

## Absolute cross sections for electron-impact excitation of $N_2^+$

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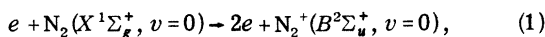
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Crossed beams of  $N_2^+$  and electrons were used to measure the absolute cross sections for the excitation,  $N_2^+(X^2\Sigma_g^+, v=0) + e \rightarrow N_2^+(B^2\Sigma_u^+, v=0) + e$ , over an electron energy range from below threshold (3.17 eV) to 91 eV. Absolute emissions of the 391.4-nm band were measured from impact of electrons on  $N_2^+$  ions in various state mixtures. Corrections were made to the data to account for state mixtures and other effects to obtain the cross section for the above process. The cross section falls from its finite threshold value of  $3.0 \times 10^{-16}$  to  $0.30 \times 10^{-16}$  cm<sup>2</sup> at 91 eV. The present values are more than an order of magnitude smaller than either the 1968 values of Lee and Carleton or the 1973 values of Dashchenko *et al.* At threshold the Gaunt-factor formula of Seaton predicts a value only 45% of that measured, but at the highest energy, the predictions of the Seaton formula have converged to within 20% of the present values of the cross section. Rate coefficients calculated from the present measurements are consistent with the recent rate-coefficient measurements of McLean *et al.* Total uncertainty at high confidence is about 18%, taken as the quadrature sum of random uncertainty (15% at 98% confidence level) with systematic uncertainties (about 8% at high confidence). The analysis leading to interpretation of the emission cross section in terms of an excitation cross section between specific states is subject to uncertainties which are not well defined, and are not included in the stated uncertainty.

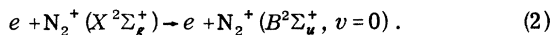
### I. INTRODUCTION

The 0-0 band of the first negative system of  $N_2^+$  located at 391.4 nm is a strong emission in nearly all nitrogen-containing plasmas, and thus enters prominently into measurements on such plasmas. It is therefore important that excitation mechanisms for this emission be understood. One might estimate that few cross sections have been measured<sup>1,2</sup> more times than that for the process of simultaneous ionization and excitation of the  $N_2$  molecule,



which is followed by emission of 391.4-nm light.

In 1968 Lee and Carleton<sup>3</sup> reported cross-section measurements for the emission of 391.4-nm radiation arising from excitation of the  $N_2^+$  ion,



This pioneering measurement gave a cross section of nearly  $10^{-14}$  cm<sup>2</sup> near the 3.17-eV threshold for the process. This large value indicated a prominence to the process (2) in plasmas not previously anticipated. In 1973 Dashchenko *et al.*<sup>4</sup> measured cross sections of similar magnitude as those of Lee and Carleton. However, in 1972 McLean, Ali, Stamper, and Dean<sup>5</sup> made rate coefficient measurements in a plasma, which gave a value almost 80 times smaller than that calculated from the Lee and Carleton data. Approximate predictor formu-

las of Seaton<sup>6</sup> and Gailitis<sup>7</sup> also indicate cross sections much smaller than those found by Lee and Carleton. On the other hand, classical calculations of Bauer and Bartky,<sup>8</sup> using the classical binary-encounter method,<sup>9</sup> lead to a cross-section curve which peaks at 50 eV with a value  $2 \times 10^{-15}$  cm<sup>2</sup> at the peak. This peak value is about 8 times larger than the value of Lee and Carleton extrapolated to 50 eV (their data extend only to about 28 eV), and is 60 times larger than given by the Seaton predictor formula.

There thus remains a question, not only of precise cross-section values for reaction (2), but of the *order of magnitude* of the cross section, and hence of the relative role it plays in various nitrogen-containing plasmas, such as the ionosphere and lasers. This paper reports new and accurate measurements of the cross section for process (2). The new values are more than an order of magnitude smaller than those of Lee and Carleton,<sup>3</sup> and of Dashchenko *et al.*,<sup>4</sup> and are consistent with values from the predictor formula of Seaton<sup>6</sup> and with the rate coefficients of McLean *et al.*<sup>5</sup>

### II. THE EXPERIMENT

The experimental approach is to collide a mass-analyzed beam of  $N_2^+$  at right angles with a magnetically confined beam of variable-energy electrons, and measure the photon flux into a cone in the third orthogonal direction. Details of the method have been presented at length in reports of previous work<sup>10,11</sup> on  $Ca^+$ , and only details peculiar

to the study of  $N_2^+$  will be given here.

The apparent emission cross section is calculated from measured quantities using the equation

$$\sigma_A = \frac{1}{Y_\Omega} \frac{\mathcal{R}}{I_i I_e} \frac{e^2 v_i v_e}{(v_i^2 + v_e^2)^{1/2}} \frac{\mathcal{F}}{D(z_0, \lambda)}. \quad (3)$$

Here  $\sigma_A$  is the apparent emission cross section,  $\mathcal{R}$  is the recorded count rate of photons,  $e$  is the electronic charge,  $I_i$  and  $I_e$  are the total currents of ions and electrons, and  $v_i$  and  $v_e$  are the respective velocities. The anisotropy correction factor  $Y_\Omega$ , which includes allowance for the finite solid angle  $\Omega$  of the detection system, is given in terms of the angle  $\theta$  between the direction of photon emission and the electron beam axis by

$$Y_\Omega = (1 - P \langle \cos^2 \theta \rangle_\Omega) / (1 - \frac{1}{3} P), \quad (4)$$

where  $P$  is the polarization of photons emitted along the observation axis and  $\langle \cos^2 \theta \rangle_\Omega$  is the average value of  $\cos^2 \theta$  over the detection solid angle. The ion and electron beams are traveling in the  $x$  and  $y$  directions, respectively, and photons are observed in a cone along the  $z$  axis. The form factor  $\mathcal{F}$  which accounts for the spatial overlap of the ion- and electron-beam density distributions,  $R(z)$  and  $G(z)$ , with the relative detection sensitivity profile  $\eta(z, \lambda)$  can be written

$$\mathcal{F} = \frac{\int R(z) dz \int G(z) dz}{\int R(z) G(z) \eta(z, \lambda) dz}, \quad (5)$$

where

$$\eta(z, \lambda) = D_R(z, \lambda) - I_1 + (e^{w_e/v_i \tau} - 1) I_2, \quad (6)$$

and here

$$I_1 = \frac{\int_0^{w_e} e^{-x/v_i \tau} D_R(x, z, \lambda) dx}{\int_0^{w_e} D_R(x, z_0, \lambda) dx} \quad (7)$$

and

$$I_2 = \frac{\int_{w_e}^{\infty} e^{-x/v_i \tau} D_R(x, z, \lambda) dx}{\int_0^{w_e} D_R(x, z_0, \lambda) dx}. \quad (8)$$

The quantity  $D(z_0, \lambda)$  [ $D(z_0, 391.4) = 0.38 \times 10^{-3}$  counts/photon] in Eq. (3) is the absolute average probability that a photon emitted in an arbitrary direction from the  $z = z_0$  plane inside the collision volume will be recorded, and  $D_R(z, \lambda)$  in Eq. (6) is the relative variation of that probability with height  $z$  such that  $D_R(z_0, \lambda) = 1$ .  $D_R(x, z, \lambda)$  is the relative probability averaged over the width of the ion beam that a photon emitted from a line parallel to the electron beam will be detected,  $w_e$  is the mean width of the electron beam, and  $\tau$  is the lifetime of the transition yielding photons of wavelength  $\lambda$ . The subtraction of  $I_1$  accommodates for the fact

that some particles do not radiate while within the limits of the electron beam. The term on  $I_2$  is added to account for those particles that radiate beyond the limits of the electron beam but are still detected. For 750-eV  $N_2^+$  the terms on  $I_1$  and  $I_2$  account for a correction to the data of about 35%. As noted, measurement of the quantities in Eqs. (3)–(8) is discussed elsewhere.<sup>10,11</sup>

Ions are formed by electron bombardment in an ion source which is similar in design to a Bayard-Alpert ionization gauge, and which has been described previously.<sup>12</sup> The operating pressure is about  $4 \times 10^{-3}$  Torr, and the mean energy of bombarding electrons is about 200 eV. Ions are mass analyzed, and the well-collimated ion beam intersects the magnetically confined electron beam in a region where the ambient pressure is typically about  $5 \times 10^{-10}$  Torr. The flight path of the ions from the source to the interaction region is about 136 cm; this parameter is important in determining state distributions of the ion beam as discussed later. Ion currents were typically 0.6  $\mu$ A.

Ions and electrons were modulated at frequencies  $F$  and  $2F$ , respectively ( $F \sim 1$  kHz), and background and signal-plus-background were recorded in dual scalars gated according to the scheme of Bacon and Hooper.<sup>13</sup> Signal count rates were typically the order of 1  $\text{sec}^{-1}$ , and background rates ranged from 4 to 60  $\text{sec}^{-1}$ , the higher rates occurring at electron energies where process (1) occurs with the background gas.

The interference filter transmission measured *in situ* has its peak at 391.5 nm; the transmission falls to half the peak value at 390.5 and 392.9 nm; and to 10% of the peak value at 389.4 and 393.9 nm. The 0-0 band under investigation has a band head at 391.4 nm and degrades to shorter wavelengths with a width of about 3 nm. Line intensities for all branches of the band for a 353 °K rotational temperature (the approximate ion source temperature) were calculated and supplied to us by Dr. D. L. Albritton.<sup>14</sup> The apparent cross sections were multiplied by the correction factor

$$\epsilon = \sum_{\lambda} I_{\lambda} / \sum_{\lambda} T_{\lambda} I_{\lambda}, \quad (9)$$

to account for the nonuniform transmission of the filter over the width of the emission band. In this equation,  $I_{\lambda}$  is the line intensity of a band member at wavelength  $\lambda$ ,  $T_{\lambda}$  is the filter transmission at  $\lambda$  relative to that at the calibration wavelength, 391.4 nm; and the summations are over significant lines in the band. For our conditions  $\epsilon = 1.43$ , with 153 band members included in the summation.

The low-signal levels in this experiment made it impractical to measure the polarization  $P$  of the emitted light which is needed in Eq. (4) to compute

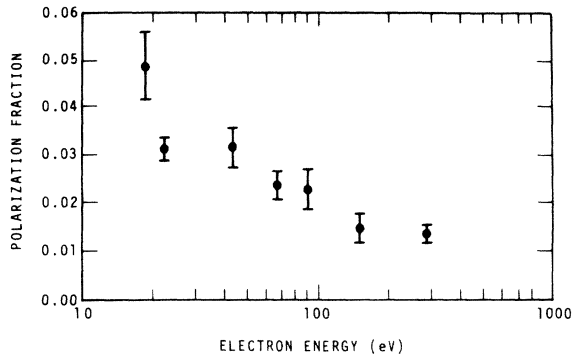


FIG. 1. Polarization fraction of light from the process  $e + N_2(X^1\Sigma_g^+, v=0) \rightarrow 2e + N_2^+(B^2\Sigma_u^+, v=0)$ , followed by  $N_2^+(B^2\Sigma_u^+, v=0) \rightarrow N_2^+(X^2\Sigma_g^+, v=0) + h\nu(391.4 \text{ nm})$  plotted versus electron energy. Bars represent statistical uncertainties at the 98% confidence level.

the anisotropy correction factor. It is noted, however, that process (1) involves excitation from a state of the same basic symmetry as process (2). The polarization of light from (1) should then be much the same as in (2), except that the variation with electron energy will be stretched out about a factor of 6 due to the difference in threshold energies. Therefore, polarization measurements were made for (1) simply by admitting  $N_2$  to the collision region and bombarding with electrons. Results are shown in Fig. 1. One sees that  $P$  is less than 5%, and given the fact that  $\langle \cos^2\theta \rangle_\Omega$  in Eq. (4) is 0.015, this implies that  $Y_\Omega$  differs from 1.0 by less than 1.5% everywhere if it is assumed that the two processes have nearly the same polarization, as discussed. Consequently,  $Y_\Omega$  has been taken to be 1.0.

### III. UNCERTAINTIES

Typically, greater than  $10^4$ -sec integration times were needed at each energy to obtain a standard deviation (SD) of the mean of 5%. At the three lowest energies, greater than  $10^5$  sec were needed to obtain even less precision. With exceptions discussed below, systematic uncertainties in measurement, calibration, etc. are effectively the same as carefully itemized<sup>10,11</sup> in the studies on  $Ca^+$ . Thus, a combination in quadrature of uncorrelated systematic uncertainties leads to values the order of 8–9% at a high confidence level [comparable to statistical 98% confidence level (CL)]. Combined in quadrature with random uncertainties of about 5% SD (15% at 98% CL), this leads to overall uncertainties at a high confidence level of 17–18%.

Lee and Carleton<sup>3</sup> found a strong dependence of their signal upon background pressure, which they attributed to excitation of slow ions formed by

charge transfer along the track of the fast ion beam. They attempted to accommodate for this by extrapolating their data to zero pressure. Variation of pressure of  $N_2$  in the collision region of the present experiment from the normal operating value of  $5 \times 10^{-10}$  Torr to  $5 \times 10^{-8}$  Torr (read on an ionization gauge) revealed no dependence on pressure. However, continuing to raise the pressure to  $2.6 \times 10^{-7}$  Torr brought forth a very unusual oscillatory structure in the apparent cross section above 11 eV. Thus, the apparent cross section rose to 10 times its normally measured value at 14 eV, decreased to a negative value at 16 eV, and shot up to very large values past 20 eV. Measurements made three years earlier with a 20-nm FWHM interference filter showed such pressure-dependent undulations even at  $10^{-9}$  Torr, possibly indicating involvement of other bands. Variation of modulation frequency between 100 Hz and 5 kHz did not change the anomalous apparent cross-section values; neither did the application of a small electric field in the collision region, applied to sweep out slow ions. Both ion and electron beams need to be present to obtain the effect, and it is very reproducible. Lee and Carleton's charge transfer model does not fit the present observations. We have arrived at no satisfactory model for the anomaly. Certainly, in the absence of evidence of a pressure dependence for more than two orders of magnitude above the operating level, we can ignore this effect in evaluating cross sections and assessing uncertainties.

Calculation of the cross sections from Eqs. (3)–(8) involves corrections due to the rapid transit of ions from the field of view of the detector. The finite lifetime<sup>15–18</sup> for the  $B^2\Sigma_u^+, v=0$  state of 59.0 nsec was used, leading to corrections of about 12% at 500 eV, 35% at 750 eV, and 60% at 2000 eV ion energies. Applying these corrections leads to emission cross sections that are consistent, independent of ion velocity. Small remaining discrepancies (a few percent) can be attributed to differences in the state distributions for beams of different flight times. In the discussion of systematic uncertainties above, no allowance was made for uncertainty in the lifetime. While the most recent measurements<sup>15–18</sup> are about 59 nsec, many measurements<sup>19–22</sup> group around 66 nsec; and values range all the way from 40 nsec<sup>23</sup> to 71.5 nsec.<sup>24</sup> If the lifetime were 68 nsec, the effect would be to raise the apparent cross sections at 500 eV by 7%, at 750 eV by 8%, and at 2 keV by 10%. After removing the effect of different state distributions associated with ions of differing velocity, the agreement among the excitation cross sections at the three ion energies is better with the 59-nsec lifetime correction than with 68 nsec; however,

precision of the data does not allow a definite choice.

#### IV. RESULTS AND INTERPRETATION

The apparent emission cross sections calculated from Eq. (3) and corrected by multiplication by  $\epsilon = 1.43$ , defined in Eq. (9), are shown in Fig. 2. Measurements taken at four different ion energies are distinguished on the plot. Bars on the points represent one standard deviation of the mean.

The results in the figure apply to the specific ion state distribution of our target, and are in need of interpretative analysis to obtain cross sections more generally meaningful.

It is assumed that only three ion states are formed by electron-impact ionization in the ion source—the ground  $X^2\Sigma_g^+$  state, the first excited  $A^2\Pi_u$  state, and the next excited  $B^2\Sigma_u^+$  state. There are, of course, many other states, but it is assumed that their contribution to the total ion number is very small. It appears,<sup>25</sup> for example, that the  $C^2\Sigma_u^+$  state contributes less than 0.1% to the

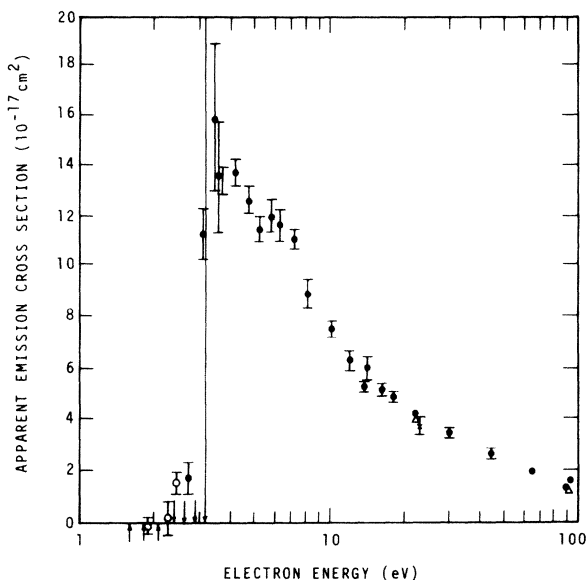


FIG. 2. Measured apparent emission cross section versus electron energy for the process,  $e + N_2^+ \rightarrow e + N_2^+(B^2\Sigma_u^+, v=0) \rightarrow N_2^+(X^2\Sigma_g^+, v=0) + h\nu$  (391.4 nm). Cross sections are from Eq. (3) corrected by Eq. (9). Measurements are for particular state distributions in the target  $N_2^+$  beam, and are somewhat different for data using:  $\bullet$ , 500-eV ions;  $\Delta$ , 750-eV ions;  $\times$ , 2-keV ions; or  $\circ$ , 3-keV ions, as shown in Table I. Thresholds for excitation from the first four vibrational levels of  $X^2\Sigma_g^+$  are shown by arrows pointing down. Arrows pointing up indicate thresholds from the first three levels of the  $A^2\Pi_u$  state. Bars indicate the standard deviation of the mean. Additional uncertainties are discussed in the text.

total ion number. All of the  $B$  state decays to the  $X$  state before the beam reaches the collision region. However, a fraction of the  $A$  state ions, for which the lifetime<sup>26</sup> of the  $v'=0$  level is 15.5  $\mu\text{sec}$ , will not decay by this time. If  $t$  is the transit time of the ions from the time of formation to reaching the target region ( $t = 23 \mu\text{sec}$  for 500-eV ions), then the fraction of the target ions in the  $k$ th vibrational level of the  $X$  state is

$$p_k^X = \xi q_{k0}^X + \beta \sum_j q_{j0}^B b_{jk}^{BX} + \alpha \sum_i q_{i0}^A b_{ik}^{AX} (1 - e^{-t/\tau_i}). \quad (10)$$

where  $\xi$ ,  $\beta$ , and  $\alpha$  are the fractions of  $N_2^+$  formed in the source in the  $X$ ,  $B$ , and  $A$  states respectively,  $q_{n0}^M$  is the Franck-Condon factor for an ionizing transition between the zeroth vibrational level of ground-state  $N_2$  and the  $n$ th vibrational level of the  $M$  state of  $N_2^+$ ,  $b_{v'v''}^{MX}$  is the branching ratio from the  $v'$  vibrational level of the  $M$  state to the  $v''$  level of the  $X$  state of  $N_2^+$ , and  $\tau_i$  is the lifetime of the  $i$ th vibrational level of the  $A$  state. Similarly, for the various fractions in levels of the  $A$  state,

$$p_k^A = \alpha q_{k0}^A e^{-t/\tau_k}. \quad (11)$$

Values of  $q_{n0}^M$  have been supplied by Dr. D. L. Albritton.<sup>14</sup> Similarly, values of  $b_{v'v''}^{MX}$  have been taken to be<sup>27</sup>

$$b_{v'v''}^{MX} = q_{v'v''}^{MX} \nu_{v'v''}^3 / \sum_{v'''} q_{v'v'''}^{MX} \nu_{v'v'''}^3, \quad (12)$$

and calculated from data supplied by Albritton. In Eq. (12),  $q_{v'v''}^{MX}$  is the Franck-Condon factor between the  $v'$  level of the  $M$  state and the  $v''$  level of the  $X$  state, and  $\nu_{v'v''}$  is the frequency corresponding to the energy interval. Lifetimes of the  $A$  state were taken from Holland and Maier,<sup>26</sup> using their values calculated with the Franck-Condon factors of Albritton *et al.* Using data from Rapp and Englander-Golden<sup>28,29</sup> on total ionization and dissociative ionization, of Borst and Zipf<sup>2</sup> for ionization and simultaneous excitation of the  $B$  state [process (1)], and of Holland and Maier<sup>26</sup> for ionization and simultaneous excitation to the  $A$  state, we arrive at  $\xi = 0.25$ ,  $\beta = 0.14$ , and  $\alpha = 0.61$ .

With these numbers Eqs. (10) and (11) give population fractions of the target beam shown in Table 1 for the several ion energies used in the experiment. Given these populations, the observed emission cross sections in Fig. 2 can be expressed

$$\sigma_{em} = \left( \sum_i p_i^X \sigma_{i0}^{XB} q_{0i}^{BX} \right) b_{00}^{BX} + \left( \sum_j p_j^A \sigma_{j0}^{AB} q_{0j}^{BA} \right) b_{00}^{BX}, \quad (13)$$

where  $\sigma_{i0}^{MB}$  is the cross section for a collision-induced

transition to the zeroth level of the  $B$  state from the  $l$ th level of the  $M$  state. If we assume that the electronic transition varies slowly with internuclear separation,<sup>26,30</sup> then above the 0-0 threshold from each state we can write

$$\sigma_{em} = \left[ \sigma^{XB} \left( \sum_i p_i^X q_{0i}^{BX} \right) + \sigma^{AB} \left( \sum_j p_j^A q_{0j}^{BA} \right) \right] b_{00}^{BX}. \quad (14)$$

Now, the threshold for excitation of the  $v' = 0$  level of  $B$  from the  $v'' = 3$  level of  $X$  is 2.37 eV. Since both populations and Franck-Condon factors are very small for  $v'' \geq 4$ , the first term in the brackets should be negligible for electron energies less than 2.37 eV. The point shown in Fig. 2 at 2.3 eV, which was taken at 3-keV ion energy where  $\sum_j p_j^A q_{0j}^{BA} \approx 0.05$ , indicates that  $\sigma^{AB}/\sigma^{XB} \sim 0.2$  with an upper limit of 1.0 allowed within the precision of the point. If the point at 1.9 eV is also considered, this cross-section ratio is even smaller. Taking  $\sigma^{AB}/\sigma^{XB} = 0.2$ , we find that with 500-eV ions (where  $\sum_j p_j^A q_{0j}^{BA} = 0.018$ ) the fractional contribution of the term on  $\sigma^{AB}$  is less than 1% at electron energies above 2.37 eV, and we ignore this term in further analysis. If  $\sigma^{AB}/\sigma^{XB}$  is as large as 1.0, then we make an error of the order of 4%. Another interpretation of the smallness of the points at 1.9 eV and 2.3 eV is that the  $p_j^A$  are much smaller than we have calculated. This point of view seems less likely, and we do not pursue it.

With these considerations we have

$$\sigma_{em} = \sigma^{XB} \left( \sum_i p_i^X q_{0i}^{BX} \right) b_{00}^{BX}. \quad (15)$$

The excitation cross section from the zeroth level of the  $X$  state to the zeroth level of the  $B$  state can be

TABLE I. Fractional beam populations  $p_v^X$  and  $p_v^A$  of the  $v$ th vibrational level of the  $X$  and  $A$  states, respectively, at the collision region when beam energies of 500 eV, 750 eV, 2 keV, and 3 keV are used.

	500 eV	750 eV	2 keV	3 keV
$p_0^X$	0.595	0.572	0.513	0.489
$p_1^X$	0.187	0.177	0.149	0.137
$p_2^X$	0.070	0.066	0.054	0.049
$p_3^X$	0.027	0.025	0.020	0.018
$p_4^X$	0.009	0.009	0.007	0.006
$p_0^A$	0.037	0.049	0.078	0.090
$p_1^A$	0.036	0.049	0.083	0.097
$p_2^A$	0.020	0.028	0.051	0.061
$p_3^A$	0.008	0.012	0.024	0.029
$p_4^A$	0.003	0.004	0.010	0.012

written

$$\sigma_{ex} = \sigma^{XB} q_{00}^{BX} = \sigma_{em} \left( \frac{q_{00}^{BX}}{\sum_i p_i^X q_{0i}^{BX}} \right) \frac{1}{b_{00}^{BX}}. \quad (16)$$

Using measured  $\sigma_{em}$  shown in Fig. 2, Franck-Condon factors supplied by Albritton,<sup>14</sup> and  $p_i^X$  given in Table I, we find with 500-eV ions,  $\sigma_{ex} = 2.02\sigma_{em}$ ; with 750-eV ions,  $\sigma_{ex} = 2.11\sigma_{em}$ ; and with 2-keV ions,  $\sigma_{ex} = 2.37\sigma_{em}$ . The results for  $\sigma_{ex}$  are shown in Fig. 3.

One of the uncertainties in the foregoing is in the value of  $\alpha$  [Eq. (10)]. If we take  $\alpha = 0.45$  (consistent with the uncertainty estimate of Holland and Maier,<sup>26</sup> then for 500-eV ions,  $\sigma_{ex} = 1.84\sigma_{em}$ ; i.e., the deduced value of the excitation cross section is about 10% lower.

Another uncertainty occurs in the assumption<sup>27</sup> that the electronic transition moment  $R_e(\nu)$  is a constant. Evidence that this is so for the  $B-X$  transition is in a recent paper by Lee and Judge.<sup>30</sup> The work of Holland and Maier<sup>26</sup> shows only a slow variation for the  $A-X$  transition. A summary of other work on  $R_e(\nu)$  is given in a review by Klemsdal.<sup>31</sup> If one were to use the relatively rapidly varying functions of Brown and Lanshoff<sup>32</sup> for the  $B-X$  transition, and of Shemansky and Broadfoot<sup>33</sup> for the  $A-X$  transition in calculating  $b_{v''v'}^{MX}$ , (and thus  $p_h^X$ ); there would result for a 500-eV ion target,  $\sigma_{ex} = 2.16\sigma_{em}$ . This makes  $\sigma_{ex}$  7% higher than the expression used, which resulted from the assumption that  $R_e(\nu)$  is constant.<sup>27,30</sup>

There thus appear to be uncertainties of about

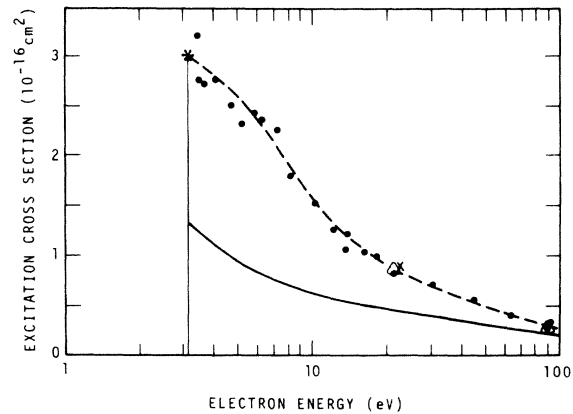


FIG. 3. Excitation cross section versus electron energy for the process  $e + N_2^+(X^2\Sigma_g^+, v=0) \rightarrow e + N_2^+(B^2\Sigma_u^+, v=0)$  derived from the emission cross section (Fig. 2) using Eq. (16). Target ion energies: ●, 500 eV; △, 750 eV; ×, 2 keV. Dashed curve is simply a visual fit through the data. The solid curve represents Seaton's (Ref. 6, 34) Gaunt-factor formula for the cross section [Eq. (17)]. The asterisk represents our estimated value of the cross section at the 3.17-eV threshold.

$\pm 10\%$  in the analysis leading to  $\sigma_{ex}$  from  $\sigma_{em}$ ; though these uncertainties are not easily pinned down.

### V. DISCUSSION

There seems to be no quantum theoretical treatment of this problem. Seaton<sup>6</sup> has offered a "universal" formula which he suggests should be more or less accurate to within a factor of 2 for dipole-allowed transitions. His expression can be written

$$\sigma_{ex}(i \rightarrow j) = \frac{8\pi^2 a_0^2 R^2 f_{ij}}{3^{1/2} (E_j - E_i) E} \bar{g}, \quad (17)$$

where  $E_j - E_i$  is the energy separation in eV,  $E$  is the impact energy in eV,  $R$  is the Rydberg,  $f_{ij}$  is the absorption oscillator strength between levels  $i$  and  $j$ , and  $\bar{g}$  is the so-called "Gaunt factor" which has been tabulated for ions by van Regemorter.<sup>34</sup> If we choose  $i$  and  $j$  to be the 0 levels of the  $X$  and  $B$  states respectively, then Eq. (17) should express the quantity given in Eq. (16) and plotted in Fig. 3. Given the lifetime, 59 nsec, of the zeroth level of the  $B$  state, we can deduce<sup>35</sup> the needed absorption oscillator strength from

$$f_{00} = \frac{1.505 \times 10^{-12}}{\tau_0} \frac{q_{00}}{\lambda_{00} \sum_{v'} q_{0v'}^{BX} / \lambda_{0v'}^3}, \quad (18)$$

if we assume the transition matrix varies slowly with internuclear separation. With this assumption, again using Franck-Condon factors and wavelengths from Albritton, we get  $f_{00} = 0.028$ . Using this in Eq. (17) with van Regemorter's  $\bar{g}$ 's, we obtain the solid curve in Fig. 3. The calculated result is 45% of the measured cross section at threshold and converges to within 20% of the measured values at 100 eV. This is not inconsistent with Seaton's estimated factor of 2 for the accuracy of the formula.

The only other theoretical estimate of the cross section for this process seems to be Bauer and Bartky's<sup>8</sup> calculation using the classical binary-encounter method. This calculation is so disparate with the present work that it cannot be shown on Fig. 3. It predicts a cross section rising from zero at threshold to a maximum of  $2 \times 10^{-15}$  cm<sup>2</sup> at 50 eV.

The data of Lee and Carleton<sup>3</sup> and Dashchenko *et al.*<sup>4</sup> seem to be analogous to our apparent emission cross section shown in Fig. 2. Again, the differences are so large that it is not meaningful to show their data here. Lee and Carleton give a cross section with a value  $80 \times 10^{-16}$  cm<sup>2</sup> at 4.5 eV, their lowest energy, and which decreases to  $5.3 \times 10^{-16}$  cm<sup>2</sup> at 27 eV, their highest energy. Dashchenko *et al.* cite values of  $39 \times 10^{-16}$  and  $9.2 \times 10^{-16}$  cm<sup>2</sup> at their energy extrema of 4.1 and 20 eV, re-

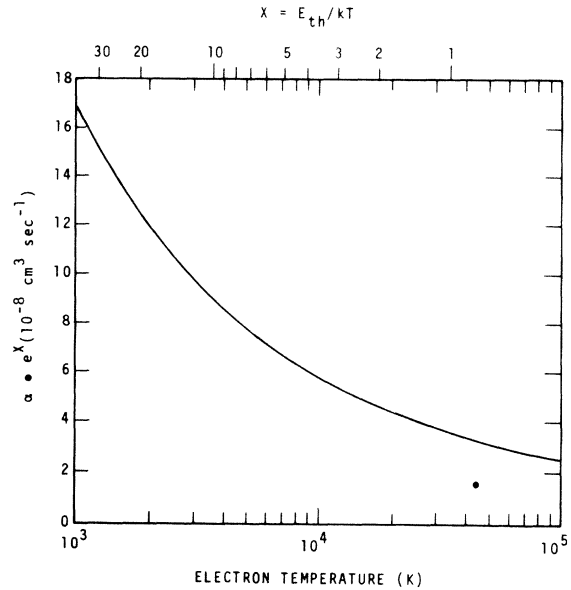


FIG. 4. Emission rate coefficient  $\alpha$  times  $e^X$  (where  $X = 36,787^\circ\text{K}/T$ ) as a function of electron temperature  $T$ , deduced from Eq. (19). Coefficient is for process  $e + \text{N}_2^+(X^2\Sigma_g^+, v=0) \rightarrow e + \text{N}_2^+(B^2\Sigma_u^+, v=0)$ , followed by  $\text{N}_2^+(B^2\Sigma_u^+, v=0) \rightarrow \text{N}_2^+(X^2\Sigma_g^+, v=0) + h\nu(391.4 \text{ nm})$ . Measurement of McLean *et al.* (Ref. 5) for unspecified vibrational temperature of ions is shown by  $\bullet$ .

spectively. There is thus no semblance of similarity between the present measurement and the two earlier ones—neither in magnitude nor shape. Both Lee and Carleton<sup>3</sup> and Dashchenko *et al.*<sup>4</sup> calibrated their apparatus using measured cross sections<sup>1,2</sup> for process (1); whereas the present experiment was calibrated<sup>10,11</sup> with the use of absolute radiometric standards. This does not explain the large discrepancy, however; since experiments in this laboratory three years ago were calibrated using process (1), and gave results within 40% of the present ones. The strong pressure dependence found by Lee and Carleton and their method of correcting the data have been discussed in Sec. III. The measurements of Dashchenko *et al.* were done with  $\sim 3 \times 10^{-7}$  Torr background pressure, and they give no discussion of a possible systematic pressure effect. As noted earlier, the present work was done at a background pressure of  $\sim 5 \times 10^{-10}$  Torr, and results were independent of pressure for more than two decades.

We have calculated the emission rate coefficient for excitation from the zeroth level of  $X$  to the zeroth level of  $B$ , with subsequent 0-0 (391.4 nm) radiation, from

$$\alpha(T) = \int_0^\infty \sigma_{ex} b_{00}^{BX} v F(v, T) dv, \quad (19)$$

where  $F(v, T)$  is the Maxwellian velocity distribu-

tion of electron velocities  $v$  at temperature  $T$ . Results of this are shown in Fig. 4 where  $\alpha e^X$  is plotted versus  $T$ . Here  $X = E_{th}/kT$ , where  $E_{th} = 3.17$  eV is the threshold energy for the process.

McLean *et al.*<sup>5</sup> have measured the rate coefficient in a laser-produced plasma. It is difficult to compare their results with the values in Fig. 4, since the vibrational temperature of their ions is not given. If their ion temperature is high, then their rate coefficient should be somewhat lower than our deduced rate for ground-state ions. This is indeed the case, as shown by their measured point plotted in Fig. 4. The agreement is considered good,

taking into account this uncertainty in interpretation of their experiment.

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