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EFFECTS OF INTERNAL ENERGY ON ION-MOLECULE REACTIONS

by

William A. Chupka

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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William A. Chupka

Argonne National Laboratory

Argonne, Illinois 60439

EXPERIMENTAL METHODS

Electron impact

Electron impact has been the most commonly used method for production of reactant ions because of its simplicity, wide applicability and good intensity. However, the standard type of electron gun usually employed in electron impact experiments suffers from several disadvantages as a general method for controlling the internal energy of ions. The relatively wide energy spread (ca. 0.5 eV), the presence of space charge, the effects of charging of surfaces, sample pyrolysis and other experimental difficulties contribute to poor control of the ionization process. The threshold law for electron impact ionization is also unfavorable for control of closely spaced internal energy states. Nevertheless significant control of internal energy can be achieved in favorable cases. Thus preparation of ions in states of electronic excitation which are widely separated in energy can often be controlled. Indeed a number of ions (e.g. B^+, C^+, F^+) have been prepared in excited electronic states only by electron impact (Koski, 1974) since the necessary high energies are not readily available to other techniques such as photoionization. Metastable electronic states which differ in spin multiplicity from the neutral molecule by more than unity can often be prepared by electron impact but not by photoionization. Also it is often easy to insure preparation of ions in the ground electronic state only. The use of electron monochromators in the future may refine the degree of control of internal energy attainable by electron impact but only at the cost of experimental difficulty and of considerable loss of intensity.

Photoionization (Chupka, 1972)

As compared with electron impact, the photoionization technique offers a number of advantages one of which is much finer control over internal energy. The typical energy resolution attained by photoionization lies in the range 1-10 meV and the photoionization cross section threshold behavior is far more favorable than is the case for electron impact. Readily constructed continuum or quasi-continuum laboratory light sources and commercial vacuum ultra-violet monochromators provide enough photon flux for many kinds of ion-molecule reaction experiments up to photon energies of about 21 eV. At still higher energies synchrotron radiation is becoming available at a number of research centers.

Parent ions are usually very readily prepared in the ground vibronic state or with less than about 10 meV internal energy. Nearly pure preparations of single excited vibronic states are practical in only a few cases (e.g. H_2^+). More commonly one may prepare ions in a known distribution of energy states which can be varied with photon energy. The internal energy distribution may sometimes be inferred reliably from the experimental photoionization efficiency curve and/or the HeI photoelectron spectrum. Measurements of photoelectron spectra at the experimental wavelengths give unambiguous internal energy distributions and such data are now becoming available or can be measured by the experimenter without great difficulty. The still more powerful technique of photoelectron-photoion coincidence measurement has been applied by a number of workers to the study of unimolecular decomposition (Eland, 1972a, 1972b; Stockbauer, 1973) and its application to the study of ion-moleucle reactions appears feasible and imminent. Successful application of this technique would provide unambiguous knowledge and ready variability of the initial internal energy of reactant ions.

Charge transfer (Lindholm, 1972)

Charge transfer has been used extensively to investigate the fragmentation of ions as a function of internal energy. More recently the technique has also been applied to the preparation of reactant ions. In favorable cases reactant ions can be prepared with a narrow range of internal energy. However only a few ions useful for charge transfer have a single recombination energy. The possibility of several recombination energies in the more typical case and the possibility of non-resonant charge transfer impose serious limitations on the usefulness of this technique.

Photoexcitation

Production of excited reactant ions from electronic ground state ions by photon absorption and the study of their subsequent reactions is a promising new development in ion chemistry. The technique has been used successfully in an ion cyclotron resonance spectrometer with a xenon arc plus interference filters serving as the light source to produce excited $C_3H_5^+$ions which subsequently were observed to react with ethylene (Kramer and Dunbar, 1972). The photoexcitation technique has the advantage that the excitation energy added to the ion is readily controlled. However, in order to exploit this advantage fully, the internal energy distribution of the absorbing ion should be very small. The example mentioned above involved electronic excitation in the visible but pure vibrational excitation by infra-red laser may be feasible in some cases. In contrast to the other techniques, photoexcitation can be used in general for fragment as well as parent ions. The electronic states optically allowed for parent ions will not include all those seen in the photoelectron spectrum but on the other hand can include others which are too weak to be seen in the photoelectron spectrum, e.g. states formed by formally two-electron processes. In the case of electronic excitation the radiative lifetime of the excited state is of importance since for a strong absorption (not followed by a radiationless transition) the lifetime will be at most of the order of, and usually much shorter than, the mean collision times for the gas densities typical of most ion-molecule reaction studies. Radiative decay will often yield vibrationally excited ions which may then react in a manned different from that of the original unexcited ion. For larger molecular ions, the lifetime of excited states may be increased by orders of magnitude by the occurrence of radiationless transitions (internal conversion and intersystem crossing) to isoenergetic vibrational levels of lower lying and especially the ground electronic states. Many larger hydrocarbon ions with many high frequency C-H stretching modes have relatively small energy gaps between electronic states and are quite likely to undergo rapid radiationless transitions (Chupka, 1974). Obviously this new field of ion photochemistry will exhibit the many complications of neutral molecular photochemistry but should add much to understanding of the chemistry and spectroscopy of gaseous ions.

Excitation of Neutral Reactant

The excitation of neutral reactants, under conditions such that the effect of a specific mode of excitation on an ion-molecule reaction can be studied, has been successfully accomplished only for vibrationally excited N_2 and electronically excited O_2 (Ferguson, 1972). The excitation has been produced by passing the gases through a microwave discharge.

GENERAL EFFECTS OF INTERNAL ENERGY

There are no generally valid, non-trivial rules governing the effects of internal energy on reaction rates. Usually endoergic reactions can be made to occur by sufficient internal excitation to overcome the endoergicity and very large effects of internal energy are often encountered in such reactions. The effect of internal energy on exothermic reactions is usually not as dramatic. In the ideal case of a collision complex of sufficiently long life and strong coupling among internal degrees of freedom all forms of energy become equivalent within the constraints imposed by conservation of linear and angular momentum and its decomposition becomes statistically controlled. For more direct reactions the observation of non-equivalence is to be expected and such observations can provide valuable information on the details of the mechanism of the reaction.

ROTATIONAL ENERGY

Very few experiments have successfully investigate the effects of rotational energy alone on an ion-molecule reaction. Sbar and Dubrin (1970) found that H_2 in the $J = 0$ state has a cross section 5% larger than that in the $J = 1$ state for the reaction with Ar^+ to produce ArH^+. These workers ascribe the effect to the reduction by rotation of the aligning ability of the long range force leading to reduction of the effective polarizability of H_2. Gislason (1972) has treated this reaction in some detail using a model which stresses the importance of potential surface crossings and avoided crossings. He attributes the Sbar-Dubrin result to a curve crossing for $Ar^+(^2P_{1/2})$ to a charge transfer product channel at their kinetic energy. Gislason has also predicted a fairly strong variation (~ 30%) with rotational state of the reaction cross section of $Ar^+(^2P_{1/2})$ with H_2 at thermal translational energy. This prediction is based on his model for which an avoided crossing of potential surfaces occurs at a distance which is rather sensitive to the rotational state of H_2. This sensitivity results from the fact that the difference in energy between the surfaces for $Ar^+(^2P_{1/2}) + H_2(\nu = 0)$ and $Ar + H_2^+ (\nu = 2)$ varies fairly strongly with the rotational quantum numbers of H_2^+ because of the large difference in rotational constants for H_2^+ and H_2. While this prediction has not yet been unambiguously confirmed experimentally, this plausible model suggests the possibility of cases for which a reaction rate may be fairly strongly dependent on the rotational state of one or both reactants.

No detectable effect ($\lesssim 10\%$) was found for small changes in the rotational energy of H_2^+ on its exothermic reaction with H_2 to form H_3^+(Chupka, Russell and Refaey, 1968a). On the other hand, rotational as well kinetic energy of H_2^+ was found to contribute to overcoming the endoergicity of the reaction of H_2^+ with He to form HeH^+ (Chupka and Russell,1968C).

Rotational energy of reactants is expected to play an important role in certain classes of reactions in which it constitutes a major fraction of the internal energy of a collision pair. Thus, in the association reaction of weakly bound diatomics such as $N_2 + 2N_2 \rightarrow N_4^+ N_2$, the rotational energy of the reactants has a strong effect on the lifetime of the N_4^{+*} collision complex and hence on the rate constant of the reaction.

VIBRATIONAL ENERGY

Exothermic reactions

For exothermic reactions with large (i.e. approximately Langevin) cross sections, the total reaction cross section has not been found to change very much with vibrational energy. In most cases the total cross section at thermal translational energies decreases with increasing vibrational energy of the reactant ion. Examples of such reactions are (Chupka et al, 1968a, 1968b): (1) $H_2^+(H_2, H)\ H_3^+$ and (2) $NH_3^+(NH_3, NH_2)\ NH_4^+$. In reaction (1) the cross section for ca. 1.0 eV vibrational energy drops to about 80% of the $\nu = 0$ value while for reaction (2) it drops to about 55% of the $\nu = 0$ value for ca. 1.0 eV vibrational excitation. Similar behavior has been observed by other workers for several other systems (LeBreton et al, 1974; Buttrill, 1974) involving $C_2H_4^+$ and $C_2H_2^+$ reactant ions. This behavior has been rationalized by a statistical phase space argument which has been discussed at length recently by Henchman (1972) and can be described briefly as follows. If the reactants have no internal energy and very little kinetic energy and the reaction is strongly exothermic, the ratio of the volume in phase space available in the product channel to that in the (backward) reactant channel is very large and the forward reaction is strongly favored. As the collision pair is formed with more internal energy, this phase space ratio decreases. Thus if the reaction is governed at least in part by phase space considerations, the overall reaction cross section may be expected to decrease with increasing internal energy although the decrease may not be large. Large effects may be expected in cases in which rearrangement is required for the forward reaction. In general large effects may be expected for cases in which there are two (or more) competing modes of decay of the collision pair (one of which may be the backward decay) one with both higher energy and entropy of activation than the other. Thus large effects on the branching ratio of certain competing forward reactions can be expected as for example in the reactions: $C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$ and $C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H$ where the second reaction would be expected to increase relative to the first as the internal energy of the reactants is increased. This is the observed behavior (Buttrill, 1974).

The applicability of a statistical theory implies the indistinguishability of the various forms of energy which can be put into the collision pair. However, by varying the vibrational energy of a reactant rather than the relative translational (or rotational) energy, one can investigate rather simply the effect of the internal energy of the collision pair without having to consider the large effect of kinetic energy on the cross section for close collision and the effects due to the variation of the total angular momentum of the collision pair. While phase space theory (Light, 1967) properly conserves angular momentum, it cannot readily be applied to complicated systems and has only been used for three-atom and four-atom reactions. RRKM theory (Forst, 1973) on the other hand is readily applied to more complicated systems but does not rigorously conserve angular momentum, although some recent progress has been made to this end (Klots, 1972).

There are exceptions to the behavior of reaction cross section with vibrational energy described above. Thus the cross section for reaction (1) increases with increasing vibrational energy at higher kinetic energies, probably due to dominance of a direct proton transfer mechanism which would be favored by vibrational energy in H_2^+. Also the cross section for the reaction $NH_3^+(H_2O,OH)NH_4^+$ appears to be nearly independent of vibrational energy in NH_3^+ and may actually increase slightly with vibrational energy. Dominance of a direct H atom transfer mechanism which would be approximately independent of NH_3^+ vibrational energy is suggested.

Some very notable exceptions have been investigated recently. Albritton et al (1973) found that the apparently exothermic thermal energy charge transfer reaction $Ne^+ + N_2 \rightarrow N_2^+ + Ne$ increases drastically in rate with increasing vibrational temperature of N_2. The suggested explanation invokes a nearly resonant and Franck-Condon favorable charge transfer from N_2 $(\nu \ \mu \ 2)$ to N_2^+ in a highly excited quartet state. The importance in charge transfer of the condition of near resonance and of Franck-Condon factors (possibly modified at close approach of reactants) implies a dependence of cross section on the vibrational states of the reactants. Schmeltekopf et al (1971) have found a very strong increase of the rate constant for the reaction $O^+(N_2,N)NO^+$ with increasing vibrational energy of N_2. While the interpretation of the many unusual characteristics of this reaction is still a matter of some controversy (Henchman, 1972), the negative temperature dependence of the thermal rate constant from

80°K to 600°K and the positive effect of vibrational excitation suggest separate low and high energy mechanisms and in any case provide a rather stringent test of any proposed mechanism. These latter two examples show how the effects of vibrational energy give important clues regarding reaction mechanism.

Association reactions

This special class of exothermic reactions will be discussed separately since these are usually termolecular, requiring deactivation of a bimolecular collision complex. Since the third order rate constant is proportional to the lifetime of the complex which is in turn a rapidly decreasing function of internal energy, strong effects of internal energy are expected and a strong negative temperature coefficient is typical of such reactions. In a few cases, the effect of vibrational energy alone on an association reaction has been studied. One such case is the dimerization reaction of the benzene ion (or its perdeuterated analogue), $C_6H_6^+ + C_6H_6 \rightarrow C_{12}H_{12}^+$ which has been the subject of much controversy and apparently conflicting observations from which various investigators have claimed the order of the reaction to be second, third, fourth and even higher (Friedman and Reuben, 1971). A large part of the confusion results from the fact that the benzene ion as usually prepared by electron impact at ~ 50 eV has a distribution in vibrational and electronic energy of about 4 eV. Photoionization experiments (Chupka and Russell, 1974) have shown conclusively that for benzene ions formed in the ground electronic state and for low conversion (< 3%) the reaction is of third order and involves almost exclusively the ground vibrational state of $C_6H_6^+$ or $C_6D_6^+$. This is readily apparent from Fig. 1 which shows the photoionization efficiency curves for $C_6D_6^+$ and $C_{12}D_{12}^+$ in the region of the ionization potential. The curve for $C_{12}D_{12}^+$ is practically flat above the initial step corresponding to the production of $C_6D_6^+$ in its ground vibrational state while the curve for $C_6D_6^+$, as well as its photoelectron spectrum, shows the formation of the ion in a range of vibrationally excited states. The vibrationally excited monomer ions react in an approximately fourth order reaction, apparently requiring an initial deactivation, while there is evidence (Jones et al, 1974) that very highly excited benzene ions produced about 3.5 eV above the ground state dimerize in a bimolecular reaction to form a dimer which is presumably much more strongly bound and thus of different structure from that formed by the ground state reactant.

Endoergic reactions

For endoergic reactions the effects of vibrational energy can be spectacularly large. Of particular interest is the determination of the relative importance of vibrational as compared with transla-

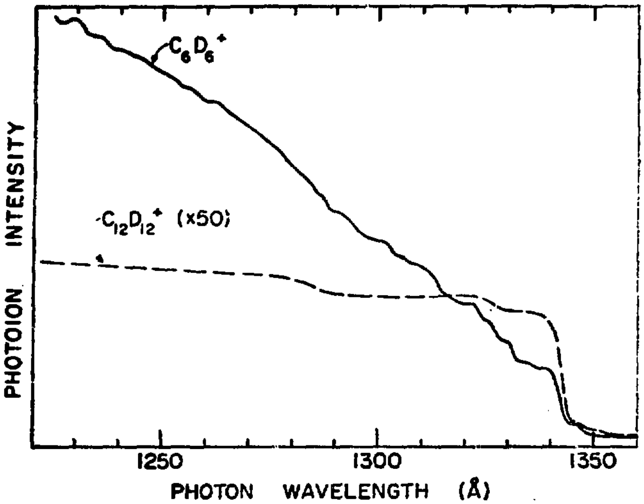

Fig. 1. Photoionization efficiency curves for $C_6D_6^+$ and for the dimerization reaction product $C_{12}D_{12}^+$.

tional energy in surmounting the potential barrier. The reactions of H_2^+ (ν = 0—5) with He have been extensively investigated (Chupka 1972) with this goal in mind. The cross section for the reaction H_2^+(He,H) HeH^+ has been measured as a function of kinetic energy for H_2^+ with ν = 0 to ν = 5. The results show that vibrational energy is much more effective than translational energy in causing reaction. The magnitude of the effect may be seen in Table 1

Table 1. Comparison of theoretical and experimental cross sections for the reaction H_2^+(He,H) HeH^+ as a function of vibrational quantum number of H_2^+ for a total internal energy of 2.0 eV in the collision complex.

ν	σ (Å^2)	
	calc.	exp.
0	0.64	0.10
1	0.76	0.34
2	0.95	0.93
3	1.17	1.70
4	1.49	2.35
4	1.94	2.49

(Truhlar 1972) which compares reaction cross sections calculated by phase space theory (which does not distinguish between translational and vibrational energy except as required by conservation of linear and angular momentum) with experimental values for a total energy of 2.0 eV in the collision complex. While the calculation yields an enhancement of a factor of about three from $\nu = 0$ to $\nu = 5$ the experimental data show enhancement by a factor of twenty-five. The greater effectiveness of vibrational energy is expected from simple theoretical considerations (Levine and Bernstein, 1974) which indicate that for reactions with a "late" barrier (i.e. in the exit part of the potential surface for the reaction) as is this reaction, vibrational energy should be more effective than translational while an early barrier should have the opposite effect. However, the detailed shape of the potential surface in the reaction region can influence the characteristics in a complicated fashion as can be seen even for very primitive idealized potential surfaces (Mahan, 1974). The potential surface for the H_2^+-He reaction has been calculated with good accuracy (Brown and Hayes, 1971) and has been used in various quantal but primitive theoretical calculations of reaction rates with some modest success in reproducing experiment (Cooper et al, 1974).

Another case of a very strong effect of vibrational energy on an endoergic reaction is illustrated by the data of Fig. 2 for the

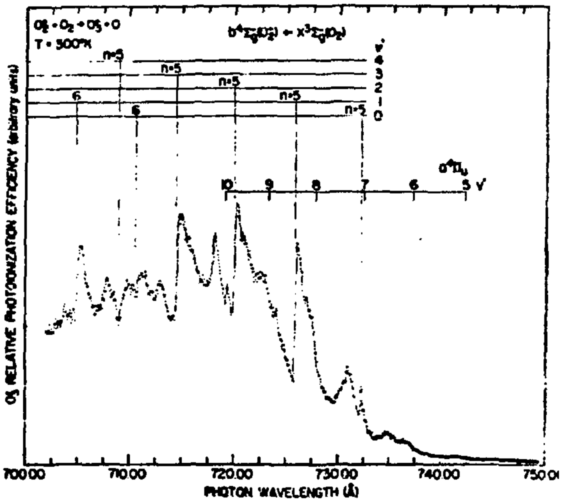

Fig. 2. Photoionization efficiency curve for O_3^+ produced by the ion-molecule reaction $O_2^+(O_2,O)\ O_3^+$.

reaction $O_2^+(^4\pi\mu) + O_2 \rightarrow O_3^+ + O$ (Dehmer and Chupka, 1974). The reactant O_2^+ ion is produced by photoionization in the long-lived metastable excited state but the reaction only becomes energetically allowed for the $\nu = 5$ level of that state. The product ion intensity rises very strongly from the $\nu = 5$ threshold through the $\nu = 9$ level. The Franck-Condon factors for the formation of these vibrational states are nearly constant and the strong rise is a measure of the strong increase in reaction cross section with vibrational energy. The presence of pronounced autoionization structure allows only a rough quantitative measurement of the effect but it is clear that the reaction cross section rises by between one and two orders of magnitude in the range. The explanation for the magnitude of the effect is not yet clear in this case. It may be in accord with statistical phase space theory for the endoergic reaction. However, the situation is complicated by the fact that the reactants are initially on an excited potential surface of the O_4^+ system which may not correlate adiabatically with the ground state products.

Electronic energy

While the effects of translational, rotational and vibrational energy can often be discussed in terms of a single potential surface for the reaction, electronic excitation in a reactant implies a different potential surface from that for ground state reactants and non adiabatic ("surface jumping") processes must be considered and are usually important. Such non-adiabatic processes can of course also be important in the case of reactants in electronic ground states since these need not even initially be on the lowest potential surface as for example the case of $Ar^+(^2P_{3/2}$ ground state) + H_2 which at large distances lies above the surface for $Ar + H_2^+(\nu = 0)$. Indeed two of the most thoroughly investigated reactions in which non-adiabatic processes are important involve ground state reactants: $H^+(H_2,H)\ H_2^+$ and $O^+(N_2,N)\ NO^+$ (Henchman, 1972).

Data on reactions of electronically excited species are relatively sparse and often consist of little more than sometimes questionable identification of the excited state involved. Franklin (1972) has reviewed some of the data on the reactions $N_2^{+*}(N_2,N)\ N_3^+$ and $O_2^{+*}(O_2,O)\ O_3^+$. The reacting state of N_2^{+*} has been assigned, probably correctly, as a theoretically expected but spectroscopically unknown metastable $^4\Sigma$ state. However, most earlier workers considered the O_2^{+*} reactant ion to be in the $^2\pi_\mu$ state which is not metastable but has its ground vibrational level at 17.045 eV or 727.4 Å which seemed to be near the crudely measured appearance potential for the reaction. The data of Fig. 2 show clearly that the reactant ion is in excited vibrational levels of the metastable $^4\pi_\mu$ state as correctly inferred by Leventhal and Friedman (1967).

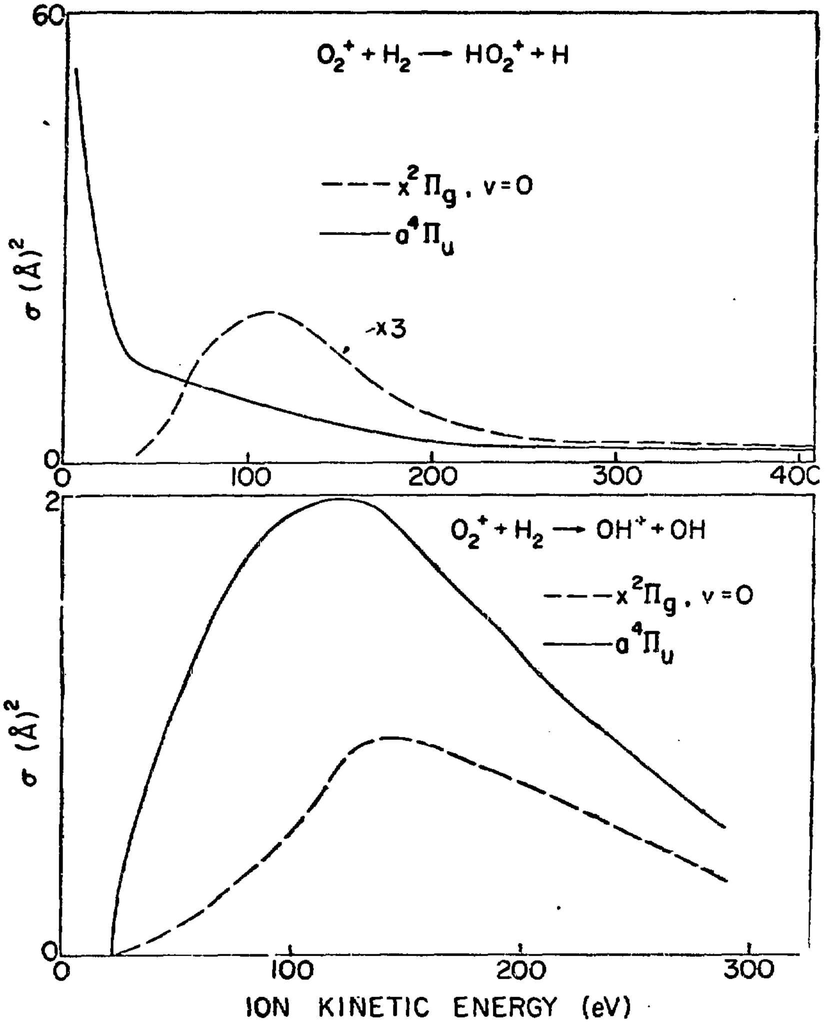

Fig. 3. Cross section as a function of laboratory kinetic energy for the reaction of O_2^+ in the ground and $^4\pi_\mu$ metastable excited state with H_2 to produce HO_2^+ and OH^+.

vibrational ground state and at about 20 eV for the large vibrational distribution actually used in the photoionization data of Fig.3. The data are in reasonable agreement with the calculated threshold.

The few examples of the effects of electronic excitation given above serve mainly to emphasize the great need for a knowledge of relevant potential surfaces for further understanding. In many cases some guidance may be obtained from a consideration of molecular orbital correlations.

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