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Electron Impact Excitation and Dissociation of N_2 via the $b\,^1\Pi_u$ State

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Electron impact excitation of the $b\,^1\Pi_u$ state in N_2 plays a prominent role in the dissociation of the molecule and thus in the production of atomic nitrogen in planetary atmospheres. Electron impact excitation cross sections combined with electron-impact-induced fluorescence measurements can yield the corresponding dissociation cross sections. Serious discrepancies exist among excitation cross sections reported in the literature. To clarify the situation, we measured these cross sections at two impact energies using electron energy loss spectroscopy. The new results are in agreement with recent values deduced from optical measurements and fall midway between previous results which are too high or low by factors of 2.

1. INTRODUCTION

Electron impact excitation of molecules to dissociative states causes significant production of neutral species in planetary atmospheres. The main path for dissociation in N_2, the major atmospheric component of Earth, Titan, and Triton, is predissociation. We report cross section measurements of the predissociative $b\,^1\Pi_u$ state of N_2 in this paper. The dissociation branching ratio for the N_2 $b\,^1\Pi_u$ state can be obtained from measurements of its total excitation (Q_{ex}) and total emission (Q_{em}) cross sections when collisional quenching can be neglected. A serious discrepancy exists, however, among electron impact excitation cross sections previously reported in the literature [*Zipf and Gorman*, 1980; *Chutjian et al.*, 1986; *Itikawa et al.*, 1986; *James et al.*, 1990], motivating the present investigation. We outline here the experimental procedures for the electron energy loss study used to determine excitation cross sections at 60 and 100 eV. The procedures used to measure the corresponding emission cross sections were described by *James et al.* [1990]. Electron impact excitation and emission cross sections obtained from these studies are reported and compared to previous results.

2. EXCITATION CROSS SECTIONS

2.1. *Experimental Procedure*

Data to determine excitation cross sections were obtained by measuring angle-resolved electron energy loss spectra. A detailed description of the apparatus and procedures has been published elsewhere [*Nickel et al.*, 1989; *Trajmar and Register*, 1984]. A gas jet of N_2 was intersected by an electron beam having an energy resolution of 50 meV full width at half maximum (FWHM). The electrons scattered into a small solid angle (about 0.003 sr) at fixed scattering angle underwent energy loss analysis. Analyzer rotation about the scattering volume allowed for scattering angles of $-30°$ to 120°. Measurements were carried out at two different electron impact energies, 60 and 100 eV. Electron energy loss spectra that include both the $b\,^1\Pi_u$ state and the elastic scattering features were obtained at several angles in the range 5°–120°. A typical spectrum is shown in Figure 1. Individual spectra were built up from multiple scans, with acquisition times varying from one to several hours for different scattering angles. Each scan was alternated with a background scan in which the N_2 gas beam was turned off and an equal amount of N_2 bled into the vacuum chamber from a side vent such that the background pressure in the chamber remained constant. This background scan was used to subtract out contributions to the data from the primary electron beam and background N_2 scattering. A time delay was introduced between the data and background scans to allow for damping of transient pressure fluctuations caused by the gas valve switching. The 50-meV overall resolution was sufficient to resolve most of the electronic states and their vibrational manifolds.

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2.2. *Data Analysis*

For the 60-eV measurements the electron detector response function was calibrated on the basis of a helium energy loss spectrum taken at 20° scattering angle and 60-eV impact energy. The ratio of intensities of the elastic and the $2\,^1P$ features in this spectrum was compared to the ratio of the known cross sections. The ratio of these two ratios gives the relative change in the detector response function for electrons of 60 eV (elastic) and 38.8 eV ($2\,^1P$) residual energy. The response function was assumed to be linear over this energy range. The energy loss spectra of N_2 (which spanned an energy loss range of 13 eV) were corrected in accordance with this response function. The correction to the $b\,^1\Pi_u$ features was about 30% with respect to elastic scattering. At 100-eV impact energy the response function can be taken to be uniform over the 13-eV energy loss range, eliminating the need for data correction at this energy.

Scattering intensities cannot be obtained for each vibrational band of the $b\,^1\Pi_u$ excitation due to blends with other electronic states. There are, however, three prominent features ($v' = 1, 2, 3$) that do not suffer spectral overlaps. A synthetic spectrum of the $b\,^1\Pi_u$ state was created in which

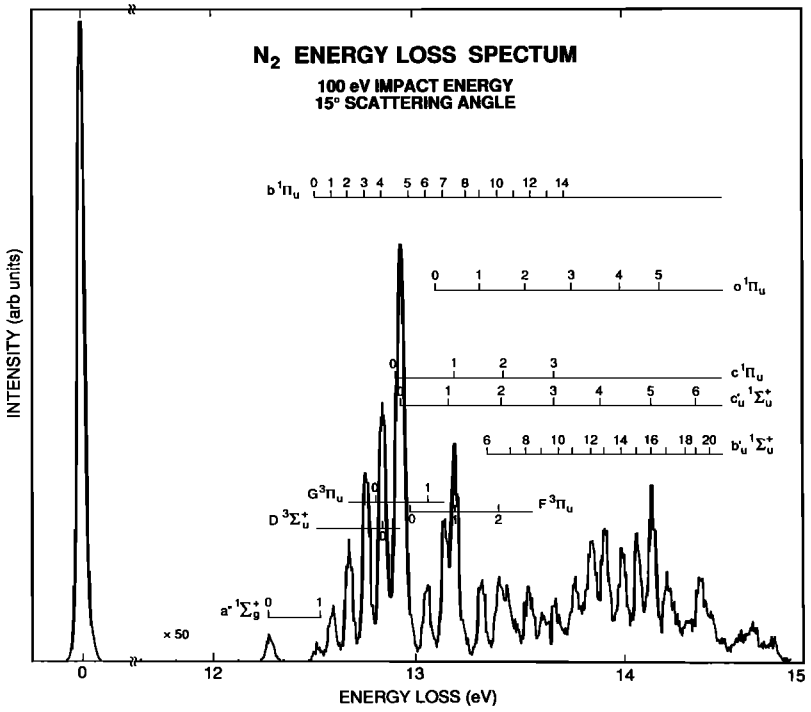

Fig. 1. A typical electron energy loss spectrum.

relative peak heights and energy spacings were taken from *Geiger and Schroder* [1969] and line shapes were taken to be that of the experimental elastic peak. A least squares routine then scaled the intensity of this synthetic peak to determine the best fit to the $v' = 1, 2, 3$ features in the data. This yielded the total $b\,^1\Pi_u$ state intensity relative to the elastic peak. The ratio of intensities is equal to the ratio of the corresponding differential cross sections (DCSs). N_2 elastic DCS data of *Shyn and Carignan* [1980] were used to place the inelastic DCS on an absolute scale. The DCS values were extrapolated to the full zero to 180° angular range and then integrated over scattering angle to obtain the integral excitation cross section Q_{ex}.

2.3. *Results and Discussion*

The present electron energy loss data yields total cross sections Q_{ex} for excitation of the N_2 $b\,^1\Pi_u$ state of $(2.78 \pm 0.42) \times 10^{-17}$ cm^2 and $(1.55 \pm 0.23) \times 10^{-17}$ cm^2 at impact energies of 60 and 100 eV, respectively (Figure 2). Previous electron scattering measurements by *Chutjian et al.* [1977] are a factor of 2 smaller at 60 eV and suggest a similarly low value at 100 eV. This is most likely due to the fact that they did not chop the target beam to obtain and subtract out the contribution to the elastic signal from background N_2 and from the unscattered electron beam. This would result in an inelastic-to-elastic intensity rato that was too small, yielding low inelastic cross sections.

Zipf and Gorman [1980] (hereinafter referred to as ZG) reported a Q_{ex} of 3.08×10^{-17} cm^2 for 100-eV impact energy. This is a factor of 2 larger than our results. The cross section $Q_{ex} = 4.18 \times 10^{-17}$ cm^2 of ZG at 60 eV is also higher than our value by about 50%. The possible presence of systematic error in their result is difficult to assess from their publication.

Itikawa et al. [1986; also private communication, 1991] have used a different combination of ZG data to obtain the $b\,^1\Pi_u$ state excitation cross section. They evaluated the equation

$$Q_{em}(v' = 1 \rightarrow v'' = 2) = \frac{A(v' = 1 \rightarrow v'' = 2)}{\sum_{v''} A(v' = 1 \rightarrow v'')}$$

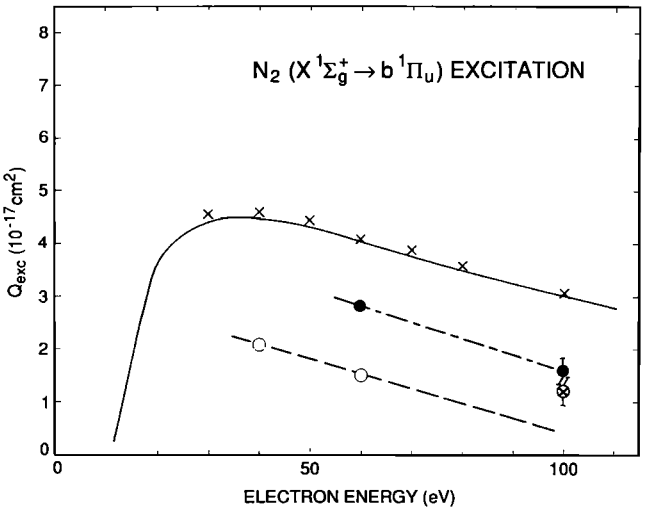

Fig. 2. Excitation cross section for the N_2 ($X\,^1\Sigma_g^+ \rightarrow b\,^1\Pi_u$) transition. Crosses, *Zipf and Gorman* [1980]; solid curve, *Itikawa et al.* [1986]; open circles, *Chutjian et al.* [1977] renormalized using *Trajmar et al.* [1983]; crossed circle, *James et al.* [1990]; solid circles, present results.

$$\cdot \frac{Q_{ex}(v''=0 \rightarrow v'=1)}{\sum_{v'} Q_{ex}(v''=0 \rightarrow v')}\, Q_{ex}(X \rightarrow b) \qquad (1)$$

to obtain the total excitation cross section Q_{ex} $(X \rightarrow b)$ as a function of energy (see Figure 2). ZG's data supplied the transition probabilities A, the excitation cross sections Q_{ex} and emission cross section Q_{em} (1, 2) at 200 eV, and the relative emission cross section Q_{em} (1, 2) of the Birge-Hopfield band as a function of energy. The ratios of these quantities, as used in equation (1), are equivalent to the Franck-Condon factors and are thus independent of energy. (It is assumed that Franck-Condon factors are valid for the $v' = 1$ level, which does not predissociate.) The values of Q_{ex} obtained from equation (1) differ very little from those of ZG.

A value of 1.21×10^{-17} cm^2 for the electron impact excitation cross section Q_{ex} at 100 eV was obtained recently by *James et al.* [1990] by rescaling and reanalyzing 200-eV Q_{ex} values for $b\,^1\Pi_u$ levels reported by ZG. This result is consistent with our excitation cross section measurement within the assumed error range of 15%.

To determine the dissociation cross section, the emission cross section must also be established. The emission cross section measured by *James et al.* [1990] at 100 eV for the $b\,^1\Pi_u$ $(v' = 1) \rightarrow X\,^1\Sigma_g^+$ $(v'' = 0\text{–}12)$ band system is 5.82×10^{-19} cm^2. This represents 95% of the total emission observed for the $b \rightarrow X$ system. The emission cross sections derived by James et al. from the measurements of ZG yield a value of 8.51×10^{-19} cm^2 at 100 eV for the same $(v' = 1)$ progression, 46% higher than that obtained from their own measurements. This discrepancy exists even though the ZG data had been corrected by James et al. by a factor of 0.597 to account for the new calibration standard in the VUV for H Ly α from dissociative excitation of H_2 [*Ajello et al.*, 1988]. The ZG results are hampered by lower spectral resolution (0.083 nm) with an unknown overlap with blended spectral components, which may account for this discrepancy.

Since cascade processes can be neglected for the $b\,^1\Pi_u$ state, we calculated a value of $(148.9 \pm 22.3) \times 10^{-19}$ cm^2 for the dissociation cross section at 100 eV for this state using the present excitation cross section and the emission cross section of James et al.

3. Conclusions

Electron impact excitation cross sections Q_{ex} have been determined for the N_2 $b\,^1\Pi_u$ state. Our measurement of Q_{ex} at 100 eV impact energy, $Q_{ex} = 1.55 \times 10^{-17}$ cm^2, is in fair agreement with $Q_{ex} = 1.21 \times 10^{-17}$ cm^2 from the reanalysis by *James et al.* [1990] of data presented by ZG. These values disagree with results of *Chutjian et al.* [1977] for reasons that are understood, and with the published results of ZG, for reasons that are not clear.

The dissociation fraction for the $b\,^1\Pi_u$ state was found to be 0.972 and 0.950 by ZG (uncorrected data) and James et al., respectively, while the present value is 0.961. Because of this high dissociation branching ratio, the most significant factor in determining the dissociation cross section is the excitation cross section. We believe that our measurement of Q_{ex} significantly reduces the uncertainty in this quantity and in the dissociation cross section.

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