Dissociation of N_2^+ and O_2^+ by Electron Impact*

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Cross sections for dissociation of N_2^+ and O_2^+ by electron impact were measured for interaction energies E between 10 and 500 eV and between 15 and 500 eV, respectively. The cross-section–versus–interaction-energy curves exhibit maxima in the vicinity of 75 eV and decrease monotonically at higher energies with an (A/E) log BE dependence. Maximum cross-section values are $4.3\pi a_0^2$ for N_2^+ and $4.1\pi a_0^2$ for O_2^+. The curves are remarkably similar at the higher interaction energies. The ion targets are typical of those formed by bombardment of gas by electrons of 150 eV and more, and some may be in excited electronic states.

I. INTRODUCTION

CROSS sections for dissociative excitation of molecules by electron impact have eluded quantitative experimental investigation until very recently. Even now, there seems to be a paucity of data except for[1,2] H_2 and for[3–5] H_2^+ and D_2^+. Probably the main difficulty lies in detection of the resultant atomic species. When the target molecules are ions, however, this difficulty is obviated, and quantitative measurements can be obtained[4] using crossed-beam techniques.

In this work the total cross sections for dissociation of N_2^+ and O_2^+ by variable energy electrons are reported. One must note, however, that the target N_2^+ and O_2^+ ions are typical of those formed by bombardment of N_2 and O_2 by high (150-eV) energy electrons in a low-pressure (10^{-3} Torr) ion source, and may thus be a mixture of ground- and excited-state molecular ions as discussed in Sec. III.

II. EXPERIMENTAL METHOD

The apparatus is the same as that used[4] for H_2^+ and is only briefly described here. Ions are formed by electron bombardment of N_2 or O_2 gas at a pressure of about 10^{-3} Torr. The bombarding electrons have energies greater than about 150 eV. The 6-keV ion beam is mass-analyzed and passed through several stages of differential pumping before entering the scattering chamber. Transit distance of the beam from ion source to collision region is about 150 cm. An electrostatic lens just in front of the collision region rejects atomic ions (N^+ or O^+) produced by background breakup of molecular ions. In the collision region, the ion beam of about 2 μA is crossed at right angles by a variable-energy intensity-modulated electron beam of about 1 mA. The spatial distributions of both beams can be simultaneously probed at the interaction region so that the degree of overlap of the beams can be determined.

Atomic ions resulting from the dissociation are separated with a 45° parallel-place electrostatic analyzer. A lock-in detector, together with a high-impedance preamplifier, are used to measure signal currents of order 10^{-15} to 10^{-14} A. All currents are integrated for preset times and their integrated values, along with other pertinent data, are punched on paper tape and reduced by a computer.

The main operational difference between this experiment and that on H_2^+ is the difference in energies of the ion beams. For the N_2^+ and O_2^+ measurements, energies of about 6 keV were used, compared to 10 keV for H_2^+. In this type of experiment it should be noted that as the ion energy is reduced, the transverse kinetic energy of dissociation causes the signal beam to diverge in space more and more. If the divergence is large enough, some atomic ions from the dissociation will not be collected. In the case of H_2^+ the limiting ion energy required to prevent this was about 5 keV; below this energy the "apparent cross section" decreased with decreasing energy.

The kinetic energies of atomic ions from dissociation of N_2^+ and O_2^+ are not known; however, they should be nearly the same as the energies from dissociative ionization of N_2 and O_2. Energies[6] of N^+ from dissociative ionization of N_2 suggest that only a small fraction (less than 7%) of N^+ will have dissociation energies larger than encountered in the H_2^+ experiment.[4] Similar considerations apply[7] to oxygen. Thus, on the basis of this comparison and the tests made on the H_2^+ data, it was concluded that little error results in the present case from use of lower ion-beam energies which are imposed by magnetic field limitations.

Cross sections are calculated from the equation

$$\sigma=\frac{eI_A}{I_iI_e}\frac{v_iv_e}{(v_i^2+v_e^2)^{1/2}\Omega}\frac{1}{}, \qquad (1)$$

where σ is the cross section, I_i is the primary ion current,

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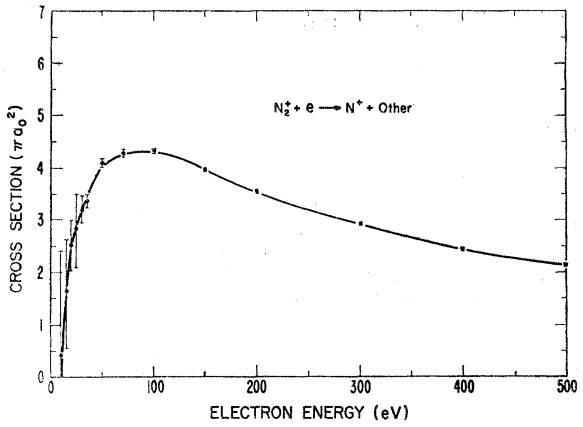

FIG. 1. Total cross section in units of πa_0^2 versus electron energy for the formation of N^+, when N_2^+ is bombarded by electrons. The solid curve at 100 eV and above can be represented by Eq. (3), and below 100 eV the curve is sketched in as the authors' guess for the extrapolation between the experimental points. Flags represent standard deviation from the mean.

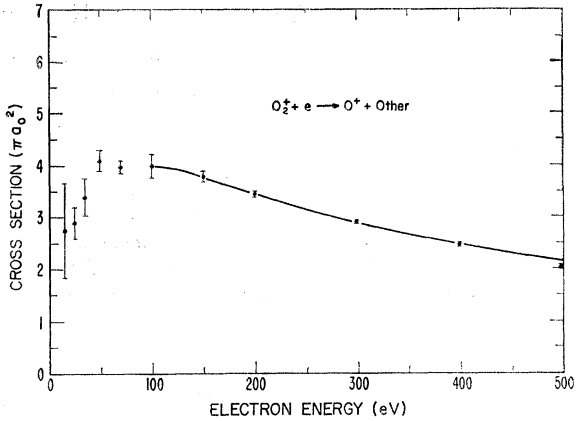

FIG. 2. Total cross section in units of πa_0^2 versus electron energy for the formation of O^+, when O_2^+ is bombarded by electrons. The solid curve can be represented by Eq. (4). Flags represent standard deviation from the mean.

I_e is the electron current, I_A is the measured atomic ion current, v_i and v_e are the velocities of the primary ions and electrons, respectively, and e is the electronic charge. The beam overlap factor Ω is given by

$$\Omega=\frac{\int R(z)G(z)dz}{\int R(z)dz\int G(z)dz}. \tag{2}$$

Here $R(z)$ and $G(z)$ are one-dimensional spatial distributions of the ion and electron beams, respectively, as determined by simultaneous probing of the beams.

With the exception of the beam energy difference discussed above, identical procedures to those used[4] in the H_2^+ experiment were employed. Possible systematic effects were discussed at length in the earlier paper. Systematic uncertainties are assumed to be about the same in this experiment. In addition to a possible 7% uncertainty associated with ion collection efficiency as discussed above, we must attach estimated uncertainties of about 18% to the points at lowest energy. This decreases to a nearly constant uncertainty of about 8% for points at 50 eV and above.

III. RESULTS AND DISCUSSION

Results for N_2^+ are shown in Fig. 1 where the cross section in units of πa_0^2 is plotted against interaction energy in eV. Flags on each point indicate the standard deviation from the mean for a number of measurements. The standard deviation becomes much larger at low energies due to loss of electron current and subsequent loss of dissociation signal.

The cross-section measurements for N_2^+ at 100 eV and above can be represented to within 1% by the expression

$$\sigma=(923/E)\log_{10}E-(1411/E), \tag{3}$$

where σ is cross section in units of πa_0^2 and E is the interaction energy in electron volts. The dominance of the logarithmic term at high energies indicates the dominant role of dipole-allowed transitions at these energies.

Results for O_2^+ are shown in Fig. 2 with the same notation as in Fig. 1. The solid curve in the figure is a representation of the expression

$$\sigma=(972/E)\log_{10}E-(1544/E). \tag{4}$$

The measurement at 500 eV is 6% below the value of this expression, but all other measurements at 100 eV and above are within 1% of Eq. (4). Again the dipole term dominates at high energies.

The O_2^+ data were more difficult to obtain, as reaction of the O_2 with the hot tungsten filament seemed to cause unstable ion-source conditions resulting in small changes in the beam's spatial profile at the interaction region. Though any change in profile [hence the factor Ω in Eq. (2)] during the course of a data run would represent a small systematic error in the measurement, no correction was made to data. Any possible error from this source has been included in the calculation of the standard deviation—i.e., all points at each interaction energy were averaged together and their standard deviation from the mean was computed.

Frank-Condon factors[8] between ground-state N_2 and the ground $X^2\Sigma_g^+$ state of N_2^+ indicate that over 99% of the N_2^+ will be in the $v=0$ and $v=1$ vibrational levels. Correspondingly,[9] for O_2^+ over 99% of the ions will be in the first five vibrational levels. This, in addition to the fact that the N_2^+ and O_2^+ potential wells are relatively deep (8.7 eV and 6.5 eV, respectively), makes these targets quite different from the H_2^+ target for which all vibrational levels of a rather

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shallow well (2.65 eV) were probably populated. This probably accounts for the difference in the gross appearance of Figs. 1 and 2 as compared to the corresponding figure[3,4] for H_2^+. Thus, in Fig. 1 and 2 for N_2^+ and O_2^+, the cross sections reach maxima at about 70 eV. For H_2^+, the cross section is a rapidly rising function with decreasing energy, even down to the lowest observed (12.3-eV) interaction energies.

One must qualify these latter considerations, however, with recognition of the fact that long-lived electronic states of N_2^+ and O_2^+ may be present in the target beams. Effects of such states (generally thought to be primarily quartet states) have been clearly observed[10,11] in ion-molecule collision studies using beams of ions. Indeed, it has been estimated[10] and shown[11] that up to 30% of an O_2^+ beam may be in an excited electronic state (presumably a $^4\Pi_u$ state). The tendency in Fig. 2, of the O_2^+ data to remain high at low energies, may be evidence of the presence of such states in this experiment.

In summary, the data of Figs. 1 and 2 represent measurements, within stated accuracy, of cross section for total dissociation by electron impact on N_2^+ and O_2^+, respectively, where the N_2^+ and O_2^+ are typical of ions formed by high-energy (150-eV) electron impact on neutral gas at low (10^{-3} Torr) pressure. Though theoretical work has been done for H_2^+, it does not seem likely that there will be theoretical work for the species reported here for some time.

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Cross Sections for Excited-State Mixing in Cesium–Noble-Gas Collisions from D_2 Optical Pumping

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Cross sections for random collisional reorientation of **J** within the sublevels of the $6^2P_{3/2}$ excited state of cesium have been measured using the D_2 optical-pumping technique. The measured cross sections σ_M^2 are: Cs-He $(3.2\pm0.6)\times10^{-15}$ cm^2, Cs-Ne $(2.9\pm0.6)\times10^{-15}$ cm^2, Cs-Ar $(6.0\pm1.2)\times10^{-15}$ cm^2, Cs-Kr $(9.2\pm1.9)\times10^{-15}$ cm^2, Cs-Xe $(11.3\pm2.3)\times10^{-15}$ cm^2. Simplified equations for D_1 and D_2 pumping with zero, partial, and complete excited-state mixing are derived for a hypothetical alkali atom with zero nuclear spin. The calculations are extended to cesium atoms with nuclear spin $\frac{7}{2}$ pumped by σ^+ D_2 radiation. The equilibrium value $\langle S_z\rangle_0$ and the time dependence $\langle S_z(t)\rangle$ of the electronic spin polarization are computed for various degrees of excited-state mixing. $\langle S_z(t)\rangle$ is found to be nearly single-exponential in the zero- and the complete-mixing cases, but shows a distinct double-exponential behavior in the intermediate region. $\langle S_z\rangle_0$ is shown to be dependent on the degree of mixing, and to change sign as the degree of mixing increases. Measurements were performed with a new transmission technique by passing a separate σ^+-polarized D_2 pumping beam and an alternately σ^+- and σ^--polarized D_1 testing beam through the cesium absorption cell. The cross sections for collisionally induced mixing were evaluated by measuring the buffer pressure at which $\langle S_z\rangle_0$ passed through zero.

I. INTRODUCTION

MOST optical pumping experiments have been analyzed either under the assumption that an alkali atom suffers no perturbation while in the excited state,[1] or that it suffers so many perturbations (i.e. collisions) during the excited-state lifetime, that it will decay with equal probability from any Zeeman sublevel of the excited state, regardless of which one it was originally pumped to.[2] In a recent article,[3] the calculation of optical pumping probabilities was extended to the region of "partial excited-state mixing," where the probability is great that an alkali atom suffers

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