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Cross Section for Excitation of the Fourth Positive Band System in Carbon Monoxide by 20–120 keV Protons*

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Excitation cross sections for the fourth positive band system in carbon monoxide have been determined from studies of the energy-loss spectra of 20–120-keV protons incident on gaseous CO targets. The energy-loss spectra had an energy resolution of about 2 eV. Prominent peaks in the spectra were observed at 8.5 and 13.8 eV. The first peak is believed to be due to excitation of the fourth positive band system of CO ($X^1\Sigma^+ \rightarrow A^1\Pi$), while the 13.8-eV peak covers a number of possible states, including the $B^1\Sigma^+$ and the $C^1\Sigma^+$ states. Changes in the slope of the ionization continuum were noted at 16.5 eV, corresponding to the $A^2\Pi_i$ state of CO^+, and at 20.5 eV, corresponding to the $B^2\Sigma^+$ state of CO^+. Absolute excitation cross sections for the fourth positive band system of CO are presented, as well as the total inelastic cross sections and the total ionization cross sections for 20–120-keV protons incident on CO.

I. INTRODUCTION

Heavy-ion energy-loss spectrometry can be used to determine inelastic collision cross sections for processes which cannot be studied by observing secondary particle or photon emission from the collision region. In this case, this technique has been applied to a study of the excitation of the fourth positive band system ($X^1\Sigma^+ \rightarrow A^1\Pi$) of carbon monoxide. This band (1140–2800 Å) is the most pronounced and extensive of all the bands (over 150) observed in carbon monoxide.[1] It is an optically allowed transition and is readily excited by proton impact.

Spectroscopic studies of proton–carbon-monoxide collisions have been very limited. Poliakova *et al.*[2] studied the light emitted (between 4000 and 6500 Å) from CO excited by 38-keV protons. Poulizac *et al.*[3,4] measured emission cross sections for transitions in the range 1900–11 000 Å for 30–600-keV proton bombardment of CO. They were able to measure cross sections for the first vibrational levels of the $B^2\Sigma^+$ and $A^2\Pi_i$ states of CO^+. In addition, they studied the Angstrom ($B^1\Sigma^+ \rightarrow A^1\Pi$) and Herzberg ($C^1\Sigma^+ \rightarrow A^1\Pi$) band systems of CO. They were, however, unable to measure these cross sections. They estimated their value at $\sim 10^{-19}$ cm^2/molecule. The fourth positive system includes ultraviolet wavelengths which were outside the range of their spectrometer; thus, the cross sections for the dominant structure in the H^+-CO collision energy-loss spectra have not been reported prior to this measurement.

Carbon monoxide is found in comet tails, stellar atmospheres, outer space, and in the solar chromosphere. It is also found in increasing concentration in the earth's atmosphere, being a major element in vehicular exhaust emissions. In addition, CO is of interest since it is isoelectronic with N_2. CO data can therefore sometimes facilitate understanding of equivalent processes in N_2.

The present experiment involves proton energies of 20–120 keV. Recent rocket measurements[5] have indicated that solar-wind protons, which are thought to play a major role in auroral excitations, enter the earth's upper atmosphere at velocities comparable to those used in the present experiment. Such studies indicate the importance of laboratory work on collisions between positive ions, especially protons in this energy range, and atmospheric gases.

In the present experiment, the determination of the excitation cross section of interest was made by a direct measurement of the energy-loss spectra of the forward-scattered ion beam. The energy-loss spectra was not affected by subsequent relaxation in the target, and was due only to processes induced by the detected ions. Thus, excitation cross sections were obtained without complications from cascade effects. The method used also assured that neutrals in the ion beam and secondary electrons in the collision chamber did not contribute to the results. By measuring the apparatus resolution function directly in the absence of target gas, absolute cross sections were obtained from the energy-loss spectra. Whereas the results of optical experiments are dependent on the calibration of detectors and on theoretical or experimental determination of transition probabilities, the present cross sections were independent of detector efficiencies and were not normalized to any other experiment or theory.

II. EXPERIMENTAL

A detailed description of the UMR heavy-ion energy-loss spectrometer has been published elsewhere.[6] A beam of ions was accelerated and focused on a target gas contained in a collision chamber. The forward-scattered beam was then

mass-analyzed and decelerated to 2 keV for energy analysis and detection. Energy analysis was accomplished using a 127° electrostatic analyzer.

During operation, the mass and energy analyses were both held fixed, while a small sweep voltage connected between the accelerator and decelerator high-voltage terminals was varied to obtain the energy-loss spectra. The raw data were obtained in the form of plots of collected ion current versus energy loss. Auxiliary experiments were performed to assure that the currents were true functions of energy loss only.[7]

The method of obtaining differential and total cross sections from the spectra has been discussed in recent articles.[7,8] The energy-loss spectrum $R(\xi)$ is a convolution of the apparatus resolution function $\Phi(\xi)$ (taken without gas in the collision chamber), and an experimental energy-loss differential cross section $d\bar{\sigma}/d\xi$; i.e.,

$$R(\xi)=n\,dx\int\Phi(\xi-\xi')\frac{d\bar{\sigma}}{d\xi}(\xi')\,d\xi',$$

where ξ is a (positive) energy loss as measured from the most probable energy of the beam of particles, n is the number density of scatterers, and dx is the effective path length.

Typical examples of the data obtained are illustrated in Fig. 1. Figure 1(a) is a plot of the resolution function, taken without gas in the collision chamber. Figure 1(b) is an energy-loss spectrum of 60-keV protons incident on CO at a target gas pressure of 8×10^{-4} Torr. The inelastic portions of both curves are shown at a gain of 100 times that of the elastic peak. In both cases, the elastic peak establishes the zero of the inelastic energy-loss scale.

In the present experiment, a slightly different data analysis has been applied than that used in prior experiments. Because of the energy analysis of the ion beam, ions which undergo an inelastic collision of any kind can be distinguished from the original beam spectra. The differential equation for the monoenergetic beam is given by

$$dI_{10}=-I_{10}(\sigma_c+\sigma_j+\sigma_e)n\,dx,$$

where I_{10} is the monoenergetic zero-energy-loss component of the proton beam, σ_c is the capture cross section, σ_j is the total inelastic cross section, σ_e is the cross section for elastic scattering beyond the acceptance angle of the apparatus, and n is the number of target particles per unit volume. The differential equation for the beam component which has undergone an energy loss corresponding to the desired excitation (I_{1a}) is given by

$$dI_{1a}=I_{10}\sigma_a n\,dx-I_{1a}(\sigma_c+\sigma_j+\sigma_e)n\,dx,$$

where σ_a is the cross section for excitation of the particular level. Exact solution of these equations yields the detected current $(I_{1a})_f$ in the energy-loss range corresponding to the desired excitation in terms of the detected current of the zero-energy-loss component of the beam $(I_{10})_f$ from which σ_a can be determined by

$$\sigma_a=(I_{1a})_f/nl(I_{10})_f=\int_{\Delta\xi_a}R(\xi)\,d\xi/nl\int_{\Delta\xi_0}R(\xi)\,d\xi,$$

where l is the effective length of the scattering chamber, $\Delta\xi_a$ is the energy interval of the energy-loss spectrum corresponding to the convolution of the desired transition with the apparatus resolution function, and $\Delta\xi_0$ is the interval in the energy-loss spectrum corresponding to the monoenergetic zero-energy-loss component of the proton beam.

The above analysis, which yields a very simple result, is valid whenever there are no competing processes which correspond to the same energy transfer. The effects of other direct excitations which fall within the resolution of the apparatus are simply additive and will be discussed later. Any other inelastic process involves an energy loss greater than 14 eV. For example, a capture-loss cycle for the incident proton would yield a continuum starting above 23-eV energy loss.

The above analysis permits data acquisition at target pressures considerably greater than those used in the prior experiments.[7,8] However, the data used to calculate the cross sections reported in this paper were taken under essentially single-collision conditions.

The data reported were obtained from 78 sets of paired energy-loss curves $[R(\xi)]$ and apparatus resolution curves $[\Phi(\xi)]$. These cruves were carefully analyzed and the numerical integrations performed by an IBM 360-50 computer. Systematic errors associated with this method are discussed in Refs. 7 and 8. In the present experiment, a capacitance-bridge manometer was taken as the laboratory standard.[9] The total systematic error

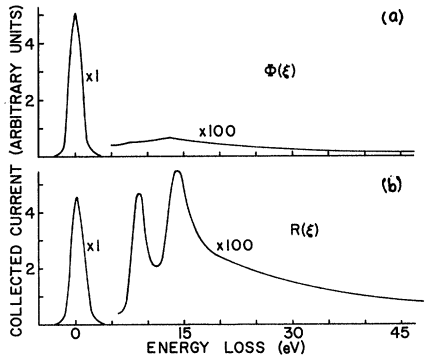

FIG. 1. Energy-loss spectrum for 60-keV protons on CO ($n\,dx=1.6\times10^{14}$ cm^{-2}). (a) Apparatus resolution function and (b) proton energy-loss spectrum.

in the present cross sections is believed to be less than ±30%, most of which is due to uncertainties in the pressure measurements.

III. ENERGY-LOSS SPECTRA

Energy-loss spectra for H^+ on CO were obtained at target gas pressures ranging from 2×10^{-4} to 3×10^{-3} Torr ($n\,dx = 4\times10^{13}$ to 6×10^{14} cm^{-2}), and at energies from 20 to 120 keV, in 10-keV increments. With each spectrum, a resolution curve was taken; the two were then used to eliminate the background before calculating the total cross sections.

Figure 2 shows the apparent energy-loss differential cross sections, $d\bar{\sigma}/d\xi$ for protons on CO at 20, 60, and 120 keV. The apparent energy-loss differential cross section is defined

$$\frac{d\bar{\sigma}}{d\xi} = \frac{R(\xi) - [\int_{\Delta\xi_0} R(\xi)\,d\xi / \int_{\Delta\xi_0}\Phi(\xi)\,d\xi]\Phi(\xi)}{nl\int_{\Delta\xi_0} R(\xi)\,d\xi}$$

It yields the cross section for energy loss by a proton colliding with a CO molecule as a function of the energy lost.

The energy-loss scale was established first by careful calibration of the sweep voltage using two differential voltmeters, and second from the location of a peak corresponding to the sum of the $1\,^1S$–$2\,^1S$ and $1\,^1S$–$2\,^1P$ transitions in the H^+-on-He spectrum. The first of these transitions occurs spectroscopically at 20.6 eV, the second at 21.2 eV. Because the two transitions cannot be separated with the present resolution, the calibration was done at a proton energy of 100 keV, where the contribution from the optically forbidden $2\,^1S$ state was expected to be small.[7]

With this calibration, the first peak in the H^+ on CO spectrum occurs at 8.5±0.2 eV. This is in good agreement with the measurements of Lassettre *et al.*[10] (8.35 eV), obtained from electron energy-loss spectra. The second, and most prominent, peak occurs at 13.8±0.3 eV. Other features of

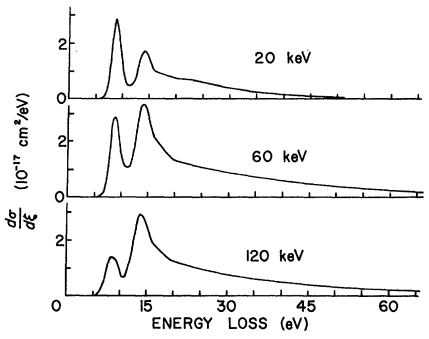

FIG. 2. Apparent differential energy-loss cross sections for H^+-CO collisions.

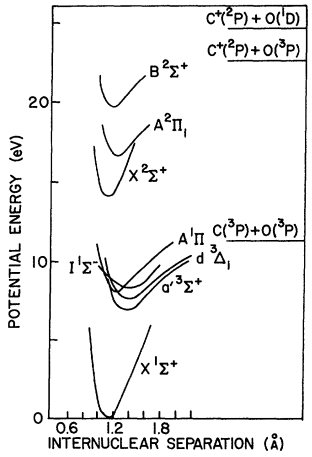

FIG. 3. Potential-energy curves for CO and CO^+ from Krupenie (Ref. 1).

the carbon-monoxide spectrum are the ionization continuum.

The potential-energy curves for CO and CO^+ are shown in Fig. 3. The well-established states which lie inside our resolution of the first (8.5 eV) peak are the $a'\,^3\Sigma^+$, $d\,^3\Delta_i$, $I\,^1\Sigma^-$, and $A\,^1\Pi$ excited states of CO. The first two cannot be reached from the ground state of CO ($X\,^1\Sigma^+$) without violating the Wigner spin rule. This rule is expected to hold in the absence of perturbations from other states which can produce a mixture of singlet and triplet terms within an otherwise pure triplet state. Poulizac *et al.*[3] reported observation of triplet-state excitation. They found a quadratic pressure dependence with no apparent excitation at very low pressures. They concluded that these states were excited by secondary electrons or neutral hydrogen and that the excitation of triplet levels from the ground state had a very low probability. Excitation of the $I\,^1\Sigma^-$ state involves a Σ^+-Σ^- transition which is forbidden for all order of multipole radiation.

The $X\,^1\Sigma^+$-$A\,^1\Pi$ fourth positive transition is optically allowed and the radiation from the fourth positive band is about a thousand times stronger than those due to the forbidden transitions which they overlap.[1] We feel the identification of the (8.5 eV) peak with this transition is well justified.

The second peak covers a number of states including the $B\,^1\Sigma^+$ and $C\,^1\Sigma^+$. These states were noted in the paper of Poulizac *et al.*[3] Since the peak is not clearly resolved from the ionization continuum, no attempt was made to determine the cross sections for the second peak.

In an energy-loss spectrum, simple ionization of the target molecule produces a continuum beginning at the ionization potential, while simultaneous excitation and ionization produces another continuum beginning at the potential required to simultaneously ionize the molecule and excite the molecular ion to

the excited level. In the energy-loss spectrum in Fig. 2, a change of slope is evident at an energy loss of about 16.5 eV which marks the $A\,^2\Pi_i$ state of CO^+. The $A\,^2\Pi - X\,^2\Sigma^+$ transition in CO^+ is the comet-tail system which is responsible for the strongest bands of CO^+. A similar change in slope at about 20.5 eV marks the $B\,^2\Sigma^+$ state of CO^+ which is the source of the $B\,^2\Sigma^+ - X\,^2\Sigma^+$ first negative system of CO^+. Since these processes involve the simultaneous excitation-ionization of the target by the projectile, the resulting features in the energy-loss spectrum are smeared out due to the variation in the energy which can be transferred to the ejected electron. Hence they do not produce distinct features in the energy-loss spectrum which could otherwise be used to determine cross sections.

IV. TOTAL EXCITATION CROSS SECTIONS

Total cross sections for excitation of the sum of the vibrational levels in the fourth positive band system of CO by proton impact are shown in Fig. 4. These were obtained by integration over the 8.5-eV peak in the energy-loss spectra. The error bars are ±2 standard deviations. No other measurements of the excitation cross section of the fourth positive bands are known to the authors.

The cross section for excitation of the fourth positive band system is large for an excitation cross section, as would be expected from the strength of the observed optical lines. The shape of the cross section curve is markedly different in shape from that obtained for the LBH of N_2.[8] They also differ markedly from the shape of the total inelastic cross sections shown in Fig. 5. This figure shows total cross sections for inelastic processes not involving charge exchange in collisions of H^+ with CO. These were obtained by integrating over the entire inelastic portion of the energy-loss spectra. Included in these measurements are all excitation, gross ionization, and dissociation.

V. TOTAL IONIZATION CROSS SECTIONS

Total gross ionization cross sections were obtained by integrating the energy-loss spectrum over

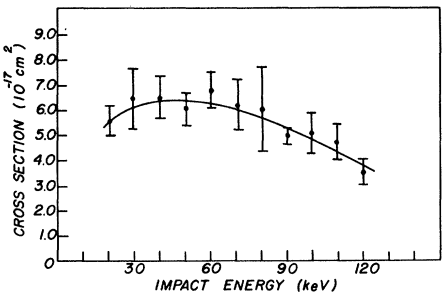

FIG. 4. Excitation cross sections for the fourth positive band system in CO.

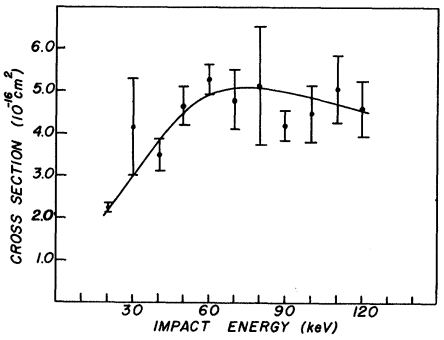

FIG. 5. Total cross section for inelastic processes in H^+-CO collisions which do not involve electron capture.

all energies greater than the ionization potential of CO. The results are shown in Fig. 6. These can be considered total cross sections for loss of energy greater than that required to remove a single electron from the CO target. They include processes such as simultaneous ionization and excitation, excitation of auto-ionizing levels, and double ionization. Shown also in Fig. 6 are data of Poulizac *et al.*,[3] who used the parallel-plate method to measure cross section for the production of electrons. These measurement were also subject to the same extraneous processes listed above. Although the shape of the two curves is quite similar, agreement is not very good. The discrepancy could be due to incomplete accounting for loss of beam by scattering in our results. However, independent checks of beam conservation similar to those discussed in Refs. 7 and 8 show that only a negligible portion of the beam was scattered out of the acceptance angle. As concerns the ionization cross sections in general, however, it should be pointed out that agreement among investigators in this energy range is not good. Of the extraneous processes that can affect ionization measurements by the conventional parallel-plate-condensor methods, many

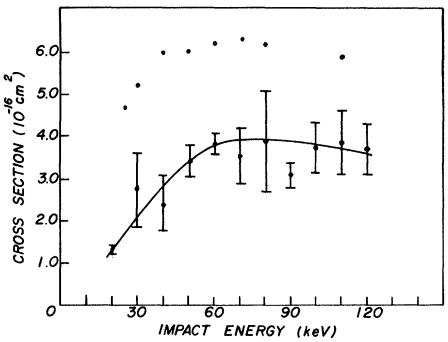

FIG. 6. Total cross section for ionization of CO by protons. Points with error bars are present data; others are from Poulizac *et al.* (Ref. 4).

become important at low energies.[11] The cross section for charge changing, for example, is comparable to that for ionization at these energies. Thus, elimination of charge-exchange effects in the parallel-plate method becomes difficult. The effects of the differences between the two types of measurements are discussed in Ref. 7. It should also be noted that the present measurement uses a M.K.S. Baratron[9] for the pressure measurement while Poulizac *et al.*[3] used a McLeod gauge.

VI. DISCUSSION

With no adequate theory and no other known experimental data available for a comparison with our excitation cross-section measurements, a complete evaluation is difficult at present. Proper determination of the relative intensities of vibrational levels in the fourth positive bands, for example, must await improved resolution.

The identification of the band within the 2-eV resolution of the system seems quite definite. Recent modifications of the energy-loss spectrometer have permitted measurements with 0.7-eV resolution. A measurement of the excitation cross section for 60-keV protons incident on CO has been made with the improved resolution. The new measurements were in agreement with the results reported here. Since the $C\,^1\Sigma^+$ state together with the smaller contribution of the $B\,^1\Sigma^+$ state are resolved in the spectra taken with 0.7-eV resolution, this agreement indicates that contributions from these states were eliminated in calculating the cross section for the fourth positive band system of CO.

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