# MOLECULAR BEAM INVESTIGATION OF ELECTRONICALLY

# EXCITED MERCURY

by

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I declare that this thesis was composed by me and that the work presented herein was carried out by me during my time as a member of the Molecular Beam Research Group at Edinburgh University.

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To Margaret and my parents .

#### ABSTRACT

Molecular beam experiments have been carried out to study the collisional interaction at thermal energies of mercury atoms, in the metastable  $Hg({}^{3}P_{2})$  electronically excited state, with a series of collision partners: Na, Ne, CO, N<sub>2</sub>, CO<sub>2</sub>, propane, propylene. Relative differential cross-section data has been collected for each system and despite the complexity of the scattering system, with possible separate potentials arising from each of the m<sub>j</sub> components of the  ${}^{3}P_{2}$  state, interference structure is observed out to wide angles (the structure for Hg\*/propane and Hg\*/propylene being, however, rather poorly defined).

The data for the Hg\*/Na and Hg\*/Ne systems was interpreted as purely elastic scattering. Potentials were obtained by use of a fitting procedure involving direct inversion of the scattering data and a good reproduction of the observed data was obtained for both systems. The Hg\*/Ne system could only be described in terms of 3 potentials, with  $\varepsilon \simeq 8$ , 14 and  $22 \times 10^{-14}$  ergs. The Hg\*/Na data could, however, be described either as a 3 potential system or as a single potential with long range softening of the outer attractive branch. In both models, a deep potential of  $\varepsilon \simeq 30 \times 10^{-14}$ ergs was required to reproduce the major features of the data, but the small angle envelope could only be accounted for either by the softening at large b (in the single potential model) or by the addition of two shallow potentials with  $\varepsilon = 1.5$ and 2.7 x 10<sup>-14</sup> ergs (in the 3 potential model).

In contrast, the observed structure for the Hg\*/CO,  $Hg*/N_2$ and Hg\*/CO<sub>2</sub> could not be interpreted as arising from purely elastic scattering. Good fits were however achieved for all three systems with the application of an adsorption function to a two potential model, the potentials being obtained in a similar manner to those for the atomic collision partner systems (with  $\varepsilon = 12 - 14 \times 10^{-14}$  ergs for the shallower potential in each case and  $\varepsilon = 38$ , 43 and 34 x 10<sup>-14</sup> ergs for the deeper potential in the Hg\*/CO, Hg\*/N<sub>2</sub> and Hg\*/CO<sub>2</sub> systems respectively). The values obtained for the quenching cross-sections in each system were surprisingly high and, in consequence, a second model was outlined. This proposes an avoided crossing at separations of  $\simeq$  8Å and with the resulting steepening of the outer attractive branch of the deflection function, quenching is not required until smaller separations than previously. Although reduced (to  $\simeq 150 \text{\AA}^2$ ), the crosssections are still very large unless adsorption is drastically reduced at impact parameters below boo

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# CHAPTER 1

# INTRODUCTION

The work presented in this thesis is an investigation of the reactions of mercury in one of its low lying metastable excited electronic states with various collision partners in a molecular beam experiment.

The importance of molecular beam experiments is that they allow the detailed study of the interaction between two atoms or molecules in a single collision environment and in a situation where the reactants are known exactly and where energy and molecular orientation can be well defined. From such a situation much information can be extracted about the type of process occurring and the potential acting between the two colliding molecules. In an elastic scattering situation a knowledge of this intermoleculer potential gives complete knowledge of the interaction.

The interest in excited atoms and molecules arises from the fact that they are very important in explosions, flames, electrical discharges and photolysis and much work is carried out in these areas in trying to understand the fundamentals of the underlying physics and chemistry. Unfortunately most of these processes are rather complex, involving several competing reactions and different excited species, which therefore makes extraction of cross-section data almost impossible. Molecular beam experiments can therefore help in the understanding of these processes by providing potential data on the individual reactions taking place between excited and ground state species and by enabling the calculation of cross-sections for both elastic and inelastic scattering. However, in order to carry out a beam experiment with one of these excited species it is essential that this species has a lifetime greater than the flight time between source and detector and this therefore necessitates the use of atoms or molecules in a metastable state.

In any molecular beam experiment, whether carried out with metastables or ground state atoms, it is much easier to look for and interpret elastic scattering data. Even the inversion of elastic scattering data to find an intermolecular potential is a complex procedure and until recently most data was interpreted in terms of simple model potentials such as the Lennard-Jones (n:6) potential which has three variable parameters. With the extension of semi-classical scattering theories, however, methods of direct inversion have been established and used quite successfully in some cases to deal with elastic scattering data.

Comparatively few molecular beam experiments have been carried out with metastable atoms or molecules and most of the investigations into elastic and inelastic scattering have involved the use of ground state atoms and ions. One metastable system which has been studied in some detail is scattering involving the inert gases, particularly He and early work in this field is reviewed by Muschlitz (MUS 66). More recent work on these metastables has been primarily aimed at investigating inelastic processes and will be discussed later. They are particularly suitable for this area of study since their metastable states have enough energy to excite or ionize most collision partners.

The thermal energy scattering of ground state Hg has also been a popular scattering system, probably because it is easy to handle, and has been extensively studied by several groups (MOR 62, PAU 64, 65a, BUC 66). In a recent more detailed piece of work, Buck and Pauly looked at the scattering of Hg ( $6^{1}S_{0}$ ) by the alkali metals and by means of a direct inversion technique obtained a set of potentials for the systems studied (BUC 71, 72, 74).

Reactions of the excited states of Hg are less well covered. The lowest of these excited states are the  $6^{3}P_{0}$ ,  $6^{3}P_{1}$  and  $6^{3}P_{2}$  states respectively 4.64eV, 4.89eV and 5.43eV above the  $6^{1}S_{0}$  ground state (see term diagram of figure 1.1). The  $6^{3}P_{2}$  states are both long lived metastable states of lifetime >  $10^{-3}$  secs (BAL 65, MCA 66), whereas the  $6^{3}P_{1}$  decays radiatively to the ground state with a lifetime of  $\simeq 10^{-7}$  secs. This means that only the  $6^{3}P_{0,2}$  states are suitable for use in a beam experiment at thermal energies.



## Figure 1.1

Term diagram for mercury

Although the 6 °P, state has been extensively studied in photochemical reactions, until very recently little work has been done on the metastable  $6^{3}P_{0,2}$  states. However, Martin et al (VAN 72) have looked at the relative intramultiple quenching of Hg  $(6^{3}P_{2}) \rightarrow$  Hg  $(6^{3}P_{1})$  by a variety of gases in a total cross-section type experiment and Kraus et al (KRA 73) have studied the velocity dependence of electronic vibronic energy conversion for Hg  $(6^{3}P_{2})$  in collisions with several gases.

Some work has also been carried out on the destruction of alignment in the  $6^{3}P_{2}$  state by collisions with several molecular partners(TIT 65, BAU 74). As part of this work, measurements of total cross-sections for collisional quenching were also evaluated.

The work presented in this thesis attempts to look at the differential elastic/inelastic cross-sections of Hg  $(6^{3}P_{2})$  in collisions with atomic and molecular partners such as the alkali metals, the inert gases, CO, CO<sub>2</sub>, N<sub>2</sub> and some small organic molecules. Since inelastic events are know to take place in some of these collisions, the possible inelastic events occurring in collisions of excited atoms will be reviewed before proceeding to discuss the experimental findings.

# Elastic and Inelastic Collisions of Excited Atoms

Several types of collisions between a metastable excited atom or molecule and another partner may be distinguished:

| a <u>)</u> | A* + XY>                   | A* + XY                        |
|------------|----------------------------|--------------------------------|
| b)         | $A^* + XY \longrightarrow$ | $A + \overline{X}\overline{Y}$ |
| c)         | $A^* + XY \longrightarrow$ | A + XY*                        |
| d)         | $A^* + XY \longrightarrow$ | $AXY^+ + e^-$                  |
| e)         | $A^* + XY \longrightarrow$ | $A + XY^+ + e^-$               |
| f)         | $A^* + XY \longrightarrow$ | $A + X^{+} + Y + e^{-}$        |
| g)         | A* + XY →                  | $A^+ + XY + e^-$               |

Reaction a) simply represents elastic scattering and reaction b) represents the conversion of excitation energy to kinetic energy of separation of the products. The remaining equations involve a transfer or rearrangement of the internal energy. Reaction c) is simply energy transfer from electronic energy of the metastable to internal vibrational/rotational energy of the collision partner. Reaction d) represents associative ionisation, reactions e) and f) are examples of Penning ionisation and reaction g) is collisional ionisation.

# Elastic Scattering

Since elastic scattering theory has been reviewed widely elsewhere (BER 66, PAU 65b), only the interpretation of

1.6

of results from beam experiments will be considered. A large number of systems have been studied and whilst direct inversion has not always been possible, potential well depths,  $\varepsilon$ , and equilibrium distances,  $R_m$ , have been obtained by assuming simple model potential forms for the intermolecular potentials (BER 67). One of the most widely used model potentials is the Lennard-Jones (n : 6) potential:

$$V(R) = 6\varepsilon/(n-6) \left[ (R_m/R)^n - (n/6) (R_m/R)^6 \right]$$
 1.1

where there are three variables Rm,  $\varepsilon$  and n available for fitting purposes.

The main steps in the interpretation of differential crosssection data are as follows:

- i) estimation of parameters from all available sources of information
- ii) identification and interpretation of key features in the data which will refine the original estimates of the potential parameters. These features include the scattering envelope which gives an indication of the power of the potential, the location of the rainbow maximum which gives a good measure of the well-depth and the locations of the supernumerary

rainbow maxima which give a measure of the curvature of the well. If the apparatus resolution is good enough to observe the high frequency oscillations, a good estimation of  $\sigma_{\rm LJ}$  can also be obtained.

iii) carrying our a statistical fitting procedure between the observed data and the scattering pattern obtained from a forward calculation using the trial potential with variable parameters.

Whereas for early experiments with relatively poor resolution the data could be fitted adequately by potentials like the Lennard-Jones, when quantum interference structure was resolved to wide angles (BUC 66) these simple forms proved inadequate. Buck and Pauly were able to fit this data by using a potential with six adjustable parameters (BUC 68) and Duren et al (DUR 68) fitted their data by a modified version of the Lennard-Jones potential which contained five additional parameters beside the well-depth and equilibrium separation. Obviously such fitting requires much more computational effort than those utilizing smaller numbers of parameters.

The difficulties involved in such fitting can be overcome if direct inversion of the data is possible. Based on a classical-mechanical inversion procedure devised by Firsov (FIR 53), Buck (BUC 71a) showed that the deflection

1.8

function can be directly related to the potential. By making use of a semi-classical uniform approximation (BER 66), Buck also outlined a method by which the deflection function could also be obtained by means of a procedure which fitted predicted and experimental positions of the supernumerary rainbow maxima. This procedure has the advantage that the positions of these maxima are largely unaffected by angular and energy averaging in the two beams. Buck and Pauly successfully applied this procedure for the analysis of the high resolution differential elastic cross-sections they obtained from the scattering between Hg (<sup>1</sup>So) and the alkali metals (BUC 71a, 71b, 72, 74) and they produced a set of intermolecular potentials.

The reduced potentials obtained for the scattering of Hg ( ${}^{\circ}S_{O}$ ) with Na, K and Cs were all similar in form (BUC 71b, 72), but the potential obtained from the Hg/Li system (BUC 74) was significantly different in both the shape and size parameters. However, the Li-Hg potential agrees surprisingly well with the results of Olson (OLS 68) who carried out an inversion procuedure utilizing the low resolution differential cross-sections obtained by Bernstein et all (BER 65) and the velocity dependence of the total cross-section reported by Rothe et all (ROT 67).

The advantage of a direct inversion procedure is that the

potential is obtained pointwise rather than as a constrained function. Indeed, the reduced potentials obtained by Buck and Pauly are significantly different in shape from the model potentials usually used to interpret scattering data.

It should be pointed out however that apart from the case when the potential, V(R), is a monotonic function of R, it is not possible to find a unique potential to account for the observed scattering. This has been shown by Boyle (BOY 71) to be true even in the case of well resolved structure. Pritchard (PRI 72) also demonstrated the possible ambiguity but suggested a method of removing it by using the envelope of the scattering data as well as the peak positions . Obviously there are many more elastic scattering experiments which could be considered including total crosssection work and collisions at greater than thermal The experiments mentioned above are however energy. those most relevant to this study of the reactions of metastable mercury. This trend will be continued in the discussion of inelastic processes.

# Excitation transfer

A great deal of the early work done on collisional quenching of excited atoms was carried out in spectroscopic bulb type experiments rather than molecular beam scattering experiments and a wide variety of experimental techniques are still used. The type of experiment is usually governed by the nature of the excited state to be studied. Molecular beam techniques are used for the study of metastables because of their relatively long lifetimes. When the excited state is short-lived the reaction may be studied by observing the emission of radiation in either a quenching or fluorescence experiment.

Before discussing experiments relevant as examples of either reaction (b) or (c) a short outline of some of the theory behind excitation transfer collisions will be given. The extension of quantum theory of scattering to inelastic processes has been carried out by Levine (LEV 69) and is based on the S matrix. The elements of the S matrix give the ratio of the amplitude of the outgoing partial wave in one channel to the incoming wave in some other. For elastic scattering only the diagonal matrix elements are non-zero, but for inelastic scattering the off-diagonal elements are also important. For a collision of the type:

 $A_i + B_i \rightarrow A_k + B_1$ 

it can be shown that the total cross section for scattering in the inelastic channel n from an incident plane wave in channel iis:

$$\sigma_{in} = \pi k_{i}^{-2} \sum_{l'm'} \left| \begin{array}{c} \Sigma (2l+1)^{\frac{1}{2}} i^{1} S_{ilm:nlm'} \right|^{2} \qquad 1.2$$

where ilm represents the entrance partial wave and nl'm' the partial wave in the exit channel.

The calculation of elements in the matrix requires the solution of the total wave function for the system. If the collision of two atoms A and B is considered, the wave equation is:

$$\left[-(\tilde{n}^{2}/2\mu)\nabla^{2} + H_{A}(r_{A}) + H_{B}(r_{B}) + V(R_{r}r_{A}r_{B})\right]\Psi = E\Psi \qquad 1.3$$

where  $\mu$  is the reduced mass of the colliding system, H<sub>A</sub> and H<sub>B</sub> are the Hamiltonians for internal motion of atoms A and B respectively and V is the total interaction potential for the two systems averaged over the electron coordinates of A and B.

For a change in internal states of  $i \rightarrow n$ , a solution of equation 1.3 is sought of the form:

$$\Psi = \sum_{n} F_{n}(R) \phi_{n}(r_{A'}r_{B}) \qquad 1.4$$

which will asymptotically have the form:

and  

$$F_{i} = \exp(ik_{i}R\cos\theta) + f_{i}(\chi,\phi)R^{-1}\exp(ik_{i}R)$$

$$F_{n} = f_{n}(\chi,\phi)R^{-1}\exp(ik_{n}R)$$
1.5

such that  $F_i$  represents an incoming plane wave and outgoing elastically scattered spherical wave and  $F_n$  represents an inelastically scattered spherical wave.

It is then possible to reduce equation 1.3 to an infinite set of coupled equations of the form:

$$|\nabla^2 + k_i^2|$$
  $F_i(R) = \sum_n F_n(R) U_{in}(R)$  1.6

where the matrix element  $U_{in}$  is given by:

In order to cut down computation on these coupled equations it is usually necessary to select only a few channels. It is then possible to calculate the S matrix elements which are given by the relationship:

$$S_{ilm:nlm} = (k_n/k_i)^2 |F_{nlm}| \exp(i\eta_{nlm})$$
 1.8

and knowing these, the differential and total crosssections for inelastic scattering from state  $i \rightarrow n$  can be found. More detailed accounts of these calculations are given by Levine (LEV 69) and Fluendy et al (FLU 73).

Whereas it is theoretically possible to use the above formalism, in the description of excitation transfer problems further simplifications are required and various approximation methods have been devised to deal with specific problems. These approximations can be generally classified into those that treat both the internal and relative motion quantum mechanically and those which introduce the concept of a classical path for the relative motion of the colliding particles. This latter method is, however, only really suitable where the energy transfer is small.

The quantum method usually makes use of a partial wave expansion when the total transition probability is given by a summation over all the angular momenta included and averaging over all the initial states. For light particles such as H or He atoms this method is ideal since there are relatively few partial waves required to define the system, but for heavier atoms the number of partial waves required becomes prohibitive. A partial wave analysis was carried out by Buckingham and Dalgarno to describe the excitation transfer for the system He\* + He (BUC 52).

The classical path method requires calculation of the transition matrix at selected impact parameters and then an average taken over all these impact parameters. This method was used by Callaway and Bauer (CAL 65) to form a theoretical base to discuss the sensitised fluorescence of alkali metals, i.e. the transition  ${}^{2}P_{3/2} - {}^{2}P_{1/2}$ due to collision of the excited alkali atoms with inert gas The assumption was made that the energy change was atoms. small enough so that a change of speed of either particle could be ignored along with the effects of elastic scattering, i.e. change in direction of the particles. The interaction was formulated in terms of a two-state calculation with an effective potential which acted to produce transitions in the alkali metal atom while leaving the inert gas in its ground state. Such an approach is a reasonable first approximation when the interaction is very weak. A more sophisticated approximation would take account of one colliding partner acting on the other at the lowest level of perturbation theory, e.g. allowing the wave functions of the ground state atom to be perturbed by the incoming excited In Nikitin's description of the same reaction (NIK 65), atom. the interaction is split into a long-range term similar to Callaway's and a short-range term, the exchange interaction, which has an exponential dependence on the interatomic separation.

One of the most general approximations of non-adiabatic collision theory is the Landau - Zener formula, arising from time-dependent perturbation theory (LAN 60). For excitation transfer to occur, two electronic states of the same symmetry have nearly the same energy at some separation and nuclear motion of the system at that separation can induce transitions between the surfaces. The probability of non-adiabatic behaviour after a single passage over the crossing point is given by:

$$P = \exp(-H_{12}^2 / (2hv|F_1 - F_2|))$$
 1.9

where  $F_1$  and  $F_2$  are the gradients of the two potential curves at the crossing point. The overall probability of non-adiabatic behaviour as a result of the collision is obtained by applying equation 1.9 on both the inward and outward path giving an overall probability of nonadiabatic behaviour of 2P(1-P).

The importance of all these approximations lies in trying to explain experimental observations. So there now follows a general discussion of experiments carried out in the field of excitation transfer processes.

In the early experiments on the study of quenching, a great deal of attention was given to the reactions of mercury vapour, especially in its  ${}^{3}P_{1}$  state. The quenching of Hg( ${}^{3}P_{1}$ ) by Ar is an example of reaction (b); the  ${}^{3}P_{1}$  state is deactivated directly to the ground state  ${}^{1}S_{0}$  by collision and all the excitation energy appears as kinetic energy of the recoiling mercury and argon atoms because the energy difference between the mercury excited and ground states in insufficient to excite Ar to any of its excited states:

 $\operatorname{Hg}({}^{3}P_{1}) + \operatorname{Ar} \longrightarrow \operatorname{Hg}({}^{1}S_{O}) + \operatorname{Ar}$ 

However, because of the large energy separation between the mercury states and because the potential surface arising from the excited state is unlikely to support an attractive well, any crossing with the ground state system potential will be high up its repulsive wall at small internuclear separation and the cross-section will therefore be small.

Studies have also been made of the sensitised fluorescence of alkali metals induced by collisions with rare-gas atoms. As early as 1928 Lechte - Holtgreven looked at the reactions between Na and Ar (LEC 28). More recently Chapman et al have studied the fluorescence from a K/Ar system (CHA 65), and Jordan (JOR 64) from reactions of Na and K with He and Ar.

1 1 6

In all these collision processes, the alkali metal atom in an excited state makes a transition to another excited state with the energy difference transferred into the relative kinetic motion of the colliding partners, e.g.

$$K(^{2}P_{3/2}) + Ar \rightarrow K(^{2}P_{1/2}) + Ar$$
 1.10

Cross-sections of the order of 40 - 100  $Å^2$  were obtained in all cases and can be explained by the fact that, unlike the Hg/Ar system, the energy mismatch is small.

Several theoretical studies have been performed on this system. Thorson (THO 61) outlined a development of general quantum theory to deal with such a situation, but Nikitin (NIK 65) showed that this is unnecessary since the main contribution to the transition probability is due to a region far from the turning point and so the relative motion can be described quite satisfactorily by the semi-classical approach. As was mentioned earlier, Nikitin and Callaway et al applied semi-classical approaches of different complexity to the Na/Ar system and both achieved reasonable agreement with the experimental cross-sections. Callaway's approach gave rise to a cross-section which was strongly dependent on the energy difference between the states, with the maximum cross-section corresponding to zero energy difference. Such a resonance theory obviously supports the experimental differences found in the Hg/Ar and alkali metal/ rare gas systems.

In all the systems mentioned so far, the excited atom has been in collision with another atom. Accurate total quenching cross-sections have, however, been measured by Deech et al (DEE 71) for the collisions of Hg  $({}^{3}P_{1})$  with a variety of partners. Typical cross-sections found for H<sub>2</sub>, D<sub>2</sub>, CO, CO<sub>2</sub> and O<sub>2</sub> were in the range 10 - 60 Å<sup>2</sup>, whereas that for Xe was < 2 x 10<sup>-3</sup> Å<sup>2</sup>, which is of the same order as the Hg/Ar case mentioned earlier. This was also found by Krause et al (KRA 73) in their study of relative quenching cross-sections for Hg ( ${}^{3}P_{2}$ ) in molecular collisions.

1.16

The cross-sections for He and Ar were found to be smaller than that for N<sub>2</sub> (and NO, CH4, H<sub>2</sub>) by at least a factor of 3 x  $10^{-3}$ . These differences in quenching efficiency by molecular and atomic gases seems to indicate that electronic energy is more readily converted into vibronic modes rather than into kinetic energy of the reacting species, i.e. internal degrees of freedom are required for significant quenching when the collision partner lacks excited states below the energy level of the excited atom.

Also in studying  $\operatorname{Hg}({}^{3}P_{1})$ , Vikis et al (VIK 72) found that most of the molecules they used as quenching partners caused the intramultiplet  ${}^{3}P_{1} \rightarrow {}^{3}P_{0}$  transitions instead of quenching to the  ${}^{1}S_{0}$  ground state. One exception was provided by  $\operatorname{CO}_{2}$  when more than 99% was directly quenched to the ground state. CO was found to cause transitions mainly to the  ${}^{3}P_{0}$ state.

The quenching of Hg  $({}^{3}P_{1'0})$  by CO and NO was also studied by Polanyi et al (KAR 67 a,b) and they were able to record infra-red emission from the excited molecules and in the case of CO estimate a set of rate constants  $k_{y}$  for the reaction:

 $Hg^* + CO \longrightarrow Hg + CO_v^{\dagger} v < 9$  1.11

The conclusion was drawn that energy matching was of no importance since a resonance conversion of electronic to vibrational energy requires k(v=20) = 1 and k(v < 20) = 0, in marked contrast with the experimental findings. It also appeared that less than half of the electronic energy involved is converted into vibrational energy, the remainder going into kinetic energy of the relative motion of the Hg and CO particles. An explanation was sought in terms of a collision complex HgCO\* which undergoes intersystem crossing onto a potential surface which correlates with the electronic ground state,  $l_{S_0}$ , in a region accessible at thermal energy and where the electronic potential energy can be released into nuclear motion of the separating particles.

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The reaction (1.11) is now believed to take place in two steps, (LON 70, CAL 71), as:

$$Hg(6^{3}P_{1}) + CO \longrightarrow Hg(6^{3}P_{0}) + CO(v = 1)$$

$$Hg(6^{3}P_{0}) + CO \longrightarrow Hg(6^{1}S_{0}) + CO(v \le 9)$$

$$1.12$$

the first of these reactions being nearly resonant. There have been several attempts to reproduce the observed vibrational distribution by theoretical applications. Levine et al (LEV 72) attempted to fit the data using an impulsive collisional model where the electronic transition was assumed to occur as a sudden process at the crossing point so that nearly all the energy was released as repulsion between Hg and the nearest atom in CO. The CO molecule then separates from the Hg atom and during the separation the vibrational and rotational excitation takes place. A reasonable fit to the experimental data was obtained.

However an even better fit was achieved by Simons et al (SIM 73) using an impulsive half-collision model modified to accommodate the possibility of changes in the potential energy functions of the separating fragments. The model assumes the intermediate formation of a Hg  $(6^{3}P_{0})$  - CO complex in which the C-O band length is increased:

 $Hg(6^{3}P_{O}) + CO \rightarrow ^{3}(HgCO) *$   $^{3}(HgCO) * \longrightarrow Hg \cdots (CO) \rightarrow Hg(6^{1}S_{O}) + CO(v \ge 0)$  1.13

The best agreement with experimental results was achieved by the extension of the C-O bond length by 0.06 Å. The process could also be applied to the Hg/NO system and again remarkable agreement was achieved with the experimental results of Polanyi (KAR 67b).

1.18

Polanyi's experiments have provided evidence against a resonance effect between the electronic energy lost by the excited species and the vibrational energy gained by the collision partner, but there is other evidence that this resonance effect is important. One of the earliest experiments carried out on the relative effectiveness of energy transfer was undertaken by Beutler et al (BEU 29) when they studied the mercury sensitised fluorescence of the diffuse series of sodium. Their results seem to show that the probability of transfer is greatest when the energy defect is least since the most favourable reaction was

$$Hg(6^{3}P_{1}) + Na(3^{2}S_{1/2}) - Hg(6^{1}S_{0}) + Na(9^{2}S_{1/2}) = 1.14$$

where the energy defect,  $\Delta E$ , was 0.019 eV. More recently, this same system was studied in more detail by Czajkowski et al (CZA 73) with low pressures of mercury and sodium vapours. They measured cross-sections ranging from  $10^{-2} \rightarrow 30\text{\AA}^2$ for the transfer of excitation energy from Hg to close lying S, P and D states of Na which exhibit a pronounced resonance with  $\Delta E$ .

Although all the experiments discussed have been either quenching or sensitised fluoresence type experiments, molecular beam experiments have also been carried out in this area. Krause et al (KRA 73) studied the de-excitation of metastable mercury in collisions with H<sub>2</sub>, D<sub>2</sub>, N<sub>2</sub>, NO, CH<sub>4</sub>, He and Ar in a modulated cross-beam experiment.

Since they were interested in the velocity dependence of electronic to vibronic energy conversion, the molecular beam was velocity selected and the photon emission at 2537Å, corresponding to the transition  ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ , was studied versus the molecular speed. The experimental results were then compared to those predicted by theory.

Two extreme theoretical models have been advanced to explain the relative intra-multiplet quenching cross-sections of Hg  $(6^{3}P)$  with different molecules. Dickens et al (DIC 62) assume no crossing of initial and final state potential energy surfaces. This simplified theory, which ignores rotational effects, is analagous in formalism to models for intermolecular vibration-vibration energy transfer and predicts cross-section magnitudes which depend resonantly on the matching of electronic energy given and vibrational energy received in the collision. Bykhovskii and Nikitin (BYK 64) assume quenching occurs when the electronicvibrational terms of the quasimolecule interest, i.e. the potential energy surfaces that describe the interactions  $Hg(6^{3}P_{2}) + M$  and  $Hg(6^{3}P_{1}) + M^{*}$  intersect. Under this assumption, quenching efficiency depends on the energy separation of initial and final states of the quasimolecule instead of the energy defect at infinite separation as in the treatment of Dickens et al. When the time dependence of the non-adiabatic interaction is considered semiclassically, the transition probability of Bykhovskii far from the threshold reduces to the form of the Landau - Zener model, which has an energy The total effective quenching crossdependence of  $E^{-\frac{1}{2}}$ . section derived from the transition probability also behaves as  $\mathbb{E}^{-\frac{1}{2}}$  well above threshold.

Krause found that the energy dependence of Dickens<sup>\*</sup> approximation, in which the quenching cross-sections are predicted to monotonically increase with increasing energy, could not explain the measured energy dependence of his experimental results in the range  $0 \rightarrow 0.3 \text{eV}$ . There was, however, a reasonable agreement between the experimental behaviour of the cross-section with energy and that predicted by Bykhovskii's treatment. Van Itallie et al (VAN 72) also studied the relative crosssections for intramultiplet quenching of Hg  $(6^{3}P_{2})$  to Hg  $(6^{3}P_{1})$ . In this experiment, crossed molecular beams were used and the phosphorescence of Hg  $(6^{3}P_{1})$  from the interaction region was monitored. Again, as with Krause's and Deech's measurements, the quenching cross-sections for the rare gases He and Xe are very small relative to those for CO, N<sub>2</sub> and CO<sub>2</sub>. They found, as had Vikis for Hg  $(6^{3}P_{1})$ , that the differences in intramultiplet cross-sections could not be explained in terms of a vibrational energy defect. They proposed that the large differences in  ${}^{3}P_{2} \rightarrow {}^{3}P_{2}$ , cross-sections could be explained by the competing quenching processes  ${}^{2}P_{2} \rightarrow {}^{3}P_{1}$ ,  ${}^{3}P_{2} \rightarrow {}^{3}P_{0}$ ,  ${}^{3}P_{2} \rightarrow {}^{1}S_{0}$  (either inelastic or reactive quenching).

There have been many other investigations carried out into excitation transfer processes, especially using the excited states of the inert gas atoms. Shahin et al (SHA 64) studied the relative rate constants for quenching of excited Ar atoms in the  $1_{P_1}$  state by  $0_2$ ,  $N_2$ ,  $H_2$ ,  $CO_2$  and  $CH_4$ , and found they were all good quenchers except N<sub>2</sub>. Fishburne (FIS 67) studied the collisions of metastable Ar  $({}^{3}P_{2,0})$ in collisions with N2 and found that the vibrational levels expected by the resonance effect are not predominantly excited. Reynolds (REY 52) measured excitation cross-sections for He, Ar and Ne metastables in collisions with other inert gases and found them all to be very small. As mentioned earlier, Buckingham et al (BUC 52) considered one of these reactions (He\*/He) theoretically by a partial wave method, and their results were in reasonable agreement with the experimental data and also supported the resonance effect.

There are many other experiments in the field of excitation transfer, but those considered are probably the most relevant to the present work. Apart from the reactions already mentioned, there are also a number of ionization processes which occur in the interaction between excited state atoms and ground state atoms or molecules and these have still to be considered.

#### Ionization processes

The following ionization processes can all take place in the reactions of excited atoms with ground state atoms or molecules:

| Associative Ionization | A* + XY | ⇒             | $AXY^+ + e^-$           |
|------------------------|---------|---------------|-------------------------|
| Penning Ionization     | A* + XY | →             | $A + XY^+ + e^-$        |
|                        | A* + XY | $\rightarrow$ | $A + X^{+} + Y + e^{-}$ |
| Collisional Ionization | A* + XY | $\rightarrow$ | $A^+$ + XY + e          |

Penning ionization and associative ionization are likely processes if they are energetically possible, i.e. if the excitation energy of A to A\* is greater than the ionization potential of XY or AXY. If  $V_+(R)$  is the potential which dissociates to A + XY<sup>+</sup>, associative ionisation will only occur if  $V_+(R)$  has a deep enough well to support bound vibrational states. The final relative translational energy in the potential  $V_+(R)$  will be E- $\varepsilon$ , where E is the collisional energy and  $\varepsilon$  is the energy carried away by the ejected electron (see figure 1.2). If E- $\varepsilon$ <0, the final relative motion in the  $V_+(R)$  potential must be that of a bound state of AXY<sup>+</sup> and this is associative ionisation. Otherwise, Penning ionisation takes place.

Penning ionization has been known for some time and was first observed experimentally by Kruithoff and Penning (KRU 37). It is an important process because it is a resonant transition and so cross-sections can be appreciable, sometimes of the order of 100  $Å^2$ , whereas those for non-resonant transitions are typically at least an order of magnitude smaller.



Figure 1.2  $V_0(R)$  is the potential which dissociates to  $A^* + XY$ ,  $V_+(R)$  to  $A + XY^+$ . For associative ionisation  $E-\varepsilon(R)<0$ , where E is the collision energy and  $\varepsilon(R)$  is the energy of the ejected electron.

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Thus Penning ionization can be an important process in atmospheric chemistry, particularly if the electronically excited species, A\*, is metastable. In this case, Penning ionization may be the key process which determines the steady state concentration of species A\*.

The Penning ionisation of the metastable states of He in particular have been studied both experimentally and theoretically because:

- (i) the  $(2^{1}S)$  and  $He(2^{3}S)$  are sufficiently energetic (  $\simeq 19-20eV$ ) to ionize most collision partners
- (ii) He is an important constituent of the atmosphere
- (iii) the radiative lifetime of these states is long enough for them to be studied using molecular beam techniques, i.e. in a single collision atmosphere.
- (iv) He is sufficiently simple electronically to allow theoretical treatment from first principles.

Studies of Penning and associative ionisation have also been carried out for several of the other inert gas metastables. In many cases absolute values of the total ionisation crosssections have not been measured, but the relative values of Penning to associative ionization cross-sections are widely measured. For example, Herman et al (HER 66) measured the relative cross-sections for Penning and associative ionisation in collisions of excited Ar\* in a metastable state with an Hg atom and found a ratio of 0.85.

Associative ionisation was first reported by Hornbeck et al (HOR 51) when they studied the appearance potentials of  $He_2^+$ ,  $Ne_2^+$  and  $Ar_2^+$  (associative ionisation) relative to those for  $He^+$ ,  $Ne^+$  and  $Ar^+$  (Penning ionisation) in collisions of He\* + He, Ne\* + Ne and Ar\* + Ar. This experiment demonstrated for the first time that the diatomic ion is generated by collision of an atom in its ground state with an atom in an excited state and not an ion.

However, if the excited atom is in a highly excited state, as well as Penning and associative ionisation, collisional ionisation is also possible, although

$$A^{**} + B \rightarrow A^{+} + B + e^{-}$$
 1.14

was only observed when B was at least triatomic, suggesting that the energy for thermal collision ionisation comes from vibrational energy in B (HOT 67). Hotop et al also found that the reaction

 $Ar^{**} + H_2 \rightarrow ArH^+ + H + e^-$  1.15

is the most favourable process with a cross-section an order of magnitude greater than that for Penning ionisation. By contrast, for He\* +  $H_2$  the roles are reversed and Penning ionisation is the most probable process, almost an order of magnitude greater than the rearrangement ionisation. Associative ionisation, although less important, is observable for the second reaction but not for the first.

Besides much experimental work there have also been several attempts to treat Penning and associative ionisation theoretically. In an attempt to fit the experimental data of Benton et al (BEN 62) who looked at the reactions of  $He(2^{3}S)$  with several atomic and molecular collision partners, Ferguson (FER 62) used a simple classical momentum transfer collision cross-section model. This model assumed that the ionisation reactions were dominated by long-range forces and only order of magnitude agreement with the experimental results was achieved.

In a more exact piece of work, Miller (MIL 70a) developed the theory of Penning and associative ionisation in a classical, semi-classical and quantum mechanical framework and produced formulae for the total cross-sections for Penning and associative ionisation, the angular distribution for Penning ionisation and the distribution of energies of the ionised electron.

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If figure 1.2 is considered again, the  $V_0(R)$  potential curve can be considered to be embedded in a continuum of electronic states of the type (AXY)<sup>+</sup> + e<sup>-</sup> (for which the  $V_+(R)$  potential is the lower limit) and will undergo autoionisation with some characteristic rate. There is thus a width,  $\Gamma(R)$ , for decay of  $V_0(R)$  into the continuum degenerate with it. Miller thus interpreted Penning ionisation, within the Born-Oppenheimer framework, as the leakage of a discrete state into the continuum state degenerate with it, but complicated by the fact that there is a simultaneous relative motion of the two nuclei.

Miller et al (MIL 70b, 72) then applied these results to the ionisation of  $H(1^2S)$  by the helium metastables,  $He(2^{1,3}S)$ . The potential curves required were calculated by a large scale configuration interaction technique and accurate potentials were obtained for the ground state  $He - H^+$  and the excited state  $He^* - H$ . The first of these potentials possesses a considerable well, so that both associative and Penning ionisation are possible. Because of difficulties in calculating the required width,  $\Gamma(R)$ , Miller first of all calculated approximate cross-sections without  $\Gamma(R)$  by using a simplified model for low collision energies (BAT 67) in which autoionisation was only allowed at the classical turning point. In a later piece of work (MIL 72), the auto-ionisation width was obtained from the golden rule type expression:

$$\Gamma(R) = 2\pi \rho | < \chi | H-E | \psi > |^{2}$$
 1.16

where  $\psi$  is the initial (discrete) electronic state,  $\chi$  is the final (continuum) electronic state, H is the total electronic Hamiltonian, E is the electronic energy of the discrete state and  $\rho$  is the density of the final continuum states (determined by the way in which  $\chi$  is normalised asymptotically). Knowing this quantity, it was possible to rigorously evaluate the total ionisation cross-section, the relative amounts of associated (HeH<sup>+</sup>) and dissociated (He+H<sup>+</sup>) products, the energy and angular distribution of the ionised electron and the angular distribution of the heavy particles.

Good qualitative agreement was obtained with the experimental results of Hotop et al (HOT 71) who measured the energy distribution of the ionised electrons.

Using the same potentials as calculated in this work, Miller et al (MIL 73) also considered the interaction between two He(2<sup>3</sup>S) atoms and for room temperature, 0.026eV, calculated a total ionisation cross-section of 94 Å<sup>2</sup>, almost 70% of which leads to He<sub>2</sub><sup>+</sup>. This agrees well with the experimental value of  $100\text{\AA}^2$  at  $300^{\circ}\text{K}$  obtained by Phelps et al (PHE 53), but is quite different from the value of  $250 \text{\AA}^2$  obtained by Johnston et al (JOH 73) in a more recent experiment. This latter value is surprising since the orbitting model should give an upper limit to the total ionisation cross-section.

The metastable atoms considered by Miller have also been extensively studied experimentally in recent years by a variety of techniques including the measurement of relative ionisation cross-sections, Penning electron energy distribution and the angular distribution of both the Penning ions and the ejected electrons.

Rothe et al (ROT 65) measured the velocity dependence of the total elastic cross-section for the scattering of  $He(2^{3}S)$  by ground state He, Ar and Kr at thermal energies. The scattering was found to be largely elastic with inelastic collisions contributing less than 10% in all three cases.

As a result of experimental findings, two different mechanisms have been preposed through which Penning ionisation can occur:

 $He^{*}(1) + B(2) \longrightarrow He(1) + B^{+} + e(2)$  $He^{*}(1) + B(2) \longrightarrow He(2) + B^{+} + e(1)$ 

where (1) and (2) refer to the electrons originally belonging to the metastable and ground state particles respectively. The first reaction can be considered as the perturbed metastable He\* atom emitting a photon which in turn is absorbed by B and leads to photoionisation.

1 27

This radiative transfer mechanism was proposed by Smirnov et al (SMI 65). The second reaction represents an electron exchange process, proposed by Hotop et al (HOT 69a), in which the He\* atom picks up an electron from B and ejects the electron which originally belonged to He. For He  $(2^{1}S)$ both channels are possible, but for He $(2^{3}S)$  the probability of the first mechanism, involving a radiative transition, would be much lower because the ground state He is singlet.

Hotop et al proposed their mechanism as a result of a series of experiments in which they measured the energy distributions of electrons ejected in thermal collisions of both He metastables with Ar, K, Xe, Hg. In another experiment (HOT 69b) they measured the ions produced in the above collisions in a mass spectrometer and obtained singlet to triplet Penning cross-section ratios which in all cases were close to unity. This was taken as evidence to support their proposed mechanism.

Muschhtz et al (SHO 62) also measured total ionisation crosssections for collisions of He metastables with a range of other gases in a crossed beam experiment. They were able to determine Penning cross-sections by monitoring the positive ion current. Separate cross-sections for the triplet and singlet atoms were also obtained by varying the beam composition and the ratio of triplet to singlet cross-sections was found to be unity, thus again supporting Hotop's mechanism.

More recent work by Schmeltekopf (SCH 70) on the same system has shown higher cross-sections for the singlet metastable – cross-sections obtained for the  $(2^{3}S)$  were similar to Hotop's, but those for He  $(2^{1}S)$  were greater by a factor of 2 or 3. Cermack (CER 66) also found that the Penning ionisation cross-section for Ar by He  $(2^{1}S)$  atoms was larger than that by He  $(2^{3}S)$  atoms. Both experiments, therefore, are indicative of the importance of the radiative transfer mechanism.

1 20
The reaction between metastable He and ground state Ar was also studied by Lee et al (CHE 74) in a thermal energy cross-beam experiment measuring both the differential elastic cross-section and the ratio of Penning to associative ionisation as a function of impact parameter. From their results, Lee et al find the singlet state more reactive than the triplet and they conclude that the mechanism of radiative transfer for perturbed metastable He should be a channel competitive with the electron exchange mechanism of Hotop.

From these experiments and their conflicting results it can be seen that there is not yet a complete understanding of the Penning ionisation process even for the simplest metastable He\* and more work is needed before the process can be fully understood.

Much recent work on ionisation processes involving metastable atoms has also been carried out by Muschlitz and his co-workers. Penton et al (PEN 68) reported an isotope effect in the production of  $H_2^+$ , HD<sup>+</sup> and  $D_2^+$  in collisions of  $H_2$ , HD and D2 with the He metastables, but this was not found by Herce (HER 68) for the ionisation of  $CH_4$  and  $CD_4$ . Kramer et al (KRA 72) measured the ratios of associative to total ionisation cross-sections for metastable He and Ne in collisions with Ar and Kr. Measurement has also been made of the velocity dependence of the total ionisation cross-section of Ar, Kr and Xe on impact of thermal energy metastable Ne  $({}^{3}P_{2,0})$  atoms (TAN 72) and the results, interpreted using a semi-empirical model, indicate that the interaction leading to ionisation is short-ranged. All these experiments by Muschlitz will be helpful in the understanding of the ionisation processes, providing as they do data which can be treated theoretically and was not previously available.

Another experiment to provide new experimental information was carried out by Ebding and Niehaus (EBD 74) when they measured the angular distribution of electrons ejected in thermal collisions of the He metastables with Ar, Kr, Xe, Hg, CO and  $N_2^{\circ}$ . These distributions were found to be approximately isotropic when the interaction between the metastable and target particle was strong, e.g. He\*/Hg. In the case where the well-depth of the He\*-B potential was small compared to the collision energy, the trajectory was determined by the hard core of the potential and the angular distribution of electrons was found to be strongly anisotropic and asymmetric, e.g. He\*/Ar. Calculations were carried out using Miller's expression for the angular distribution and assuming a hard core collision, and a good fit was obtained with the observed laboratory results.

This is the first reported experiment in which the angular distribution of Penning electrons has been measured and good agreement is obtained with theory. As experimental techniques improve and the data provided by experiment becomes more detailed, then there will obviously be an even better opportunity of understanding these ionisation reactions. The experimental work carried out so far seems to indicate that Miller's work in particular already goes a long way to providing a good theoretical approach to Penning and associative ionisation.

Unfortuneately, as was seen earlier, the situation in the case of the excitation transfer reactions is not so well defined. Formal theory involves vast computational difficulties and most of the approximate theories forwarded have been applied to only very specific cases, e.g. Simons and Taskers explanation of Polanyi's results for quenching of Hg ( $6^{3}P_{1,0}$ ) by CO, NO (SIM 73). A better general understanding of these processes is, however, gradually being achieved , but obviously much more work is required in this area, both experimentally and theoretically. High resolution molecular beam experiments are especially important since they provide an ideal technique for stutying the collisions of individual atoms and molecules in that photon, ion or excited atom emission from the collision region can all be monitored. This information can be used to test formal theories or provide necessary information to use in approximation methods. In this way it may be possible to resolve the argument concerning the importance of a resonance effect in excitation transfer collisions.

The systems studied in this work are unlikely to supply any useful information on ionisation processes since the Hg  $({}^{3}P_{2})$  state is not sufficiently energetic to ionise most small molecules (the only system studied where ionisation is possible was Hg\*/Na). Also, because of the complexity of the systems, each with several possible potentials (which will be asymptotically degenerate) arising from the M<sub>J</sub> components of the J = 2 state, the experimental data can only easily be interpreted by adopting a simple model corresponding to some dominant process. It was an important objective of this work to test whether such interpretations can be satisfactorily used to reproduce the observed data. It was also hoped that further information on excitation transfer processes could be obtained from perturbations of the elastic differential cross-sections measured. CHAPTER 2

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APPARATUS

The apparatus used in this work was originally designed for the study of alkali metal systems by the measurement of high angular resolution differential cross-sections at small angles using a velocity selected main-beam. It was later converted for its present purpose of studying metastable mercury, formed by electron bombardment of a ground state mercury beam (DAR 71). In this conversion the velocity selector was removed due to the fact that electron bombardment is rather an inefficient process and the main-beam intensity recorded was much lower than in the original experiment. With the removal of the velocity selector, however, the intensity was found to be high enough to allow the measurement of differential cross-sections.

The apparatus is shown in figure 2.1 and can be seen to consist of two differentially pumped chambers, the main scattering chamber and an U.H.V. detector chamber.

The main scattering chamber consists of a stainless steel box whose removable sides are approximately 55 cm long and 36 cm high. One of these sides contains an ion gauge for pressure measurement and feed-throughs for electrical connections and water and gas lines, another contains a perspex viewing window and a third a valved connection to the metastable atom detector chamber. The top of the

2 1



Figure 2.1

chamber contains a liquid nitrogen cold trap from which are suspended copper shields which completely surround the oven assemblies. This lid is easily removable and, like the sides, can be bolted into place, the vacuum seal being made by a rubber oring. From the bottom of the chamber is suspended a 12 inch oil diffusion pump with a water-cooled chevron baffle. Without the help of cryo-pumping a pressure of  $1 \times 10^{-5}$  torr. can easily be obtained in this chamber, and when the liquid nitrogen trap is filled a pressure of  $10^{-6}$ -  $10^{-7}$  torr. can be achieved if the cross-beam material is readily condensible.

The detector chamber, which is connected to the main chamber by a valve which opens over a narrow slit, is made completely from polished stainless steel and is pumped by the combination of an ion pump and a liquid nitrogen cooled titanium sublimation pump. After the chamber has been baked at  $100^{\circ} - 120^{\circ}$ C for several hours with the slit to the main chamber open, a pressure of  $< 10^{-3}$  torr. can be achieved in the valved-off chamber and this pressure is maintained easily by the ion pump alone. Even with the valve to the main chamber open, only a slight rise in pressure is obtained.

This apparatus, as shown in figure 2.1, has been slightly modified from the original apparatus used to study the metastable mercury system in that the whole detector

chamber has been removed from one wall of the main chamber and shifted through  $90^{\circ}$  on to the wall facing the perspex viewing window. The value between the two chambers has also been changed, shortening the distance between the scattering centre and the detector.

With this apparatus the detector remains fixed and the two beam sources, set at right angles to each other and mounted on a turntable, can be rotated through a wide angular range about the scattering centre. One of the advantages obtained from the fore-mentioned modifications is that the angular range able to be scanned has been increased from under 20° to approximately 40°. This increase was necessary because, at the very low collision energies capable of being reached by the source ovens, rainbows for some systems could occur at very wide laboratory angles.

Since the distance from the scattering centre to the detector was reduced, another improvement made by the modifications was in the total signal and the signal to noise ratio seen at the detector. The intensity of the detected signal for a cross-beam experiemnt is given by:

2 1

$$S = \frac{I_{1}T_{1}I_{2}T_{2}W_{1}W_{2}h_{0}j(E,\theta)(v_{1}-v_{2})T_{3}A_{d}q}{v_{1}v_{2}I_{1}^{2}I_{2}^{2}I_{3}^{2}}$$
2.1

where:

| $I_1, I_2$                                     | are the fluxes of main and cross-beam      |
|------------------------------------------------|--------------------------------------------|
|                                                | respectively                               |
| $W_1$ , $W_2$                                  | are the respective beam widths             |
| $\mathbf{v}_1$ , $\mathbf{v}_2$                | are the respective velocities of particles |
|                                                | in the beams                               |
| $T_{1}, T_{2}, T_{3}$                          | are the transmissions of filters           |
| h                                              | is the beam height                         |
| σ <sub>j</sub> (E,θ)                           | is the laboratory differential cross-      |
|                                                | section for process j                      |
| Ad                                             | is the area of the detector                |
| q                                              | is the detector efficiency                 |
| l <sub>1</sub> ,l <sub>2</sub> ,l <sub>3</sub> | are the distances from sources and         |
|                                                | detector to the scattering centre          |

Since the only major alteration in any of these factors was the reduction of the distance,  $l_3$ , from the scattering centre to the detector from 61 cm to 34 cm, the ratio of signals after and before the modifications is given by:

$$S(\text{new})/S(\text{old}) = [1_3(\text{old})/1_3(\text{new})]^2 \approx 3.2$$
 2.2

So the total signal seen at the detector has been trebled. Of more importance than the total signal, however, would be any improvement made in the signal to noise ratio observed.

The noise counting rate arises from two main sources from the partial pressure of the species being detected that is present in the detector region and from scattering of the beams from background gas molecules. For the first of these the contribution to the noise counting rate will be:

$$Nn = n_{i} T_{3} A_{d} q v_{b} / 3$$
 2.3

and for the second, where the densities of the target beam and the background gas are of concern, the contribution will be:

Nn = 
$$n_b I_1 T_1 W_1 W_2 h \sigma_b(\theta) T_3 A_d q$$
  
 $1_1^2 I_3^2$ 
2.4

where  $\sigma_{b}(\theta)$  is the differential cross-section for scattering into angle  $\theta$  from the background gas and  $n_{b}$  is the number density of the background gas.

These noise count rates represent the mean counting rate. But, because it is possible experimentally to measure the signal plus noise and the noise separately, the signal can be estimated by subtraction of one from another with an uncertainty which depends on the standard deviation

of the noise. If the noise is completely random, its standard deviation can be taken as the square root of the mean counting rate and so the signal to noise ratio is given by:

$$S/N = \left[ \frac{I_{1}T_{1}I_{2}T_{2}W_{1}W_{2}h\sigma_{j}(E,\theta)(v_{1}-v_{2})}{v_{1}v_{2}l_{1}^{2}l_{2}^{2}l_{3}^{2}} \right] \times \left[ T_{3}A_{d}q \right]^{\frac{1}{2}}$$
$$\times \left[ \frac{3 l_{1}^{2}l_{3}^{2}}{3 n_{b}I_{1}T_{1}W_{1}W_{2}h\sigma_{b}(\theta) + l_{1}^{2}l_{3}^{2}n_{i}v_{b}} \right]^{\frac{1}{2}} 2.5$$

Any improvement in the signal to noise ratio will have arisen from the change in  $l_3$  and the relationship between the signal to noise ratio and  $l_3$  is given by:

S/N 
$$1_{3}^{-1}/\bar{K} + K' 1_{3}^{2}/\bar{J}^{-\frac{1}{2}}$$
 2.6

If the noise due to the partial pressure in the detector chamber is neglected, the S/N ratio is proportional to  $l_3^{-1}$  and the apparatus modifications will mean an improvement of  $\approx 1.8$  in the ratio. If, however, the noise due to the scattering of background gas is neglected the S/N ratio is then proportional to  $l_3^{-2}$  and the modifications give an improvement of  $\approx 3.2$ . In reality, neither noise source is zero and the improvement achieved by the modifications will lie somewhere between the two figures given above.

One disadvantage which could arise from shortening the distance from scattering centre to the detector is that the apparatus resolution would be decreased. This decrease of resolution is not important, however, since the geometric resolution is much higher than the broadening of the differential cross-section structure due to the velocity spread in the cross-beam.

The detailed experimental set-up used in the present work is illustrated schematically in figure 2.2. A ground state mercury beam is formed by effusion from a thermal source oven and then passed through an exciter which produces a beam of mercury atoms in excited electronic states. After collimation this beam comes into collision with a modulated target beam and is scattered. The scattered signal, after further collimation, is measured by a fixed detector, the angle of scattering being determined by the orientation of the turntable with respect to the zero position when the main-beam is firing straight at the detector.

The components of this experimental set-up will now be discussed separately:

#### Sources

The ground state mercury beam is formed by effusion through a glass capillary array mounted in the front



2.9

9

face of a carefully thermostated single chamber oven. The advantage of using a capillary array instead of a thin slit is that the intensity in the forward direction is much improved, provided the pressure in the oven is not raised too high. In the arrays used in this experiment, the capillaries had a diameter of 50µm and a length of 1.25mm and the arrays themselves were cut to 0.3cm in diameter. The beam was given a rectangular shape of the desired width by a pair of defining slits mounted on the face of the oven and covering the capillary array. The oven, made throughout of stainless steel, was designed by Darwall (DAR 71). A temperature range of between 120°C and 150°C was found to be the most suitable conditions for providing a good steady main beam with a maximum forward intensity.

The type of source used to provide the cross-beam was dependent on the nature of the cross-beam material but both types used were effusive sources. For solid cross-beam material such as the alkali metals an oven was used similar to that described by Cowley (COW 68) but of a much larger capacity. As for the mercury source, this oven was carefully thermostated and the running temperature was different for each material used. For gaseous cross-beam material an oven was used which could be fed externally from a gas-line. In this case, the pressure of gas feeding the oven could be monitored from the exit end of the gas-line using a Piranni gauge and a constant pressure could therefore be main-

tained throughout the experiment. The oven was also well thermostated and had the same arrangement of a capillary array and defining slits as for the mercury oven. The pressure at which the oven was operated depended on the gas used and was chosen to give the best attenuation of the main beam (ideally 10-15%) that was possible without seriously raising the pressure in the main scattering chamber.

### Exciter

The mercury beam is excited by bombardment from an electron gun by a magnetically collimated stream of electrons of controlled energy. The electron gun, mounted immediately in front of the source oven but separate from it, consists of an anode with a slit running down its entire length through which the beam is fired. The cathode is fixed below this slit, separated from the anode by thin mica strips, and is heated indirectly by a heating element which runs through the centre of the cathode. Both the cathodes and heating elements were supplied by Mullard, the cathode being standard uncured metal oxide cathodes from PL36 pentode valves. A magnetic field of 600 gauss in the anode-cathode direction is supplied by two Eclipse C magnets causing electrons which leave the cathode to travel in a helical path. This arrangement is illustrated in figure 2.3.



The cathodes and heaters have to be changed before every experiment and after a pressure of approximately 10<sup>-6</sup> torr. is reached the cathodes are cured by slowly raising the heater current over the period of about an hour until the operating conditions are reached. At an anode-cathode voltage of 10V and with a heater voltage of approximately 30V, an emission current of 4-8mA is obtained.

Electron bombardment is rather an inefficient method of excitation since perhaps only 1 in  $10^5$  of the atoms in the beam are excited, but it has the advantage of being more selective than discharge sources. With electron bombardment, only those states with energies less than the excitation energy can be excited whereas with discharge sources if the atom has more than one metastable state then they all tend to be populated.

For a beam of mercury atoms, electron bombardment leads to the production of two or possibly three metastable states depending on the excitation energy. These states are the  ${}^{3}P_{0}$ ,  ${}^{3}P_{2}$  and  ${}^{3}D_{3}$  states located at 4.64, 5.43 and 9.05 eV respectively above the ground state. However, an experiment by Borst (BOR 69), in which he measured the trapped electron current corresponding to inelastic scattered electrons as a function of electron-beam energy for electron impact of mercury,

indicated that the excitation cross-section for the  ${}^{3}P_{0}{}_{,2}$  states was approximately two orders of magnitude greater than for the  ${}^{3}D_{3}$  state. Since all the other states produced will be short-lived, the only important constituents of the beam at excitation energies around loV will be the  ${}^{3}P_{0}$  and the  ${}^{3}P_{2}$  metastable states.

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McConnellet al (MCC 68) have calculated theoretical cross-sections for the excitation of  $Hg(6^{1}S_{0})$  to the  $Hg(6^{3}P_{0,2})$  states brought about by electron bombardment and found that the cross-sections for the excitation of the  ${}^{3}P_{2}$  state was five times larger than for the  ${}^{3}P_{0}$  state, i.e. in the statistical ratio for the states if the different  $m_{j}$  components are considered. This was experimentally confirmed by Davidson (DAV 73) who carried out experiments to determine the life-times of the  ${}^{3}P_{0}$  and  ${}^{3}P_{2}$  states using the same source and exciter as in the present work.

Taking account of these findings, the electron gun can be assumed to produce a mercury metastable beam consisting mainly of the  $6^{3}P_{2}$  state with a relatively small percentage of the  $6^{3}P_{0}$  state. Any other excited states in the beam are either short-lived or of a negligible amount.

### Metastable Detector

This piece of equipment was designed by Darwall and has been described fully by him (DAR 71).

The detector is based upon the fact that electronically excited atoms in collision with a metal surface are capable of ejecting electrons from these surfaces with fairly high efficiencies. For this Auger process to take place, the energy carried by the metastable must be greater than the work function of the metal. McDermott et al (MCD 60) were the first to use this type of detection system for a beam system when they used the alkali metals for the detection of the  ${}^{3}P_{0,2}$ states of mercury.

In the present work the metal surface used is potassium deposited on a tungsten peg. The measured work function for potassium is 2.2 eV and the depth of the bottom of the conduction band is 4.6 eV (LIC 58), so the  ${}^{3}P_{0}$  and  ${}^{3}P_{2}$  metastable states of mercury have sufficient energy to eject any electron in the potassium conduction band since they have energies of 4.64 eV and 5.43 eV respectively. Sodium can also be used since it has a work function of 2.3 eV, but will be less efficient since the

bottom of the conduction band lies at 5.3 eV for sodium. The actual efficiency of the ejection of electrons has only been measured in a few cases, e.g. Hasted et al (HAS 58) found an efficiency of 0.14 for He (2<sup>3</sup>S) atoms incident on a tungsten surface, which has a work function of 5.8 eV (RIV 67).

As was mentioned previously, the detector is mounted in a separate U.H.V. chamber capable of reaching pressures of  $<10^{-9}$  torr. This has the advantage that once an alkali surface has been prepared it can be maintained in an active condition for long periods.

The detector assembly consists of a tungsten peg mounted so that it can be moved transversely by means of a rotary feed-through from a position in the path of the mercury metastable beam to a position in front of a small alkali oven (see figure 2.4). The tungsten peg is insulated from ground by means of a P.T.F.E. sleeve so that it can be held at a required voltage. When in position on the beam centre, the peg is surmounted by a three-element electrostatic lens assembly which is used to focus ejected electrons into the cone of a B419BL Mullard Channel Electron Multiplier (C.E.M.). Copper shielding is positioned around the C.E.M. and in front of the alkali oven in order to prevent the alkali metal being sprayed on to the lens assembly while the tungsten peg is being coated. This whole detector



assembly is mounted on to a 6" diameter flange to enable easy removal from the vacuum chamber for cleaning or topping-up of the alkali oven.

For coating the peg, an adequate film of potassium can be deposited after 30 minutes exposure to the potassium beam with the oven at  $230^{\circ}$ K. Once settled, this surface can last for several months if it is not exposed to "poisonous" gases such as So<sub>2</sub>, I<sub>2</sub>, SF<sub>6</sub>, etc. which react with the potassium layer.

When the peg is in the path of the mercury beam, an excited mercury atom striking the potassium surface causes an electron to be ejected. These ejected electrons are focussed by the lens system into the cone of the C.E.M., where each incoming electron produces an avalanche of electrons which is treated as a single pulse. The cone of the C.E.M. is held at earth and the output end is typically held at 3.0 KV. The rate of arrival of electrons depends not only on these voltages, but also on the lens voltages. A typical set of voltages is given in table 2.1 and with these voltages typical main-beam counts of 2.5-3.5 x  $10^5$  s<sup>-1</sup> were recorded, with typical background noise counts of 1.0-1.5 x  $10^3$  s<sup>-1</sup>. This background noise is mainly due to photons emitted from the hot cathode and cathode heater and is seen only near the main beam centre. Typical background count rates of 20-30  $s^{-1}$  are seen at wide angles.

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Table 2.1

| Unit                   | Voltage      |
|------------------------|--------------|
| Peg<br>lens l          | -75V<br>-99V |
| lens 2                 | +93V         |
| lens 3<br>CEM entrance | +100V<br>0V  |
| CEM collector          | 3.OKV        |

Since the collector end of the C.E.M. is at 3.0 KV, the output pulses are taken off by a  $0.001\mu\text{F}$ capacitor, followed by a protection circuit. This is shown in figure 2.5. The output from this circuit is fed into a Keithley 111 amplifier, a zero-gain amplifier which is used for impedance matching and for broadening the output pulse. This is followed by a Hewlett Packard HP462A amplifier and a discriminator and pulse shaper circuit. Each signal pulse is then counted by one of two scalers, which during an experiment are automatically switched on and off for pre-set periods of time by the modulation electronics (which will be described later).







By plotting the observed metastable signal against the exciter voltage, the excitation function for metastable mercury may be obtained. The excitation function for a potassium surface is shown in figure 2.6. At each voltage the signal I(V) has been multiplied by the factor i(Vmax)/i(V), where i(V) is the exciter current at voltage V, in order to compensate for the larger currents flowing at higher voltages which give rise to higher signals. The plot has a threshold at about 6V and exhibits two maxima at 9.5V and 15V, the former being the larger of the two. This curve is in good qualitative agreement with the results obtained by Lichten (LIC 58) who saw a threshold at  $\simeq 4.5$  eV and peaks at 7V and 11.5V for the same system. In a later experiment McDermott and Lichten (MCD 60) assigned the peak at 7V to the  $P_{\theta_{1,2}}$ states, whereas the second peak is attributed to contributions from the  $P_{0,2}$  and  $D_3$  states. At higher voltages there is an increasing contribution from photons originating from the exciter.

In a more detailed experiment using a partly contaminated W surface, Borst (BOR 69) was able to show that the lowest energy metastables capable of liberating electrons were those in the  $6^{3}P_{2}$  state and that the contribution from the  $6^{3}P_{0}$  state was negligible. He also assigned the second group of emission to photons from the  $7^{3}P_{1}$  state at 8.64eV and reported very little if any contribution from the  $6^{3}D_{3}$  metastable state.





#### Alignment

Exact alignment of the components involved in a molecular beam experiment is of critical importance. With the apparatus described above, the task of alignment has been considerably eased by the use of a He/Ne laser.

For this purpose, the rear flange of the detector chamber is removed and the tungsten peg moved out of its position under the electrostatic lenses. The laser, situated at the rear of the detector chamber, is then adjusted until the horizontal laser beam passes freely through the narrow channel in the exciter intended for the main-beam. At this stage, all defining slits will be wide open. The mercury oven is then placed in position on its mount and the mount is adjusted in height and position until a well defined image of the capillary array is produced in the back of the oven. The oven slits and collimating slits are then closed down to their operating widths, which vary between 0.02 cm and 0.07 cm, while maintaining the slit image in the back of the oven. The detector peg is then moved to a position where it interrupts the laser beam and any necessary adjustment can be made to the detector until the peg lies directly under the concentric holes in the electrostatic lenses.

This part of the alignment is only carried out relatively infrequently since the whole turntable assembly is mounted on optical rails and so can be removed and replaced easily without disturbing the alignment.

The alignment of the components mounted on the turntable can be checked optically by removing the turntable to an optical bench. A small electric bulb is placed in the mercury oven and if this light is seen through the oven slits, the exciter and the collimating slits when viewed through a telescope then the alignment is correct. The alignment of the cross-beam oven is checked by rotating the turntable through  $90^{\circ}$  and performing the same operating, ensuring that there is no discrepancy in the heights of the two ovens.

This alignment check was carried out fairly frequently since for each experiment the oven(s) have to be recharged and the exciter exchanged, all of which involve removing the relevant component from its mounting on the turntable.

# CHAPTER 3

## EXPERIMENTAL PROCEDURE

Before each experiment the exciter cathode and cathode heater were replaced, the mercury oven was filled and all components inside the vacuum system were checked to ensure working order. The lid was then bolted down and after roughing out by the rotary pumps to a pressure of < 0.1 torr, the diffusion pumps were switched on. When a pressure of  $1-2 \times 10^{-5}$  torr. had been achieved, the liquid nitrogen cold trap was filled, causing an immediate drop in pressure. After both ovens were outgassed by heating to  $50-60^{\circ}$ C, a pressure of  $10^{-6}-10^{-7}$ torr. was generally achieved.

At this stage, the oxide cathode heater was gradually brought up to an operating voltage of  $\approx 30V$  and the mercury oven slowly heated to its operating temperature of  $130-150^{\circ}C$ . This temperature was rigorously controlled by the operation of a platinum resistance thermometer bridge linked to a power supply unit. Changes in resistance of the platinum are proportional to temperature and, once the bridge has been zeroed with the oven at the required temperature, this property can be used to maintain the oven at the set reading.

When both the exciter and the oven were at their operating conditions and if the exciter was performing adequately (i.e. giving an emission current of several milliamps

at an anode to cathode voltage of  $\simeq$ 11V), then a search was made for a main-beam by rotating the turntable and observing the count rate at the detector. With the turntable positioned at the beam centre, the signal was then tuned up by altering the lens voltages and possibly sightly altering the voltage on the collector end of the C.E.M. (normally kept at a setting of 3.OKV). The optimum settings are those which give the highest signal to noise ratio, calculated as the ratio of the signal count rate to the square root of the noise count rate. A count rate of anywhere between 1.0-3.5 x  $10^5$  second<sup>-1</sup> was regarded as an acceptable signal, while a reasonable noise rate while sitting at the main-beam centre was  $0.2-3.0 \times 10^3 \text{ second}^{-1}$ . This was mainly due to photons from the exciter heater and the wide variation probably due to differences in the position of unshielded parts of the heater projecting outside the cathode. This noise count rate fell away rapidly as the turntable was turned away from the main-beam position and typical noise counts at wide angles were 10-30 second<sup>-1</sup>.

With a reasonable main-beam, the cross-beam was switched on. For a solid cross-beam material, such as an alkali metal, this again means bringing an oven slowly up to its operating temperature, but for a cross-beam material which is gaseous at room temperature all that is involved is opening a tap to a gas-line. Ideally,

an attenuation of the main-beam by the cross-beam of 10-15% was desired. With the alkali metals this should be achieved if the oven was at the correct operating temperature, but with gaseous cross-beam materials the situation is different.

If the cross-beam gas is condensible at liquid nitrogen temperature, e.g.  $CO_2$ , there is no problem and good attenuation can be achieved while maintaining a pressure of  $\simeq 10^{-6}$  torr. in the scattering chamber. However, if the cross-beam gas is not condensible, e.g. Ne, CO, the pressure in the scattering chamber will start to rise as the cross-beam intensity is increased. This is undesirable because the main-beam count rate is rapidly cut as the pressure rises beyond  $\simeq 5-6 \times 10^{-6}$ torr. The operation of the exciter can also be affected by relatively high pressures causing a gradual fall-off in the emission current over a period of several hours. So, in these cases a compromise has to be made between the attenuation achieved and the reduction in main-beam intensity due to the rising pressure. In most cases a smallish attenuation of  $\simeq 3-5$ % has to be accepted, with pressures in the range of 0.5-2 x  $10^{-5}$  torr.

The situation is complicated further by the nature of the cross-beam material. If it is an oxidising agent, e.g.  $I_2$ ,  $SO_2$ , then the background noise seen

at the detector is very much increased and to minimise this noise the cross-beam has to be run at as low an intensity as possible. If it is a reducing agent, e.g.  $CO_{,} CO_{2}$ , then the emission current and consequently the main-beam intensity are improved because the presence of the reducing agent appears to enhance the cathode and makes the exciter work more efficiently.

The attenuation observed also depends upon the excitation voltage, because at high anode to cathode voltages the production of photons appears to become more important, probably due to the formation of the 6<sup>1</sup>P<sub>1</sub> state which is radiatively connected to the ground state. These photons have very little probability of being attenuated. Table 3.1 shows the percentage attenuation for several exciter voltages during the same experiment and indicates that increasing the excitation voltage above a critical voltage seriously reduces the percentage attenuation observed.

| Exciter Voltage | <pre>% Attenuation</pre> |
|-----------------|--------------------------|
| 10V             | 12%                      |
| 11V             | 12%                      |
| 12V .           | 10%                      |
| 15V             | 5%                       |

Table 3.1

The critical voltage was found to be just below 12V and so most experiments were run with an excitation voltage of between 11V and 11.5V. This was found to give a maximum main-beam count rate with a maximum attenuation.

Once a steady main-beam, cross-beam and attenuation had been achieved, angular sweeps were started during which data was collected automatically, controlled by the modulation electronics. These sweeps were always started a few degrees on the anti-clockwise side of the main-beam centre position and carried through in a clockwise direction to as wide an angle as was permitted by the apparatus dimensions. The permittable angular sweep was  $16-17^{\circ}$  before the apparatus was modified and  $\simeq 40^{\circ}$  after these modifications. At the end of each sweep the turntable was returned to the main-beam position to check for any drift in the intensity of either beam.

The turntable is rotated by a stepping motor which can be made to drive the turntable shaft accurately in steps varying from  $0.05^{\circ}$  to  $0.5^{\circ}$ . The angular position of the turntable is monitored by an S.G. Brown "Minitac" shaft rotation indicator whose rubber-tyred friction wheel runs along a quadrant attached to the turntable

shaft (see figure 3.1). The motion of the minitac against the quadrant produces a set of Moiré fringes which are counted by two photodiodes and recorded on an electronic counter. The set up is such that 200 counts displayed on the counter is equivalent to one degree of rotation of the turntable.

In addition to the "minitac" there are two electromagnetic switches, one positioned about a degree to the anti-clockwise side of the main-beam centre and the other almost at the end of the angular sweep allowed by the apparatus dimensions. The first of these has the effect of zeroing the angle counter at the same position in each sweep, so that there is a fixed reference point at the beginning of each sweep and just before the beam centre. The second of the switches supplies another reference point at the end of each sweep, with a fixed angular separation between this and the initial zeroing point. This is necessary because the levels of the photodiodes in the minitac sometimes drift if they overheat in the vacuum system, causing the minitac to count low. However, since the stepping motor drives the turntable by accurate angular increments, the position of the turntable relative to the initial zero position can be worked out. The second reference point gives a check on these calculated angular positions since it registers on the counter at a known angular position relative to the first.

Figure 3.1 TURNTABLE DRIVE SYSTEM (viewed from underside)



(a) Stepper Drive Motor (SIO-Syn).
(b) Optical Shaft Encoder (Minitic) (H.G. BROWN).
(c) 36:1, Reduction Gearbox (S.H. Muffet).
(d) 6"radius, Quadrant.
(e) Limit Stops.
(f) Micro-switch.
(g) Turntable driveshaft.
## Modulation System and Data Collection

The employed modulation scheme used a chopper disc, rotating at 35 cycles per second, mounted in front of the cross-beam oven. The chopper had two blades so that at the instant it interrupted the cross-beam it also intercepted a light beam between a small electric bulb and a photocell. The output from this photocell, a square wave pulse of period 14.3 ms and width 7.2 ms, was used to drive an "in-phase" detector system consisting of two width delay lines, two counters (Hewlett Packard 5245L and 3734A units) and a switching network. This counting system is illustrated schematically in figure 3.2.

A positive signal from the photocell, indicating that the cross-beam was on, triggered the delay of the signalplus-noise line (yellow chain) which was set at ≃0.3 ms. This delay is necessary in order to avoid counting as many photons as possible since any photons should arrive almost instantaneously. The output from this delay was fed into a width unit, set at 6.25 ms, in the signal-plus-noise line and into a delay unit of the noise line (blue chain). This delay unit was set to 7.2 ms and its output was fed to another width unit, also set



at 6.25 ms. The outputs of both width units were fed through an amplification stage to operate "and" gates feeding two counters. The effect of the width delay lines were such that the yellow chain counted only when the cross-beam was on and the blue chain counted only when the cross beam was off (see figure 3.3).

To compensate for any possible slight differences in the open time of the two counters, the roles of the two width counter lines were switched after every 100 modulation periods. So if for one batch of 100 periods a counter registered signal plus noise, then for the next batch it registered noise. At the end of each batch, the totals registered on each counter were output on paper tape (these were the signal plus noise and the noise accumulated over a total period of 0.63 seconds). The number of modulation periods was counted by a clock counter which not only triggered the interchange between width counter lines after 100 pulses, but also triggered the punch unit and then reset the counters to zero.

After each batch of 100 modulation periods, a set of information was presented in parallel to the punch by the interface. This set of information consisted of a sentence of sixteen lines and was set out in binary code as follows:





- 5 lines for counts from the 3734 counter or for angle or manual codes
- 6 lines for counts from the 5245 counter
- 2 lines for condition codes
- 3 lines for separator codes

This was always output with the same pattern so that any corruption in the data could be noticed and dealt with by the handling programme. The composition of the sentence depended on exactly at which point of the sweep the data was being output, and the actual type of information being output could be recognised by the use of different condition codes.

In general, manual codes were only used to mark the beginning and end of a sweep, though in principle they could be used to output any sort of information. At any angle during the sweep the same collection routine was carried out automatically, although the number of times that any particular type of information was recorded could be decided by the operator.

First of all the angular position of the turntable was punched together with the relevant condition code. This was recorded several times to ensure that the turntable had come to rest. The next piece of information output was the background noise, counted with the cross-beam on and off by the two scalers. Since the voltage between anode and cathode in the electron gun is switched off at this time, these two count rates should be the same. This therefore supplies a useful check as to whether there is any "in phase" signal arising from some source other than the main-beam.

Finally, with the main-beam switched on by supplying an excitation voltage, measurements were taken of the noise when the cross-beam was off and signal plus noise when the cross-beam was on. The number of times each of these measurements were taken depended on the relative position of the turntable, because the wider the angle the weaker was the scattered signal. So, in order to try to improve the signal-to-noise ratio at wide angles by reducing the standard deviation in both noise and signal-plus-noise counts, a greater number of each type of count were taken as the sweep progressed.

After the required measurements at a particular angle were recorded by the punch, the turntable was automatically moved to a new position at a pre-set angular separation from the previous position. The step size was controllable by the operator and was usually kept constant throughout the sweep.

This whole procedure was then repeated for the new turntable position. A complete sweep during an experiment involved stepping through an angular range of over  $40^{\circ}$  with a typical step size of 0.3-0.4 degrees and could take as long as two hours to complete. A step size of as low as  $0.05^{\circ}$  could have been achieved accurately by the stepping motor but this would have meant taking eight times as long to complete a sweep. Since the main-beam is checked only once per sweep this would be undesirable because fluctuations in beam intensities might go unnoticed.

However, a finely separated mesh of points covering the whole angular range could be achieved by taking as many as a dozen sweeps of data for each system. The starting point for each sweep was different, although several degrees to the anti-clockwise side of the mainbeam centre, so that when all the sweeps were processed together there would be a dozen data points within the step size of 0.3-0.4 degrees. Thus a mesh much finer than the actual step size was produced.

## Data Analysis

The data is analysed in two stages, the first of which looks at the data from each individual sweep separately and the second of which combines the individual sweeps into a complete data set.

In the first stage of processing, the data from a sweep, held on paper tape in binary code, is translated to decimal and each sentence is checked for consistency. If any part of a sentence does not conform to a set pattern, then the whole sentence is rejected.

At each angle, the means and standard deviations of the noise, signal-plus-noise and background noise are calculated. The original data is then compared with its mean value and any point lying outwith plus or minus two standard deviations is rejected. The means and standard deviations are then re-calculated and these values stored in an array, along with the corresponding angle. When the whole angular range of a sweep has been covered, this multi-dimensional array is then output and is stored on disk for easy access in the second stage of processing.

The second phase takes these arrays of means and standard deviations as input data and combines them into a complete data set. First of all, using a sweep in which the range over the main-beam centre has been covered by small angular steps, the beam-centre is located and all angular information is then referred to this zero point. The beam width and attenuation of the main-beam signal by the cross-beam are then

calculated.

Each sweep is then considered individually and the set of data corresponding to each angle is checked. If the difference between the background noise signals (measured with the exciter voltage at zero and with the cross-beam on and off respectively) is greater than twice the standard deviation of either signal, or, if the noise at one angle is considerably greater than at the preceding angle, then all the data for this angle is rejected. At small angles the scattered signal appears to be negative since the detector has recorded the main-beam signal attenuated by the cross-beam. Α correction is made for this by using the value of attenuation already calculated and a good approximation to the signal is achieved by adding on this correction at every angle.

After normalising individual sweeps by the area swept out by the scattered signal over a fixed laboratory angular range, the data for a complete experiment is assembled by merging the individual sweeps, ensuring that the beam centres of all the different sweeps coincide. (An alternative method of normalisation consists of normalising over the main-beam signal - both methods were used and very little difference was found in the results). The raw data is then smoothed using an

exponential smoothing routing which computes the smoothed signal and standard deviation in this signal for each data point in the array.

The smoothed signal,  $NS_i$ , is obstained by considering a smoothing window of n points on either side of the data point in question,  $S_i$ , and finding the mean of these signals weighted by an exponential function of their angular separation. Thus:

$$NS_{i} = \sum_{j=i-n}^{i+n} (S_{j}Z_{j}/N_{j}) / \sum_{j=i-n}^{i+n} (Z_{j}/N_{j}) 3.1$$

where  $N_j$  is the counting standard deviation in  $S_j$  (as provided by the initial processing program) and  $Z_j$  is the exponential smoothing factor, given by:

$$Z_{i} = \exp \{0.5/[(\theta_{i} - \theta_{i})/\sigma_{i}]^{2}\}$$
 3.2

where  $\theta_i$ ,  $\theta_j$  are the laboratory angles corresponding to signals  $S_i$ ,  $S_j$  respectively, and  $\sigma$  is the half-width of the exponential distribution function. The extent of the smoothing of the signal is governed by the choice of value for  $\sigma$  (n is chosen large enough that  $Z_{i+n} \neq 0$ ).

The variation of the signal given by this sample of points is given by:

$$VAR = \sum_{j} (s_{j}^{2} z_{j}^{/N} j) / \sum_{j} (z_{j}^{/N} j) - \langle \sum_{j} (s_{j}^{2} z_{j}^{/N} j) / \sum_{j} (z_{j}^{/N} j) / \sum_{j} (z_{j}^{/N} j) / \sum_{j} (z_{j}^{/N} j) / \sum_{j} (z_{j}^{/N} j) - \langle \sum_{j} (s_{j}^{2} z_{j}^{/N} j) \rangle_{j}^{2} / \langle \sum_{j} (z_{j}^{/N} j) / \sum_{j} (z_{j}^{$$

and the standard deviation of the averaged signal,  $NS_i$ , is then given by the relation:

$$SD_{i} = \sqrt{VAR} \left\{ \sum_{j} (Z_{j} / N_{j}) - 1 \right\} - \frac{1}{2}$$
 3.4

The value of the signal, standard deviation and the corresponding laboratory angle can then either be output or subjected to the process of further smoothing followed by deconvolution.

For the purpose of convolution and deconvolution a filter function is calculated which is based on the mainbeam profile, since the resolution obtainable in the scattered signal will depend on the beam width. Although the true apparatus resolution depends on several factors, this filter function is used to represent experimental broadening in the convolution equation:

$$h(x) = \int_{-\infty}^{\infty} f(x - y) g(y) dy = f*g$$

where h(x) is the measured structure, f(x-y) is the corresponding ideal structure and g(y) is the apparatus resolution function.

3.5

A method of solution of this equation has been described by Morrison (MOR 63) and this method has been utilised to find the deconvoluted experimental structure, where h(x) is the observed scattered signal and g(y) is the calculated filter function.

Whether or not the convolution/deconvolution steps have been included, the next stage in processing is the transformation of the signal and standard deviation from the laboratory to the centre-of-mass frame of reference. This is necessary because the differential crosssections must be presented in the centre-of-mass frame before inversion of the scattering data to find the intermolecular potential can occur. When this has been completed, both line-printer and graphical outputs are produced.

## Laboratory (LAB) to Centre-of-Mass (CM) Transformation

The relationship between the centre-of-mass and laboratory angles has been considered by several authors and has been known for some time. Morse and Bernstein (MOR 62) have presented a treatment which is not confined to scattering in the plane defined by the incident beams and is applicable to elastic, inelastic and reactive scattering of crossed molecular beams.

If two collimated beams of particles of masses  $m_1$  and  $m_2$ and with volocities  $v_1$  and  $v_2$  intersect at an angle  $\Psi$ , then the relative velocity of the colliding particles is:

$$v_{R} = (v_{1}^{2} + v_{2}^{2} - 2v_{1}v_{2} \cos \Psi)^{\frac{1}{2}}$$
 3.6

The CM velocity of the incident primary beam particle is then given by:

 $w_1 = v_R m_2/(m_1 + m_2)$  3.7 and the velocity of the cross-beam particle relative to the centre of mass by :

$$W_2 = v_{\rm p} m_1 / (m_1 + m_2)$$
 3.8

The speed of the centre of mass is given by :

$$v_{CM} = \left[ W_1^2 + V_1^2 - 2W_1 V_1 \cos \xi_1 \right]^{\frac{1}{2}}$$
 3.9

where  $\xi_1$  is the angle between the vectors  $v_1$  and  $W_1$ .

The geometric relationship between these quantities is shown in figure 3.4 (which is appropriate for all of the experimentally studied systems since the mercury atoms of the main-beam were always slower and heavier than the cross-beam molecules). The relative velocity vector,  $W'_1$ , for the scattered primary beam particle is shown rotated through the CM scattering angle,  $\chi$ , with respect to the incident primary beam,  $W_1$ . Correspondingly, the laboratory vector,  $V'_1$ , for the scattered particle is rotated through the experimentally observed angle  $\theta$ from the incident main-beam vector,  $V_1$ .

For the special case of in-plane scattering, the CM angle is given in terms of the LAB angle by the relationship:

$$\chi = \cos^{-1} \left[ \left( W_1^2 + W_1^{\prime 2} - V_1^2 - V_1^{\prime 2} + 2V_1 V_2 \cos \theta \right) / 2W_1 W_1^{\prime} \right] - 3.10$$

and:

$$V'_{1} = V_{CM} \cos \alpha_{1} \pm / \bar{V}_{CM}^{2} \cos^{2} \alpha_{2} - V_{CM}^{2} + W_{1}^{2} / \bar{Z}^{2}$$
 3.11

where  $\alpha_1$  is the angle between the vectors  $V_1$  and  $V_{CM}$  and is given by:

$$\alpha_{1} = \cos^{-1} \left( \left( V_{CM}^{2} + V_{1}^{2} - W_{1}^{2} \right) / 2V_{1} V_{CM} - 7 - \theta \right)$$
 3.12



Figure 3.4 Newton diagram of typical elastic scattering system.

If the scattering is elastic, equation 3.10 is simplified since the initial and final relative velocities will be equal in magnitude, i.e.  $|W_1| = |W_1'|$ , and the relationship reduces to:

$$X = \cos^{-1} \left[ (2W_1^2 - V_1^2 - V_1^2 + 2V_1V_2 \cos\theta) / 2W_1^2 \right]$$
 3.13

For the experimental set-up described earlier where the two beams are set at right angles, i.e.  $\Psi = 90^{\circ}$ , there is the further simplification that:

$$V_{\rm R} = (V_1^2 + V_2^2)^{\frac{1}{2}}$$
 3.14  
and:

$$V_{CM} = (W_1^2 + V_1^2 - 2W_1V_1^2 / V_R)^{\frac{1}{2}}$$
  
=  $(m_1^2V_1^2 + m_2^2V_2^2)^{\frac{1}{2}} / (m_1 + m_2)$  3.15

In this case it is therefore easy to calculate the CM angle corresponding to a given laboratory angle.

The transformation of the differential cross-sections from LAB to CM is given by:

$$\sigma(\chi) = \sigma(\theta) \frac{d\Omega}{d\omega} \qquad 3.16$$

where  $d\omega$  is the solid angle subtended at the detector centre-of-mass system and  $d\Omega$  is the solid angle in the laboratory system. The Jacobian is calculated by considering an area, dA, on the centre-of-mass ring. This subtends a solid angle in the CM system of:

$$d\omega = dA/W_1^{2}$$

and in the laboratory system of:

$$d\Omega = dA \cos\beta / V_1^{/2}$$
 3.18

so that:

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$$\frac{\mathrm{d}\Omega}{\mathrm{d}\omega} = \left(\frac{W_1}{V_1}\right)^2 \cos \beta \qquad 3.19$$

But since, for elastic scattering:

$$\cos \beta = (V_1^{\prime 2} + W_1^{\prime 2} - V_{CM}^{2})/2W_1^{\prime} V_1^{\prime} \qquad 3.20$$

the solid angle ratio is therefore given by the easily calculable relationship:

$$\frac{d\Omega}{d\omega} = W_1 (V_1'^2 + W_1^2 - V_{CM}^2) / 2V_1'^3 \qquad 3.21$$

The LAB to CM transformation of observed signals can thus be achieved if the molecular masses and laboratory velocities are known.

But since this experiment uses a thermal source without velocity selection, account has to be taken of the resulting main-beam velocity distribution. This takes the form of the normal Maxwell-Boltzmann distribution, modified by an experimental factor to account for decay of the metastable mercury atoms:  $I(V)dV = 4\pi I_0 (m/2\pi kT)^{3/2}V^2 \exp(-mV^2/2kT)\exp(-l_0/\tau V)dV$  3.22 where  $\tau$  is the lifetime of the metastable state and  $l_0$  is the distance from exciter to detector. The distribution takes this form because although the effusion process adds a factor of V to the normal distribution, the probability that a molecule will be excited by electron impact is proportional to  $V^{-1}$ .

To determine the velocity distribution, a value has to be found for the lifetime,  $\tau$  , of the metastable mercury atoms. Davidson (DAV 74), in an experiment carried out on the same apparatus as used in this work, carried out flight time measurements on the metastable beam and established a value of  $3 \times 10^{-3}$ s for the lifetime of the metastable beam. (Even if this is not a true lifetime, it is the correct value to use in this case since it is the effective lifetime of the metastable mercury atoms under these experimental conditions). This corresponded to a substantial deficit of slow atoms (probably at least partly due to recollimation losses of the slower atoms after excitation) and as a result, the velocity distribution is substantially narrower and the most probable velocity 35% greater than that expected from an effusive beam in the same temperature range, with an observed most probable velocity of  $2.48 \times 10^{2} \text{ms}^{-1}$ .

This value is only valid for the old experimental configuration, but in the new configuration (where  $l_0$  is shorter) the extra exponential factor of equation 3.22 incorporating the lifetime has the similar, but smaller, effect of increasing the most probable velocity and narrowing the distribution. Using Davidson's value for the lifetime, the most probable velocity was found to be increased from its expected value by just over 20% to a value of 2.25 x  $10^2 \text{ ms}^{-1}$ .

These two most probable velocities are the values used in all subsequent calculations or LAB to CM transformations for the various target gases.

There is, however, one further problem in the LAB to CM transformation. The relative masses and velocities are such that at a given laboratory angle of observation there are contributions from two CM angles, leading to fast and slow scattered components. This occurs because  $W_1$  (corresponding in this work to the mercury beam) is less than  $V_{CM}$  and so, as can be seen from figure 3.5, a particle can emerge at an angle of observation,  $\theta$ , with two different velocities,  $V_f$  and  $V_s$ . These two velocities correspond to scattering at different angles,  $\chi_f$  and  $\chi_s$ , in the CM system, so that the measured differential cross-section  $\sigma(\theta)$  will correspond to the sum of  $\sigma(\chi_f)$  and  $\sigma(\chi_s)$ , weighted by their individual Jacobians.



Figure 3.5 Fast and slow components for scattering into laboratory angle  $\theta$ .

However, partly because of the ratio of the Jacobians which favours the fast component and also because of a greater decay since the metastable atoms take longer to reach the detector, the slow component is <10% of the fast component. Since the forward and backward scattered contributions correspond to the same laboratory angular range (for typical example, see figure 3.6) it is therefore possible to achieve an estimate of the forward scattered distribution by the following iterative procedure.

For each laboratory angle,  $\theta_i$ , the corresponding CM angles, CMF<sub>i</sub> and CMB<sub>i</sub>, and their Jacobians for transformation to the CM system, JF<sub>i</sub> and JB<sub>i</sub>, are calculated. CMF<sub>i</sub> represents the angle for forward scattering and CMB<sub>i</sub> represents the angle for backward scattering. As an initial estimate for the forward signal, the backward contribution is neglected and so the forward signal, SIGF<sub>i</sub>, is given by:

 $SIGF_{i} = SIG_{i} * JF_{i}$ where SIG<sub>i</sub> is the observed LAB signal corresponding to angle  $\theta_{i}$ .

But for every backward scattering angle, CMB<sub>i</sub>, there is an equal forward angle, CMF<sub>j</sub>, and so a better estimate to SIGB<sub>i</sub> would be to equate it to SIGF<sub>j</sub>. This is not





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true, however, if decay is important because of the different laboratory velocities,  $(V_s)_i$  and  $(V_f)_j$ , in the two cases. In such a situation the observed signal, attenuated from the expected intensity  $I_o$ , is given by:

 $I_{obs} = I_{o} \exp(-l_{0} / \tau V)$  3.24 and the backward contribution is therefore calculated as:

 $SIGB_i = SIGF_j \exp \{-(1/(V_s)_i - 1/(V_f)_j\}$  3.25 There is another possible modification to this estimate since the beam is also attenuated by the background gas both by quenching of the metastable atoms and by scattering out of the beam. If the effective crosssection for attenuation by the background gas is markedly velocity dependent, the slow component will be attenuated to a different extent from the fast one. This would probably have the effect of reducing the magnitude of the background contribution as calculated in equation 3.25.

Having obtained a better estimate for SIGB<sub>i</sub>, the forward contribution is then re-calculated as:

 $SIGF_i = (SIG_i - (SIGB_i/JB_i)) * JF_i$  3.26 so a new set of estimates for  $SIGF_j$  are produced for all angles. The whole procedure is then repeated until the value for the forward scattered signal converges. This convergence takes place very rapidly.

It was found to make <10% difference in the value obtained for  $SIGB_i$  when the velocity dependence of the cross-section for attenuation of the observed signal by the background gas was varied between zero and  $V^{-1}$ dependence. This in turn led to only 1-2% difference in the values obtained for SIGF.

The above method was used to produce the CM differential cross-sections for all of the experimental data discussed in the remaining chapters.

## CHAPTER 4

RESULTS

The scattering of the metastable mercury atoms from a variety of both atomic and molecular collision partners was studied in this work in the hope of observing not only differential elastic scattering phenomena but also quenching of the metastable mercury atoms. Such quenching would be observed in any attenuation of the differential scattering envelope which is due to transitions from the metastable excited state to the ground state in inelastic processes, as described in chapter 1. The observed scattering pattern would be attenuated because the ground state atoms thus produced are not counted by the detector which selectively detects only excited particles.

These detected particles can be assumed to be in the  $P_2$  state for several reasons. As was shown in chapter 2, both calculations and experiments have pointed to electron bombardment cross-sections for the  ${}^{3}P_{R}$  and  ${}^{3}P_{0}$  states in approximately the ratio of 5:1. Also, Borst found that the detection of the  ${}^{3}P_{2}$  state using a contaminated tungsten surface was relatively efficient, whereas the <sup>3</sup> P<sub>n</sub> state was not able to be detected at all. So, although the potassium coated tungsten peg will have a lower work function than simply a contaminated tungsten surface, the efficiency of detection <sup>3</sup>P<sub>2</sub> state should still be higher than that of the of the <sup>3</sup>P<sub>0</sub> The combination of the two effects should be enough to state. make any contributions to the scattered signal from the  ${}^{3}P_{0}$ metastable negligible in comparison to that from the  ${}^{3}P_{2}$  state.

This conclusion is confirmed by some time-of-flight measurements carried out by Davidson (DAV 74) using the same apparatus as in this work. Analysis of the experimental data suggested a lower limit of 86% for the  ${}^{3}P_{2}$  percentage at excitation energies of between 9eV and 14eV.

The collision partners chosen for study were as follows: Ne, Ar, Na,  $I_2$ ,  $O_2$ ,  $N_2$ , CO,  $CO_2$ ,  $SO_2$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $C_3H_6$ , and  $SF_6$ . The simple atomic systems were chosen since here the scattering would probably be purely elastic, although for the case of Na there was a possibility of Penning or Associative ionisation taking place. CO,  $\mathrm{N}_2$  and  $\mathrm{CO}_2$  were chosen because they were all fairly simple molecules which were known to have fairly large, i.e. observable, quenching cross-sections with mercury in the  $6^{3}P_{2}$  state (VAN 72,  $SO_2$  was chosen because it is isoelectronic with  $CO_2$ , KRA 73). and I $_2$  and O $_2$  because they are symmetrical diatomics similar to N $_2$ (and possibly could be expected to be more reactive). The other molecular collision partners were all chosen mainly for their simple symmetrical shapes, ready availability and because, being polyatomics, they have many vibrational and rotational states in the correct energy range if energy matching is important for excitation transfer.

For each of these systems the experimental procedure was basically that outlined in the previous chapter, but the actual data collection times varied considerably.

First of all, some of the experiments were carried out before the apparatus modifications outlined in chapter 2 so that the data collection time per sweep was less than half that of later experiments. Most of these experiments were later repeated but the Na and I<sub>2</sub> systems have only been studied in the shorter angular range.

The overall experimental time also depended on the nature of the cross-beam material being studied. For the Na and I<sub>2</sub> systems which involved filling the cross-beam oven outside the vacuum system the length of an experiment was limited by when this oven would run out and, in a successful experiment, data could be collected for a maximum of only 12 - 15 hours. But for systems where the cross-beam oven was constantly being externally recharged from a gas-line, a successful experiment could run for up to a week, in which time several systems could be studied.

During such an experiment, however, data collection would not be continuous. When changing cross-beam material, time had to be allowed for the system to pump away any remnant traces of the previous material. Also, in the cases where the cross-beam material is not efficiently trapped at liquid nitrogen temperatures, e.g. Ne, N<sub>2</sub>, CO, and maintaining a working pressure was therefore a problem, time was allowed between sweeps for the detector chamber to be pumped back down to its normal pressure. This procedure was carried out even for the more easily condensible

gases in the hope of cleaning up the detector surface and saving it from deterioration.

The number of sweeps collected for each experimental system also varied although ideally 6 - 10 sweeps should have been sufficient for any system. This occurred because in some experiments difficulties such as low beam counts, high noise counts or electronic mal-functions were encountered. Collecting more sweeps than ideally required allowed the noisiest data to be thrown away. In some cases, however, the data collected was so noisy that entire experimental runs were rejected after initial processing, and the experiment had to be This was especially true for the non-trappable gases. repeated. In these cases in order to obtain a workable attenuation of the main beam the experiment had to be carried out with cross-beam intensities which resulted in an overall pressure in the scattering chamber higher than desirable. This had the effect of reducing the signal because of an increase in back-ground gas scattering and because the main-beam exciter was forced to operate at pressures above its ideal working So these systems suffered from the two-fold disadvantage conditions. of lower beam and higher noise counts simply because of the pressure problem.

Because of these and other difficulties, it was not possible to collect meaningful data for all of the fore-mentioned experimental systems.

In the cases of argon, oxygen and ethylene, weak beams and high scattering chamber pressures gave rise to an unacceptable signal to noise ratio and the data collected was not processed beyond the initial calculation of means and standard deviations. However, with a strong main-beam, all of these systems should have been workable.

With  $SO_2$  there was no pressure problem since it is readily condensible at liquid nitrogen temperatures and on at least one occasion a strong main-beam signal was recorded. However, although there was no increase in scattering chamber pressure there was a gradual build-up of noise seen at the detector and the signal away from the main-beam became obscured during only the second sweep. The noise problem off the main-beam centre was even more severe with both  $I_2$  and  $SF_6$ even though, as with  $SO_2$ , the experiment was otherwise ideal with a strong main-beam signal, good attenuation and no pressure problem. Some data was collected for I2 in the hope of the noise abating but as for  $SO_2$  the situation deteriorated. With  $SF_6$ , the initial noise was so bad that no data at all was taken. A possible explanation for the above situation with SO<sub>2</sub>,  $I_2$  and SF<sub>6</sub> is that cross-beam material leaking into the detector chamber is somehow reacting with the potassium on the surface of the detecter peg and causing the emission of electrons. This being the case, it is difficult to see how these systems could be studied except by using a completely different detector system.

Successful experiments were carried out with the remaining collision partners, i.e. Ne, Na, N<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> and the laboratory results are shown in figures 4.1 - 4.7. The data in these figures has undergone a preliminary analysis in which after rejection of noisy points the cross-sections are exponentially smoothed and standard deviations are calculated.

In each of these experiments, the main-beam oven was maintained at a temperature between  $135 - 140^{\circ}$ C (see Table 4.1 for running temperatures of both main and cross-beam ovens) and with no crossbeam on, a pressure of approximately  $10^{-6}$  torr could be maintained in the scattering chamber. Despite this the main-beam recorded varied widely with the system under investigation. This can be explained by the following reasons:

- (a) the emission current obtained from the electron gun was not always consistent even before the cross-beam was initially switched on and so the main-beam intensity could fluctuate from experiment to experiment
- (b) the efficiency of operation of the electron gun was sometimes affected by the cross-beam material. For the cases of CO, ethane and ethylene the emission current was slightly enhanced by the introduction of the cross-beam, with a resulting increase in the main-beam intensity
- (c) for the cases of Ne, CO and N<sub>2</sub> which cannot be cryo-pumped at liquid nitrogen temperatures, in order to gain a workable



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METASTABLE HG 3P / NE SCATTERING Velocity= 723.0M/S NUMER OF SCANS= 6.0 FILTERED DATA SIGMA= 0.20  $\cdot$ \*SIN(TH)\*TH\*\*4 Ъ. Ň ENS I F 4(

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METASTABLE HG ЗP N2 SCATTERING VELOCITY= 614.0M/S NUMER OF SCANS= 4.0 • \*\* FILTERED DATA SIGMA= 0.20 INTENSITY\*SIN(TH)\*TH\*\*4/3 Figure 4.4 lφ Φ e e F. 7 40






TABLE 4.1

| System              | Main-beam<br>oven temp | X-beam<br>oven temp |  |  |
|---------------------|------------------------|---------------------|--|--|
| Hg*/Na              | 135 <sup>0</sup> C     | 424 <sup>0</sup> C  |  |  |
| Hg*/Ne              | 136 <sup>0</sup> C     | 153 <sup>0</sup> C  |  |  |
| Hg*/N2              | 135 <sup>0</sup> C     | 148 <sup>0</sup> C  |  |  |
| Hg*/CO              | 137 <sup>0</sup> C     | 146 <sup>0</sup> C  |  |  |
| Hg*/CO <sub>2</sub> | 135 <sup>0</sup> C     | 145 <sup>°</sup> C  |  |  |
| Hg*/propane         | 137 <sup>0</sup> C     | 146 <sup>0</sup> C  |  |  |
| Hg*/propylene       | 136 <sup>0</sup> C     | 144 <sup>0</sup> C  |  |  |

attenuation of the main-beam it was necessary to operate at pressures higher than desirable, with a consequent fall-off in main-beam intensity due to the reasons discussed earlier.

The various main-beam intensities recorded for each experiment are listed in Table 4.2, which also gives the main-beam attenuation at which the experiment was run and the back-ground noise count rate on the main beam centre, bgn<sub>0</sub>, and at approximately 20<sup>0</sup>, bgn<sub>20</sub>.

The effect of pressure on the main-beam intensity can be demonstrated by considering the cases of the N<sub>2</sub> and Ne systems. For the N<sub>2</sub> case, before the introduction of the cross-beam a main-beam of  $350,000 \text{ s}^{-1}$ was recorded which was reduced to  $180,000 \text{ s}^{-1}$  under operating conditions, and for the Ne system a beam of  $330,000 \text{ s}^{-1}$  was reduced to  $110,000 \text{ s}^{-1}$ . In both cases the pressure rose to approximately  $1 \times 10^{-5}$  torr and only 3% attenuation was achieved. By contrast, for CO<sub>2</sub> an attenuation of up to 30% was attainable without any rise in pressure and the main-beam remained steady at the intensity recorded before the introduction of the cross-beam.

As can be seen from Table 4.2, there is a large noise count rate at zero degrees. This noise is artificially high in some cases because, depending on slight variations in assembly of the electron gun, the detector was sometimes given a direct line of sight to the glowing filament of the cathode heater. This is consistent with the fact

TABLE 4.2

| System                            | Mb signal/s <sup>-1</sup> | bgn <sub>o</sub> /s <sup>-1</sup> | bgn <sub>20</sub> /s <sup>-1</sup> | Attenuation |
|-----------------------------------|---------------------------|-----------------------------------|------------------------------------|-------------|
| Hg*/Na                            | 55,000                    | 250                               | <20                                | 12 - 15%    |
| Hg*/Ne                            | 110,000                   | 2,000                             | 30 - 40                            | 3%          |
| Hg*/CO                            | 135,000                   | 1,400                             | 30 - 40                            | 4%          |
| Hg*/N <sub>2</sub>                | 180,000                   | 1,000                             | 30 - 40                            | 3%          |
| Hg*/CO <sub>2</sub>               | 80,000                    | 2,000                             | 25 - 30                            | 16%         |
| Hg*∕C <sub>3</sub> H <sub>6</sub> | 150,000                   | 1,600                             | 25 - 30                            | 18%         |
| Hg*∕C <sub>3</sub> H <sub>8</sub> | 90,000                    | 4,000                             | 30 - 40                            | 18%         |

that the noise rate for the Hg\*/Na system, where the glowing filament was much further away from the detector, was much lower than for the other systems. In all cases, however, this high noise count was only recorded for approximately the first degree and dropped off rapidly to a more acceptable level as the turntable was rotated.

It can be seen that the quality of the differential cross-section data collected depends not just on the main-beam intensity but also the noise level and percentage attenuation of the main-beam that were recorded. This can be easily seen by considering the data for the Ne and  $C_3H_8$  systems, where, despite a lower main-beam intensity, the standard deviation in the signal for the  $C_3H_8$  system is noticeably better than in the Ne system.

However, before any meaningful interpretation of the data can take place, it has to be transformed from laboratory to centre-of-mass co-ordinates. This was done following the algorithm outlined in the previous chapter and the results are shown in figures 4.8 -4.14. (The factor  $\chi^{4/3} \sin \chi$  multiplying the scattered intensity is used since this factor renders the envelope of scattering from an R<sup>-6</sup> potential horizontal.) The sharp fall-off in envelope at small angles (under 10<sup>°</sup>) is due to attenuation of the main-beam which masks the scattering.







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METASTABLE HG SP / PROPANE SCATTERING VELOCITY= 466. M/S NUMER OF SCANS= FILTERED DATA SIGMA= 0.20 .6.0 m (\*SIN(TH)\*TH\*\*4) Figure 4.13 INTENSITΥ Μ 18(



Figure

The data shown in the above figures was shown to be reproduceable by processing completely separate sets of five to six scans for a given experiment or from a repeat experiment and comparing the results. Although not identical, the major features such as the overall shape of the scattering envelope and the positions of maxima and minima in this envelope were always reproduced to within the stated experimental accuracy of  $0.5^{\circ}$  in the laboratory frame. The main difference between sets of scans lay in slight alternations in peak to valley amplitudes of the observed structure.

Although the data could have been "cleaned up" and standard deviations improved by means of convolution and deconvolution with a suitable filter function, it was felt that this exercise would have been meaningless because of the slight differences mentioned earlier and because, with the fairly complex scattering structures observed, only the main features could be expected to be reproduced by any simple model of the system.

## Preliminary Analysis

As mentioned above, one of the most striking features of all the centre-of-mass plots i.e. figures 4.8 - 4.14, is the presence of oscillatory structure out to wide angles. In most cases the oscillations in the envelope occur at regular intervals for the entire range mapped by the experiment, e.g. for sodium, strong oscillations

exist out to almost 80° where experimental measurement was stopped and in the case of CO, structure is observed over almost the entire measureable range of 180°. The only cases where this structure is not so strongly evident are the propane and propylene systems where the envelope tends to be flatter. Some structure does exist, but it is not nearly as strong or as regular as in the other cases.

The regular angular spacing of the observed structure in the Na, Ne,  $\mathrm{N}_2$  , CO and CO  $_2$  systems can be seen from figure 4.15 where the angular positions of successive maxima in the differential cross-section structure are plotted against an arbitrary indexing which assigns the maxima to integer values, the highest observed maximum being given a value of one. The gradient of each of these plots can be seen to decrease slowly as n is increased, i.e. the angular spacing of the maxima slowly increases as we move to wider angles. The positions of maxima in the Hg\*/CO<sub>2</sub> system are only plotted out as far as approximately 80<sup>0</sup> although experimental data exists out to approximately 145<sup>°</sup>. This is because the experimental data, which up to  $80^{\circ}$  is very well defined and very regular, suddenly becomes much noisier and irregular. It should also be noted that the graph for the Hg\*/Ne system is much less smooth than any of the others and has several sudden changes of gradient due to irregularities in the spacing of the maxima in the scattering pattern.

In some cases, apart from the most obvious structure pointed out





above, two other frequencies of oscillations can be picked out. For the Na, Ne and CO systems, a high frequency structure of approximately constant angular spacing can be weakly observed in the angular range below 20<sup>°</sup> (provided the width of window of experimental smoothing is not too large), the spacing between minima being approximately 1.0<sup>°</sup>, 2.05<sup>°</sup> and 1.25<sup>°</sup> respectively.

Also, if any of the molecular collision partner systems is considered, a very low period frequency of undulation can also be observed. (As for the intermediate oscillations, this low period structure is less evident in the Hg\*/propane and Hg\*/propylene differential crosssections.) It is difficult to pick out the exact location of the maxima and minima of this slow oscillation because of the higher frequency structure superimposed on it, but the approximate location of these minima for the N<sub>2</sub>, CO and CO<sub>2</sub> systems are shown in Table 4.3. Unlike the intermediate frequency oscillations, the spacing between minima appears to decrease slightly as the scattering angle,  $\theta$ , is increased.

If the assumption is made that the system can be described in terms of a single potential, two of these observed frequencies can be used in an attempt to construct a deflection function for the system. Both the high frequency and intermediate frequency structures can be explained as arising from interference between different branches of the deflection function (see figure 4.16). Thus, the intermediate

TABLE 4.3

| Hg*/N <sub>2</sub> | Hg*/CO Hg*/CC |      |
|--------------------|---------------|------|
|                    |               |      |
| 28.4               | 20.5          | 24.8 |
| 41.7               | 33.8          | 43.3 |
| . 54.0             | 46.8          | 57.0 |
| 66.2               | 60.0          | 68.9 |
| 78.8               | 72.2          | 80.0 |
| 90.9               | 82.7          |      |

Minima Location of Low Period Structure



Figure 4.16 Deflection function

structure at an angle of observation,  $\theta$ , would arise from interference between the two attractive branches of the deflection function at  $l_1$ , and  $l_2$ , and the high frequency structure at the same angle from interference between the two innermost branches at  $l_2$  and  $l_3$ . Making use of semi-classical scattering theory, the angular spacing between adjacent maxima in the differential crosssection can be related to the spacing across the bowl of the deflection function, and is given by the expression:

$$\Delta \chi = 2 \Pi / (1_1 - 1_2)$$
 4.1

with  $l_1$  and  $l_2$  as above. (Thus as the deflection function well grows narrower,  $l_1 - l_2$  will decrease and the angular spacing of maxima will increase as was observed in the experimental data.) Similarly, the value of  $l_0$ , the location of the zero-crossing point of the deflection function (important since it determines the range of the potential) can be estimated from the angular spacing of the high frequency structure. The spacing is given by the relation:

$$\Delta X_{\rm HF} = 2 \Pi / (1_2 + 1_3)$$
 4.2

and since  $l_2$  and  $l_3$  converge for  $\chi = 0$ , at small angles the relationship reduces to :

$$\Delta X_{\rm HF} \simeq \Pi / l_0 = \Pi / kb_0 \qquad 4.3$$

If the structure for the Hg\*/CO system is taken as an example, a rough deflection function for the system can be produced. The high frequency structure as mentioned earlier , has an approximately constant angular separation of  $\simeq 1.25^{\circ}$  which leads to a value of lo  $\simeq$  144 (bo  $\simeq$  5.7 Å). The angular separation of the maxima in the cross-section and the resulting  $\Delta 1$  separation across the well of the deflection function are given in Table 4.4. From these, a deflection function has been constructed and is shown in figure 4.17. Unfortunately, there is no clear indication in the data of the rainbow angle and so a guess has to be made of a reasonable value by projection of the deflection function beyond the experimentally mapped angular range. Also since this method gives no alternative method of calculating it, the repulsive branch is obtained from a Lennard-Jones 12-6 potential giving rise to a deflection function with identical  $l_0$ value and comparable well-depth.

The potential corresponding to this deflection function can be calculated using the Firsor inversion procedure (FIR 53), as:

$$V(r) = E(1 - b^2 / r^2)$$

where E is the kinetic energy of relative motion and the separation, r, is given by:

$$r = b \exp \{ \prod_{b}^{-1} \int_{b}^{\infty} \chi(b') db' / (b'^{2} - b^{2})^{\frac{1}{2}} \}$$
  
= b exp{[ I(b') / ]] }  
4.5

TABLE 4.4

| x           | Δχ  | ۵1     | ۵۵   | X    | . Δχ | ۵1    | Δb   |
|-------------|-----|--------|------|------|------|-------|------|
| 153.9       |     |        |      | 64.2 |      |       | -    |
|             | 9.4 | 38.3   | 1.61 |      | 4.6  | 78.3  | 3.09 |
| 144.5       |     |        |      | 59.6 |      |       |      |
|             | 7.7 | 46.8   | 1.85 |      | 3.8  | 94.7  | 3.74 |
| 136.8       | 7 0 | 50.0   |      | 55.8 |      |       |      |
| 129.6       | 1.2 | 50.0   | 1.98 | 51.0 | 4.0  | 90.0  | 3.56 |
| 125.0       | 7.1 | 50.7   | 2 00 | 51.8 | 3 0  | 02.2  | 2 65 |
| 122.5       |     |        | 2.00 | 47.9 | 5.5  | 94.0  | 3.03 |
|             | 6.4 | 56.3   | 2.23 |      | 3.5  | 102.9 | 4.07 |
| 116.1       |     |        |      | 44.4 |      |       |      |
|             | 5.8 | 62.1   | 2.45 |      | 2.9  | 124.1 | 4.91 |
| 110.3       |     |        |      | 41.5 |      |       |      |
|             | 5.0 | 72.0   | 2.85 |      | 3.0  | 120.0 | 4.74 |
| 105.3       | F 6 | 64.0   | 0.54 | 38.5 |      |       |      |
| 99.7        | 5.0 | 64.3   | 2.54 | 25.0 | 3.3  | 109.1 | 4.31 |
| 55.7        | 5.0 | 72.0   | 2.85 | 35.2 | 3 /  | 105 0 | 4 10 |
| 94.7        |     | / 21 0 | 2.00 | 31.8 | 5.4  | 103.9 | 4.19 |
|             | 5.5 | 65.5   | 2.59 |      | 3.4  | 105.9 | 4.19 |
| 89.2        | ļ   |        |      | 28.4 |      |       |      |
|             | 4.8 | 75.0   | 2.96 |      | 2.7  | 133.3 | 5.27 |
| 84.4        |     |        |      | 25.7 |      |       |      |
|             | 4.5 | 80.0   | 3.16 |      | 2.7  | 133.3 | 5.27 |
| 79.9        |     | 75 0   |      | 23.0 |      |       |      |
| 75 1        | 4.8 | /5.0   | 2.96 | 20.0 | 3.0  | 120.0 | 4.74 |
| , , , , , , | 5.3 | 67.9   | 2.68 | 20.0 | 27   | 133 3 | 5 27 |
| 69.8        |     |        | 1.00 | 17.3 | 6.1  | 100.0 | 5.27 |
|             | 5.6 | 64.3   | 2.54 |      | 2.7  | 133.3 | 5.27 |
| 64.2        |     |        |      | 14.6 |      |       |      |



Since the inversion is based on semi-classical principles, the potential can at best only be obtained up to the classical turning point.

(In order to avoid the singularity which occurs at b' = b, the integration in the above expression is best written in a new form by means of the transformation  $b^2 = b^2 + \sigma^2$  which yields:

$$I(b) = \int_{0}^{\infty} \chi \{ (b^{2} + \sigma^{2})^{\frac{1}{2}} \cdot d\sigma / (b^{2} + \sigma^{2})^{\frac{1}{2}}$$
 4.6)

The potential thus produced can be used to perform a forward calculation of the differential cross-ection, which should hopefully correspond to the experimental data.

However, the differential cross-section produced from such a potential differs quite drastically from the experimental data for the Hg\*/CO system as given in figure 4.10 (and from the experimental data for the other molecular collision partner systems).

First of all, only the high and intermediate frequencies of oscillatory structure are reproduced, with no possibility of the observed low frequency oscillations. Moreover, a single attractive potential gives rise to interference structure not only of a regular angular frequency, but also of regular amplitude. In contrast, in the experimental data the relative amplitude of adjacent peaks can be seen to be most irregular. (The only possible exception to this general statement is

4.35

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the Hg\*/Na data at CM angles beyond  $\approx 25^{\circ}$  where the oscillatory structure is quite regular).

The overall envelope of the differential cross-sections has also to be For a single attractive potential the envelope (when considered. multiplied by the factor  $\Theta^{4/3} * \sin \Theta$  rises monotonically with  $\Theta$ to a fairly pronounced peak at the rainbow angle. The data collected for the Hg\*/Na system can be seen to possess such an envelope in the angular range from  $\simeq 25^{\circ}$  to  $80^{\circ}$  (the limit of experimental observation) but without the pronounced peak expected for the rainbow, which must be assumed to lie at a deeper angle. In contrast, the envelope for the Hg\*/CO system (and the other molecular collision partner systems) decreases fairly steadily over the whole observable This shape of envelope could however be produced angular range. from a single attractive potential if a suitable quenching function were to be applied.

But there are several noticeable features of the envelope in the experimentally observed data which cannot readily be produced from such a simple model for the scattering system.

In the Hg\*/Na data, and to a much less extent the Hg\*/Ne data, there is a pronounced "hump" in the scattering envelope at small angles (over the first 25<sup>0</sup>) which cannot at first sight be explained by a single potential surface. The "hump" could be due to

scattering from a very deep well giving rise to a rainbow angle of  $2\pi \pm \theta$ with  $\Theta \approx 20^{\circ}$ . But such a deep well would complicate the scattering pattern since the number of interferences would be greatly increased and the regular interference structure at angles greater than  $25^{\circ}$  would therefore not be possible. But, as can be seen by considering the classical expression for the scattering envelope:

$$\sigma(\theta) = \sum_{i=1}^{3} b_i / (\sin \theta \left| \frac{d\theta}{db} \right|_i)$$
 4.7

the experimentally observed increase of scattering intensity at small angles could also be produced if the derivative of the deflection function,  $d \theta/db$ , at those angles was reduced (such a reduction in  $d\theta/db$  having most effect on the envelope at the largest values of  ${\sf b}_i$  ). Thus the experimental hump can be produced by a softening of the attractive branch of the deflection function at large values of b, as shown in There is, however, another possible explanation for figure 4.18. the increase of intensity at small scattering angles. In the presence of a field, the Hg <sup>3</sup>P <sub>2</sub> state, which is the dominate state in the beam, can be split into the components  $m_i = \pm 2, \pm 1, 0$  depending on how the angular momentum vector, J, is aligned in the field, and the Na $^{2}$ S, ground state can similarly split into the components  $m_1 = \pm \frac{1}{2}$ , The molecular states arising from these various m<sub>i</sub> components may be coupled together to form a single effective potential for the system, as assumed earlier, but could also lead to distinctly different potential surfaces.



Figure 4.18 Deflection function with long range softening of outer attractive branch to produce greater intensity at narrow angles. The form of the interaction between two atoms depends on the strength of the axial interatomic field. If the field is strong, then the angular momenta of both atoms are coupled to it and the total angular momentum of the system precesses around this axis with a constant component along the axis which is given by:

$$\Lambda = \left| M_{L_1} + M_{L_2} \right|$$

$$4.8$$

where  $M_L$  is the projection of the atomic angular momentum, L, along the internuclear axis. Similarly, the spin angular momentum, S, will have a component along the axis given by:

$$\Sigma = \left| M_{S_1} + M_{S_2} \right|$$
 4.9

The total angular momentum of the system will then be given by:

$$\Omega = |\Lambda + \Sigma| \qquad 4.10$$

This type of coupling is known as Hund's case (a).

If, however, the spin orbit coupling between L and S in individual atoms is strong compared with the axial interatomic field, then L and S will couple to give the total angular momentum, J, for each atom and only the components of J along the internuclear axis will couple together. So the total angular momentum of the system is given by:

1 20

$$\Omega = \left| M_{J} + M_{J} \right|$$
 4.11

This type of coupling is known as Hund's case (c).

In a collision between two atoms, the system will start in a state corresponding to Hund's case (c) and as the internuclear separation decreases will move towards a state resembling Hund's case (a). Even at the distance of closest approach, however, the atoms may only have achieved some intermediate form of coupling.

If Hurd's case (c) is assumed for the  $Hg^{3}P_{2}/Na^{2}S_{1}$  system, then there results a system of 5 doubly degenerate states which may be characterised by:

$$\Omega = 2 * (5/2, 3/2, 3/2, 1/2, 1/2)$$
 4.12

This shows that there may be up to 5 different potential surfaces operating for the system, each with a separate contribution to the observed scattering patter. The observed "hump" in the experimental envelope can be explained if these potentials have radically different well-depths. Thus even two potentials, one leading to a rainbow angle of  $\approx 20^{\circ}$  and the other to a rainbow angle beyond the experimental limit (i.e. >  $80^{\circ}$ ), could give rise to the desired envelope. Even if the potentials are very similar in depth, the observed envelope could be produced if there were selective quenching of some of the molecular states, with the onset of hard quenching at an angle of  $\simeq 30^{\circ}$ .

The shape of the envelope in the Hg\*/Ne system is also difficult to rationalise with a single potential system. As can be seen from figure 4.9, the envelope increases monotonically with the scattering angle up to a limit of  $\simeq 65^{\circ}$ , but beyond this angle the envelope decays slowly until an angle of  $\simeq 115^{\circ}$ , beyond which there is a rather sharper fall-off in intensity. It is also noticeable that there is a strong oscillatory structure up to the angle of  $\simeq 115^{\circ}$  and beyond this angle the envelope is comparatively smooth, so that the peak at 115<sup>°</sup> can almost certainly be interpreted as a rainbow peak with the region beyond corresponding to the dark side of a rainbow. However, the overall shape of the envelope is not what would be expected from a single attractive potential, where the envelope would be monotonically increasing over the whole range up to the rainbow angle and the rainbow peak itself would be the dominant feature. The shape could perhaps be explained by the onset of a strong quenching function from the angle of 65<sup>0</sup> outwards, but for inert gas collisions with metastable mercury atoms quenching cross-sections are known to be very small (VAN 72, KRA 73) and could not therefore give rise to the observed falloff in the scattering envelope. Also, in contrast to the Hg\*/Na system, the angular spacing of the extrema of the interference structure is not regular (as was shown in fig 4.15) and consequently no single reasonably-shaped potential could account for the observed

scattering pattern.

But because of the 5 m<sub>j</sub> components of the  $Hg^3P_2$  state there are several potential surfaces for the Hg\*/Ne system, which if the coupling between them is weak, need not necessarily be considered as a single effective potential. Thus if Hurd's case (c) is used to describe the interaction between the  $Hg^3P_2$  and  $Ne^1S_0$  states, there results one singly degenerate and two doubly degenerate states with total angular momentum given by:

$$\Omega = 0, 1, 1, 2, 2 \qquad 4.13$$

Assuming the m states to be present in their statistical proportions j this gives rise to a system described in terms of three potentials weighted in the ratio of 2 : 2 : 1. The experimental envelope could be explained in terms of these three potentials if they gave rise to rainbow angles at  $\approx 70^{\circ}$ ,  $100^{\circ}$  and  $115^{\circ}$  respectively. (The first of these angles marks the start of the fall-off in the envelope, the second is the approximate position of a pronounced double peak which is followed by a deep minimum and slight increase in the rate of fall-off of the overall envelope and the third is the final pronounced peak in the scattering pattern, after which the envelope drops sharply away towards zero intensity.) The differential cross-sections arising from each of these potentials can be thought of as simply added together, so that below  $70^{\circ}$  there are three different contributions

(i.e. on the light side of all three rainbows), beyond  $70^{\circ}$  one contribution will start to become negligible (i.e. the dark side of the shallowest rainbow peak has been reached) and beyond  $100^{\circ}$  there will only be a major contribution from the deepest potential (i.e. the dark side of the second rainbow has now also been reached). The rapid fall-off beyond  $\approx 120^{\circ}$  will be due to the fact that this angular region corresponds to the dark side of all three rainbows. This addition of the scattering patterns of the three potentials will also give rise to an overall confused and irregularly spaced oscillatory structure as the interference patterns from the separate potentials move in and out of phase with one another. Thus, representation of the Hg\*/Ne system in terms of a three potential model could explain both the experimentally observed envelope and scattering pattern.

As has been shown, both the atomic systems, despite unusual envelopes can be explained in terms of totally elastic scattering. Further consideration must now be given to the molecular collision partner systems. As was pointed out earlier, the fall-off in envelope with increasing scattering angle observed in these systems can be explained by the onset of strong adsorption on the outermost branch of the deflection function at relatively small angles. An alternative explanation similar to that for the Hg\*/Ne system might be sought, but if the scattering envelopes for that system and the Hg\*/N<sub>2</sub>, Hg\*/CO and Hg\*/propylene systems are compared, it can be seen that in each of the molecular collision partner systems, the envelope falls

monotonically over nearly the whole observable angular range without a region of "normal" envelope behaviour as in the first 70° of the Hg\*/Ne data. Thus the fall-off in intensity is attributed to quenching of the metastable  $Hg^{3}P_{2}$  atom. Such a situation, where quenching is important for the molecular collision partner systems and negligible for an inert gas system, is confirmed by the relative quenching cross-section work of Van Italie et al and Krause et al, both of which reported cross-sections for intramultiple quenching of the  $Hg^{3}P_{2}$  state by the inert gases smaller than those for CO and  $N_{2}$ by a factor of at least  $3 \times 10^{-3}$ . Van Italie et al also give a relative cross-section for  $Hg^{3}P_{2} \rightarrow Hg^{3}P_{1}$  quenching for CO<sub>2</sub> which is a factor of  $3 \times 10^{-2}$  smaller than that for N<sub>2</sub>. However, they suggest that; as for the  $Hg^{3}P_{1}$  state (VIK 72) where the intramultiple transition to the  ${}^{3}P_{O}$  state is a minor process in quencing by CO $_{2}$ , the total quenching cross-section of  $Hg^3P_2$  by  $CO_2$  is of the same order of magnitude as the  $\mathrm{N}_{2}$  and CO total quenching cross-sections. Thus, although similar to the Hg\*/Ne envelope, the shape of the experimentally observed envelope for the Hg\*/CO<sub>2</sub> system can also be confidently attributed to the effects of quenching.

Although the overall shape of the scattering patterns could be reproduced simply by the effect of some suitable adsorption function on a single attractive potential, there are other features of the experimental data for the molecular systems which cannot.

In both the CO and N<sub>2</sub> data, there is a pronounced maximum at  $\simeq 100^{\circ}$ , whilst in the CO<sub>2</sub> data there is a less pronounced maximum at  $\simeq 125^{\circ}$ . These maxima do not correspond to the structure expected from typical rainbow peaks since the envelope does not fall off sharply enough beyond the maximum and since there is also definite oscillatory structure visible all the way out to the limit of the observations. There are however two possible explanations. In the first, a deflection function is required with a well depth greater than 180° so that the observed maximum is in fact a rainbow peak corresponding to a scattering angle of  $\simeq 260^{\circ} - 270^{\circ}$ . Thus, interference structure would be expected over the complete 180° range and the fall-off in intensity on the dark side of the rainbow would be hidden by scattering at lower angles. The second explanation assumes, as in the explanation for the Hg\*/Ne system, that more than just a single effective potential is operational in the scattering system. If two potentials are used to describe the system, there will be superposition of scattering from the separate potentials and the observed maximum in the envelope is explained as the rainbow peak of the shallower. The rapid intensity fall-off beyond the rainbow angle is thus masked by the structure of the deeper potential. In all three systems (i.e. Hg\*/CO, Hg\*/N<sub>2</sub>, Hg\*/CO<sub>2</sub> ) scattering from the deeper well probably extends beyond  $\ \ensuremath{\mathbb{I}}\$ , but due to adsorption (which can quite reasonably be expected to increase as the inter-molecular separation decreases on the outermost branch of the deflection function - see figure 4.19) the rainbow peak of this second potential has only a small





perturbation on the scattering pattern. Indeed the small increases in scattered intensity apparent in the N<sub>2</sub> and CO data at  $\approx 135^{\circ} - 145^{\circ}$  can be thus explained, i.e. a deeper second potential with a rainbow angle of  $\approx 220^{\circ} - 230^{\circ}$ . In the case of CO<sub>2</sub>, the second potential might be even deeper and its effect on the scattering pattern would then be less apparent due to the relatively increased intensity of scattering from smaller angles. Thus, both a single effective potential explanation and a multi-potential explanation can account for the observed maximum as a rainbow peak (whose half-width is  $\approx 20^{\circ}$ ) which has superimposed on it an oscillatory structure of  $\approx 5 - 6^{\circ}$  period arising from interference across a deflection function well - in the single potential case at an angle  $2 \pi - \theta_{\rm R}$  and in the two potential case, at the angle  $\theta_{\rm R}$  (the rainbow angle of the shallower potential) for the deeper potential.

But, account has also to be taken of the interference structure observed in the scattering data. As was shown earlier, three frequencies of oscillatory structure can be picked out and only two of these would normally be associated with a single attractive deflection function. The first of the models suggested above, i.e. a single deflection function with a rainbow angle in the range  $\Pi \rightarrow 2\Pi$ , fails to explain the low period structure and the fact that the intermediate structure observed (which is typical of structure arising from interference across the deflection function bowl) is also clearly disturbed by some other frequency, as evident in the irregular
amplitudes of successive peaks. An explanation for these features might be sought by extending the depth of the well to  $>2 \Pi$  (or, in the limit, to an orbitting situation), but such a situation would lead to a great number of interferences between the different branches of the deflection function. For example, a well depth of  $2 \Pi + 110^{\circ}$  for CO and N<sub>2</sub> (so that the rainbow peak corresponds to the observed maximum) would give rise to 15 different frequencies from interferences across the well. These will, however, lead to contributions to the differential crosssection of different intensity, as can be seen by considering the following semi-classical expression for the differential cross-section:

$$\sigma(\theta) = \left| \sum_{j=j}^{\Sigma} f_{j} \exp(i\beta_{j}) \right|^{2}$$
4.14

where  $\beta_j$  is the phase angle for the j<sup>th</sup> contributing branch and  $f_j$  is the scattering amplitude for the j<sup>th</sup> branch, as given by the classical expression:

$$f_{j} = (\sigma_{L})_{j}^{\frac{1}{2}} = (b_{j} / \sin \chi | \frac{d\chi}{db} |_{j})^{\frac{1}{2}}$$
 4.15

The above expression for the differential cross-section can be rewritten in the form:

$$\sigma(\theta) = \sum_{i,j}^{n} f_i f_j \cos(\beta_i - \beta_j) \qquad 4.16$$

where n is the total number of interfering branches of the deflection

function. Maxima and minima appear in the cross-section as the phase difference (  $\beta_{i}$  -  $\beta_{.j}$  ) changes through multiples of  $~\Pi$  , and the sizes of the contribution from interference between any two branches are given by the terms  $2f_{i}f_{i}\cos(\beta_{i}-\beta_{i})$  obtained when the above equation is expanded. The magnitude of any oscillation must therefore depend on the individual amplitudes f; arising from each branch and the contributions from the outermost branches would thus be expected to dominate. For the example being considered, there would be at least five or six such terms, all giving rise to interference structure at a different frequency, which might be expected to be of the same order of magnitude. In such a situation it is doubtful whether any oscillatory structure would survive the superposition of the individual contributions and even more unlikely that regular spacing of the oscillatory structure would be observed.

Thus, an explanation of the observed data has to be sought in a two potential model in which deflection functions similar to those in figure 4.20 (b) are required (the two deflection functions must have very similar zero crossing points, bo, if high frequency structure is to be observed and can be expected to be very similar at large separations where a C / R<sup>6</sup> dependence of the potential is expected). Since there will be different potentials for the various  $m_j$  states, the weighting of these two effective potentials will probably not be equal.

If there is no correlation between the potentials (as in the case of the





potentials from the different Hg<sup>3</sup>P<sub>2</sub> m<sub>j</sub> states in the Hg\*/Ne system) there will simply be superposition of the two interference patterns arising from the individual potentials and since both these patterns are regular and of not too dissimilar angular spacing, a "beat" frequency may result. This is the observed low frequency oscillation. The observed intermediate frequency is simply the interference structure of the deeper (and wider) deflection function which has a higher frequency than that of the shallower well and is therefore easier to identify. The irregular amplitude of this intermediate frequency is due to the effect of the interference structure from the shallower well.

With two potentials, however, there is also the possibility of mutual interference. This interference could be expected to be small compared to the interference across the bowls of the deflection functions since it depends on off-diagonal elements in the Hamiltonian of the system. Correlation will stop as the separation between the states increases and so any such interference will be strongest between the outer branches of the two deflection functions. Since these branches are relatively close together, the interference structure produced will be of lower angular frequency than that across the bowl of each deflection function well. This provides an alternative explanation for the origin of the "low" frequency oscillations.

Whether or not mutual interference exists, the observed high frequency oscillations will arise from interference between the positive and

negative repulsive branches of the deflection functions.

In order to test that the type of structure shown in the experimental data can be produced from a two potential system as above, a test case was computed using two Lennard-Jones 12 : 6 potentials giving rise to deflection functions with similar b<sub>0</sub> values but different well depths. As can be seen from figure 4.21, the interference structure across the deeper well is reproduced but that from the shallower is not so evident. The presence of low frequency undulations is not as clear as would be expected from the experimental data. However, the frequency of the observed intermediate oscillations suggest much wider deflection function wells than those produced by the Lennard-Jones potentials and this in turn would allow a greater separation between outer branches, giving not quite such a low frequency in the interference pattern as that shown in figure 4.21.

It would also be possible to produce the observed structure with more than two potentials in the system, but only two of these could be widely different, e.g. there might be two deep potentials which are very similar, but with slightly different rainbow angles, but which still produce very similar interference patterns in the observed range.

In conclusion, it can be seen that all the observed data can be devided into two classes - the atomic systems which are almost totally elastic and the molecular systems in which quenching plays an important role.

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The data for all the systems is however different from that expected from a normal single attractive potential. For the atomic systems, explanations can be found either in terms of a single effective potential for the system (with a modified attractive branch) or in terms of a set of potentials arising from the different m, states in the  $Hg^3P_2$ beam. (A discussion of which is more likely will be left till later.) For the molecular systems, a multi-potential explanation is necessary and the simplest explanation lies in a two potential system. (Again, the origins of these two potentials will be discussed later.)

In each case, the procedure of inversion from observed data to scattering potential(s) will be similar. Firstly, the intermediate and high frequency interference structure (and envelope where possible) will be used to construct a single deflection function for the system by means of a fitting procedure which minimises the angular positions of maxima and minima of the intermediate oscillatory structure. Any other necessary deflection function will then be fitted to reproduce the observed interference structure as closely as possible and, if necessary, a quenching function will also be introduced to reproduce the observed envelope as closely as possible. The deflection function(s) thus produced will then be inverted to the potential(s) for the system by means of the Firsor inversion procedure described previously.

## CHAPTER 5

## DETAILED ANALYSIS AND DISCUSSION

The contents of this chapter splits logically into three sections. In the first, details will be given of the general inversion procedure used to construct a deflection function from measured differential cross-sections. The second and third will be devoted to the application of this technique to the data obtained from the scattering of metastable mercury with, respectively, the various atomic and molecular collision partners outlined in the previous chapter. Both sections will also contain details of any amendments or additions to the general procedure required when the system cannot be adequately described in terms of a single effective potential. The results obtained in each section will then be discussed.

## A. Detailed Inversion Procedure

There are two possible methods of interpreting the observed differential cross-sections in terms of intermolecular potentials. The first involves using some parameterised form of the potential and working forward from this to produce differential cross-sections, which are then fitted to the observed structures. The second involves starting with the observed scattering patterns and trying to invert to unique potentials for the systems. For the forward calculations from potential to scattering pattern, it was found (BUC 68, DUR 68, etc.) that the usual simple parameterised forms of the potential, e.g. Lennard-Jones 12: 6 potential, were not sufficient and instead some formulation involving seven or eight parameters had to be used, thus greatly increasing the amount of computational time required. This difficulty is, however, overcome by inversion directly from the cross-section to the potential. This is done in two stages : firstly the construction of a deflection function from the differential cross-section and then the inversion of this deflection function to a unique potential by means of the Firsor inversion procedure (outlined in the previous chapter).

The procedure used in this work to construct a deflection function from an experimental cross-section is based on the inversion procedure outlined by Buck (BUC 71a). This was first used successfully to interpret the experimental data obtained by Buck and Pauly for the Hg ground state / alkali metal systems (BUC 71b, 72, 74). The starting

point of the inversion procedure is the uniform approximation of Berry (BER 66) which gives a formulation for the cross-section,neglecting high frequency oscillations, in terms of the deflection function and which is valid for the whole angular range. For the lit region,  $\theta < \theta_R$ , the cross-section is given by:

$$\sigma(\theta) = \pi(\sigma_{1}^{\frac{1}{2}} + \sigma_{2}^{\frac{1}{2}}) |z|^{\frac{1}{2}} \operatorname{Ai}^{\frac{1}{2}}(-|z|) + \pi(\sigma_{1}^{\frac{1}{2}} - \sigma_{2}^{\frac{1}{2}}) |z|^{-\frac{1}{2}} \operatorname{Ai}^{\prime 2}(-|z|)$$
 5.1

where  $\sigma_{\rm r}$  is the classical differential cross section given by:

$$\sigma_{i} = b_{i} / (\sin \theta \left| \frac{d \theta}{d b} \right|_{i})$$
 5.2

Ai and Ai are the Airy function and its first derivative, respectively, and z is given by:

$$z = 0.75 \{ 2 \eta (b_2) - 2 \eta (b_1) + k \theta (b_2 - b_1) \}^{2} 3 5.3$$

where  $\eta(b_i)$  is the phase shift at impact parameter  $b_i$  (as shown in figure 5.1) and k is the wave number.

Far from  $\theta_R$  the phase differences of the interfacing partial waves is large. Thus z is large and the Airy functions can be replaced by their known asymptotic approximations. Also, very near to the rainbow angle, z is small and the first term of equation 5.1 dominates the second, which can therefore be neglected. If these steps are carried out for large and small values of z, the differential cross-section given by equation 5.1 reduces to the result obtained by





Ford and Wheeler (FOR 59).

Since the phase-shift and deflection function are related as:

$$k \Theta(b) = 2 d \eta(b) / db = 2 \eta'(b)$$
 5.4

the differential cross-section obtained from equation 5.1 can be seen to be a function only of the impact parameter b and the angle  $\theta$ . If, however, there exists for the deflection function  $\theta = f(b)$  an inverse function  $b = f^{-1}(\theta)$ , then the cross-section can be defined solely in terms of  $\theta$ , and so can be compared directly with the experimental cross-section  $\sigma_{exp}(b)$ . It is much easier to find such an inverse function if the deflection function is split into several regions each characterised by a simple function form  $f_i(b)$  which can be easily inverted, so that the deflection function as a whole is given by:

$$\Theta(b) = \sum_{i} f_{i}(b) \qquad 5.5$$

where each  $f_i(b)$  contains coefficients which need to be evaluated before the deflection function is defined. The procedure is to calculate the differential cross-section (or some feature of the crosssection), X, at several angles using the above expression and to evaluate the coefficients by minimising the expression:

 $\sum_{j} (X_{j} \text{(experimental)} - X_{j} \text{(calculated)})^{2}$  5.6 where the expression is summed over j data points.

In the minimization procedure for the attractive region of the deflection function, Buck and Pauly used the angular positions of the rainbow oscillations because, if resolved, they are easily measured and their positions are almost completely unaffected by velocity and angular averaging (BAR 66). (This is not true about the amplitudes of the rainbow oscillations which are strongly dependent upon the velocity and angular distributions of the primary and secondary beams.) From equation 5.1 it can be deduced that the maxima of the rainbow oscillations are given by the values of z which give rise to the zeroes of Ai' and the minima by values of z which give rise to the zeroes of Ai . These can be found in literature, but if maxima are counted as integers and minima as half-integers (starting with the classical rainbow as N = 1) the positions of the extrema, z  $_{\rm N}$ , can also be calculated from the approximate formula (which arises from Ford and Wheeler's theory for the cross-section curve) :

$$(N - 3/4) 2\pi = (4/3) z_N^{32}$$
 5.7

This provides good values for the zero positions,  $z_N$ , in all cases above N = 2 (see table 5.1). Minimization is carried out between these calculated values and the experimental quantity  $z_N$ , which is exactly analogous to equation 5.3:

$$z_{N} = (0.75\{2n[b_{2}(\theta_{N})] - 2n[b_{1}(\theta_{N})] + k\theta_{N}[b_{2}(\theta_{N}) - b_{1}(\theta_{N})] \})^{23}$$
5.8

and which can easily be calculated for each of the regions f<sub>i</sub> (b). Buck and Pauly split the deflection function up into 5 different regions

TABLE 5.1

| 5   |                      |                       |  |
|-----|----------------------|-----------------------|--|
| N   | Z <sub>N</sub> (lit) | Z <sub>N</sub> (calc) |  |
| 1   | 1.019                | 1.115                 |  |
| 1.5 | 2.338                | 2.320                 |  |
| 2   | 3.248                | 3.261                 |  |
| 2.5 | 4.088                | 4.081                 |  |
| 3   | 4.820                | 4.826                 |  |
| 3.5 | 5.520                | 5.516                 |  |
| 4   | 6.163                | 6.166                 |  |
| 4.5 | 6.788                | 6.783                 |  |
| 5   | 7.372                | 7.373                 |  |
| 5.5 | 7.944                | 7.941                 |  |
| 6   | 8.488                | 8.489                 |  |
| 6.5 | 9.023                | 9.019                 |  |
| 7   | 9.535                | 9.535                 |  |
| 7.5 | 10.04                | 10.04                 |  |
| 8   | 10.53                | 10.53                 |  |
| 8.5 | 11.02                | 11.01                 |  |
| 9   | 11.47                | 11.47                 |  |
| 9.5 | 11.93                | 11.93                 |  |
| 10  | 12.39                | 12.38                 |  |

as shown in Figure 5.2, each being represented by a simple mathematically invertible function. Thus the attractive well of the deflection function is represented by a straight line in the region of zero crossing, a parabola in the region of the rainbow angle and an inverse power for the outermost branch (giving way to a  $C/b^6$  representation in the asymptotic region), as:

Region 2: 
$$\Theta = -a_1 (b - b_0)$$
,  $a_1 > 0$   
3:  $\Theta = -\theta_R + q (b - b_R)^2$   
4:  $\Theta = -c_1 b^{-C_2}$   
5:  $\Theta = -(15.\pi . V / 16.E) b^{-6} = -C b^{-6}$ 

where V is the van der Waal's constant and E is the interaction energy. The quantities  $\dot{z}_N$  are then given in the region of the minimum (i.e. between b<sub>2</sub> and b<sub>3</sub>) by:

$$z_{\rm N} = k^{2/3} q^{1/3} (\theta_{\rm R} - \theta_{\rm N})$$
 5.10

and in the regions next to the minimum (i.e. between  $b_0$  and  $b_2$  and at impact parameters  $>b_3$ ) by:

$$z_{N} = 0.75^{2/3} \left[ 2\eta_{0} + kb_{0}\theta_{N} + 0.5ka_{1}^{-1}\theta_{N}^{2} - k\beta^{0}(1-\alpha)^{-1}\theta_{N}^{1-\alpha} \right]^{2/3} 5.11$$

where  $n_0$  is the maximum phase (corresponding to impact parameter bo); for impact parameters  $b_3 < b < b_4$ :

$$\alpha = 1 / c_{2}, \beta = c_{1}$$

and for impact parameters  $b > b_4$ :

$$\alpha = 1/6$$
,  $\beta = C$ 



Figure 5.2 Parameterised deflection function proposed by Buck and Pauly.

At first sight, this leaves nine coefficients  $(n_0, b_0, b_R, \theta_R, q, a_1, c_1, c_2, C)$  to be evaluated in the minimisation procedure. The number of coefficients can, however, be reduced since boundary conditions (i.e. continuity in the deflection function and its first derivative) must apply at the intersection of regions and the van der Waal's constant, V, can be obtained from calculations. There are therefore only five coefficients remaining and these can be determined in the minimisation procedure from a minimum of five measured rainbow extrema. (These can be reduced still further if  $b_0$  is determined from high frequency oscillations.)

For the repulsive region of the deflection function at angles  $\theta > \theta_R$ , Buck and Pauly used the cross-section itself as the function, X, in the minimisation procedure and the actual functional form of the deflection function was given by:

Region 1: 
$$\Theta(b) = \pi - a_2 b - a_3 b^2$$
 5.12

The deflection function for small +ve values of  $\theta$  was taken as a continuation of the attractive region between impact parameters  $b_0$  and  $b_2$ , and the intermediate region was interpolated to provide a smooth function.

After testing the algorithm against differential cross-sections obtained from known Lennard-Jones potentials, Buck and Pauly successfully

applied the procedure to experimental data from the scattering of ground state Hg<sup>1</sup>So with Na, K, Cs, Li (BUC 716,72,74). Intermolecular potentials for each system were then produced from the calculated deflection functions by means of the Firsov inversion procedure (outlined in the previous chapter).

An attempt was made to apply this procedure to the data obtained from the Hg\*/Na system. The initial values required for the variable coefficients in the minimisation procedure were, however, more difficult to set, mainly because the data did not extend right out to the rainbow angle. A reasonable guess of the rainbow angle could be obtained by performing a rough fit for the deflection function from the equations:

$$\Delta \theta = 2 \pi / (1_1 - 1_2)$$

$$\Delta \theta_{\text{HF}} = 2 \pi / (1_2 + 1_2)$$
5.13

(as detailed in the previous chapter) and projecting both negative branches beyond the observed region. In this way it is also possible to obtain a reasonable guess for the initial values of the other variable parameters and also for the indexing of the rainbow peaks. Since there is no data beyond the rainbow angle, however, the positive branch of the deflection function had simply to be parameterised as in equation 5.12 and the coefficients  $a_2$  and  $a_3$  evaluated in terms of the other variable parameters from boundary conditions. The procedure was tested against structure produced by known Lennard-Jones potentials and against the

data of Buck and Pauly (BUC 71 b) and was found to be very effective. In the calculation for the experimentally obtained data, the value of the van der Waal's constant obtained by Darwall (DAR 71), i.e.  $590 \times 10^{-60}$  ergs cm<sup>6</sup>, was used and a good estimate of the zero crossing point of the deflection function, bo, was obtained from the high frequency structure noted earlier. Although several different indexings and rainbow angles were used, unfortunately only a reasonable fit to the angular positions of the rainbow extrema could be achieved (evaluated by comparison of the experimental data with the approximately apparatus averaged differential cross-section produced by a forward calculation from either the deflection function or the potential). This fit is shown in graph B of figure 5.3, with the corresponding deflection function and potential shown in curve A of figures 5.4 and 5.5 respectively.

This is not too surprising, however, when it is considered that the experimental data considered by Buck and Pauly had typical rainbow angles of  $30^{\circ} - 40^{\circ}$  and contained, on average, only twelve rainbow extrema whereas the data for the metastable Hg\*/Na system covers an angular range of  $80^{\circ}$  and has twice the number of extrema. Indeed, it appears that Buck and Pauly used only five extrema positions to evaluate the five variable parameters in the minimisation procedure and did not appear to check the potential obtained by running a forward calculation (although this might not have been necessary since the same potential was obtained from data at five different energies).





Figure 5.4 Deflection functions obtained from various fitting procedures for the Hg\*/Na data.





For the present system, to obtain a reasonable fit in the minimisation procedure, more flexibility was therefore required, i.e. more variable coefficients in the parameterisation of the deflection function. Accordingly, the deflection function was split into 7 regions as shown in figure 5.6, where each region is again represented by an easily invertible mathematical function, as:

Region 1 : 
$$\Theta = \pi - a_{\mu}b - a_{5}b^{2}$$
  
2 :  $\Theta = -a_{4}(b - b_{0}) - a_{3}(b - b_{0})^{2}$   
3 :  $\Theta = -\Theta_{b} - a_{1}(b - b_{1})$   
4 :  $\Theta = -\Theta_{R} + q(b - b_{R})^{2}$   
5 :  $\Theta = -c_{1}b^{C_{2}}$   
6 :  $\Theta = -\Theta_{c} + c_{3}(b - b_{4}) - c_{4}(b - b_{4})^{2}$   
7 :  $\Theta = -Cb^{6}$ 

where C takes exactly the same value as in equation 5.9. For Buck and Pauly's formalisation of the deflection function, two equations (5.10 and 5.11) were sufficient to define the quantity  $z_N$  for any negative value of the angle of observation. In the above formalisation, however, because  $\theta_b$  and  $\theta_c$  are variable, it is possible for one region of the deflection function to correspond to one of several regions on the opposite branch of the deflection function well. It is therefore necessary to evaluate the contributions for each region,  $X_N$  and  $Y_N$ for, respectively, inner and outer branches of the deflection function well. The quantity  $z_N$  is then formed in the minimisation procedure only after the values of  $\theta_b$  and  $\theta_c$  have been determined, as:





$$z_{\rm N} = 0.75^{2/3} (x_{\rm N} + Y_{\rm N})^{2/3}$$
 5.15

(The one exception is region 4, i.e. for angles of observation greater than  $\theta_a$ , where it is possible to calculate  $z_N$  directly and the result of equation 5.10 is obtained.) The quantities  $X_N$  for regions 2 and 3 were calculated (from equation 5.8) as:

Region 2: 
$$X_{N} = 2\eta_{0} + k\theta_{N}b_{0} + k\theta_{N}\beta - \frac{1}{2}ka_{2}\beta^{2} - ka_{3}\beta^{3}/3$$
  
3:  $X_{N} = 2\eta_{1} + k\theta_{N}b_{1} + k(\theta_{N} - \theta_{b})^{2}/2a_{1}$ 
5.16

and  $Y_{\mathrm{N}}$  for regions 5, 6 and 7 as:

Region 5 : 
$$Y_{N} = -2\eta_{+} + \kappa c_{1} b_{+}^{1-C_{2}} (c_{2} - 1)^{-1} - \kappa \theta_{N}^{1-\alpha} c_{1}^{\alpha} (1 - \alpha)^{-1}$$
  
6 :  $Y_{N} = -2\eta_{-} - \kappa \theta_{N} b_{+} + \kappa (\theta_{C} - \theta_{N}) \gamma_{-} - \kappa c_{3} \gamma^{2} / 2 + \kappa c_{4} \gamma^{3} / 3$   
7 :  $Y_{N} = -1.2 \kappa \theta_{N}^{5/6} C^{1/6}$ 

where 
$$\alpha = 1/c_{2}$$
 5.17  
 $\beta = \{ (a_{2}^{2} + 4a_{3}\theta_{N})^{\frac{1}{2}} - a_{2} \}/2a_{3}$   
 $\gamma = \{ c_{3}^{2} - |c_{3}^{2} - 4c_{4}(\theta_{C} - \theta_{N})|^{\frac{1}{2}} \}/2c_{4}$ 

and  $n_0$ ,  $n_1$  and  $n_4$  are the phase shifts corresponding to impact parameters bo, b1 and b4 respectively. Since the deflection function is a continuous function of impact parameter, however, the phase shifts  $n_1$  and  $n_4$  can both be calculated as functions of  $n_0$  if the boundary conditions between regions are used. Alternatively, if the asymptotic region is assumed only to contribute to the angular region in which the scattering data is obscured by the main beam profile,  $n_4$ can be arbitrarily set to zero since every expression for the quantity  $z_N$  will then contain a term of the form  $n_0 - n_4$  or  $n_1 - n_4$  The continuity condition at  $b = b_1$  need then only be applied to obtain:

$$n_1 = n_0 - ka_2 (b_1 - b_0)^2 / 4 - ka_3 (b_1 - b_0)^3 / 6 5.18$$

The set of equations for  $\Theta$  and  $z_N$  therefore contain the following variables:

which can be reduced to a sub-set of 9 if the deflection function is assumed to be continuous and smooth (as earlier for the deflection function of Buck and Pauly). Again, the van der Waals constant can also be calculated and the zero crossing point, bo, can be estimated (to the value  $b_0 = 6.05$ Å) from high frequency structure (see chapter 4) so that the following 7 coefficients are left as variables in the minimisation procedure:

 $a_1$ ,  $a_2$ ,  $b_R$ ,  $c_2$ ,  $\theta_b$ ,  $\theta_c$ ,  $\eta_0$ .

as compared to four variables when Buck's parameterisation of the deflection function was used.

The procedure was again first tested against structure produced by a known Lennard-Jones potential and the potential was accurately reproduced. For the experimental data from the Hg\*/Na system, the same data restrictions concerning the rainbow angle and supernumeracy indexing obviously still apply and the same procedure is used to obtain

5.19

initial values. Several sets of initial values and indexings were used with varying degrees of success (see figure 5.7 for graph of minimum value achieved in the fitting procedure against the indexing of rainbow maximum at 69.5°). The differential cross-section corresponding to the best fit achieved in the minimisation procedure is shown in figure 5.3, curve C. Neglecting the first  $25 - 30^{\circ}$ , it can be seen that the angular positions of the rainbow oscillations have been fairly well reproduced (see table 5.2 for comparison of experimental and calculated values of  $z_{\rm N}$ ), but that the envelope of the differential cross-section rises too steeply.

But as was pointed out by Boyle (BOY 71) and Pritchard (PRI 72) it is not really sufficient to fit only the angular positions of the supernumerary rainbow structure. Although it is possible to fix the position of  $b_0$ , by fitting only the positions of the extrema in the cross-section all that is really being determined is the value of the quantity  $\{b_1(\theta)-b_2(\theta)\}$ . It is therefore possible to construct several deflection functions which would give the same interference structure because the value of  $\{b_1(\theta)=b_2(\theta)\}$  at every  $\theta$  was the same, but which would be completely different in shape and would give rise to different potentials (see figure 5.8). In practice, it is possible to obtain reasonably accurate deflection functions if the gradient through  $\theta = 0$  is known and is then extended smoothly to fit the quadratic approximation at the minima. This gradient at  $\theta = 0$  can be found from the amplitude of glory oscillations in the total cross-section or, if the repulsive branch



Figure 5.7 Plot of minima values obtained versus indexing of peak at 69.5<sup>0</sup> in Hg\*/Na data.

TABLE 5.2

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| N    | z <sub>N</sub> (exp) | z <sub>N</sub> (fit) | θ <sub>N</sub> (exp) | θ <sub>N</sub> (fit) |
|------|----------------------|----------------------|----------------------|----------------------|
| 8    | 10.53                | 10.45                | 69.5                 | 69.0                 |
| 8.5  | 11.01                | 10.98                | 66.1                 | 66.0                 |
| 9    | 11.48                | 11.61                | 62.1                 | 63.0                 |
| 9.5  | 11.94                | 11.94                | 60.0                 | 60.1                 |
| 10   | 12.39                | 12.52                | 58.3                 | 57.2                 |
| 10.5 | 12.83                | 12.89                | 56.0                 | 56.3                 |
| 11   | 13.26                | 13.22                | 53.8                 | 53.5                 |
| 11.5 | 13.69                | 13.65                | 51.0                 | 50.8                 |
| 12   | 14.11                | 14.12                | 48.0                 | 48.1                 |
| 12.5 | 14.53                | 14.50                | 45.6                 | 45.4                 |
| 13   | 14.94                | 14.84                | 43.4                 | 42.8                 |
| 13.5 | 15.34                | 15.34                | 40.2                 | 40.3                 |
| 14   | 15.74                | 15.63                | 38.4                 | 37.7                 |
| 14.5 | 16.13                | 16.17                | 35.0                 | 35.3                 |
| 15   | 16.52                | 16.59                | 32.4                 | 32.8                 |
| 15.5 | 16.91                | 16.91                | 30.4                 | 30.4                 |
| 16   | 17.28                | 17.28                | 28.3                 | 28.3                 |
| 17   | 18.03                | 18.02                | 23.5                 | 23.7                 |
| 17.5 | 18.40                | 18.43                | 21.4                 | 21.5                 |
| 18   | 18.77                | 18.87                | 19.0                 | 19.3                 |

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has been fitted to data beyond the rainbow, by extrapolating the repulsive branch to zero angle.

If the gradient of  $b_2(\theta)$  cannot be found by either of the above methods, the deflection function can only be determined correctly if at least two experimentally determined functions of angle are used in the minimisation procedure. Apart from the extrema positions, Pritchard suggested that suitable functions were the average cross-section and the ratio of the lower envelope to the upper envelope of the supernumerary oscillations. The average cross-section i.e. the classical envelope, is given by:

$$\langle \sigma(\theta) \rangle = \sigma_1(\theta) + \sigma_2(\theta) + \sigma_3(\theta)$$
 5.19

where

$$\sigma_{i}(\theta) = b_{i} / (\sin \theta_{i} | \frac{d\theta}{db} |_{i})$$

Since expressions for  $b = b(\theta)$  and  $\Theta = \Theta(b)$  exist, values of  $\langle \sigma(\theta) \rangle$  can be easily evaluated. But because the absolute value of the cross-section was not measured, both experimental and calculated values of the envelope have to be normalised, as:

$$g_{j}(\theta) = \langle \sigma(\theta_{j}) \rangle / \langle \sigma(\theta_{j}) \rangle \quad i = 1 - j \qquad 5.20$$

Thus, in the minimisation procedure fitting will now be performed not only on the extrema positions but also on the relative size of the classical envelope at each angle corresponding to one of these extrema. The function to be minimised is therefore given by:

$$\sum_{j} \{ |z_{N_{o}j}(exp.) - z_{N_{o}j}(cal)|^{2} + S. |g_{N_{o}j}(exp) - g_{N_{o}j}(cal)|^{2} \}$$
 5.21

where j is the number of data points and S is a scaling factor allowing variation in the relative importance of fitting the angular positions or the envelope.

With this revised procedure, and using as initial values the return values of the variables obtained from the previous best fit, the deflection function and potential (both labelled C) shown in figures 5.4 and 5.5, respectively, were produced (the potential is also listed in table 5.3). Both can be seen to be slightly deeper than those for the best fit obtained without considering the envelope. The differential cross-section produced from this potential is shown in figure 5.3, curve D, and, for angles above thirty degrees, can be seen to match the experimental data fairly accurately in both the shape of the envelope and the angular positions of the supernumerary rainbows. (The experimental and calculated values of  $Z_N$ ,  $g_N$  and  $\theta_N$  are shown in table 5.4.)

At this stage it is worth carrying out a check on the consistency of the minimisation procedure by calculating the area enclosed by the deflection function thus produced. The spacing between two maxima is equivalent to a change of  $2\pi$  in the area bounded by the deflection function for the angular range separating the maxima and so the total number of maxima, N, supported by the deflection function between the rainbow angle and the angle of observation,  $\theta$ , is given by:

TABLE 5.3

,

| R∕xI0 <sup>®</sup> cm | V / x 10 <sup>14</sup> ergs |
|-----------------------|-----------------------------|
| 3.77                  | - 2.0                       |
| 3.80                  | - 15.2                      |
| 3.83                  | - 21.2                      |
| 3.86                  | - 27.8                      |
| 3.95                  | - 30.2                      |
| 4.23                  | - 27.7                      |
| 4.73                  | - 22.1                      |
| 5.44                  | - 15.3                      |
| 6.39                  | - 9.1                       |
| 7.50                  | - 4.2                       |
| 8.47                  | - 1.4                       |
| 9.13                  | - 0.35                      |
| 9.56                  | - 0.05                      |

TABLE 5.4

| N    | Z <sub>N</sub> (exp) | Z <sub>N</sub> (fit) | g <sub>N</sub> (exp) | g <sub>N</sub> (fit) | θ <sub>N</sub> (exp) | θ <sub>N</sub> (fit) |
|------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 12   | 14.11                | 14.11                | 1.39                 | 1.54                 | 69.5                 | 69.5                 |
| 12.5 | 14.53                | 14.57                | 1.37                 | 1.40                 | 66.1                 | 66.4                 |
| 13   | 14.94                | 15.15                | 1.35                 | 1.36                 | 62.1                 | 63.6                 |
| 13.5 | 15.34                | 15.46                | 1.32                 | 1.32                 | 60.0                 | 60.9                 |
| 14   | 15.74                | 15.72                | 1.32                 | 1.30                 | 58.3                 | 58.2                 |
| 14.5 | 16.13                | 16.08                | 1.31                 | 1.27                 | 56.0                 | 55.5                 |
| 15   | 16.52                | 16.38                | 1.27                 | 1.23                 | 53.8                 | 52.9                 |
| 15.5 | 16.90                | 16.80                | 1.24                 | 1.19                 | 51.0                 | 50.3                 |
| 16   | 17.28                | 17.24                | 1.18                 | 1.14                 | 48.0                 | 47.7                 |
| 16.5 | 17.66                | 17.60                | 1.13                 | 1.11                 | 45.6                 | 45.2                 |
| 17   | 18.03                | 17.93                | 1.09                 | 1.08                 | 43.4                 | 42.7                 |
| 17.5 | 18.40                | 18.40                | 1.04                 | 1.03                 | 40.2                 | 40.3                 |
| 18   | 18.77                | 18.68                | 1.00                 | 1.00                 | 38.4                 | 37.9                 |
| 18.5 | 19.13                | 19.20                |                      |                      | 35.0                 | 35.4                 |
| 19   | 19.48                | 19.59                |                      |                      | 32.4                 | 33.1                 |
| 19.5 | 19.84                | 19.90                |                      |                      | 30.4                 | 30.8                 |
| 20   | 20.1 <b>9</b>        | 20.17                |                      |                      | 28.3                 | 28.2                 |
| 20.5 | 20.54                | 20.46                |                      |                      | 26.4                 | 25.9                 |
| 21   | 20.88                | 20.91                |                      |                      | 23.5                 | 23.7                 |
| 21.5 | 21.23                | 21.24                |                      |                      | 21.4                 | 21.5                 |
| 22   | 21.57                | 21.62                |                      |                      | .19.0                | 19.4                 |

$$2\pi(N-1) = k \int_{b}^{b_{2}} \chi db$$

where :  $\theta = \chi(b_1) = \chi(b_2)$ 

The consistency check is important because in the minimisation procedure no account is taken of the angular region between the rainbow angle and the highest supernumerary maximum observed. Since fits were obtained with several different indexings of the supernumerary bows (the lowest value of the sum of squares being selected as the best fit) and since the rainbow angle was allowed to vary in the minimisation procedure, it is possible that the indexing and the area under the deflection function do not correspond.

Thus the areas contained by the deflection function between the rainbow angle ( $\theta_R = 165.6^{\circ}$ ) and angles of observation of  $19^{\circ}$ ,  $40^{\circ}$  and  $70^{\circ}$  (all approximating the positions of rainbow extrema) were calculated in order to compare the experimental value of N to that calculated using equation 5.22. The results, as given in table 5.5 below, show that the two compare very favourably (for the Hg\*/Na system under consideration, k was calculated as  $29.28^{\circ}A^{-1}$ ): Table 5.5? Comparison of supernumerary index numbers

| Region<br>(degrees)       | Area<br>(arbitrary units) | N<br>(calculated) | N<br>(index) |
|---------------------------|---------------------------|-------------------|--------------|
| $19^{\circ} - \theta_{R}$ | 18.96                     | 22.07             | 22           |
| $40 - \theta_R$           | 14.87                     | 17.52             | 17.5         |
| $70^{\circ} - \theta_{R}$ | 9.77                      | 11.85             | 12           |

5.28
It should also be noted that none of the attempted fits for the metastable Hg\*/Na system used data from the entire angular range observed experimentally. Thus in fitting the angular positions,  $z_N$ , of the extrema, only the data above 19° was used because below that angle the interference structure is not readily distinguishable. When fitting to the classical envelope only the region above 32°, where the envelope rises monotonically with angle, was used.

Another important point still to be considered is the fact that the inversion procedure has been carried out assuming a mono-energetic beam, whereas the experiments were carried out without velocity selection. As was shown earlier, the main-beam has a reasonably narrow velocity spread and a most probable velocity of 2.475 x  $10^{2}$  ms<sup>-1</sup>. Cross-beam velocities were, in general considerably higher and would have the normal Maxwellian velocity distribution expected from an effusive source, so that the major contribution to the energy spread will be from this source. It might be expected that because of this energy spread no interference structure could be resolved, but when forward calculations were run with cross-beam velocities of 30% either side of the most probable velocity (corresponding to the halfwidth of the distribution) it was found that although the positions of the rainbow and first supernumerary peaks were shifted slightly, the other supernumerary bows remained in fixed angular positions. (The fact that the angular locations of supernumerary bows and high frequency glory oscillations are largely unaffected by velocity and

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angular averaging was of course reported by Buck et al (BAR 66) and was the basis of Buck's choice of using the function  $z_N$  in the minimisation procedure).

Although the extrema positions in the CM frame are not affected by the velocity distribution, it is also necessary to check that structure is resolvable in the laboratory frame of reference since the transformation from one set of co-ordinates to the other involves the beam velocities. Thus transformation of a given CM angle,  $\chi$ , to the scattering angle,  $\theta$ , in the laboratory frame is carried out for the same range of velocities as above (the CM angle chosen is  $35^{\circ}$  since this is approximately the mid-point of the observed angular range). The results for the Hg\*/Na system are shown in Table 5.6 below and it can be seen that any structure with a period of  $\approx 1^{\circ}$  should be easily resolvable.

Table 5.6

| Cross-beam velocity                  | х                 | θ                 |
|--------------------------------------|-------------------|-------------------|
| $7.5 \times 10^2 \text{ ms}^{-1}$    | 35 <sup>0</sup>   | 5.54 <sup>0</sup> |
| $8.7 \times 10^2 \text{ ms}^{-1}$    | 35 <sup>0</sup>   | 6.00 <sup>0</sup> |
| $11.5 \times 10^{2} \text{ ms}^{-1}$ | . 35 <sup>0</sup> | 6.53 <sup>0</sup> |

## B. Atomic Systems

In this section, the results obtained from the scattering of the metastable  $Hg^3P_2$  beam with Na and Ne are analysed and discussed. Both systems are expected to be almost totally elastic, although there is the possibility of quenching by ionisation or electronic excitation of the collision partner for Hg\*/Na. Since the sodium data was used as a test case in the previous section, this system will be discussed first.

As was shown, a good fit to the sodium experimental data in both the scattering envelope and the angular positions of extrema could be achieved by the general inversion procedure if the differential cross-section below  $\approx 30^{\circ}$  was ignored. But in the experimental data the envelope of the differential cross-section, instead of dropping off smoothly with angle as could be expected, rises again to a distinct double maximum. In the previous chapter, two explanations were put forward to explain this "hump", one involving a single effective potential with a softening in the outer branch in the appropriate angular region and the other involving a multi-potential system with the different potentials arising from different m<sub>j</sub> components of the Hg<sup>3</sup>P<sub>2</sub> beam.

If the single effective potential is assumed, an alteration has to be made to the fitting procedure to allow for the necessary softening of the outer branch of the deflection function, which may take the form of a point of inflection or, since two maxima are distinguishable, a second shallow minimum. The parameterisation of the deflection function is,

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therefore, the same as in equation 5.13 until region 6 is reached, when three additional regions are included, as:

region 6: 
$$\theta = -\theta_{c} + c_{3}(b - b_{4}) - c_{4}(b - b_{4})^{2}$$
  
7:  $\theta = -\theta_{d} - c_{5}(b - b_{m})^{2}$   
8:  $\theta = -\theta_{e} + c_{6}(b - b_{n})^{2}$   
9:  $\theta = -\theta_{f} + c_{7}(b - b_{7}) - c_{8}(b - b_{7})^{2}$   
10:  $\theta = -Cb^{-6}$ 

This parameterisation is shown in figure 5.9 and provides the necessary flexibility to enable the "hump" to be fitted. Unfortunately, Berry's uniform approximation only takes account of two branch interference effects and in the minimisation procedure only those extrema positions used previously can therefore be included. It is possible, however, to take account of the scattering envelope over the entire observed angular range if care is taken to avoid the singularities which arise in the classical envelope from extrema in the deflection Both these restrictions make it difficult to obtain a sensible function. deflection function from the minimisation procedure unless very good initial estimates of the variable parameters are used. In such a situation, it was found easier to obtain a good fit to the experimental data by intelligent guesswork (i.e. starting with the deflection function shown in graph C of figure 5.4, modifying the attractive branch at angles below 20  $^{\rm O}$  and then running a forward calculation to obtain the differential cross-section for comparison with the experimental data) and then using the minimisation procedure to optimise this fit. In

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this way, the deflection function shown in figure 5.10 was obtained and the Firsov inversion procedure was then used to yield the potential shown in figure 5.11.

In the limit of strong coupling between the potentials arising from the different m<sub>j</sub> components of the mercury beam, a single effective potential, as above, can describe the scattering system (FLU 74). But in other cases it is necessary to describe the system in terms of several potentials. Thus an attempt was also made to represent the Hg\*/Na scattering in terms of two and three potential systems. In both cases it was assumed that there was one deep potential giving rise to a rainbow angle of  $> 80^{\circ}$  and that the other potentials were much shallower with all scattering confined to the region  $0 - 25^{\circ}$ .

The "hump" in the envelope at low angles is thus explained as super - position of the scattering patterns of these shallow potentials (and especially their rainbow peaks) on top of the interference structure of the deep potential. The deep potential was assumed to be that produced by the general fitting procedure. Since very little information other than the approximate position of the rainbow peak(s) could be obtained from the observed data, the shallow potentials were given a simple parameterised form, i.e. the Lennard-Jones 12 : 6 potential:

$$V(R) = 4\varepsilon \left[ (\sigma/R)^{12} - (\sigma/R)^{6} \right]$$
 5.24

and the values of  $\varepsilon$  and  $\sigma$  chosen so that the potential had the









required well-depth and approximately the same  $C_6$  asymptotic behaviour as the deeper potential. A forward calculation was then performed in which the structure from all the potentials representing the system were superimposed and the resulting differential crosssection compared with the experimental data.

For the two potential system, several different valuations of the potential parameters were tested and the best fit was achieved with:

 $\sigma = 5.5 \text{ Å}$ ,  $\epsilon = 2.5 \times 10^{-14} \text{ ergs}$ 

The two potentials are shown in figure 5.12, with the corresponding deflection function in figure 5.13.

The best fit for the three potential system was achieved in similar manner, the potential parameters being:

 $\sigma_1 = 5.45 \text{ Å}$ ,  $\varepsilon_1 = 1.54 \times 10^{-14} \text{ ergs}$  $\sigma_2 = 5.45 \text{ Å}$ ,  $\varepsilon_2 = 2.73 \times 10^{-14} \text{ ergs}$ 

The potentials and corresponding deflection functions are shown in figures 5.14 and 5.15 respectively. Initially the potentials were given equal weighting, but variation of the weighting to 2:2:1 (with the shallowest potential singly degenerate) only has any noticeable effect on the maximum at  $10^{\circ}$ .

Figure 5.16 shows the differential cross-sections obtained from the







Figure 5.13 Hg\*/Na deflection functions arising from the two-potential model for the system.





5 40



Figure 5.15 Hg\*/Na deflection functions arising from the three-potential model for the system.



5.42

general, modified single-potential, two-potential and three-potential fitting procedures, labelled A, B, C and D respectively. By comparison with the experimental data, it can be seen that graphs B and D are in good agreement with the observed envelope and oscillatory structure.

There is one other possible explanation of the observed data which has not yet been fully considered i.e. that the decrease in intensity of the differential cross-section above  $25^{\circ}$  is due to some quenching process. A rough estimate of the quenching cross-section involved can be obtained from Greene's formula for the probability of an inelastic collision at angle  $\Theta$  (ACP 66) :

$$P(b) = \left[\sigma_{calc}(\Theta(b)) - \sigma_{obs}(\Theta(b))\right] / \sigma_{calc}(\Theta(b))$$
 5.25

where  $\sigma_{calc}$  and  $\sigma_{obs}$  are the calculated and observed differential cross-sections, respectively. The total inelastic collision cross-section is then given by:

$$\sigma = 2\pi \int_{0}^{b_{T}} P(b) \cdot b \cdot db \qquad 5.26$$

where  $b_{T}$  is the impact parameter corresponding to the threshold of quenching. From the experimental data, P(b) can be estimated to be  $\simeq 0.3$  and  $b_{T}$  to be  $\simeq 9.5$ Å (corresponding to  $\Theta = 25^{\circ}$ ), which gives a value of  $\simeq 90$ Å<sup>2</sup> for the inelastic cross-section.

There are three possible inelastic processes: intramultiplet transitions between the different J states, transfer of electronic

excitation and ionisation (either Penning or associative). Since the internal energy change arising from intramultiplet transitions is quite large ( $\Delta E_{21} = 0.57$  eV and  $\Delta E_{20} = 0.79$  eV) the cross-sections are likely to be small (CZA 73), unless a molecular collision partner, which has internal degrees of freedom, is used (KRA 73). Czajkowski (CZA 73) al so found that cross-sections for the reaction:

$$\text{Hg}({}^{3}\text{P}_{1}) + \text{Na}({}^{2}\text{S}_{1/2}) \rightarrow \text{Hg}({}^{1}\text{S}_{0}) + \text{Na}^{*}$$

exhibited a pronounced resonance with the energy defect between the excited levels of the two atoms. Cross-sections in the range  $10^{-2} \text{\AA}^2$  - 30  $\text{\AA}^2$  were found for the various excited levels of Na. The energy mismatch between the Hg(<sup>3</sup>P<sub>2</sub>) state and the first excited state of Na is 3.33eV and no excited state of Na lies within 0.3eV (since the ionization potential of Na is 5.14eV) and so cross-sections for this process will also be small. The one remaining possibility is Penning ionisation of the Na atom. However, Hotop et al (HOT 70) have reported a cross-section of  $\simeq 15 \text{\AA}^2$  for the Penning ionisation of the cross-section for Hg(<sup>3</sup>P<sub>2</sub>) is unlikely to be much greater.

Thus, the experimental data is explained by either a single effective potential with softening in the attractive branch or by a system of three separate potentials, two of which give rise to rainbow angles in the angular region of  $0 - 30^{\circ}$ . It is now worth considering whether either or both of these explanations are chemically acceptable.

As was pointed out in the previous chapter, the interaction between two atoms depends on the strength of the axial interatomic field and, therefore, also on the internuclear separation. At large separation, the components of each atom's total angular momentum along the internuclear axis,  $M_J$ , will couple together to give the total angular momentum of the system (Hund's case (c)), as:

$$\Omega = \left| M_{J} + M_{J_{2}} \right|$$
 5.27

As the internuclear separation decreases and the axial field increases in strength, the angular momenta and spin angular momenta of both atoms are coupled to the field, with constant components along the axis,  $\Lambda$  and  $\Sigma$  respectively (Hund's case (a)). The total angular momentum is then given by:

$$\Omega = \left| \Lambda + \Sigma \right|$$
 5.28

If Hund's case (a) is applied to the interaction between ground state Na and the  ${}^{3}P$  and  ${}^{1}P$  excited states of Hg, the 24 states shown in table 5.7 below are produced.

Table 5.7

| Atomic states | molecular states                                                    | number           |
|---------------|---------------------------------------------------------------------|------------------|
| ²S + ³P       | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$               | 8<br>4<br>4<br>2 |
| ²S +¹P        | $^{2}\pi$ , $\Omega = 3/2$ , $1/2$<br>$^{2}\Sigma$ , $\Omega = 1/2$ | 4<br>2           |

F 1F

Although there is no method of determining the ordering of these states in energy, some idea of the relative positioning of states can be obtained if the atomic orbitals are considered. Thus it might be assumed that one of the  ${}^{2}\Sigma$  states will lie lowest in energy, whereas the other will be highest, since these resemble most closely the normal bonding and anti-bonding situations. The  ${}^{2}\pi$  state with pairing of electrons between the 4s and 6s orbitals would also be expected to lie second lowest in energy. The other  ${}^{2}\pi$  state could also be expected to be close in energy with the  ${}^{4}\pi$  state since the only difference is in  $\pi$  p-orbital. The  ${}^{4}\pi$  state might also be assumed to lie lower than the  ${}^{4}\Sigma$  state because of the lower electronelectron repulsion of the Na(s) orbital with the Hg (p- $\pi$ ) orbital than with the Hg (p- $\sigma$ ) orbital.

If Hund's case (c) is applied to the same set of atomic states, a set of 24 states is again produced as shown in table 5.8

| Ta | bl | e | 5 | • | 8 |  |
|----|----|---|---|---|---|--|
|    |    |   |   |   |   |  |

| Atomic states                                                                                                                               | Molecular states                                                                                                                                                                                                              | number            |
|---------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| ${}^{2}S_{1} + {}^{3}P_{0}$ ${}^{2}S_{1} + {}^{3}P_{1}$ ${}^{2}S_{1} + {}^{3}P_{2}$ ${}^{2}S_{1} + {}^{2}P_{2}$ ${}^{2}S_{1} + {}^{2}P_{1}$ | $\Omega = \frac{1}{2}$ $\Omega = \frac{3}{2}, \frac{1}{2}, \frac{1}{2}$ $\Omega = \frac{5}{2}, \frac{3}{2}, \frac{3}{2}, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}$ $\Omega = \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ | 2<br>6<br>10<br>6 |

In attempting to produce a correlation diagram, the only certainty is that the  ${}^{4}\pi_{5/2}$  state must arise from the  ${}^{3}P_{2}$  atomic state. It is also fairly certain that the  ${}^{3}P_{0}$  state will correspond to the low

lying  ${}^{2}\Sigma$  state, and the 'P, to the high  ${}^{2}\Sigma$  state. A possible correlation diagram for the system is shown in figure 5.17.

In a collision between two atoms, the system will start in a state corresponding to Hund's case (c) and as the internuclear separation decreases, will move towards a state resembling Hund's case (a), although this form of coupling may never be achieved even at the distance of closest approach. For the interaction of Hg  $({}^{3}P_{2})$  and  $Na({}^{2}S_{\frac{1}{2}})$  at very large separation, electron exchange will provide only a small contribution to the interaction energy and the potentials might be expected to split into three groups weighted 2 : 2 : 1 corresponding to the different  $M_{\ensuremath{\mathsf{I}}}$  states of the Hg atom (with the state of maximum M<sub>T</sub> lying lowest in energy if electron-electron repulsion is more important than dispersion forces). As the interatomic separation decreases and electron exchange becomes important, the pairs of degenerate states will split into their  $\Omega$  components. At small separations, the potentials will be classed in terms of the two states  $^{2}\Sigma$  and  $^{4}\pi$ , with the different  $\Omega$  levels essentially degenerate. (Note that figure 5.17 is only one possible configuration diagram and that the  $({}^{2}P_{2} + {}^{2}S_{\frac{1}{2}})$  interaction could lead to three separate molecular states  ${}^4\pi$  ,  ${}^4\Sigma$  and  ${}^2\pi$  ). At thermal energies, however, only the larger interatomic separations are studied where the atomic interaction is smaller than spin-orbit coupling (  $\simeq 10^{-12}$  ergs) and so splitting into three effective potentials could be expected. If the splitting between the three potentials is sufficiently small it may be



Figure 5.17 Possible correlation diagram for the Hg\*/Na system.

possible to represent the system in terms of a single effective potential.

Both fits are equally good (see figure 5.18 where the experimental, single potential and three potential cross-sections are labelled  $a_g$  b and c respectively) and both explanations would seem to be equally acceptable if some explanation can be found for the softening in the outer branch of the single effective potential. Similar potentials have been noted for some of the excited states of the inert gas dimers (MUL 70, COH 74), but here a potential barrier near  ${\tt R}_{\tt m}$  is typical and is generally associated with penetration of the ground state partner by the excited electron of the other partner, which is usually in a high electronically excited With metastable  $Hg(6^{3}P_{2})$ , however, the excited electron does state. not change its valence state and the softening of the potential curve is required at long range (R\*  $\simeq$  2R\*<sub>m</sub>). A more reasonable explanation would therefore lie in an avoided curve crossing, but inspection of the correlation diagram does not reveal any sharply plunging state which would cross the  ${}^{3}P_{2}$  levels at large separation. Curve-crossing is possible if, for example, the  ${}^{4}\Sigma$  state lies below the  ${}^{4}\pi$  state, but such a crossing would be expected at small separations where coupling between the atoms is strongest. The only other reasonable explanation is that the crossing is with some deeply plunging ionic surface, but again the crossing would seem to be at an unexpectedly large The three state explanation would therefore seem to be separation. the more likely (in agreement with the long range part of the correlation diagram for Hund's case (c) coupling).

E 10



Figure 5.18

For the Hg\*/Ne system, there is however such doubt and the only explanation of the experimental data requires the superposition of the scattering patterns of three effective potentials since both the extrema positions and the scattering envelope are unlike those normally seen from a single elastic potential. Because the experimental data was unusually noisy due to pressure difficulties, a case might be put forward for disregarding the irregularity of the interference structure and the anomalous envelope might then be explained by the onset of quenching at angles above 70°. For the Hg\*/Na system, three sources of possible quenching were identified, but two of these can be completely discounted for the Hg\*/Ne system. Excitation transfer is not possible because Ne has no excited states at a low enough energy to be reached by the 5.46eV available from the  $Hg(^{3}P_{2})$  state and ionisation is also impossible since the Ne atom has an ionisation potential of 21.56eV. Thus the only channel left open for quenching in the Hg\*/Ne system is the conversion of excitation energy to kinetic energy of the colliding particles. Such cross-sections have been shown to be very small unless the energy transfer is also small and the 0.57eV and 0.79eV available from intramultiplet transitions of the Hg atom would thus lead to only very small amounts of guenching. Thus the experimental results of Krause and Martin mentioned in the previous chapter are to be expected and the Hg\*/Ne interaction can be regarded as purely elastic scattering.

The origins of the three potentials required if the experimental data is

6 63

to be reproduced can be found if a correlation diagram is produced for the first few excited states of the system.

At small internuclear separations, the interaction between the ground state Ne ( $2^{1}$ So) atom and electronically excited  ${}^{3}P$  and  ${}^{1}P$  mercury atoms can be described in terms of Hund's case (a) coupling, resulting in the molecular states shown in table 5.9 below.

Table 5.9

| Atomic states         | molecular states               | number |
|-----------------------|--------------------------------|--------|
| · 'S + <sup>3</sup> P | $^{3}\pi$ , $\Omega = 2,1,0$   | 6      |
|                       | ${}^{3}\Sigma$ , $n = 1, 1, 0$ | 3      |
| 'S + 'P               | $\pi$ , $\alpha = 1$           | 2      |
|                       | 'Σ , Ω = 0                     | 1      |

This would appear to be an ideal situation where Hurd's rules on the ordering of states can be applied. Thus for molecular states evolving from the same atomic states, the states with highest multiplicity lie lowest in energy and, for states with the same multiplicity, the state with the highest angular momentum lies lowest, i.e.  $\Sigma > \pi$ . For splitting of the molecular states by spin-orbit into  $\alpha$  substates, the lower the value of  $\Omega$  the lower is the energy.

At larger separations, the interaction can be described in terms of Hund's case (c) coupling, when the molecular states shown in table 5.10 are obtained.

5 52

Table 5.10

| ' Atomic states                                           | molecular states         | number |
|-----------------------------------------------------------|--------------------------|--------|
| <sup>1</sup> S <sub>0</sub> + <sup>3</sup> P <sub>0</sub> | <b>Ω</b> = 0             | 1      |
| <sup>1</sup> S <sub>0</sub> + <sup>3</sup> P <sub>1</sub> | $\mathfrak{A} = 1, 1, 0$ | 3.     |
| <sup>1</sup> S <sub>0</sub> + <sup>3</sup> P <sub>2</sub> | n = 2, 2, 1, 1, 0        | 5      |
| <sup>1</sup> S <sub>0</sub> + <sup>3</sup> P <sub>1</sub> | Ω = 1,1,0                | 3      |

The correlation diagram in figure 5.19 can then be drawn with much more certainty than that for the Hg\*/Na system, and as expected shows that the system can be represented by a system of three potentials weighted 2:2:1.

Approximate well-depths for the three deflection functions are known if the three maxima in the experimental envelope at  $\simeq 65^{\circ}$ , 100° and 115° are interpreted as the rainbow peaks of the three potentials. (It is fairly certain that the last of these extrema must correspond to a rainbow angle since the cross-section, which up to this angle is oscillating strongly, starts to decay smoothly as would be expected on the dark side of a rainbow.) There is also some evidence of high frequency structure in the low angle region which if interpreted as glory oscillations leads to a bo value of  $\simeq 4\text{\AA}$  (10 = 88). The presence of these glory oscillations in a three potential system makes it necessary that all three deflection functions have very similar zero It might also be expected that the three potentials crossing points. would be similar at large separation and degenerate in their asymptotic regions.





Using the above facts it is possible to obtain a reasonable fit to the First of all, the deepest deflection function can experimental data. be obtained if the two peaks at 103<sup>0</sup> and 93<sup>0</sup> are assumed to be the first and second supernumerary bows superimposed on the rainbow peak of the middle potential, whose rainbow peak is situated at If the general fitting procedure is used (without fitting  $\simeq 100^{\circ}$ . of the scattering envelope) there are therefore six angular positions available to determine the six variable parameters (  $\Theta_{\mathsf{R}}^{}$  being held This should ensure a reasonable deflection function, although fixed). the low angle region is not tightly constrained. It is almost impossible, however, to use the fitting procedure to obtain the other two deflection functions because of the fact that the interference structure is very irregular. As a result, both these deflection functions were obtained as reduced forms of the deepest deflection function, with rainbow angles of 72<sup>0</sup> and 106<sup>0</sup>, instead of 126<sup>0</sup>. Forward calculations were then performed in which the scattering patterns corresponding to the three deflection functions were weighted in the ratio of 2 : 2 : 1, each potential in turn being given the single The best fit to the observed data was thus achieved with weighting. the deepest potential awarded a weighting of 1 (though as for the Hg\*/Na system, almost as good a fit can be achieved with the shallow potential singly weighted). Small modifications were then made to the deflection functions obtained as above in order to obtain a better fit to the experimental extrema positions and scattering envelope. With these limitations the fitted scattering pattern shown

in figure 5.20 was adjudged to be quite reasonable since it reproduces the main features of the experimental data. The sets of three deflection functions and potentials from which the scattering pattern is derived are shown in figures 5.21 and 5.22 respectively.

It has been shown that the experimental data for the Hg\*/Na and Hg\*/Ne systems can in both cases be best described in terms of a system of three potentials. The Hg\*/Na system could also be described in terms of a single effective potential (similar to the deepest potential in the three-state system), although no suitable explanation could be found for the required long-range softening in the attractive branch of this potential.

If the splitting in energy between the potential surfaces arising from the different m<sub>j</sub> states in the mercury beam is sufficiently small, it has been shown by Fluendy et al (FLU 74) that the coupling between the states can become strong enough to mix the states and the system can then be described in terms of a single effective potential. A useful measure of the extent of mixing of the states is given by:

$$p = \sigma \Delta \varepsilon / \hbar v$$
 5.29

where  $\sigma$  is the zero crossing point of the potential,  $\Delta \epsilon$  is the energy difference between the potentials and v is the relative velocity of the two atoms. A critical impact parameter for the onset of adiabatic motion, b<sub>c</sub>, can then be defined (assuming the potential is essentially



Figure









 $\propto R^{-6}$  near R = b) as:

$$b_c^* \simeq (3p/8)^{1/5}$$
 5.30

so that a single effective potential can describe the system for collisions in which  $b > b_C$  (and, conversely if  $b < b_C$  the collisions have to be defined in terms of separate adiabatic potentials). Thus, the three potential model requires that  $b_C > b_R$ , the rainbow value for the innermost deflection function bowl, if the three rainbow peaks are to be observed.

If the three potentials for the Hg\*/Na system are used, the two shallow potentials give a value of  $p \simeq 8$  which in turn gives  $b_c^* \simeq 1.25$ . Similarly for the deeper of the two shallow potentials and the deep potential, values of  $p \simeq 180$  and  $b_c^* \simeq 2.3$  are obtained. Since reduced glory and rainbow impact parameters are typically 1.05 - 1.1 and 1.1 - 1.2 respectively, the conditions for scattering from separate potentials are satisfied.

It is also possible to calculate the maximum splitting which would allow the system to be described in terms of a single effective potential. The condition for a single potential is that  $b > b_C$  and since interference structure in the experimental data is observed down to small angles, the requirement is therefore that  $b_C \simeq b_0$ , the zero crossing point of the deflection function, i.e. that  $b_C^* \simeq 1.05 - 1.1$ . For the Hg\*/Na system this yields a value of  $p \simeq 3.4 - 4.3$  which gives a maximum energy splitting of  $\simeq 0.7 - 1 \times 10^{-14}$  ergs if the system is to be described by a single effective potential.

If the results of equations 5.29 and 5.30 are applied to the potentials obtained for the Hg\*/Ne system, values of p = 22 and  $b_c^* \simeq 1.55$  are obtained for the two shallower potentials : for the deeper of these and the remaining potential, values of p = 28 and  $b_c^* \simeq 1.6$  are obtained. There can be no doubt therefore that separate scattering patterns should be observed for the three potentials obtained by the fitting procedure.

Thus for the collisions of metastable mercury with both Na and Ne, the experimental data can be interpreted as totally elastic scattering from a system of three separate adiabatic potentials.

Nothing has yet been said about the accuracy of the potentials obtained by the inversion procedure. There are three major sources of inaccuracy:

(a) In all systems studied, there is a sharp fall-off in the crosssections at small angles due to attenuation of the main beam which masks the scattering. As a result, this region is not used in the fitting procedure and there is therefore some inaccuracy in the asymptotic behaviour of both the parameterised deflection function and the potentials obtained

from them.

- (b) Because no fitting is done to the envelope beyond the rainbow angle, the repulsive branch of the deflection function,  $b_{i}(\Theta)$ , for positive angles of observation is obtained simply by evaluation of the variable coefficients  $a_4$  and  $a_5$  (see equation 5.14) from boundary conditions. It is possible to devise other parameterised forms for this region which will result in a completely different shape for this branch without noticeably altering the other two branches or invalidating the fitting procedure. In the Firsov inversion procedure it is seen that practically the whole repulsive branch of the potential is obtained from this positive branch of the deflection function. As a result, therefore, very little confidence can be placed in the repulsive branch of the potential from just above the minimum (and as a result the value of  $\sigma$  obtained is only approximate).
- (c) For the Hg\*/Na system there is also the disadvantage that the region around the minimum of the deep deflection function and the actual value of the rainbow angle are obtained by interpolation. This leads to inaccuracy in the well-depth of the potential and also in the location of the minimum, i.e. the interatomic separation Rm. The size of the error is probably reduced by the fact that the minimisation procedure

r ()

fits not only the extrema positions but also the scattering envelope and achieves good agreement between the area bounded by the deflection function and the extrema indexing used (see table 5.5).

It is difficult to assess the size of the error arising from each of the above sources but it is felt that the major source of error in the potential must be the repulsive branch which is also the region least likely to be probed in a thermal scattering experiment. Confidence in the potential is probably as shown in figure 5.23, where the size of the error limits shown are only approximate and were obtained by variations in the fitting procedure. Another source of possible error is, of course, the value of  $b_0$  obtained from high frequency structure and used as an initial value in the minimisation procedure. If doubts are expressed on this structure, then the value of  $b_0$  could be inaccurate, leading to inaccuracy in the values obtained for Rm and  $\sigma$  of the potential

Finally, it is fashionable to compare calculated potentials with some of the standard forms previously used in an attempt to reproduce experimental data. Thus figures 5.24 and 5.25 show the deepest of the three potentials for the Hg\*/Na and Hg\*/Ne systems, respectively, plotted beside the Lennard-Jones 12 : 6 potential having the same values of  $\varepsilon$  and  $\sigma$ . It is very noticeable in both cases that the calculated potentials have a much wider bowl and appear more attractive at intermediate angles. This behaviour was also noted by










Figure 5.25 Comparison of deepest Hg\*/Ne potential with LJ potential of same  $\epsilon,\,\sigma.$ 

Buck (ACP 75) for ground state mercury / alkali metal potentials but is not found in the inert gas ground state / metastable systems (WIN 76). The value for  $\sigma$  of 3.75 Å found for the Hg\*/Na system is also almost identical to the value found by Buck and Pauly (BUC 71b), but the value obtained for  $\varepsilon$  is much larger, with a value of 30.6 x 10<sup>-14</sup> ergs compared to the value of 8.79 x 10<sup>-14</sup> ergs obtained from their experimental data. It is difficult to explain this unless the unpaired electrons of the excited state give rise to some sort of binding not available to the ground state with its paired outer electrons.

## C. Molecular Systems

The scattering results obtained from the molecular collision partner systems will now be discussed in detail. As was shown in the previous chapter, each of these systems requires at least two potentials (with or without mutual interference) to explain the observed interference structure, with the simultaneous application of an appropriate quenching function to enable the experimental envelope to be reproduced. In every case, the general fitting procedure detailed in section A will be used to produce one of the potentials from the observed intermediate oscillations and from this potential and the low period oscillations, a second potential will be produced. A quenching function will then be applied to produce the required shape of the scattering envelope.

For use in the general fitting procedure, initial estimates for the variable parameters in the minimisation can be obtained by producing rough deflection functions (as outlined in chapter 4). Values for  $b_0$  and  $C^{(6)}$  are thus required. For the Hg\*/CO system, high frequency structure was observed with an angular spacing of  $1.25^{\circ}$ , which therefore gives rise to a  $b_0$  value of approximately 5.7Å (since k = 25.3 Å<sup>-1</sup>). No such structure was however observed in either the Hg\*/N<sub>2</sub> or Hg\*/CO<sub>2</sub> experimental data. Since CO and N<sub>2</sub> are isoelectronic and their reported molecular range parameters are very similar (3.65 and 3.7 Å respectively), it would seem reasonable to assume that the zero-crossing point in both systems would be

5 68

similar. The range parameter reported for  $CO_2$  is larger (3.95 Å) and the value for  $b_0$  might therefore reasonably be expected to be correspondingly larger than that for CO, a value in the range  $b_0 = 6.0 - 6.5$  Å thus being used as an initial estimate.  $C^{(6)}$ values of 83 x 10<sup>-60</sup>, 77 x 10<sup>-60</sup> and 112 x 10<sup>-60</sup> ergs cm<sup>6</sup> for Hg\*/CO, Hg\*/N<sub>2</sub> and Hg\*/CO<sub>2</sub> were also produced by using literature values of molecular polarisabilities and ionisation potentials and applying them to the London dispersion force formula.

The general fitting procedure was then applied to the angular positions of the maxima and minima of the intermediate structure (the shape of the classical envelope cannot be used because of the effects of quenching). Again, as for the Hg\*/Na system, since no definite rainbow angle is visible, an arbitrary indexing has to be assigned to the first discernable maximum (estimated by smooth extension of the negative branches of the rough deflection functions beyond the experimentally observed range). The best fits (the deep deflection functions shown in figures 5.26, 5.27 and 5.28) were obtained with the maximum at 154<sup>°</sup> for Hg\*/CO assigned to N = 6, the maximum at 163<sup>°</sup> for Hg\*/N<sub>2</sub> to N = 6 and at 78<sup>°</sup> for Hg\*/CO<sub>2</sub> to N = 19.

Although the dominant interference structure can be seen to arise from interference across the well of the above deflection functions for each system, a second potential is required in each case to reproduce the observed low period oscillations and the irregularity in amplitude of





- a,b addition
- c partial interference









the intermediate oscillations. (This second potential can also explain the maximum observed in the envelopes of both the Hg\*/CO and  $Hg*/N_2$  system at 90<sup>°</sup> - 110<sup>°</sup> if it is interpreted as arising from the rainbow peak of the shallower potential.) With two potentials, however, there is the possibility of mutual interference and different shallow potentials can be found, with and without inter-state interference.

When the scattering pattern is assumed to arise merely from the superposition of scattering from the deep and shallow potentials, the minima of the low frequency structure can be assumed to correspond to minima in the scattering pattern of both potentials. The number of maxima arising from interference across the deflection function well between the minima of the low frequency structure can be assumed to be less for the shallow potential than for the deep potential. These maxima must also lie on a smooth curve, their separation increasing with angle (cf indexing plots of figure 4.15) and so a reasonable guess can be made as to their location. With  $\theta_{p}$  and bo approximately known (bo will be similar to that for the deep potential if high frequency structure is observed), the general fitting routine can then be used to produce a shallow deflection function and potential. A forward calculation is then performed with the differential cross-sections from the two potentials added together and the results checked against the experimental structure. Although the method is rather crude, a reasonable fit can be achieved after

several attempts and the computational time for an exact fit would be excessive.

The deflection functions giving the best reproduction of the oscillatory structure observed for the Hg\*/CO, Hg\*/N<sub>2</sub> and Hg\*/CO<sub>2</sub> systems are labelled a, b in figure 5.26 and a in figures 5.27, 5.28 and the potentials arising from these are shown, with corresponding labelling, in figures 5.29 - 5.31. Two different shallow potentials are given for the Hg\*/CO system because that labelled b, although giving a slightly better fit, has a different b<sub>0</sub> value from the deep potential. This might be important if the experimentally observed high frequency structure is to be believed since deflection function b would give rise to high frequency structure with a spacing  $0.2^{\circ}$  different from the experimental.

If interference, between the outer attractive branches of the two deflection functions is assumed to lead to the observed low frequency structure, the spacing between these branches can be obtained from the same type of semi-classical approximation used to fit the interference structure across the deflection function well, i.e.

$$\Delta \chi = 2\pi / \Delta l \qquad 5.31$$

where  $\Delta \chi$  is the angular separation of two low frequency structure minima and  $\Delta 1$  the separation of the two outer branches. Since the outer branch of the deep deflection function is already known, the



Figure 5.29 Potentials for the Hg\*/CO system

a,b addition

c partial interference



Figure 5.30 Potentials for the Hg\*/N<sub>2</sub> system

a addition b partial interference





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outer branch  $b_i(\Theta)$  of the shallow deflection function is thus fixed. With  $\Theta_R$  and  $b_0$  also known, the remainder of the deflection function can be reasonably interpolated and the potential obtained by the Firsov inversion method. The scattering pattern arising from the interfering potentials can be produced from the semi-classical relationship:

$$\sigma(\Theta) = \sum_{i,j} W_{ij} f_i f_j \cos(\beta_i - \beta_j)$$
 5.32

where  $W_{ij}$  is the weighting for each contribution. W will have a value in the range  $0 \rightarrow 1$  for interference between the outer branches and 0 for all other cross-potential terms.

The only difficulty in the method is that an arbitrary point has to be chosen where the phase of the two outer branches start to diverge (assuming that both potentials have the same asymptotic  $C^{(6)} / R^6$ dependence) and two or three attempts are possibly needed before a good fit to the experimental oscillatory structure is achieved.

The deflection functions and potentials obtained for Hg\*/CO, Hg\*/N<sub>2</sub> and Hg\*/CO<sub>2</sub> are again plotted in figures 5.26 - 5.31, with the plots for Hg\*/CO labelled c and those for the Hg\*/N<sub>2</sub> and Hg\*/CO<sub>2</sub> labelled b. In each case, the best reproduction of the observed structure was obtained with only partial interference between the outer branches, i.e.  $W_{ij} = 0.05 - 0.4$ .

Although both these methods reproduce the positions and irregular structure of the extrema of the observed cross-sections, the overall shape of the envelope is wrong and has to be modified by the application of a suitable quenching function. In a full quantum mechanical treatment, the effect of quenching on the elastic differential cross-section can be shown by the equation:

$$\sigma_{P1}(\theta) = (1/4k^2) \Sigma (21+1)^2 P_1^2(\cos \theta) (1-2a(1)\cos 2n(1)+a(1)^2) 5.33$$

where the probability of non-adiabatic collision at separation 1, P(1), is given by  $(1.0 - a(1)^2)$ . The total elastic cross-section is then given by:

$$\sigma_{\text{elastic}} = (\Pi / k^2) \Sigma (21+1) (1 - 2a(1) \cos 2n(1) + a(1)^2) 5.34$$
  
and the total non-adiabotic cross-section by:

$$\sigma_{non-ad} = (\Pi / k^2) \Sigma (21+1) P(1) \approx 2 \Pi \int_{0}^{\pi} b P(b) db$$
 5.35

It only remains therefore to find an appropriate function P(1) or P(b)and to apply this to equation 5.33 to obtain the elastic differential cross-section. This will be the observed cross-section since only excited metastable mercury atoms are detected.

A common functional form for P(1) arises from the optical model of quenching, which gives:

$$P(1) = P_{LIM} / [1.0 + \exp((1 - 1_{ST})/d_1)]$$
 5.36

where  $P_{LIM}$  is the limiting probability of attenuation (i.e. takes the values 0 - 1),  $1_{ST}$  is the 1 value for which P(1) = 0.5 and  $d_1$  governs how quickly  $P_{LIM}$  is obtained. Figure 5.32 shows plots of P(1) in which  $P_{LIM} = 1$ ,  $1_{ST} = 220$  and  $d_1$  takes the values of 1, 10, 25, 50 and 100, the last of these curves being the least step-like.

Attempts to reproduce the experimental scattering envelopes using the above functional form for P(1) were reasonably successful, but it was found that a better fit could be obtained by specifying P(1) pointwise and calculating a smooth curve through the given points. Although no minimisation procedure was used (since the computation would have again been prohibitive), it was found that reasonable fits to the observed data could be produced readibly easily. The experimental cross-sections and the various fits to them are shown in figures 5.33, 5.34 and 5.35 (for the Hg\*/CO, Hg\*/N<sub>2</sub> and Hg\*/CO<sub>2</sub> systems respectively), with the labelling corresponding to that of the deflection functions and potentials of figures 5.26 - 5.31. There would appear to be very little to choose between the different fits obtained, with perhaps a marginal improvement when inter-state interference is included.

It should be pointed out that the potentials obtained cannot be considered to be unique since it is insufficient to fit only the angular positions of the interference structure (see section A). For the atomic collision

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partner systems, this problem was resolved by using the shape of the scattering envelope as a second experimentally determined function in the fitting procedure. If, however, the shape of the scattering envelope is affected by non-adiabatic processes, this second minimisation function cannot be used. Such is the case for the systems considered above, where the observed envelope could only be reproduced by the application of an adsorption function. It is clear that if the potentials produced by fitting only the maxima locations (and their corresponding differential cross-sections) are wrong, then the adsorption functions P(b), required to reproduce the experiment al scattering envelopes will also be incorrect, i.e. if the cross-section obtained from a potential is too large, then the adsorption function has to be correspondingly too large in order to give the observed envelope.

The adsorption functions used in the Hg\*/CO, Hg\*/N<sub>2</sub> and Hg\*/CO<sub>2</sub> systems are shown plotted in figures 5.26 - 5.28, and each can be seen to be fairly long ranged, rising to >0.9 at almost 9 Å. Not surprisingly, therefore, the non-adiabatic cross-sections obtained are also large, with values of  $325\text{Å}^2$  for CO,  $304\text{\AA}^2$  for N<sub>2</sub> and  $265\text{\AA}^2$  for CO<sub>2</sub>. These are considerably larger than the values reported by Baumann et al (BAU 74), who reported total quenching cross-sections of  $11\text{\AA}^2$  and  $63\text{\AA}^2$  for collisions of Hg(<sup>3</sup>P<sub>2</sub>) atoms with N<sub>2</sub> and CO<sub>2</sub> respectively. They also reported much larger values for depolarisation collisions (up to 600  $\text{\AA}^2$ ) but these probably arise

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from a long range angle dependent term in the potential which is unlikely to be important in electronic state quenching.

A lower cross-section implies a much shorter ranged quenching function (a maximum impact parameter for quenching of less than 5Å is required if a cross-section of  $60Å^2$  is to be achieved) and a shorter ranged potential would therefore also be required for any detectable effect on the cross-section. This could be achieved if the zero-crossing point of the deflection function was reduced, but would also mean that the high frequency structure observed for the Hg\*/CO system could not be reproduced. To produce quenching crosssections of under  $100^{100}$  would require a reduction in b<sub>0</sub> of almost  $4\overset{\text{O}}{\text{A}}$  for each of the systems considered, resulting in very low crossing points since values of  $b_0 = 5.7 - 6.2$  Å were obtained for the best fits of the three deep deflection functions. Although perhaps not too much reliance should be placed on the bo values obtained from the high frequency structure, the range parameters obtained in all of the inverted potentials are in reasonable agreement with those obtained by simple combining rules (using literature values of atomic range parameters). as can be seen from table 5.11 below.

Table 5.11

| System              | o (calculated) | ♂ (experimental) |
|---------------------|----------------|------------------|
| Hg*/CO              | 3.65 X         | 3.0 - 3.8 Å      |
| Hg*/N <sub>2</sub>  | 3.7 Å          | 3.0 - 3.7 Å      |
| Hg*/CO <sub>2</sub> | 3.9 Å          | 3.65 - 3.9 Å     |

Clearly if  $b_0$  were reduced by  $4^{\circ}$  the potentials obtained would have unacceptably low range parameters.

The potentials obtained are also very wide (the deep Hg\*/CO potential is shown plotted with a Lennard-Jones potential of the same well-depth and  $R_m$  value in figure 5.36) and smaller quenching cross-sections would be obtained from a narrower well. This is not possible, however, if the intermediate frequency oscillations are to be interpreted as interference structure across the deflection function bowl since the range of the outer branch of V(R) comes directly from the range of the outer branch of  $\Theta$ (b).

A smaller value of quenching cross-section could be obtained however if the adsorption function had a different shape from that shown in figures 5.26 - 5.28. With the low energy of the experiments (in the region of 6 - 10 x 10<sup>-14</sup> ergs), the experimental information for the low impact parameter region, i.e. below bo, is very poor and the adsorption function could conceivably be restricted to a narrow band in the region of the deflection function well (as in figure 5.37). With such an adsorption function, the cross-sections obtained would be in the region of 140 - 180  $A^2$ .

If the potentials obtained from the fitting procedure are correct, it appears that very poor agreement with Baumann's cross-sections is therefore obtained in interpretation of the three systems by a two

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of same  $\sigma$  and  $\epsilon.$ 

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potential model. A second model has therefore been proposed (COS 76) in which the diabatic Hg( ${}^{3}P_{2}$ ) - AB ( ${}^{1}\Sigma$ ) state is depressed by interaction with another close lying state. Thus the rather pronounced dip observed in the scattering envelope of each system at angle  $\chi_{1}$  (see figures 5.33 - 5.35) is interpreted as the point of an avoided crossing. The scattering at angles below  $\chi_{1}$ is interpreted as arising from a single state (such as the shallow potentials obtained in the original model). The motion over the crossing point is assumed to be sufficiently adeabatic that most of the trajectories follow the second deeper surface, but with sufficient left following the upper state that the shallow rainbow at  $\chi_{2}$ will be observed at very low amplitude. Adsorption is assumed to occur only on the lower surface.

The proposed deflection functions and adsorption function are shown in figure 5.38, with the shallow deflection function that shown in graph (a) of figure 5.26 for the Hg\*/CO system. The steepness of the attractive branch on the lower surface is greater than in the deep deflection function of the original model in order to permit a much reduced P(b) at large b. Strong absorption is however still required from approximately  $b = b_R$ .

From this model, quenching cross-sections of  $160 - 200 \text{ }^{A^2}$  should be obtained if a high value of P(b) is assumed to b = 0. But if an adsorption function similar to that of figure 5.37 is assumed, then





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cross-sections of 40 - 75  $Å^2$  could be expected. Besides supplying more reasonable quenching cross-sections, the model also seems capable of reproducing most of the experimentally observed features, the only slight problem being the low frequency oscillations observed in the Hg\*/CO<sub>2</sub> data at angles below  $\chi_1$ . A possible explanation lies in interference between the outer branch of the shallow deflection function with the inner branch of both surfaces.

So far no mention has been made of the possible states arising from the interaction between the metastable  $Hg({}^{3}P_{2})$  state and the AB ground state. In the linear configuration, the correlation diagram is likely to be similar to that for the Hg\*/Ne system, with the  $\Omega = 0, 1, 2$  states from Hund's case (c) coupling correlating with  ${}^{3}\Sigma$  and  ${}^{3}\pi$  states arising from Hund's case (a). It is therefore possible to interpret the results in terms of a two or three state system (or indeed in terms of a single effective potential if the  $\Omega = 0, 1, 2$  states are similar enough).

The source of the configuration interaction responsible for quenching of the Hg( ${}^{3}P_{2}$ ) state is most likely the interaction of the Hg( ${}^{3}P_{2}$ ) - AB( ${}^{*}\Sigma$ ) state with a state dissociating to Hg( ${}^{1}S_{0}$ ) and one of the electronically excited levels of the molecular collision partner. CO, N<sub>2</sub> and CO<sub>2</sub> each have a  ${}^{*}\pi$  or  ${}^{3}\pi$  state close to 6eV as their first excited state and this level is nearly resonant with the Hg( ${}^{3}P_{2}$ ) state at 5.43eV, so that interaction is possible.

CHAPTER 6

# CONCLUSIONS

One of the major aims of this work was to investigate whether a complex multi-state system of asymptotically degenerate potentials could be interpreted in terms of some simple potential model. In general the interpretation was relatively successful and good agreement was obtained with the experimental differential cross-section in every system.

Both the Hg\*/Na and Hg\*/Ne systems were interpreted as being purely elastic (despite the fact that ionization is energetically possible for Na), with the superposition of scattering of three weighted potentials. Both sets of potentials were produced by considering not only the extrema positions of the differential cross-sections but also the overall scattering envelopes, so that a reasonable amount of confidence can be held in their uniqueness.

All of the molecular collision partner systems exhibited signs of quenching, but the data for propane and propylene was not adequately resolved to be interpreted. Although good fits were obtained for the Hg\*/CO, Hg\*/N<sub>2</sub> and Hg\*/CO<sub>2</sub> systems in terms of a two potential model with the application of a long range adsorption function to both surfaces, the values obtained for the total quenching cross-sections were unusually large. In an attempt to explain the experimental results while producing an acceptable value of the quenching cross-section, a second model was produced in which an avoided crossing was assumed on the long range attractive branch of

a shallow potential. The model is perhaps more realistic in that quenching by a shorter-ranged adsorption function is only required on the deeper adiabatic surface and the values of cross-sections obtained would be favourably comparable with previous experimental results. The two models are not incompatible and the first method could be used to produce the required potentials for the second if a restraint is placed on the shape of the outer branch of the deep deflection function. (It was also proposed that the shallow deflection function of the first model could be used unchanged in the second.) This emphasises the fact that the potentials obtained in the first model by the general fitting procedure (without the constraint of fitting the classical envelope) cannot be unique. Little confidence can be given to the quenching cross-sections thus obtained since P(b) and V(R) are directly related.

A general feature of the results for each system was that the potentials produced were all very long range, their bowls being much wider than Lennard-Jones potentials of comparable range and well-depth. It was found that an  $R^{-6}$  potential dependence could not be used for impact parameters much less than 10Å. A similar situation was reported by Buck (ACP 75) for the scattering of ground state  $Hg({}^{1}S_{O})$  atoms.

Some doubt also exists about the values of  $b_O$  used as input to the minimisation procedure for some of the systems fitted. High

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frequency structure of approximately the same spacing as the apparatus resolution was weakly discernible in the experimental cross-sections of only three systems. This situation could be improved by examining the low angle region of every system in more detail.

Modifications to the experimental set-up to include velocity selection of both beams and state selection of the mercury beam should help to provide the required detail. After the reductions due to velocity and state selection, the current beam intensity would probably still be high enough to enable the low angle range near the beam centre to be examined, but it might be necessary to collect more data at every point on a scan.

The intensity problem would be solved by the introduction of a nozzle source. This would have the advantage of producing variable energy beams and at higher energies than available from a thermal source, but would probably require extensive alterations to the experimental apparatus with the introduction of differential pumping. Such a source would, however, allow scans over the whole angular range of the apparatus even with velocity and state selection.

Much work obviously remains to be carried out on these and other systems before a complete understanding can be obtained of the interactions of the  $Hg(^{3}P_{2})$  state. In particular it would be interesting to investigate each of the systems studied in this work

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with the complexity of the states of the colliding particles reduced by state selection of the mercury beam. Differential cross-section results over a full  $180^{\circ}$  CM scan for each individual  $m_j$  component of the beam would help enormously in the understanding of each of the systems. More confidence could also be given to the potentials produced if the experimental results were obtained at more than a single interaction energy for each system.

Even with such data it is difficult to see how, for systems in which the scattering envelope is strongly perturbed by non-adiabatic processes, the interaction potential(s) and adsorption function can be obtained unambiguously. However, the data could perhaps be used as a check on whether conflicting theoretical models are equally valid.

## APPENDIX A

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# Elastic scattering of slow electronically excited mercury atoms from neon and alkali-metal atoms: the interatomic potentials

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Abstract. A modulated crossed-beam technique has been used to study the thermal-energy elastic scattering of electronically excited mercury in the  $6^{3}P_{2}$  state from Ne, Na, K and Rb. Relative differential elastic cross sections have been measured and interpreted to yield interatomic potentials. In the alkali-metal/Hg\* systems, two models based on spherical potentials were in excellent agreement with observation. In both models, a potential (tentatively ascribed to an  $\Omega = \frac{5}{2}$  or  $\frac{3}{2}$  state) with  $\epsilon = 30 \pm 2 \times 10^{-14}$  erg and  $R_{\rm m} \simeq 40$  Å (Na/Hg\*),  $R_{\rm m} \simeq 4.6$  Å (K/Hg\*) was responsible for the major features in the observed cross sections. Small-angle structure, however, could be interpreted in two ways, either as arising from a soft region at large R in the single potential or due to the operation of two additional rather shallow potentials ( $\epsilon = 2.7 \pm 0.5$  and  $1.5 \pm 0.5 \times 10^{-14}$  erg) ( $\Omega = \frac{3}{2}$  and  $\frac{1}{2}$  states).

In contrast, the Ne/Hg<sup>\*</sup> system could not be fitted by any plausible single potential and three potentials having  $\epsilon = 8 \pm 4$ ,  $14 \pm 4$  and  $22 \pm 2 \times 10^{-14}$  erg tentatively identified as  $\Omega = 0$ , 1 and 2 states, respectively, were required.

In neither case was there any evidence for quenching (J transitions) of the metastable atom on the attractive branch of the potential.

#### 1. Introduction

In Davidson *et al* (1973) we reported the first results of differential elastic scattering experiments in the study of the interaction of electronically excited mercury atoms with other species. In this paper these results are extended to include a closed-shell atom (neon) and are interpreted to yield interatomic potentials.

There are two low-lying states of mercury with sufficiently long lifetimes to travel through a scattering apparatus, the  $6^{3}P_{0}$  and  $6^{3}P_{2}$  states with energies of 4.64 and 5.46 eV respectively. The  $6^{3}P_{1}$  at 4.89 eV radiates in  $10^{-7}$  s, which is too short for detection. Magnetic analysis of the beam gives a lower bound on the fraction of  ${}^{3}P_{2}$  atoms of 85% but, since no state selection is used in the scattering experiments, all the  $M_{J}$  states of the  ${}^{3}P_{2}$  atom are represented in the beam. As the collision proceeds  $M_{J}$ , in a space-fixed frame of reference, ceases to be a good quantum number but, replaced by  $\Omega$  (the total electronic angular momentum about the interatomic axis), may conveniently be used to label the different adiabatic potentials which evolve from each atomic  $M_{J}$  state as they interact with the target atom. The collisions

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thus take place over a manifold of surfaces. In this situation, the Coriolis force arising from the relative motion of the atoms can induce transitions between these  $M_J$  states. Transitions between J states, which can then lead to quenching of the metastable, are also possible but, because of the large spin-orbit splitting, are relatively less frequent. Collisions with the alkali metals can also result in their ionization or electronic excitation.

In contrast, collisions between ground-state  $Hg({}^{1}S_{0})$  and these target atoms are necessarily elastic at thermal energies and involve a single potential surface, so that scattering measurements may be inverted to yield an accurate potential. However, even in these systems, restrictions on the range of data or lack of an absolute calibration may result in ambiguities in the derived potential (Buck 1975).

The systems studied here are, in comparison, very complex with a large number of exit channels open, as well as possible interference effects between trajectories which sample two or more of the asymptotically degenerate potentials. The interpretation must correspondingly be more model-dependent, and indeed an important objective of this work is to discover whether a simple potential model corresponding to some dominant process is a useful approximation in describing these collisions (Fluendy *et al* 1974).

#### 2. Experimental

#### 2.1. Crossed-beam apparatus

The crossed-beam apparatus used has already been described (Cowley et al 1969) and only the essential features need be discussed here. The excited Hg atom beam was produced by bombarding a ground-state Hg beam effusing from a glass capillary array with a magnetically collimated electron beam of controlled energy. After recollimation, the excited Hg atoms entered the collision zone where they intersected the modulated target beam from a multichannel array. The target beam produced typically 10-15% attenuation of the Hg\* flux, except in the case of Ne where pumping constraints limited the attenuation to 3%-the data for this system being consequently rather more noisy. The scattered excited Hg atoms were detected by Auger ejection of electrons from a clean potassium surface (coated in situ) located in a differentially pumped UHV chamber. Ejected electrons were detected by a channeltron and thence counted into a gated dual scaler system. The experiment was conducted by recording the scattered signal as a function of angle at intervals of about 0.3°, a single sweep over the range of angles explored taking approximately 3 h. Individual scans of this type were repeated until sufficient precision had been achieved. The angular resolution of the apparatus was 0.5°. Since both beams were from effusive sources and not velocity-selected, there was broadening in the relative velocity distribution in addition to that arising from the angular divergence of the incident beams. Forward calculations, in which a model centre-of-mass (CM) differential cross section function was convoluted with the appropriate distribution of centre-of-mass vectors, showed that structure with a CM period of 1° would just be observable in the laboratory.

### 2.2. Hg\* beam composition

The excitation function for Auger ejection from the potassium surface in the detector was measured over a range of electron energies in the Hg atom exciter. A threshold
## Elastic scattering of electronically excited Hg atoms

at around 6 eV rising to a maximum at around 10 eV was observed, in agreement with previous work. Time-of-flight measurements showed that higher excitation energies produced large quantities of photons without improving substantially the yield of metastables. In these experiments the exciter was operated at energies less than 9 eV, the electron energy scale being calibrated by extrapolating the excitation function to 5.46 eV. At about 9 eV,  ${}^{3}P_{0}$  and  ${}^{3}P_{2}$  are the only long-lived states accessible, the  ${}^{3}D_{3}$  (also long-lived) being at threshold (about 8.7 eV) (Borst 1976).

Theory (McConnell and Moiseiwitsch 1968) suggests that the ratio of cross sections for the direct production of  ${}^{3}P_{0}$  and  ${}^{3}P_{2}$  by electron impact is close to statistical (i.e. 1:5) though, at the excitation energies used, cascade from higher levels may also be important. Measurements to investigate this point were made using a two-wire configuration inhomogeneous magnetic field between the metastable source and the detector. Calculation (Davidson 1973) and saturation experiments showed that this field could be operated as a shutter for  $\mu = 0$  states so that the ratio [( $\mu = 0$ ) states/all states] could be determined for the metastable atoms at various excitation voltages. Contributions from photons produced in the source were eliminated by using the flight time of the metastable, so that counting was only permitted during periods when the exciter voltage was off. The results of experiments of this type are shown in table 1; more detailed flight-time measurements showed that this ratio was independent of metastable-atom velocity.

This data, without further knowledge of the relative population of magnetic substates in the  ${}^{3}P_{2}$  level, does not allow the J-state composition of the scan to be determined. If the magnetic substates of  ${}^{3}P_{2}$  are equally populated—a reasonable approximation for (i) direct excitation with a very poorly collimated electron beam having a relatively high (approximately 0.3 V) energy spread (Ottley and Kleinpoppen 1975) or (ii) for population by cascade from a range of higher states produced at higher voltages—the  ${}^{3}P_{2}$  composition shown in the table can be computed. If cascade from the 7<sup>3</sup>S is important, enhanced populations in the  $M_{J} = 0$  state will be produced and lead to even larger estimates for the  ${}^{3}P_{2}$  fraction. It should be noted that the observed composition agrees closely with that expected for purely statistical excitation and detection of these states (83%  ${}^{3}P_{2}$ ), further supporting this analysis and confirming the predominant  ${}^{3}P_{2}$  composition of the beam.

Partly for simplicity and also in view of the lower detection efficiency for the  ${}^{3}P_{0}$  state, the scattering data are attributed solely to the  ${}^{3}P_{2}$  level. Where appropriate the  $M_{J}$  states are assumed to be populated equally (Krause *et al* 1975).

#### 2.3. Velocity distribution

Flight-time measurements on the metastable-atom beam were made to distinguish photon production from genuine metastable atoms (§2.2) and also to determine their

| Excitation voltage | Signal magnet on magnet off | Percentage ${}^{3}P_{2}$ assuming all $M_{J}$ equi-populated |
|--------------------|-----------------------------|--------------------------------------------------------------|
| 8                  | 0.43                        | 71                                                           |
| 9                  | 0.31                        | 86                                                           |
| 11                 | 0.32                        | 85                                                           |
| 14                 | 0.31                        | 86                                                           |

Table 1.

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most probable velocity. The measurements were made by pulsing the electron excitation current to produce pulses of metastable atoms approximately 100  $\mu$ s long (a period determined by the length of the excitation region). The channel advance of a multiscaler was triggered simultaneously with the exciter pulse and the channel address incremented every 20  $\mu$ s by a crystal clock. Metastable arrivals incremented the appropriate channel, so that by repetition of this sequence an arrival-time spectrum was constructed. The most probable flight time was found to be about 1.5 ms.

In comparison with the expected  $v^2$  Maxwellian distribution (the exciter has an efficiency  $\propto 1/v$ ) a substantial deficit of slow atoms was seen, possibly due to recollimation losses of the slower atoms following excitation. As a result of this loss, the velocity distribution is substantially narrower and the most probable velocity was 38% greater than that expected for an effusive beam at a similar temperature. The measured most probable velocity of  $2.48 \times 10^2$  m s<sup>-1</sup> was used in subsequent calculations of the relative velocity of collision with the target atoms studied.

#### 2.4. Treatment of data

The data reported, relative differential elastic cross sections, are the result of averaging six or more individual angle scans of the type described. The scans were first approximately normalized to each other and then merged by summing in successive smallangle increments (approximately half the angular resolution in width) to yield a mean value for the cross section in the angle increment. The mean laboratory cross sections computed in this way were then transformed into the centre-of-mass frame, using the Jacobian appropriate to the most probable relative velocity.

As can be seen from the Newton diagram, two centre-of-mass (CM) angles  $\chi$  contribute to the scattering  $I(\theta)$  at every laboratory angle  $\theta$ , so that

$$I(\theta_1) = J(\theta_1, \chi_{\mathsf{F}})I(\chi_{\mathsf{F}}) + J(\theta_1, \chi_{\mathsf{B}})I(\chi_{\mathsf{B}})$$
(1)

where  $J(\theta, \chi)$  is the Jacobian transforming between laboratory angle  $\theta$  and CM angle  $\chi$ .  $I(\chi_F)$  and  $I(\chi_B)$  are the forward and back CM scattering intensities which contribute at  $\theta_1$ . For the systems studied here, every angle  $\chi_B$  also appears at some other laboratory angle  $\theta_2$  as a forward-scattered component. Now  $J(\theta, \chi_F) > J(\theta, \chi_B)$ , while  $I(\chi_F) \gg I(\chi_B)$  since  $\chi_F < \chi_B$ , so that the backward contribution in equation (1) is small. An iterative scheme can therefore be used to extract the separate forward and back contributions.

A first estimate

$$I'(\chi_{\rm F}) = J(\theta_1, \chi_{\rm F})^{-1} I(\theta_1)$$

is made for all laboratory angles. This estimate is then corrected by

$$I''(\chi_{\rm F}) = I'(\chi_{\rm F}) - J(\theta_1, \chi_{\rm F})^{-1} J(\theta_1, \chi_{\rm B}) I'(\chi_{\rm B})$$
(3)

where  $I'(\chi_B)$  is found via (2) at the appropriate laboratory angle  $\theta_2$ . Equation (3) is then iterated until convergence is complete; typically only three iterations are required. The results of this analysis are finally plotted as relative differential elastic cross sections in the CM frame in the various figures.

(2)

# 3. Results and discussion

As already indicated, interpretation of elastic scattering in the present systems is subject not only to the usual difficulties associated with inverting limited data to yield a unique potential, but also to uncertainty as to the appropriate model for the process.

The data for the alkali-metal systems are presented in figures 1, 2 and 3. It supercedes the data presented, but not analysed, in Davidson (1973), in that a number of angle calibration errors affecting the superposition of different scans has been corrected. A striking feature of the scattering pattern is the wide-ranging and rather regular oscillatory pattern. This pattern is very reminiscent of the supernumerary



Figure 1. Relative differential elastic cross section for  $Hg({}^{3}P_{2})/Na$ . Curve A, experimentai; curve B, single-potential fit; curve C, three-potential fit. Fitted curves are shifted on arbitrary amount upwards. Data is deconvoluted with the main beam profile and the representative error bars are twice the standard deviation of the signal based on the counting statistics. Velocity = 895 m s<sup>-1</sup>; number of scans = 6.



Figure 2. Relative differential elastic cross section for Hg  $6^{3}P_{2}/K$  (experimental). Velocity = 660 m s<sup>-1</sup>; number of scans = 3; filtered and deconvoluted data.

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Figure 3. Relative differential elastic cross section for Hg  $6^{3}P_{2}/Rb$  (experimental). Velocity = 470 m s<sup>-1</sup>; number of scans = 6; filtered and deconvoluted data.

bows seen in simple elastic scattering inside the rainbow. Although individual oscillations are distorted by noise, the sequence and approximate location of peaks are reasonably secure. In contrast, the rather noisy Ne/Hg\* data (figure 4), which might naively be expected to be less complex, show a much less regular and also a less pronounced structure although the smaller amplitude of the oscillations makes it difficult to identify specific features. The sharp fall-off in the cross section at small angles seen in all the systems is simply due to over-compensation for the attenuation of the main beams. This angular region is not used in subsequent fitting operations.



Figure 4. Relative differential elastic cross section for Hg  $6^{3}P_{2}/Ne$  (full curve is threepotential fit). Velocity = 723 m s<sup>-1</sup>; number of scans = 6.

## 3.1. Potential fitting

A number of techniques have been used to tackle the 'practical' inversion problem the extraction of a potential in accord with limited experimental scattering data. The uniqueness of this potential depends upon the quantity and quality of data available. Inversion methods have recently been reviewed by Buck (1975) and in

# Elastic scattering of electronically excited Hg atoms



Figure 5. Schematic deflection function showing parametrization regions.

this work we use a version previously exploited by him in which a parametrized form for a deflection function is adjusted to produce agreement with the scattering data. The deflection function can then be inverted using the Firsov technique to yield the fitted potential. Buck has shown that the location of supernumerary rainbows and high-frequency glory oscillations is not affected significantly by apparatus averaging so that these features are particularly useful for fitting. In the Na, K and Rb data there are 21, 37 and 10 extrema, respectively, available for fitting; Buck's technique was therefore extended to allow a more flexible parametrization of the deflection function. The parametrization regions are shown in figure 5 and correspond to the following functions:

| Region | Form $\pi = a b = a b^4$                              | Adjustable<br>parameters |
|--------|-------------------------------------------------------|--------------------------|
| П      | $a_{1}(b - b_{0}) - a_{3}(b - b_{0})^{2}$             | $b_{0}, a_{2}$           |
| III    | $-\chi_b - a_1(b-b_1)$                                | $a_1, \chi_b$            |
| IV     | $-\chi_R + q(b-b_R)^2$                                | $b_R, \chi_R$            |
| V      | $-C_1b-C_2$                                           | $C_2$                    |
| VI ·   | $-\chi_{c} + C_{3}(b - b_{4}) - C_{4}(b - b_{4})^{2}$ | χc                       |
| VII    | $\frac{15}{56}\pi(C_{(6)}/E)b^{-6}$                   |                          |

The phase at  $b_0$  (i.e.  $\eta_{max}$ ) is also a variable. The value of  $C_{(6)}$  calculated by Darwall *et al* (1970) was used to constrain the function at large *b*. The other parameters were determined to join smoothly the different regions of parametrization.

The information used from the cross section was:

(i) locations  $\chi_N$  of supernumerary bows,

(ii) smoothed cross section at  $\chi_N$ ,  $\overline{\sigma}_N$ , and

(iii) high-frequency oscillation period  $\Delta \chi_{HF}$  in the small-angle region.

The extrema locations provide rather precise information on the area enclosed in the deflection-function bowl while  $\vec{\sigma}_N$  corresponds to the classical cross section and is primarily sensitive to the shape of the outer branch of  $\chi(b)$ ; as with the extrema locations this property is not affected significantly by apparatus resolution. The glory oscillations  $\Delta\chi_{\rm HF}$  provide an initial estimate of the parameter  $b_0 = (k\Delta\chi_{\rm HF})^{-1}$ .

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Fitting is carried out using a uniform approximation to calculate the quantities (i)-(iii) from the parametrized deflection function which is then adjusted to produce the best fit. The  $\chi(b)$  function is considerably over-determined since seven parameters are constrained by 40 or more input values.

3.1.1. The  $Hg^*$ -alkali-metal system. The degeneracy of the  $Hg^* M_J$  states is removed by the collision partner and five different molecular states evolve from the separated atoms (figure 6). Previous calculations (Fluendy *et al* 1974) have suggested that, in the limit of strong coupling between the different potential surfaces evolving from the mixture of  $M_J$  states in the incident beam, a single spherical effective potential can describe the scattering. In other cases interference effects between the different surfaces will be seen, but it is likely that the separate scattering features of each surface, e.g. rainbows, will remain important features in the total scattering. A model based on summing one or more single-surface elastic scattering cross sections is thus a natural starting point.



Figure 6. Suggested correlation diagram for Hg\*/alkali atoms. The ordering of the levels at the right-hand side is appropriate for small separations and the framed portion is suggested for intermediate values of R where Hund's case (c) is appropriate, i.e.  $V(R) \ll$  spin-orbit coupling energy. States dissociating to M\*/Hg are omitted and all the levels shown are embedded in a continuum of states dissociating to M<sup>+</sup> +  $\epsilon$  + Hg(<sup>1</sup>S).

The alkali-metal cross sections show an unusual hump near  $16^{\circ}$  which, at least in the case of Na, seems to be resolved into two peaks. This feature can be reproduced in two principal ways, using either a single-potential model with a small maximum in its deflection function at large impact parameters (full curve in figure 7), or a three-potential model in which this feature is constructed by the addition of two primary bows (dotted curve in figure 7). It was not found possible to reproduce the small-angle scattering pattern by a combination of two normal (i.e. with only one rainbow) deflection functions, or by a single such function. The fits obtained with the inflected single-potential and the three-potential models are compared with the experimental data in figure 1; some deviation at wide angles is seen due to the restrictions of the parametrization, but both are in excellent agreement with the envelope and oscillation structure.



Figure 7. Fitted deflection functions for Hg\*/Na scattering (full curve is single deflection function fit with small maximum; dotted curves are deflection functions for the three-potential model). The deepest function is common to both fits except where shown at the largest ranges. The labelling of states corresponds to the correlation diagram (figure 6).

The potentials calculated by Firsov inversion of these deflection functions are seen in figure 8. The deeper potential is very similar in both models, differing only in the softening seen at large separations in the single-potential fit.

The K/Hg\* cross section had been analysed in a similar way, though in this case no small-angle high-frequency oscillations could be seen. The extrema spacing



Figure 8. Potentials calculated from the fitted deflection functions for the Hg\*/sodium system. The full curve is the single-potential model; the dotted curves are the three-potential fit, note that the deepest potential for each of these models only differ at very large R; the broken curve is the ground-state Hg/M potential reduced to the same  $\epsilon$  and  $R_m$  (Buck 1975). The labelling of the states corresponds to that in the correlation diagram (figure 6). For Na/Hg\*,  $\epsilon = 3 \times 10^{-13}$  erg,  $R_m = 40$  Å; for Na/Hg  $\epsilon = 8.8 \times 10^{-14}$  erg,  $R_m = 4.72$  Å. The potentials are shown over the range determined by the data.

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in the Na and K data, which relate to the phaseshift difference across the deflection bowl, can be reduced to a common plot if  $R_m(K) = 1.17 R_m(Na)$ . The potential in this region is correspondingly likely to be reducible, though the large number of extrema in the K data make it difficult to obtain a precise fit with the parametrized deflection function used. The Rb/Hg\* data is rather poor and quantitative interpretation is difficult, the same general features—small-angle hump and supernumerary bows—as for the other alkali metals can, however, be seen.

The data available from experiment is primarily sensitive to the potential bowl, though the failure to observe primary bows in the angular range accessible means that the bottom of the bowl is rather poorly probed. The absolute location of the zero crossing to the potential is also only weakly determined by the data.

3.1.2. The Hg<sup>\*</sup>-inert-gas systems. The correlation diagram for inert-gas/Hg<sup>\*</sup> is shown in figure 9. Three potential states evolve from the Hg J = 2 state. In contrast to the alkali metals, the states correlating with excited Ne lie at much higher energies than the states of interest here and the collisions can be expected to be almost entirely elastic.



Figure 9. Correlation diagram for  $Hg^*/Ne$ . The ordering of the levels at the right (small separations) is assumed to be dominated by electron/electron repulsion and the classification there corresponds to Hund's case (a).

The Ne/Hg\* cross sections shown in figure 4 are noisy due to difficulties in pumping the inert gases and it proved impossible to obtain satisfactory data for the heavier members of this series. A clear division is seen between an angular region in which the cross section is oscillating strongly and a wide-angle zone where it decays smoothly. Since quenching cross sections for inert-gas collisions are small, this large-angle zone is almost certainly the dark side of a rainbow. A sequence of high-frequency oscillations is just visible at small angles from which a sensible  $b_0$  value can be deduced. In contrast with the alkali metals, the extrema positions in the oscillating part do not fit a simple supernumerary bow sequence while the low-resolution envelope is also unlike that normally seen in atom/atom elastic scattering. No reasonable shape of deflection function capable of reproducing the overall behaviour could be found.





A three-potential model was therefore sought, using the techniques already described. The complexity of the data as well as the presence of some noise make it unrewarding to search for a perfect fit. The agreement obtained in figure 4, which reproduced the main features including the overall shape quite well, is therefore satisfactory. This was computed as the sum of three cross sections weighted 2:2:1 calculated from the potentials plotted in figure 10, the two deepest potentials each being awarded a weight of 2.

## 4. Discussion

## 4.1. Hg\*-alkali-metal pairs

The most striking feature of the experimental results is the comparative simplicity of the scattering patterns. In §3, two models were shown to lead to a good fit of  $\sigma(\chi)$ , one involving a single potential with an unusual softening of the outer attractive branch and the other a three-potential model. The depth and location of the well of the single potential was very similar to the deepest potential of the second model. In neither case was it necessary to invoke quenching.

A possible correlation diagram is given in figure 6. In the case of weak interactions (large R), the electron spin of the alkali atom is only weakly coupled with that of Hg\* and only three different potential energy states evolve from the separated atoms. As R decreases, Hund's case (c) is replaced by case (a) and at intermediate separations the five-fold degeneracy of the parent  ${}^{3}P_{2}$  level is completely removed, to be replaced by a simpler splitting at small R where the  ${}^{4}\Sigma_{1/2}$  and  ${}^{4}\Sigma_{3/2}$  states become very nearly degenerate. No information is available on the ordering of the

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 ${}^{4}\Sigma$  and  ${}^{4}\Pi$  levels and it is assumed that the lower electron-electron repulsion in the  $\Pi$  states (i.e. between Hg(p<sub>±1</sub>) orbitals and the M(s) orbital) places them below the  $\Sigma$  states (where the Hg(p<sub>0</sub>) orbital is occupied) in the limit of Hund's case (a).

At very large separations, where the interaction energy is entirely determined by dispersion forces, the greater polarizability in the bond direction,  $\alpha_{zz}$ , of the  $M_J = 0$ state may result in the  $|\Omega| = \frac{1}{2}$  levels initially lying lowest and the  $(\frac{3}{2}, \frac{5}{2})$  pair highest. However the anisotropy in the polarizability is small ( $\leq 10\%$ , Levine *et al* 1968) and this order would be easily reversed as the overlap between the two atoms increased, to give the order shown in figure 6.

Of the two models used in fitting the data, a single potential implies that the splitting in the manifold of levels remains small down to  $R_m$  ( $\simeq 4$ Å in the case of Hg\*-Ne) even though the interaction is strong ( $\sim 0.2$  eV). Outer maxima in the potential energy curves of excited diatomics have been reported (e.g. Cohen and Schneider 1974, Mulliken 1970) but in association with the penetration of a diffuse orbital occupied by a promoted electron (e.g. in the <sup>3</sup>P states of an inert-gas atom). The effect would not be expected at long ranges in the much more compact 6s6p configuration of <sup>3</sup>P Hg. Also, there seems no obvious state, e.g. a charge-transfer one, that could cross the states (b)-(f) (figure 6) at a separation of about  $2R_m$  and hence perturb them in that region. The possible re-ordering of some of the <sup>3</sup>P<sub>2</sub> manifold due to the onset of overlap referred to above would be expected around  $R_m$ , when repulsion forces begin to dominate.

The three-potential model is thus to be preferred on theoretical grounds and is in accord with the correlation diagram for Hund's case (c) and with relatively little contribution to the spin-orbit coupling energy from the electron in the still largely unperturbed valence shell of the alkali metal. The spectroscopic designation of the three groups of states is not settled by these scattering experiments since the fitting is not sufficiently sensitive to the weighting of each state, but on experimental grounds we favour the higher weight for the deeper states.

On either model a deep potential is required, possibly accompanied by shallower ones, having a well depth approximately  $30 \times 10^{-14}$  erg. This value is considerably greater than that of the ground state (x<sup>2</sup> $\Sigma$ ) where  $\epsilon = 9 \times 10^{-14}$  erg (Buck and Pauly 1971) and points to a specific interaction in this excited state.

## 4.2. Hg\*-Ne

The probable correlation diagram for Hg<sup>\*</sup> interacting with a <sup>1</sup>S atom is given in figure 9. At large separations  $M_J$  ( $\equiv \Omega$  for a <sup>1</sup>S partner with the quantization axis along the interparticle vector) is a good quantum number. At large separations the state of maximum  $M_J$  lies lowest if, as discussed in §4.1, electron-electron repulsion dominates over dispersion forces. As R decreases and the coupling passes to Hund's case (a), the  ${}^{3}\Sigma_{0}$  and  ${}^{3}\Sigma_{1}$  states become degenerate, the *e* state being forced up in energy in energy by interaction with the *c* state (both  $\Omega = 1$ ).

The observation that the scattering data are best fitted by three potentials is thus entirely consistent with the correlation diagrams and indicates that, at the range of separations scanned experimentally (essentially down to the inner zero of the potential), Hund's case (c) is appropriate because pure case (a) would predict only two potentials. Once again the spectroscopic labelling of the three states cannot be decided unambiguously from these scattering experiments, but we favour giving a weight of 2 to the two deeper states, indicating that the lowest state has  $|\Omega| = 2$ .

# Elastic scattering of electronically excited Hg atoms

The Ne-Hg<sup>\*</sup> and Na-Hg<sup>\*</sup> potentials exhibit a much wider bowl than a Lennard-Jones potential having the same  $\epsilon$ ,  $R_m$  values (figures 8 and 10). This behaviour has been noted by Buck (1975) for ground-state Hg/alkali-metal potentials; it is not found in the ground/metastable state pairs of the inert gases (Winicur *et al* 1976).

#### 5. Conclusions

The elastic scattering of Hg<sup>\*</sup> in all the systems studied can, on a combination of theoretical and experimental evidence, best be interpreted in every case as the scattering from three distinct potential energy states. This is consistent with the partial removal of the degeneracy of the  ${}^{3}P_{2}$  state at separations around 4Å. The potential minima are sufficiently separated for it to be meaningful to assign separate deflection functions to each state, i.e. Hund's case (c) rather than case (e) applies when molecular rotation is taken into account.

In the case of the alkali metals, the absence of any marked attenuation due to ionization, which is energetically allowed in each system, is noteworthy. Coupling to the continuum is evidently small and one can continue to use the concept of a deflection function even when the classical path is embedded in a continuum.

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# APPENDIX B

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PUBLISHED PAPER (2)

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62/21

# The Scattering of $Hg(6^{3}P_{2})$ by CO, N<sub>2</sub> and CO<sub>2</sub>

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#### Received 3rd May, 1976

The differential scattering pattern of a thermal beam of  $Hg(6^3P_2)$  from CO, N<sub>2</sub> and CO<sub>2</sub> has been measured from 10° to 160° (CM). Pronounced and regular oscillations are observed over the whole angular range in each system. However, the envelope is not that of purely elastic scattering, the  $\chi^{4/3} \sin \chi I(\chi)$  plot showing an almost monotonic decrease over the whole angular range. The spacing of the oscillations indicates a deflection function with an unusually broad bowl, interfering branches being 3 Å apart. Two models are put forward; both include partial adsorption of the wave front and the operation of two potentials. Detailed fitting of one model shows that a highly attractive long range potential (well depth  $\approx 10 kT$ ) is needed, but although the interference structure is well reproduced, the necessary range of the optical potential is not consistent with known quenching cross sections. A second model is given in outline and involves an avoided crossing around 8 Å producing a rapid steepening of the potential gradient at that point. Quenching begins at impact parameters  $\sim 7 Å$  thus indicating a very large quenching cross section unless a rather sharply peaked adsorption function is postulated with a width of only  $\sim 1 Å$  to give the known values of  $\sigma_{qu}$ .

The scattering of many ground electronic state species has now been thoroughly explored over a wide energy range by crossed beam techniques. The scattering of low lying excited electronic species remains largely unexplored and is, in a sense, complementary to ground state scattering in the 10–100 eV range in that there electronic excitation is frequently observed in the products. By starting with an excited state (of necessity a metastable one for beam work), curve crossings and diabatic state mixing become accessible at thermal kinetic energies, and may be expected to lead to marked inelastic scattering. So far, excited state phenomena have largely been studied through kinetic spectroscopic observation of quenching or collision induced fluorescence<sup>1,2</sup> though the more energetic metastable species (those of the inert gases) have been used in elastic<sup>3</sup> and Penning ionization studies.<sup>4</sup> Only relative quenching cross sections for Hg( ${}^{3}P_{2\rightarrow 1}$ ) have been measured in a beam experiment.<sup>5</sup>

 $Hg(6^{3}P_{2})$  is an attractive candidate for beam studies in that the nearest electronic state (the  ${}^{3}P_{1}$ ) is only 0.57 eV away and provides a route for quenching. The J = 2state is not sufficiently energetic (5.4 eV above the ground state) to ionize most small molecules. The following studies of the thermal elastic scattering (or, rather, scattering without change of electronic state) of Hg\* by CO, N<sub>2</sub> and CO<sub>2</sub> were undertaken to see if more light could be cast on the known quenching processes in these systems by examining the perturbation of the elastic scattering differential cross section.

### EXPERIMENTAL

The crossed beam apparatus has been described before.<sup>6</sup> Hg\*( ${}^{3}P_{2}$  with less than 15% of the  ${}^{3}P_{0}$  state<sup>7</sup>) is generated by electron bombardment (at 10 eV) of an effusive beam of Hg and crosses a thermal effusive beam of the target gas. The angular resolution is 0.5° LAB.

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The detector, a fresh K surface, responds to the  ${}^{3}P_{2}$  state, to the  ${}^{3}P_{0}$  state with probably lower efficiency but not to the ground state. The  ${}^{3}P_{1}$  state decays in flight between scattering centre and detector (transit time  $5 \times 10^{-3}$  s) and so is not detected. Typical main beam signals were  $10^{5}$  c.p.s. and counting techniques were used.

The CM scattering patterns, averaged over the stated number of scans, are reproduced as the lowest curve in fig. 1, 2 and 3. The factor  $\chi^{4/3} \sin \chi$  multiplying the scattered intensity conveniently places all the observations within the compass of a linear scale and renders the envelope of scattering from an  $R^{-6}$  potential horizontal. The location of the major maxima and minima is reproduced in independent sets of four or five scans, though the peak-to-valley amplitude ratio varies. The envelope is unchanged by selecting different scans for averaging. The sudden fall-off in intensity at less than 16° is due to imperfect unfolding of the main beam coupled with the attenuating effect of the  $\chi^{4/3} \sin \chi$  term at small angles. In the case of CO, closer examination of the data shows a barely visible high frequency structure in the 16-20° CM region with a period  $\approx 1.25^\circ$ .

## INTERPRETATION AND FITTING

The three scattering patterns are broadly similar (CO and N<sub>2</sub> being very similar) in the following respects: (i) the envelope is basically monotonically decreasing across the whole angular range, though in each case there is a maximum around 90–100° (arrowed as  $\chi_2$ ) and there is a pronounced perturbation of the envelope at 20° in the case of CO and N<sub>2</sub> and at  $\approx 80^{\circ}$  for CO<sub>2</sub>, labelled as  $\chi_1$ , (ii) oscillatory structure with an only slowly increasing period extends across the whole angular range, but the amplitude is not regular and is clearly perturbed by another frequency.

The envelope must be compared with that expected from purely elastic scattering. For a potential with an  $R^{-3}$  attractive branch a horizontal (s = 6) or slowly rising (s < 6) envelope with increasing  $\chi$  is found. The absence of a well defined rainbow (the features at  $\chi_2$  do not fall away quickly enough on the dark side to be typical rainbows) may either mean orbiting, the superposition of scattering from several rather different potentials with an overlapping rainbow structure or extensive adsorption of the incident wave front beginning at impact parameters somewhat greater than the rainbow value.

The fact that interference structure is visible at all makes it unlikely that several rather different potentials are operating, for then the supernumerary spacing would be confused by the multiplicity of interfering branches. Although orbiting cannot be ruled out, it would upset the regularity of the supernumerary spacing by introducing further interfering branches (albeit of small amplitude). The same considerations apply to rainbow angles greater than 180°.

The near regularity of the interference structure across such a wide angular range (especially noticeable in the case of  $N_2$ ) is unusual because supernumerary rainbow spacing (or inter-branch interference in general when both branches correspond to deflections in the same sense) usually decrease markedly with falling angle of observation as the two branches diverge in impact parameter. The present structure seems to indicate a dominant deflection function with nearly parallel sides, *i.e.*, that the rainbow angle is very large. The fact that the period of oscillation of  $\sigma(\chi)$  nevertheless slowly increases with angle indicates that we are not observing interference structure arising between the positive and negative branches of a deflection function.

Putting the remaining experimental observations and the above deductions together, we arrive at the simplest model (I) for a trial fitting:

(i) The scattering is predominantly from a single deep potential that gives rise to a rainbow  $\geq 180^{\circ}$ .

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(ii) The dominant potential must lead to a deflection function in which the separation of the two attractive branches is  $\approx 3$  Å at small angles (from  $\Delta \chi = 2\pi/k\Delta b$ ).

(iii) Scattering from a second, shallower potential is needed to account for the maxima in the envelopes of the CO and N<sub>2</sub> date around  $\chi_2$  and the change of gradient of the CO<sub>2</sub> scattering in this region. These rainbow positions serve to fix the well depths of the shallow potentials.

(iv) Adsorption sets in early on both surfaces and is responsible for the falling envelope of  $\sigma(\chi)$ .

(v) The very high frequency structure with poorly resolved periodicity of  $\sim 1.25^{\circ}$  is interpreted as glory oscillations (interference between the positive and negative branches of the deflection function around  $\chi = 0^{\circ}$ ) and serves to assign the impact parameter  $b_0$  for the inner zero of the deflection function at 5.3 Å in all cases. In fact, there is not too much latitude in this value if a sensible length parameter (position of the inner zero,  $\sigma$ ) is to be obtained for the potential especially when very highly attractive potentials are operating.

With two potentials the possibility of mutual interference arises. Two different fits were obtained, with and without inter-state interference. Such structure, being predominantly between the outer attractive branches of two deflection functions, is inevitably of much lower angular frequency than that originating across a single deflection function unless the two deflection functions are considerably displaced from each other—in this case by  $\sim 3$  Å. In the present model the dominant source of interference structure is between the two negative branches of the deep deflection function; inter-state interference produces only a small change in the scattering pattern, but agreement with experiment is marginally improved.

In order to fit the scattering pattern, a flexible deflection function divided into 7 sections was employed. In each section a simple functional form was adopted subject only to the constraint of a smooth join to the neighbouring sections. In order to complete the partial wave summation, the deflection function was smoothly joined to a tail resulting from the following  $C^{(6)}$  values;  $Hg^*/CO$ ,  $0.83 \times 10^{-77}$  J m<sup>6</sup>;  $Hg^*/N_2 0.77 \times 10^{-77}$  J m<sup>6</sup> and  $Hg^*/CO_2$ ,  $1.12 \times 10^{-77}$  J m<sup>6</sup>. It was found in all three systems that an  $R^{-6}$  potential could not be used for impact parameters less than  $\sim 10$  Å since it gave too slowly varying a deflection function for  $\chi > 15^{\circ}$ , but  $C^{(6)}$  is not well determined by the present experiments.

The best fits are shown as the upper curves in fig. 1, 2 and 3, the associated deflection functions in fig. 4, 5 and 6. The potentials derived by Firsov inversion of these deflection functions are plotted in fig. 7, 8 and 9.

#### DISCUSSION

The overall fits are good. Both the dominant angular structure and the envelope are well reproduced, with only isolated features such as the dips in  $I(\chi)$  at  $\chi_1$  unaccounted for. However, this agreement is achieved only with the aid of a pair of unusually long range potentials and an equally long range adsorption function.

In fig. 7 the Hg\*/CO potential is contrasted with a Lennard-Jones potential with the same well depth and  $R_m$  value. The much greater width of the potential bowl is apparent. The range of the outer branch of V(R) comes directly from the range of the outer branch of  $\chi(l)$  and this, in turn, comes inescapably from adding the glory  $l_0$  value to the width  $\Delta l$  across the bowl dictated by the dominant interference structure. Thus, at  $\chi = 40^\circ$  a  $\Delta l$  value of 90–100 is required, giving an impact parameter for this deflection of  $\sim 7$  Å.

The adsorption function P(b) has to be similarly long range, rising to 0.9 at 9–10 Å,



FIG. 1.—Observed angular scattering plot for Hg\*/CO (lowest trace), velocity = 680 m s<sup>-1</sup>, number of scans = 9. Calculated curves (a) and (b) differ only in the upper state deflection function while (c) incorporates interference between upper and lower states (see fig. 4). A displacement of the upper state clearly has little effect on the calculated scattering pattern.



FIG. 2.—Scattering in the Hg\*/N<sub>2</sub> system. Experimental, lowest trace velocity = 614 m s<sup>-1</sup>, number of scans = 4. (a) is calculated from the sum of scattering from a deep and shallow potential (see fig. 5), (b) includes interference between them.

so that the scattering down to  $\sim 20^{\circ}$  is affected. The behaviour of P(b) for  $b < b_0$ is not really probed by the present experiments. The maximum adsorption cross section implied by the above adsorption function is  $\approx 350 \text{ Å}^2$  and the minimum  $270 \text{ Å}^2$  in the case of N<sub>2</sub>, where the two possible shapes of P(b) are sketched in fig. 5. Implied quenching cross sections are slightly larger in the other two systems. Other quenching and depolarization cross section measurements on Hg( ${}^3P_2$ ) are few and may be summarized by saying that with N<sub>2</sub> as partner the total quenching cross section (*i.e.*, to all possible final states) is  ${}^{8,9,5}$  11–19 Å<sup>2</sup>; with CO<sub>2</sub> as partner the cross section for  ${}^3P_2 \rightarrow {}^3P_1$  is  $\approx 0.4 \text{ Å}^2$  and with CO as partner the cross sections for the  $J = 2 \rightarrow 1$  transition is similar to that with N<sub>2</sub>. The depolarisation cross sections are all much larger<sup>8</sup> (up to  $\sim 600 \text{ Å}^2$ ) but they seem to be due to a long range angle dependent term in the potential, probably a quadrupole-quadrupole term not cornected with electronic state quenching.

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FIG. 3.—Scattering in the Hg\*/CO<sub>2</sub> system. Experimental, lowest trace velocity = 466 m s<sup>-1</sup>, number of scans = 6. (a) Is calculated from the sum of scattering from a deep and shallow potential (see fig. 6), (b) includes interference between them.



FIG. 4.—Deflection and adsorption functions for fig. 1 (Hg\*/CO). The two functions  $\cdots$  give rise to the plots (a) and (b) in fig. 1, --- to plot (c), both taken in connection with the lower state —; b-scale in Å.

An observed quenching cross section of  $\sim 20$  Å<sup>2</sup> implies a maximum impact parameter for quenching rather less than 3 Å. This range of attentuation function would, however, produce no detectable effect on the elastic scattering in the angular range of the present experiments unless the intermolecular potential were of rather short range. However, the interference structure points to an unusually long range potential.

In interpreting an elastic scattering envelope, there is a direct relationship between V(R) and the adsorption function necessary for a fit. Classically, the differential cross section is proportional to  $|d\chi/db|^{-1}P(b)$  and without an independent knowledge of P(b) one cannot unambiguously separate the two terms. In the present case, if a

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FIG. 5.—Deflection and adsorption functions for fig. 2 (Hg\*/N<sub>2</sub>). The function  $\cdots$  gives rise to the best fit including interference, --- to the best fit without interference with the lower state ----. Two possible continuations of P(b) are shown leading, respectively, to the maximum and minimum quenching cross sections compatible with the postulated deflection function.



FIG. 6.—Deflection and adsorption functions for fig. 3 (Hg\*/CO<sub>2</sub>). The ··· function gives the best fit without interference with the lower state ----, --- optimises the fit with interference.

less steeply rising P(b) is required, a more steeply falling deflection function must be employed. In order to preserve the periodicity of the observed interference structure the inner negative branch of the deflection function must be softened as the outer branch is hardened.

A rapidly varying potential at 8 Å (close to the smallest angle of observation) suggests an avoided crossing in which the diabatic  $Hg(^{3}P_{2}) - AB(^{1}\Sigma)$  pair state is depressed by interaction with another close lying state. A rather sudden change in gradient of the potential would produce a dip in  $\sigma(\chi)$  and tentatively we assign the perturbations at  $\chi_{1}$  in each of the systems to this cause.

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FIG. 7.—Potentials for Hg\*/CO. The two upper state potentials  $\cdots$  and --- are derived from the corresponding deflection functions in fig. 4. Inset is the Lennard Jones function having the same  $\varepsilon$  and  $R_m$  values; R scale in Å.



FIG. 8.—Potentials for  $Hg^*/N_2$ . The upper state potentials  $\cdots$  and --- are derived from the corresponding deflection functions in fig. 6.





# Faraday Discussion 62—Potential Energy Surfaces—62/21—Costello—4B

Trying to accommodate the quenching data within the limits set by the scattering results, we construct model II:

(i) The small angle scattering  $(\chi < \chi_i)$  is from a single potential identified with the shallow state of model I.

(ii) This state is perturbed by a second state at a separation  $R_e \approx 8-8.5$  Å. The crossing is sufficiently avoided for the motion to be almost adiabatic and most of the trajectories follow the lower surface. Nevertheless, sufficient amplitude (~10%) is found in the upper state for the shallow rainbow at  $\chi_2$  to be observed, though with low amplitude. At some impact parameter less than  $b_e$ , adsorption ensues on the lower surface and reaches 90% by the time the forward glory on the lower surface is reached.



Fig. 10.—The type of deflection functions needed to minimise the opacity function. The upper state  $\chi(b)$  is taken unchanged from fig. 4. The lower state function is sufficiently steep to produce the observed envelope of  $\sigma(\chi)$ . Two possible extrapolations of P(b) are shown, the lower one leading to  $\sigma_{qu} \sim 30 \text{ Å}^2$ .

(iii) The steepness of the attractive branch of the lower surface is at least three times greater than in model I in order to permit a much reduced P(b) function at large b. The broad features of the deflection function and P(b) function indicated by this model are given in fig. 10. The softening of the inner attractive branch is apparent, though it must be remembered that phase shifts in the presence of an optical potential do contain a contribution from the imaginary part of the potential and it is by no means clear that the ordinary semi-classical analysis holds. The inner branch to the potential must thus be regarded as conjectural. Even with an almost vertical outer branch to  $\chi(b)$  adsorption must set in rapidly at  $b \approx b_r$  (the rainbow value) and unless the P(b) function is restricted to a band of b values between 5 and 6 Å the implied value of the quenching cross section is still  $\approx 150$  Å in each system.

The configuration interaction responsible for the perturbation of the outer branch of the potential energy function is still a matter of conjecture. A steeply plunging ionic state (Hg<sup>+</sup>AB<sup>-</sup> seems the more likely charge distribution<sup>10,11</sup> in view of the high I.P. of the molecular partners) has been postulated in the quenching of Hg( ${}^{3}P_{2}$ ) by Na, but none of the present molecular partners has a positive electron affinity<sup>13</sup>

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and a crossing of the  ${}^{3}P_{2}$  state at  $\approx 8$  Å hardly seems feasible. More likely as the source of the perturbation is the interaction of the  $Hg(^{3}P) - AB(^{1}\Sigma)$  pair state with the state dissociating to  $Hg(^{1}S_{0}) - AB(^{1.3}\Pi_{g})$ . All three molecular partners have excited states close to 6 eV in which the  $1\pi_g$  orbital is occupied and this level is nearly resonant with the Hg  ${}^{3}P_{2}$  level at 5.4 eV. Although the overlap of the relevant orbitals would be small at 8 Å (neither the 6p nor  $1\pi$  orbitals are grossly different from highest occupied orbitals in the ground electronic states)<sup>13</sup> the interaction energy need only be lowered by  $4 \times 10^{-14}$  erg from the normal dispersion energy at this separation to give the observed potential.

### CONCLUSIONS

The thermal scattering of  $Hg(^{3}P_{2})$  from CO, N<sub>2</sub> and CO<sub>2</sub> exhibits a fairly simple interference structure that persists out to the largest angle of observation, nearly 180° (CM). Each system also shows evidence of quenching or an attenuation of the elastic scattering compared with that expected from a normal  $R^{-6}$  potential which begins at quite small angles of scattering. The very fact that structure is observed at all points to the conclusion that either the three molecular states evolving from the separated species ( $\Omega = 0^-$ , 1 and 2 in the linear configuration) have very similar potentials or that selective quenching on some branches simplifies the scattering pattern.

The spacing of the interference oscillations leads almost inescapably to a deflection function and hence to a potential that is very broad compared with the Lennard-Jones form. The simplest detailed model that fits most of the scattering data is a two state one correlating with degenerate levels at infinite separation. Adsorption is needed on both surfaces from  $\sim 10$  Å inwards. Suitably broad potentials give a good fit to the observed angular structure which is interpreted as supernumerary bows in a deep well. The model, however, leads to unacceptably large values of the quenching cross section ( $\sim$ 300 Å<sup>2</sup>) and a second model is therefore proposed in which the outer branch of the deflection function is considerably steepened at separations  $\approx$ 8-8.5 Å to account for some of the fall-off of the elastic scattering with increasing angle. A second, shallow potential is still needed to account for some of the features of the scattering. Even with an outer branch of almost infinite gradient [vanishing contribution to  $\sigma(\chi)$ ], an adsorption function has to be applied to the inner attractive branch which now becomes the dominant one. Quenching cross sections  $\approx 150$  Å<sup>2</sup> would thus follow unless the adorption function was rather sharply peaked around 6 Å.

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