Collision Cross Sections for the Excitation of the Schumann-Runge Dissociation Continuum in Molecular Oxygen by 20-110-keV Protons*

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Absolute cross sections for the excitation of the Schumann-Runge dissociation continuum of molecular oxygen have been obtained from inelastic energy-loss spectra induced by 20–110-keV protons incident on gaseous targets of molecular oxygen. Apparent differential energy-loss cross sections, ionization cross sections, and total inelastic cross sections are also obtained from the energy-loss spectra. The proton energy-loss spectra have an energy resolution of about 2 eV. The energy location of the first peak in the energy-loss spectra of O_2 is in general agreement with the findings of photoabsorption and electron energy-loss-spectra measurements. The cross section for the Schumann-Runge dissociation continuum for 20–110-keV protons varies between 5 and 7×10^{-17} cm^2 and has a broad maximum at about 60 keV. Existing theoretical treatments show poor agreement with these reported cross sections for the excitation of the dissociation continuum with respect to both absolute magnitude and curve shape.

I. INTRODUCTION

Heavy-ion energy-loss spectrometry can be used to study many processes occurring as a result of heavy-ion–atom inelastic collisions. The method is of particular value when the collision process does not result in a unique secondary particle which can be unambiguously attributed to the process under study. In this paper, heavy-ion energy-loss spectrometry has been applied to the Schumann-Runge dissociation continuum of molecular oxygen.

The Schumann-Runge continuum has previously been studied by optical measurements of photoabsorption coefficients[1–4] and by electron energy-loss spectrometry.[5] Energy-loss spectrometry, both for heavy ions and electrons, and photoabsorption spectra measurements are similar in that the secondary particle need not be detected. Hence, a dissociation continuum can be studied even if that continuum can lead to several different final-state configurations.

The Schumann-Runge dissociation continuum is important in understanding the production of atomic oxygen formed in the upper atmosphere. This continuum is excited by solar ultraviolet radiation and by the electrons, protons, and other heavy ions in the solar wind. Rocket experiments[6] indicate solar-wind proton energies of 30–240 keV at altitudes above 100 km, an energy range which overlaps the proton energies used in the present experiment.

In the present experiment the determination of the excitation cross section is made by a direct measurement of the energy-loss spectra of the forward-scattered ion beam. The energy-loss spectra is not affected by subsequent relaxation in the target, and is due only to processes induced by the detected ions. Thus, excitation cross sections are obtained without complications from cascade effects, and it is assured that neutrals in the ion beam and secondary processes in the collision chamber do not contribute to the results. By measuring the apparatus resolution function directly in the absence of target gas, absolute cross sections can be obtained from the energy-loss spectra. Whereas the results of experiments involving the detection of secondary products of the collision process are often dependent on the calibration of detectors and on theoretical or experimental determination of transition probabilities, the present cross sections are independent of detector efficiencies and are 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.[7–9] A beam of ions was accelerated and focused on 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 by a 127° electrostatic analyzer.

During operation, the mass and energy analyzers 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 vs energy loss. Auxiliary experiments were performed to assure that the currents were true functions of energy loss only (see Refs. 7–9).

The method of obtaining differential and total cross sections from the spectra has been discussed in recent articles.[8,10] 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.,

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

where n is the number density of target molecules, l is the effective path length, and ξ is the (positive) energy loss of the ions measured from the most probable energy of the unscattered monoenergetic beam.

The cross section σ_a, for a process for which there are no competing processes which correspond to the same energy transfer, can be found by exact solution of the differential equations for the various beam (specific energy-loss) components. The resulting equation[10] is

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

where $(I_{1a})_f$ is the detected current in the energy-loss spectrum. $\Delta\xi_a$ is determined by the energy width of the convolution of the cross section for the transition with the apparatus resolution function $\Phi(\xi)$. $(I_{10})_f$ is the detected current of the zero energy-loss component of the beam. $(I_{10})_f$ can be determined by integrating the energy-loss spectrum over the energy interval $\Delta\xi_0$, where $\Delta\xi_0$ corresponds to the energy interval which accounts for 99.99% of the area under the apparatus resolution function.

Application of this analysis permits data acquisition at target pressures considerably greater than pressures corresponding to single-collision conditions. The data used in obtaining the cross sections reported in this paper were, however, taken under essentially single-collision conditions.

Systematic errors associated with this method are discussed in Ref. 8. In the present experiment a capacitance bridge manometer[11] was taken as the laboratory pressure standard. The total systematic error in the reported cross sections is believed to be less than 30%, most of which is due to uncertainties in the pressure measurement.

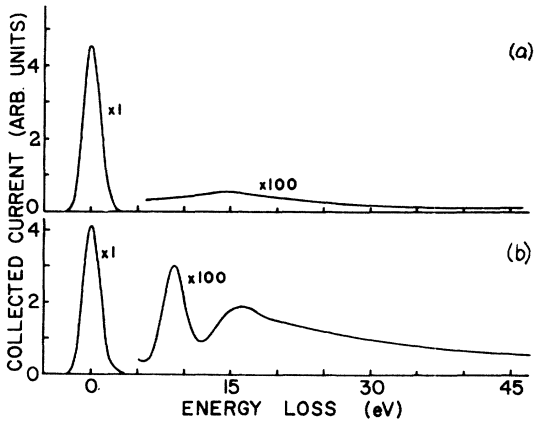

FIG. 1. Energy-loss spectrum for 60-keV protons incident on O_2 ($ndx = 1.24 \times 10^{14}$ cm^{-2}): (a) apparatus resolution function $\Phi(\xi)$; (b) proton energy-loss spectrum.

III. ENERGY-LOSS SPECTRA

Energy-loss spectra for H^+ on O_2 were obtained at target gas pressures ranging from 2×10^{-4} to 1×10^{-3} Torr ($ndx = 4\times10^{13}$ to 2×10^{14} cm^{-2}), and at energies of 20–110 keV, in 10-keV increments. The target gas pressure range was chosen so as to fall in the region where the scattered intensities varied linearly with pressure. With each spectrum, a resolution curve was taken and the two were used in conjunction to eliminate the background for calculating total cross sections.

An energy-loss spectrum for impact of 60-keV protons on O_2, at a pressure of 6.2×10^{-4} Torr, is shown at a gain 100 times that of the elastic peak (Fig. 1). The elastic peak establishes the zero for the inelastic energy-loss scale. Figure 2 shows apparent differential energy-loss cross sections defined[10] as

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

where the differential cross section for elastic scattering with zero energy loss has been removed. The differential energy-loss cross-section curves give the cross section for loss of energy as a function of the energy lost. Differential cross sections are shown for 20-, 60-, and 110-keV protons incident on molecular oxygen.

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 is expected to be small.[8]

With this calibration, the first peak in the H^+ on O_2 spectrum occurs at 8.7 ± 0.2 eV and the second at 15.5 ± 0.3 eV. A change in the slope of the ionization continuum can be observed at 19 eV.

Potential energy curves for O_2 and O_2^+ are shown in Fig. 3. The curves are due to Gilmore.[12] The Schumann-Runge continuum is believed to be due to the excitation of O_2 from the ground state to high vibrational states of the $B^3\Sigma_u^-$ band of O_2 followed by dissociation to $O(^3P) + O(^1D)$. Small contributions to this continuum may also arise from excitation to the optically allowed $^3\pi_u$ state follow[illegible]

by dissociation to $O(^3P)+O(^3P)$ or the optically forbidden $^1\Delta_u$ state which dissociates into $O(^1D)+O(^1D)$. The dashed lines in Fig. 3 indicate an excitation taking place without a change in internuclear separation of the O_2 molecule, i.e., an excitation satisfying the Franck-Condon principle. The excitation energy indicated for the $B^3\Sigma_u^-$ state is consistent with our observation of 8.7 eV for the peak of the Schumann-Runge continuum particularly if a small contribution from a low-intensity higher energy-loss peak, discussed below, is considered. Other experiments and theory yield peak values near 8.7 eV. Lassettre *et al.*[5] obtained a value of 8.44 eV while experiments with photoabsorption spectra[1-4] have revealed values varying from 8.57 to 8.73 eV. The theoretical calculations of Steuckelberg[13] yielded a value of 8.47 eV.

Lassettre *et al.*[5] found a number of additional peaks in the electron energy-loss spectra. It should be noted, however, that the possibility of electron exchange permits the excitation of states by electron impact which are not allowed for proton impact. Lassettre *et al.* found a peak at 9.94 eV. The final excited state corresponding to this peak was not identified. Detailed study of our energy-loss spectra curve shapes indicated the probability of a similar peak for proton impact. Preliminary data taken with improved resolution obtained from recent apparatus modifications indicate that this peak makes a contribution of approximately 8% to the 8.7-eV peak. A survey of the well-established levels corresponding to a 9.9-eV energy loss indicates that the probable excited level is the $^1\Delta_u$ state which dissociates to $O(^1D)+O(^1D)$. The potential curves of all the established levels near 9.9 eV are very flat and lead to dissociation if the Franck-Condon principle is obeyed. The data reported below includes this estimated 8% contribution to the dissociation continuum from the higher level.

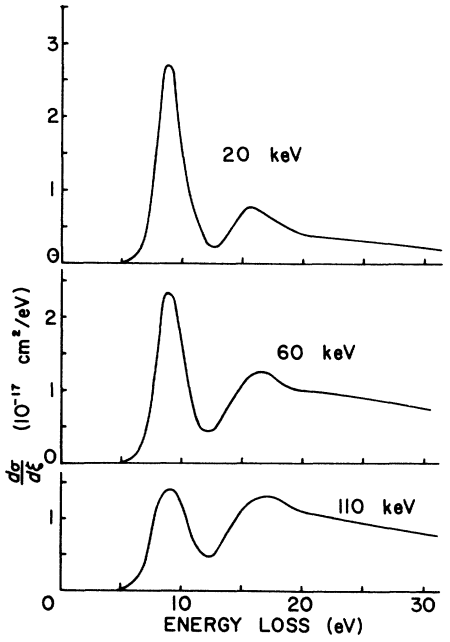

FIG. 2. Apparent differential energy-loss cross sections for H^+-O_2 collisions.

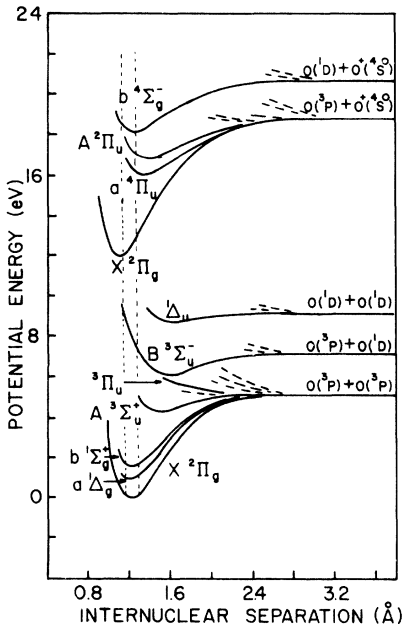

FIG. 3. Potential energy curves for O_2 and O_2^+ taken from Gilmore, Ref. 12.

The peak at 8.7 eV may also include contributions from the Schumann-Runge bands. These bands cover an energy range in the spectra from 6.1 to 7.1 eV. The excitation of these bands requires a sizable increase in the internuclear separation of the oxygen atoms in the molecule. The cross section for excitation of these bands is expected to be much smaller than the cross section for excitation of the continuum. Their absorption coefficients vary from 0.0001–0.02 of the peak in the absorption of the continuum.[3] For these reasons, the contribution of these bands is believed to be very small and has, therefore, been ignored in determining the cross section for excitation of the Schumann-Runge continuum.

The peaks Lassettre *et al.*[5] reported in the electron energy-loss spectra at 12.9, 15.4, and 17.0 eV are not individually detectable. They may contribute as a group to the broad 15.5-eV peak observed in Figs. 1 and 2. The change in the slope of the energy-loss spectra at 19 eV corresponds to a peak reported by Lassettre *et al.* at 19.1 eV.

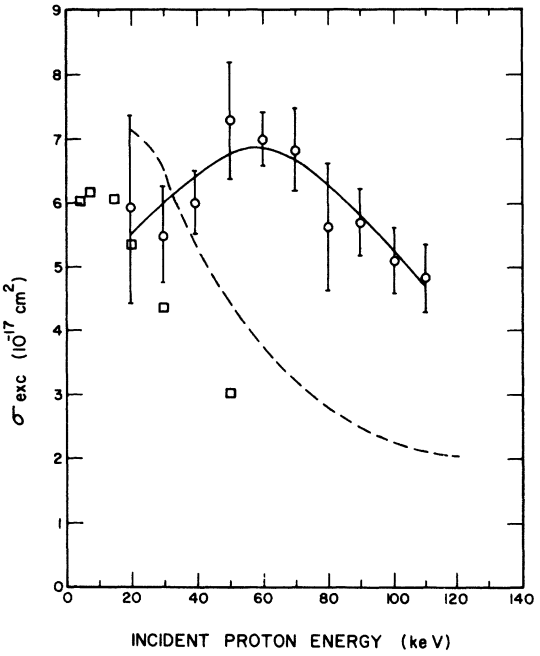

FIG. 4. Total cross section for excitation of the Schumann-Runge dissociation continuum of O_2 (see text) ○: present data; □: theoretical calculations of Breene (Ref. 15); dotted line: theoretical calculations of Green divided by four (Ref. 16).

IV. TOTAL EXCITATION CROSS SECTIONS

Cross sections for the excitation of the Schumann-Runge dissociation continuum by 20- to 110-keV proton impact are shown in Fig. 4. These data were obtained by integrating over the 8.7-eV peak in the apparent energy-loss differential cross sections. The error bars shown are ±1 standard deviation. The reported cross sections as noted above are primarily due to excitation of the $X^3\Sigma_g^- - B^3\Sigma_u^-$ transition in O_2, where the excited $B^3\Sigma_u^-$ state dissociates into $O(^3P)+O(^1D)$, but also includes an estimated 8% contribution due to excitation of a higher (~9.9 eV) state. Also shown in Fig. 4 are theoretical calculations due to Breene[14,15] and Green.[16] The theoretical curves of Breene use the impact-parameter method. The curve of Green (which is shown reduced by a factor of 4) was determined from generalized oscillator strengths obtained by Lassettre *et al.*[5] from inelastic electron scattering experiments. The agreement of our data with these theoretical results is not good with respect to either magnitude or curve shape. The lack of agreement is not unexpected as the approximations employed in both types of calculations are not valid for 20- to 110-keV protons.

V. IONIZATION AND TOTAL INELASTIC CROSS SECTIONS

The total cross section for loss of energy greater than that required to remove a single electron from the O_2 molecule may be compared to the total gross ionization cross section. A discussion of the differences between our measurements and those made using the parallel-plate method is given in Ref. 8. These data are shown in Fig. 5. Also shown are the data of de Heer *et al.*,[17] unpublished data of Crooks and Rudd,[18] and the lowest point in the data of Hooper *et al.*[19] Our data could be low as a result of incomplete accounting for loss of beam by scattering. See the discussion section below. The agreement between the four measurements of ionization cross sections is not very good but is not atypical for ionization cross section measurements in general.

Figure 6 shows the total inelastic cross section obtained by integrating over the apparent differential energy-loss cross section. It represents the cross section for loss of energy by any process which leaves the incident proton charge unchanged.

VI. DISCUSSION

Heavy-ion energy-loss spectrometry permits the measurement of processes such as, in this case, the excitation of the Schumann-Runge continuum which can not be readily measured by experiments detecting the ejected secondary particles. In several cases this method has provided the only known collision cross sections. The major uncertainty in the present set of experiments using the heavy-ion energy-loss spectrometer is the effect of angular scattering. This was discussed in the first of this group of papers (Ref. 8) and in detail in Ref. 20. The argument is that if the inelastic cross sections have very strong angular dependence, so that the major contribution to

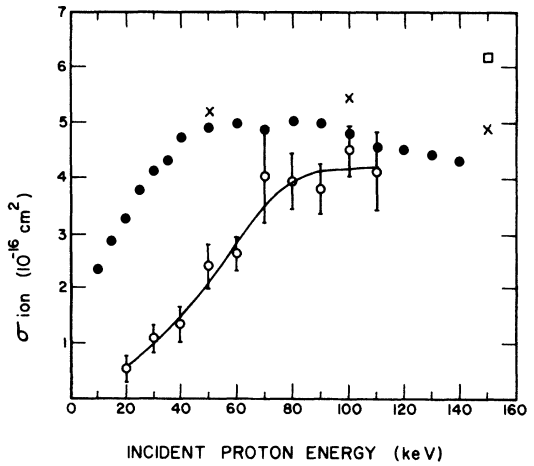

FIG. 5. Total cross sections for ionization of O_2 by protons. ○: present data; •: de Heer *et al.* (Ref. 17); □: Hooper *et al.* (Ref. 19); ×: Crooks and Rudd (Ref. 18).

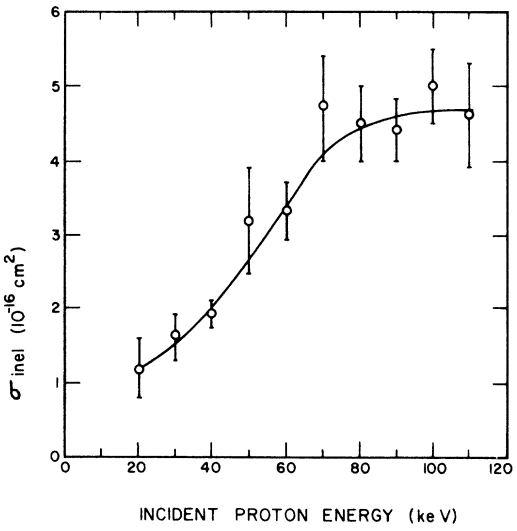

FIG. 6. Total cross section for inelastic processes in $H^+ - O_2$ collisions which do not involve charge exchange.

an inelastic cross section occurs at large angles, then our results for that specific process are not for the total cross section but only represent the beam which was not scattered outside of our acceptance angles. We have performed several experiments to explore this possibility.

We have checked to determine the fraction of the ion beam lost to the system by comparing the detected ion current with gas in the scattering chamber plus the charge-exchanged neutral beam to the beam detected without gas in the scattering chamber. The mean ratio was 0.97 ± 0.098 with ratios greater than, and smaller than, one occurring with almost equal frequency. These ratio measurements include data taken at pressures two orders of magnitude higher than gas pressure used for the energy-loss-spectra measurements reported above. Within the errors of the measurements no trend with pressure could be detected. Considering the uncertainty in the measurements and in the charge-exchange cross section, this result is consistent with the assumption that no appreciable fraction of the beam is scattered out of the acceptance angle.

Beam-profile measurements have been performed at the entrance to the analyzer using deflection plates located near the entrance to the decelerator column. No detectable increase in the observed size of the beam at the entrance to the analyzer was observed even with gas pressure ten times those used in this experiment.

The acceptance angle in the vertical plane ($\sim 2\times10^{-3}$ rad) is defined by the analyzer slits modified by the focal properties of the decelerator column. In the horizontal plane, the acceptance angle of the decelerator-analyzer system ($\sim 1.5\times10^{-2}$ rad) is modified by the focal properties of the magnet and because the 127° analyzer slits are horizontal, the acceptance angle in the horizontal plane is larger than the angle of divergence of the beam. Thus the system samples a fixed horizontal slice across the total beam interacting with the target gas with possible complications due to scattering out of and scattering into these acceptance angles. Theoretical estimates of total scattering[20] indicate that in our ion energy and target pressure range, less than 1% of the beam would be scattered outside of our acceptance angle due to both elastic and inelastic scattering, a result which is collaborated by the data of Barat and Houver.[21] It should also be noted that some ions which would not have reached the analyzer could be scattered into the acceptance angle and partially compensate for those scattered out of the acceptance angle.

We are in the process of modifying our apparatus to make it possible to measure the energy-loss spectra of scattered ions. Until this experiment has been performed we know of no way to definitely determine if the inelastic scattering corresponding to a particular process is entirely within our acceptance angle. This experiment should provide a definite answer on the angular dependence of inelastic excitation cross section.

At present we do not believe our excitation cross sections will be significantly affected by underestimates of a possible enhanced cross section for beam scattered out of our acceptance angles. The relative magnitude of the total ion beam scattered beyond our acceptance angle is very small, and if it is assumed that the inelastic cross sections are independent of the elastic cross section, other than their common dependence on impact parameter, a very strong angular dependence in the cross section would be required if the scattered beam were to affect the results. Even this effect would be partially compensated by beam scattered into the acceptance angle. For these reasons, it seem reasonable to expect that the energy-loss spectra obtained are representative of the weighted average over all scattering angles and that the cross sections reported are equivalent to the total cross sections.

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