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Excitation of nitrogen by fast H_3^+ ions

S. Bashkin
Department of Physics, University of Arizona, Tucson, Arizona 85721

E. Träbert*
Experimentalphysik III, Ruhr-Universität Bochum, D-4630 Bochum 1, Federal Republic of Germany

D. A. Thiede, P. C. Sercel,† P.-C. Lin, M.-L. Li, and D. G. Jenkins
Department of Physics, University of Arizona, Tucson, Arizona 85721

D. E. Shemansky and K. Wells
Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721

R. Bruch, S. Fülling, and D. DeWitt
Department of Physics, University of Nevada, Reno, Reno, Nevada 89557

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The visible spectrum emitted from N_2 under bombardment by 1-MeV H_3^+ ions has been studied with higher spectral resolution (linewidths down to 0.01 nm) than employed in comparable earlier work. The light yield versus gas pressure has been investigated in the 2–225-mTorr range (0.3–30 Pa) for a number of prominent spectral features attributed to atomic ions and to neutral and ionic molecules. The pressure functions are interpreted in terms of the constituents of the composite projectile. A considerable kinetic broadening observed for emission from N^+, but not for other radiators, corroborates findings by Aarts and de Heer [Physica **52**, 45 (1971), using electron impact] that this excited species results from the breakup of highly excited N_2^+ ions into electronically excited ionic fragments.

I. INTRODUCTION

The excitation of nitrogen by the impact of energetic ions has been studied by a number of investigators. Such excitation is of interest because of the need to understand the basic physical mechanisms which are operative in the collisions and because there is direct application to auroral phenomena.[1–7] The molecular spectra of nitrogen, in particular those of N_2 and N_2^+, have been well known since the early comprehensive studies of low-pressure electric discharges.[8,9] The data on these molecules and their spectra have been summarized by Lofthus and Krupenie[10] and by Pearse and Gaydon.[11]

Because the auroral phenomena in the upper atmosphere are expected to be caused by particle impact (mostly electrons and protons from the solar wind), laboratory spectra have been produced for comparison purposes using projectiles of electrons,[1,2,12–19] hydrogen [atoms, atomic ions (proton, deuteron), or hydrogen molecular ions[3,5,12,16,17,20–42]] or other light ions (He^+, Li^+, N_2^+, Ne^+)[2,12,23,26,33,34,37,38,43–45] on nitrogen or nitrogen-containing gases. The primary goal of many of the above papers was either to measure emission cross sections or to deduce details of the collision process, especially at low collision velocities.

Thomas[46] has surveyed the collision physics extracted from such early experiments. Most of those studies were made for gas pressures in the range 0.01–1 Pa. Several investigators found that the intensities of some of the emission features were not proportional to the target pressure: this indicated excitation processes which went beyond direct excitation or ionization excitation of the target molecules by the projectiles.[20,27,30,35,36,40,43]

The above studies of nitrogen under particle impact were all done with much lower spectral resolution than the classical spectroscopic work which led to the detailed understanding of the atomic and molecular spectra. For a weak light source such as the aurora, this poor resolution caused problems for the interpretation of the intensity distribution in the molecular bands.[4] Only in a few of the laboratory experiments[26,32–34,44] a resolution sufficient, for example, to resolve the rotational components of the N_2^+ $1N(0,0)$ band (first negative band, $v=0$ to $v'=0$ vibrational level) was reached.

We are engaged in a series of experiments directed towards the measurement of excitation cross sections as a function of incident particle type and energy. Preliminary results of this experiment have been published elsewhere.[47–50] The present paper describes the effects of incident ions of H_3^+ at 1 MeV on a target of nitrogen gas, that is at an energy per nucleon which is important in aurorae. H_3^+ ions of lower energy play a key role in the chemistry of many planetary atmospheres.[51] We obtained data on spectral distributions of monoatomic and molecular emissions, the pressure dependence of certain excitations which elucidate the roles of ions and electrons, and the rotational temperature in the target; we also searched for broadening effects of selected spectral lines.

II. EXPERIMENTAL DETAILS

Molecular ions of H_3^+ were accelerated to 1 MeV by a 2-MV Van de Graaff generator. Following magnetic deflection and thus charge state and mass separation, the ion beam traversed a 2.8-cm-long differentially pumped target cell (Fig. 1) through two collinear channels each 3 mm in diameter and 7 cm long. The particle beam was ultimately collected in an unshielded Faraday cup; data were accumulated for a preselected amount of charge per point.

The pressure in the gas target was measured with an MKS capacitance manometer and stabilized to ±0.1 mTorr through an MKS pressure controller. The target pressure ranged from 2 to 225 mTorr (roughly 0.3–30 Pa). These pressures are higher than in most (but not all) experiments aiming at cross sections: this was deemed necessary in order to observe spectral details neglected in most of the earlier studies. With a pressure of 200 mTorr in the gas cell, the pressure in the surrounding volume was 0.4 mTorr, and better than 10^{-5} Torr (about 1 mPa) in the beamline before the target. Because of charge-changing and molecule-breaking collisions in the target gas, the beam current into the cup was measured at each operating pressure and also without gas in the cell. This allowed us to normalize data taken with a given incident ion beam at different target pressures.

The light generated in the gas cell appeared as a luminous horizontal cylinder, a rich purple in color for a nitrogen target. It was viewed through a quartz window; an uncorrected quartz lens focused the light onto the entrance slit of a 1 m, air, Czerny-Turner, scanning monochromator equipped with a 1200-line/mm grating blazed at 500 nm. Since the spectrometer slit was at right angles to the axis of the light source, only a small slice of the luminous gas in the center of the target was examined. The width of that slice was determined by the width of the spectrometer's entrance slit.

A thermoelectrically cooled photomultiplier tube (type EMI 9659QB) served as the detector, the signals from which were recorded in synchronization with the stepping of the spectrometer drive. We covered the spectral range from 320 to 800 nm, with a linewidth as narrow as 0.03 nm for selected portions of the spectrum. The instrumental linewidth [full width at half-maximum (FWHM)] of 0.028 nm has been obtained with 25-μm-wide slits in measurements on the 313.1-nm lines from an Hg pen ray lamp observed in second diffraction order.

An echelle spectrograph was made available by the Lunar and Planetary Laboratory. The detector was a CCD camera which was position sensitive in two dimensions. The spectrograph covered spectral sections of only 1.3 nm at a time, but with high resolution. The linewidth (FWHM) achieved with this instrument using 50-μm-wide slits was less than 0.01 nm for a stationary light source (a built-in Th-Ar hollow cathode discharge lamp); this was sufficient to study line-broadening effects (see below).

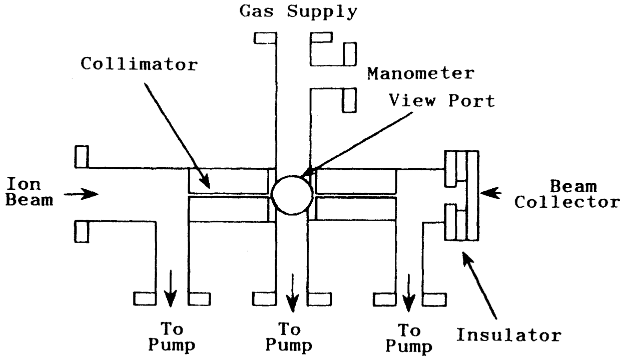

FIG. 1. Experimental arrangement.

No calibration of the relative sensitivity of the optical system was carried out, because the optical coupling of the light source to the spectrometer suffered from mechanical and geometric problems. Hence, although relative intensities within multiplets extending over narrow wavelength intervals (< 10 nm) may be approximately correct, the present data provide no basis for quantitative comparisons over larger spectral regions. The observation of the continuum emitted by a tungsten filament lamp showed only one anomaly near $\lambda = 619$ nm, and thus it ascertained that no efficiency anomalies hampered our observations.

III. DATA

Figure 2 shows a spectrum of nitrogen under bombardment with 1-MeV H_3^+ ions. The spectrum was obtained using the Czerny-Turner spectrometer and covers our full wavelength range; it shows the wealth of structure we observed. Most of the spectral features already appear at low gas pressures. A wide-band detection system as used in most of the earlier studies probably recorded some of this light as background. Atomic lines identified are given in Table I (a detailed list of identified molecular bands is available on request). Data similar to those in Fig. 2 were obtained for many target pressures in the range 10–240 mTorr (1–32 Pa). Components of particular interest, such as those studied for pressure effects, were also observed with considerably higher resolution than in the overall spectral surveys. None of the Balmer lines from hydrogen appeared, despite the use of H_3^+ particles to initiate the events, whereas other investigators have reported the presence of Balmer lines under comparable conditions.[25]

The spectra show both molecular and monatomic sources contributing to the data. However, there is an interesting apparent selectivity of the light source, which also has been noted by Doering[24] for $N_2^+ + N_2$ collisions and which differs from the excitation of N_2 by electrons.[52] Among the many monatomic lines, we see but one from the neutral atom; it is quite weak. Most of the strong lines of N I lie in the vacuum uv. While some of the principal lines of N I (Ref. 53) which lie in our wavelength range might be obscured by strong molecular radiations, the fact is that none at all is found to be particularly intense, although many are seen in the electron experiments. (We mention in passing that a similar experiment on oxygen, which will be published separately, shows a substantially different behavior.) The strong

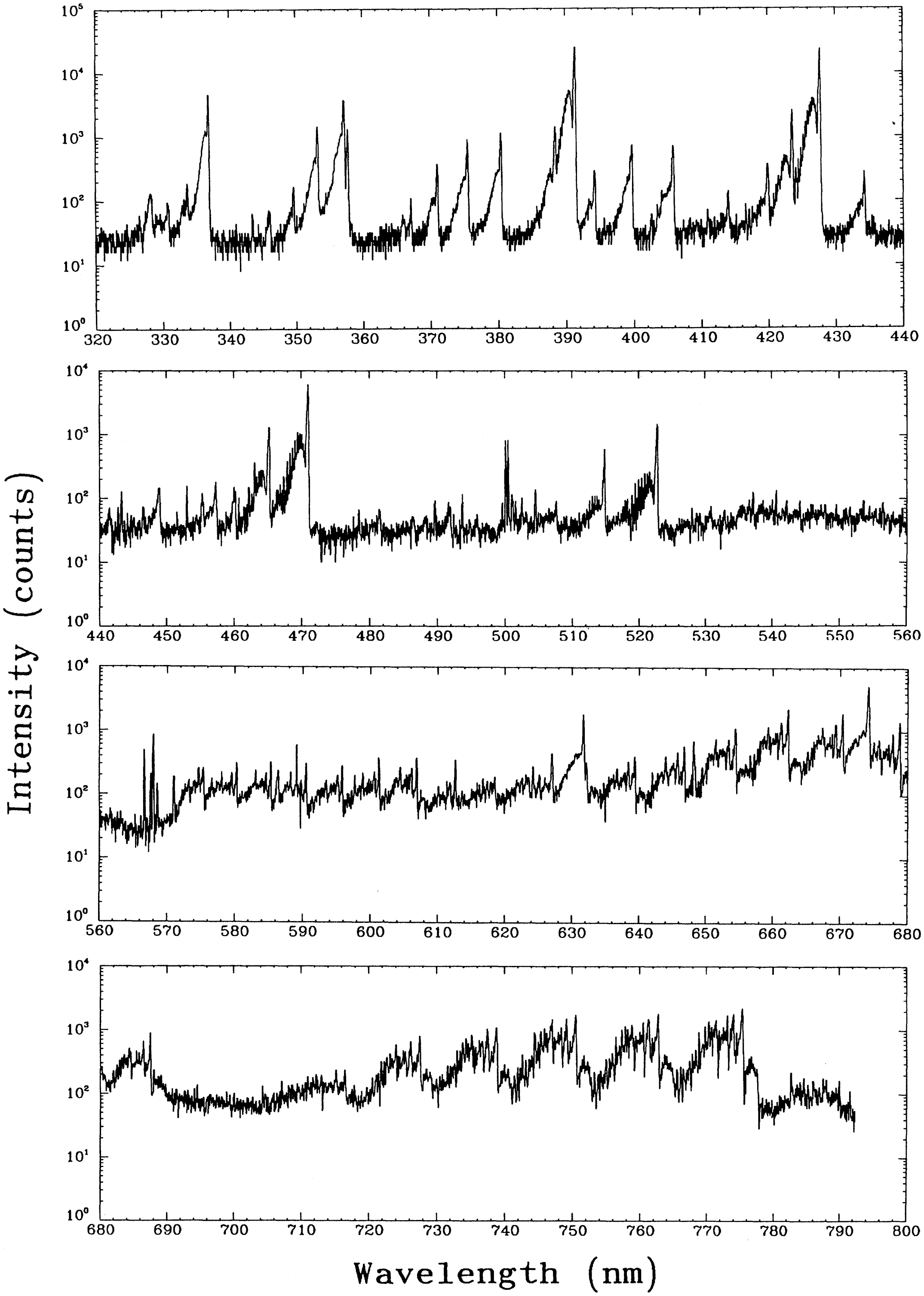

FIG. 2. Spectrum of N_2 at 200 mTorr (26 Pa) pressure under bombardment with 1-MeV H_3^+ ions, with the spectrometer slits set to a width of 150 μm and a height of 10 mm. Linewidth (FWHM) is 0.12 nm; logarithmic intensity scale.

TABLE I. List of observed atomic lines (N and N^+). The atomic line wavelengths are from Striganov and Sventitskii (Ref. 53). Of the monatomic lines, only those are given which can be positively identified among the multitude of components of the molecular bands. For the molecular bands, see the ranges of bands discussed in the text. A detailed listing can be obtained from the first author.

Spectrum	Transition	Wavelength (nm)
N I	$3s\ {}^2P_{3/2}-4p\ {}^2S^{\circ}_{3/2}$	493.5
N II	$3d\ {}^1F^{\circ}_3-4f\ G_{(9/2)4}$	453.04
	$3s\ {}^3P^{\circ}_1-3p\ {}^3P_0$	462.14
	$3s\ {}^3P^{\circ}_2-3p\ {}^3P_2$	463.05
	$2s\ {}^2p^3\ {}^1D^{\circ}_2-2s^2\,2p\,({}^2P^{\circ})3p\ {}^1P_1$	489.51
	$3p\ {}^3D_1-3d\ {}^3F^{\circ}_2$	500.11 (partly blended with next entry)
	$3p\ {}^3D_2-3d\ {}^3F^{\circ}_3$	500.15
	$3p\ {}^3D_3-3d\ {}^3F^{\circ}_4$	500.51
	$3s\ {}^3P^{\circ}_1-3p\ {}^3D_2$	566.66
	$3s\ {}^3P^{\circ}_0-3p\ {}^3D_1$	567.60
	$3s\ {}^3P^{\circ}_2-3p\ {}^3D_3$	567.96
	$3s\ {}^3P^{\circ}_1-3p\ {}^3D_1$	568.62
	$3s\ {}^3P^{\circ}_2-3p\ {}^3D_2$	571.08
	$3s\ {}^3P^{\circ}_2-3p\ {}^3D_1$	573.06
	$3s\ {}^3P_2-3p\ {}^3D^{\circ}_3$	589.32 (very weak, uncertain)
	$3s\ {}^3P_1-3p\ {}^3D^{\circ}_2$	589.73 (very weak, uncertain)
	$3s\ {}^3P_0-3p\ {}^3D^{\circ}_1$	589.98 (very weak, uncertain)

lines from N^{2+} and higher ionization stages are too short in wavelength for us to detect. Thus, only N II (N^+) transitions appear among the monatomic lines we clearly see.

Of those, the intense lines at 500.1 and 500.5 nm come from the multiplet $3p\ {}^3D-3d\ {}^3F^{\circ}$. Their presence guarantees that the $3p\ {}^3D$ level is populated, and transitions downward from that level are clearly seen. The fact that the $3p\ {}^3D^{\circ}_J$ decays appear so much weaker than the $3p\ {}^3D_J$ decays (which are fed by cascades from the $3d\ {}^3F^{\circ}_J$ levels), plus the absence of any quintet lines, suggest that very specific reaction channels through the intermediate molecular states are involved (see below and Ref. 17).

The higher pressure we used, compared to earlier work done elsewhere, was effective in intensifying the molecular bands, and apparently our spectra show more of the known bands than any of the earlier studies. The molecular portions of our data include bands from the neutral nitrogen molecule N_2 [$1P(2,0)$ to $1P(12,9)$, $2P(0,0)$ to $2P(5,5)$], and from the singly ionized molecule ${N_2}^+$ [$1N(0,0)$ to $1N(3,5)$]. One can account for the absence of other contributions in terms of the wavelengths, blending, or small transition probabilities. For example, the $1P(6,3)$ band with band head at 660.8 nm, is not resolved from the intense $2P(2,2)$ and $1N(2,0)$ transitions, both of which appear in second-order diffraction. In addition, the Einstein A coefficient for $1P(6,1)$ is only about 3% of that for $1P(6,2)$, which, itself is quite weak. We do not observe the Meinel band of ${N_2}^+$ either; the radiative transition rates for this band system are lower than that for the ${N_2}^+$ $1N(0,0)$ band by about 2 orders of magnitude, and the cross section for quenching collisions with N_2 ground-state molecules is large.

IV. DISCUSSION

A. Monatomic lines

One set of N II transitions, consisting of five members of the $3s\ {}^3P^{\circ}-3p\ {}^3D$ multiplet, near 570 nm, is clearly resolved from neighboring contributors (except for a minor blend of the shortest-wavelength component), as is shown in Fig. 3. The wavelength span of these lines is only 6 nm, so the wavelength dependence of our detection sensitivity should not significantly affect our relative results. At our densities of the emitting species, there cannot be any self-absorption. The peak heights of the lines as detected using a target pressure of 200 mTorr (~26 Pa) and a linewidth of 0.1 nm, have been obtained from computer fits to the line profiles. They compare well (within our statistical uncertainty of 3% for the stronger and 5% for the weaker components) with the relative intensities expected from the transition probabilities compiled by Wiese, Smith, and Glennon[54] or predicted from first principles.[55]

The agreement implies that the fine-structure levels of the upper terms are statistically populated. This finding agrees with the observation of little or no polarization detectable in the emission from an ion-irradiated gas target.[31] The agreement with the intensities listed in the Striganov and Sventitskii tables,[53] however, which are mostly based on visual estimates and which contain data from a variety of light sources, is poor. We emphasize that—in contrast to many other light sources—the beam-gas light source seems to be well suited for precise determinations of relative line intensities in transition arrays. It thus offers the opportunity to make reliable com-

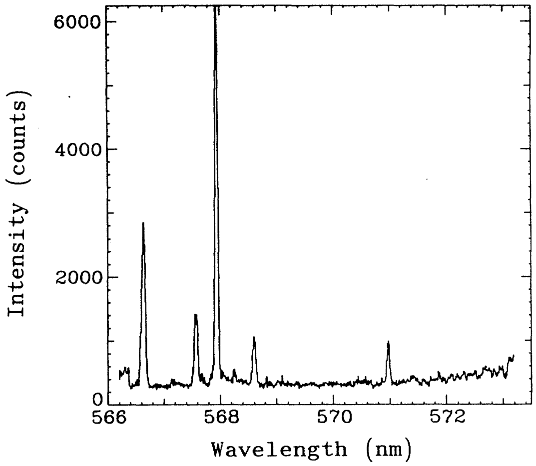

FIG. 3. Detailed spectrum of the multiplet N II $3s\ ^3P^\circ$–$3p\ ^3D$, near 570 nm. Czerny-Turner spectrometer, slit width is 50 μm, and linewidth (FWHM) is 0.06 nm.

parisons between experimental and theoretical determinations of those numbers. With molecular gases, however, only a subset of the atomic multiplets appears to be excited.

Turning to the N II $3d\ ^3F^\circ$ level, the decay to $3p\ ^3D$ at 500.51 nm is nominally blended with a transition at virtually identical wavelength from $3s\ ^5P_2$–$3p\ ^5P_2^\circ$. However, we see no evidence for other components of the latter multiplet, and thus we assume that the quintet transitions were absent. The $3p\ ^3D_2$–$3d\ ^3F_3^\circ$ and $^3D_1$–$^3F_2^\circ$ transitions lie within 0.034 mn of each other at 500.1 nm, and appear as a broadened line in our observations (blended, but reflecting the relative intensities of the components), well separated from the $3p\ ^3D_3$–$3d\ ^3F^\circ$ component at 500.51 nm (for a spectrum, see Ref. 56). The fact that the blend was incompletely resolved even when using narrow spectrometer slits was puzzling at first, since this would imply a linewidth clearly wider than the instrumental one.

In an attempt to reach even higher spectral resolution than possible with the Czerny-Turner spectrometer, we used an echelle spectrometer, with an instrumental linewidth of 0.01 nm, to record spectra of the N II lines near 500 nm. These lines, indeed, turned out to be considerably broadened (to linewidths of order 0.03 nm),[56] thus confirming the results obtained with the Czerny-Turner spectrometer. In contrast, the N_2^+ 1N(0,0) emission band, which was studied with the Czerny-Turner spectrometer in second diffraction order, with a resolution equivalent to first diffraction order linewidths of 0.015 nm, did not show any significant broadening.

The large widths of the monatomic lines imply either pressure broadening or Doppler broadening. Since the linewidths proved to be independent of pressure from 1 to 26 Pa, we attribute the widths to the Doppler effect; the effect indicates kinetic energies of the order of 10 eV. It relates to the energy distribution which follows the disintegration of predissociative or repulsive states of N_2^+, or the Coulomb explosion of the N_2 molecule after multiple inner-shell ionization. Aarts and de Heer[17] find the same spectral features to be enhanced after bombardment of N_2 with electrons of energies exceeding 50 eV.

The primary particle responsible might ionize and excite N_2 molecules to form N_2^+, $(N_2^+)^*$, or N_2^{2+}:

$$e,p + N_2 \ggg e,p + (N_2^+ + e), ((N_2^+)^* + e), (N_2^{2+} + 2e) .$$

If the $(N_2^+)^*$ molecule is highly or the N_2^{2+} molecule is moderately excited, dissociation is probable. Although radiative transitions between states of N_2^{2+} have been observed,[57–60] this system is not stable and breaks up due to Coulomb repulsion. Since N_2^{2+} is a much rarer species than N_2^+, we assume that the latter dominates in our light source. Anyway, a highly excited N_2^+ molecular ion (resulting, e.g., from inner-shell ionization and subsequent electron rearrangement processes) can be seen as an N_2^{2+} core with a Rydberg electron (in agreement with the interpretation by Aarts and de Heer of their electron-excitation results).[17] This core then can undergo Coulomb explosion, leading to two N^+ ions and a free electron. Such energetic residuals have been observed recently after inner-shell photoionization of nitrogen molecules.[61–63] Because of momentum conservation, the monatomic fragments each carry half of the surplus excitation energy of the parent highly excited molecule.

We observe transitions in energetic excited nitrogen atomic ions, $(N^+)^*$. If our conjecture about the origin of the $(N^+)^*$ ions from the breakup of $(N_2^+)^*$ molecules is correct, we expect the same gross dependence on target pressure for the production of $(N^+)^*$ as for $(N_2^+)^*$. This is, indeed, what we observe (see below). The lack of notable emission from the neutral atom, N, means that the branching ratio of such decays minimizes excited neutral atoms as reaction products.

Since the lifetime of the $3d\ ^3F^\circ$ level is of order 8 ns,[54] and the collision times are of order 10^{-5} s, the $3d \rightarrow 3p$ transitions are most likely to occur before the ions slow down. Thus the same line broadening as observed on the $3p$-$3d$ transitions has to be expected for the subsequent $3s$-$3p$ transitions, and this was, indeed, found, using the Czerny-Turner spectrometer. This agrees with the observations by Aarts and de Heer,[17] who found the $3d\ ^3F^\circ$ levels to be particularly strongly populated after electron excitation and to give rise to a most notable intensity of the decay chain $3d \rightarrow 3p \rightarrow 3s$, etc.

The N^+ $3p\ ^3D_J$ level population appears to be statistical (see above), without any indication of J-dependent population effects from the production process. In order to find out whether the $3d\ ^3F^\circ$ levels are the highest lying ones populated by the above mechanism, one would like to study the $3d$-$4f$ transitions, and so forth, but those transitions are outside the detection range of our present experiment.

Independent support for this picture can be found in other studies: Fan and Meinel[2] note the role of the number of projectile electrons in the excitation. Our conclusion rather is that it is the higher degree of excitation of N_2^+ which is responsible for generating the excited states of N^+ and that the crucial step is the intermediate excited state reached in the N_2^+ ions. This concept is supported by the threshold behavior of the production of excited N^+ ions by electron excitation.[17]

Comtet, Fournier, and Lassier-Govers[64] studied the collision of N_2^+ molecular ions of 5–10 keV with He atoms, using the technique of translational energy spectroscopy. They observed breakup fragments (N,N^+) with kinetic energies comparable to our findings. Comtet, Fourier, and Lassier-Govers, as well as Suzuki and Saito,[61,62] use particle detectors (for ions and atoms) which cannot detect whether a particle is electronically excited. They associate their energy distributions with reaction products in either the ground state or low-lying excited levels, and thus are led to assume intermediate excited N_2^+ states which should lie about 30 eV above the ground state of the neutral molecule, N_2.[61,62,64] We see that the fragments can carry substantial amounts of electronic excitation energy, a fact that points to intermediate states which are even higher lying by about 10 eV, the sum of the energies needed to emit the $3d \rightarrow 3p \rightarrow 3s$ decay chain and the subsequent $n=3 \rightarrow n'=2$ transition. Similarly highly excited intermediate states, charged and excited atomic fragments, and breakup reactions involving the doubly charged nitrogen molecule have been found by Eberhardt *et al.*[63] in an Auger electron study of the fragmentation of N_2 by soft x rays.

B. Molecular bands

The density of bands showing in our spectra is much higher than that apparent in the poor spectral resolution, low gas pressure work of most of the earlier studies, where only a few outstanding spectral features were treated, the multitude of other bands being smeared out and considered as background. Our work suggests that satisfactory determinations of relative band yields, and hence excitation cross sections, cannot presently be made with either our present equipment or with that used in some other studies, because the branches, which are especially numerous for the neutral molecule, often overlap.

Oldenberg[56] observed that the rotational level population of molecules might be indicative of the ambient temperature, whereas the less regular populations of vibrational levels apparently relate to the collisional process in which the molecular species was formed. Any such observations can be meaningful only if the radiative lifetime of the molecular states is considerably shorter than the collision time or quench rate. For the N_2^+ $B\Sigma$ bands, of which we discuss the $1N(0,0)$ band, the typical lifetime has been measured to (61.35±0.3) ns,[66] which is close to the results of recent calculations of about 55 ns.[67] This is clearly shorter than the collision time at our maximum pressure.

We have evaluated the relative intensities of the rotational transitions in the $1N(0,0)$ band of N_2^+ by comparing a model calculation with our high-resolution spectroscopic data.[49,56] A comparison of the computed and measured spectra gives a source rotational temperature of 350±50 K, with no significant variation of this rotational temperature with the target gas pressure over the range 1–26 Pa. Similar deductions have been made previously for both auroral and laboratory spectra of the same molecular band.[3–5,14,20,22,23,26,31,32,34,44,45] Systematic studies of the apparent rotational temperature showed a slight variation with projectile energy when excited by electrons[14] and a notable effect of the ionic projectile species at low energies.[23,44,45]

C. Pressure dependence of the light yield

We determined the pressure dependence of both monatomic and molecular features in terms of the variation of a particular peak height with pressure (Fig. 4); refer to

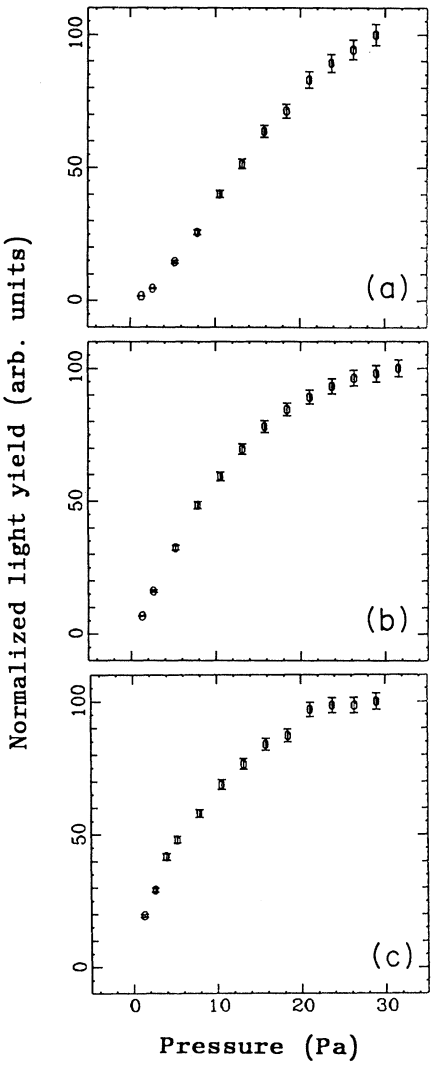

FIG. 4. Normalized light yield (observed intensity corrected for the pressure effects on the normalizing beam charge) vs pressure for prominent lines and bands. (a) N_2 $1P(4,1)$, (b) N_2^+ $1N(0,0)$, (c) N^+ $3p\,^3D$–$3d\,^3F^\circ$. The 1σ error bars relate to counting statistics, Faraday cup current readings and pressure readings and take the evaluation procedure into account.

Fig. 2 to see the relative line intensities of the various spectral features in perspective and to Figs. 2 and 6 and Refs. 49 and 56 for high-resolution spectra. The bands studied include the N_2 bands $1(P)(2,0)$, $1P(3,1)$, $1P(4,1)$, $1P(5,2)$, $1P(6,4)$, $1P(9,6)$, and $2P(0,0)$, $2P(0,1)$, $2P(1,4)$, $2P(2,4)$, and the N_2^+ bands $1N(0,0)$ and $1N(1,0)$. The signal obtained for each feature at each pressure was corrected by multiplying each measurement of intensity I by the ratio of Faraday cup currents at the given pressure and at $p=0$, $i(p)/i(p_0)$, in order to relate the data to similar numbers of projectiles, and by subtracting a background contribution measured with zero target pressure. The resulting pressure curves clearly show different shapes. In a second step, each peak yield was divided by the pressure p. This removes any underlying linear pressure dependence of the data and enhances the nonlinearities of the pressure trends (Fig. 5).

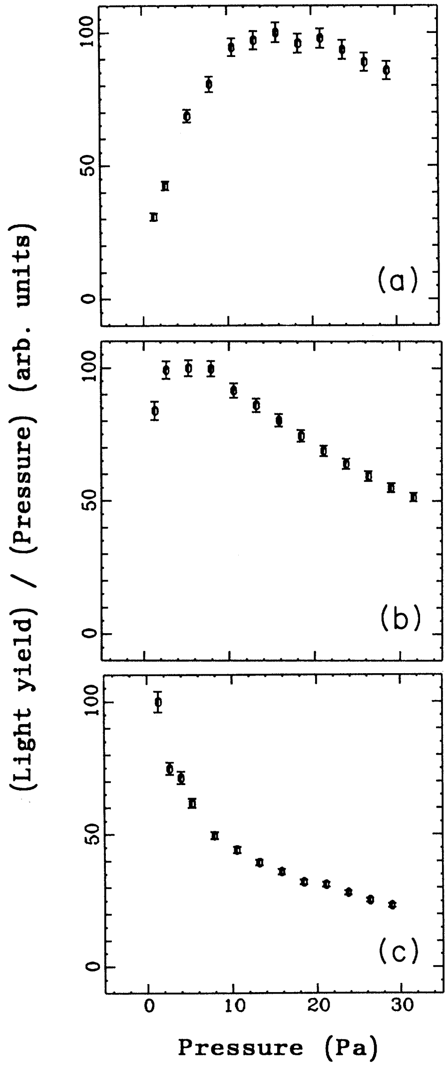

FIG. 5. Light yield data divided by the pressure vs pressure for the data shown in Fig. 4. (a) N_2 $1P(4,1)$, (b) N_2^+ $1N(0,0)$, (c) N^+ $3p\,^3D-3d\,^3F°$.

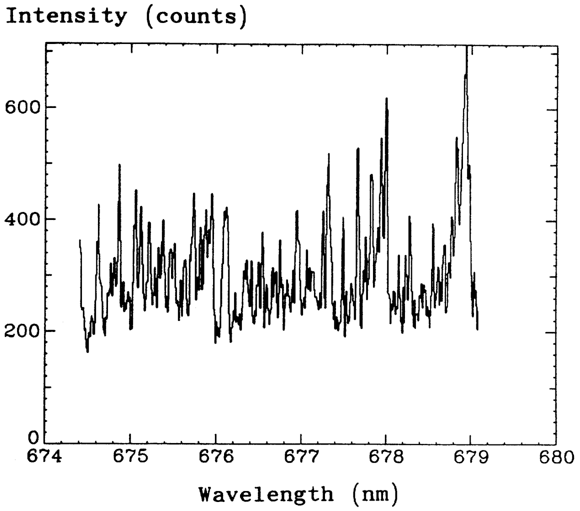

FIG. 6. Detailed spectrum of the N_2 $1P(4,1)$ band, near 679 nm, and of the adjacent spectral features. Czerny-Turner spectrometer, slit width is 30 μm, linewidth (FWHM) is 0.05 nm. The complexity evident in this spectrum is typical for most of the spectral features of Fig. 2 when studied with higher spectral resolution.

The error bars in both figures relate to counting statistics and to the uncertainties of the pressure and current measurements.

Our results show that the curves for the first and second positive bands of the neutral molecule are fairly similar to one another, but that they differ significantly from the others.[56] According to Fig. 4, the intensity of emission from the neutral molecule rises less strongly with pressure than the intensities of the molecular and atomic ion emissions. Although there are almost straight sections in the pressure curves, the overall shape is not just linear, but indicates a quadratic pressure dependence up to about 10 Pa. This might be caused by a projectile species which is itself dependent on pressure, like slow secondary electrons.

On the other hand, the pressure dependencies of the monatomic lines and the first negative bands have almost the same general appearance; their excitation rises steeply with pressure for low pressures (up to about 7 Pa). Then the gradient of the increase lessens until the light yield becomes only weakly dependent on pressure (flat curve for the pressure-normalized data in Fig. 5) above about 25 Pa. Figure 4 suggests that the excited states in N^+ and N_2^+ might share a common production mechanism (at least in part), whereas the excited states in N_2 arise from a different kind of interaction. The data reduction presented in Fig. 5, however, shows a notable difference in the details of the pressure curves of the N_2^+ and N^+ light emission. The N_2^+ curve (Fig. 4) is dominated by a linear term for $p > 3$ Pa. The N^+ curve starts out with a steep slope (Figs. 4 and 5) which then decreases, as if the excitation process is less and less efficient at higher gas pressures. In Sec. IV D, we consider explanations of these similarities and differences.

We note that Dufay *et al.*,[27] working with linewidths of 0.4 nm, reported the pressure dependence of the N II $3s\ ^1P^\circ - 3p\ ^1D$ line at 399.5 nm and of the molecular $2P(1,4)$ band from N_2 with a band head at 399.8 nm. In our data, however, taken with a linewidth of 0.03 nm, the monatomic ion line is clearly contaminated by the molecular band contribution. An example of our data on this spectral region is included in Fig. 2.

D. Excitation-deexcitation processes

The observed light yields from nitrogen under H_3^+ bombardment result from two separate factors, namely, the excitation cross sections and the decay processes. Both the excitation and the deexcitation may show (different) pressure effects if multistep processes, including cascades, are involved. As regards the excitation process(es), the major contributors are the following:

(1) Direct interaction between the incident ions and the target molecules, which may include ionization and simultaneous excitation, and would be proportional to the target pressure.

(2) Interaction between the electrons which accompany the incident ions and the target. The number of electrons stripped off the projectiles is proportional to p, up to the pressure (or the target mass per unit area) at which there is equilibrium of electron loss and capture. By collisions with target molecules these electrons lose energy, and initially fast electrons first become more effective as they approach the optimum energy for excitation,[68] then less effective when they are slowed down to energies below the various excitation thresholds.

(3) Excitation by electrons released from target molecules by ionization events (secondary electrons). The number of these electrons is proportional to the kinetic energy of the ionizing particles, and their density is roughly proportional to the square of the target pressure.

(4) Various dissociation and recombination processes among the target particles.

(5) Possible pressure-dependent geometrical effects in the plasma which is generated close to the ion beam.

The decay modes include radiative emission, recombination, collisional quenching, and diffusion out of the region of observation (which can be significant for long-lived states).

Several simple models have been described for electron excitation in the low-pressure range ($p < 1$ Pa),[15,68] but for higher pressures it seems virtually impossible— considering the complexity of the problem—to make a quantitative assessment of the role of the individual factors which contribute to the observed emission intensities. In the following we note a few features and develop a scenario for our case.

At a target gas pressure of 26 Pa, protons of energy 333 keV (that is the energy per proton in the 1-MeV H_3^+ projectiles) can be estimated to lose about 500 eV of their energy until they reach the field of view of the spectrometer in the center of the gas target,[69] and proportionately less at lower pressures. Thus the projectile ion velocity is hardly affected by the change in target pressure. For projectile molecular ions which do not dissociate in the target, the energy loss will be even lower, because of the lower charge-to-mass ratio.

The situation for electrons is very different. We consider as an example electrons of 180 eV, that is, bound or free electrons with the velocity of the projectile ions. Typical cross sections for inelastic collisions (dominated by ionizing collisions)[70] of 180-eV electrons on N_2 are of the order of 10^{-16} cm^2. At a pressure of about 2.6 Pa (a tenth of our typical maximum pressure) the mean free path of such electrons would be equal to the target length. In other words, at higher pressures the majority of the initially fast electrons will suffer one or more collisions with the target gas, many of which may ionize the target molecules. Each of these violent collisions will take about 30 eV from the kinetic energy of the fast electron; thus they will soon drop below the threshold energy necessary to ionize and excite the target gas. At the same time, slow secondary electrons are set free.

From all this, the following interpretation of the pressure curves emerges: The nonlinearities of the pressure curves result from the electronic component of the projectiles and from secondary electrons. The influence of the latter shows as an overproportional pressure trend in the low-pressure part of the light yield curve of N_2^0 [see Fig. 4(a)]. The positive bands of the N_2^0 molecule require the lowest electron energies (although a spin-flip), and their intensities continue to rise (albeit more slowly) at our highest pressures. The excitation of N_2^+ needs higher energy, and the fraction of these higher-energy electrons is depleted in favor of the slower ones at higher pressures. This effect is even more pronounced for high excitation states of N_2^+, which dissociate and lead to $(N^+)^*$ excited ions. This interpretation agrees fully with the results of the electron excitation study by Aarts and de Heer.[17]

We suggest, therefore, that there is (at least) a two-component energy distribution for the electrons, and that this is responsible for the (basically) two groups of pressure curves we measure, in addition to the projectile-related processes discussed in the literature for which it is usually assumed that the projectile beam consists of monoenergetic ions or electrons only. The observation of this picture is complicated by the fact that the first of these collisions can happen anywhere along the projectile trajectory, so that a mixture of fast and slow electrons is always present, with the balance clearly being shifted towards the slower electrons for higher target pressures and for observations in the center of the extended gas target.

V. CONCLUSION

By varying the pressure in a gas target under H_3^+ ion bombardment over a wider range than previously used with other projectiles, it was shown that complex physical processes are involved which may render this type of laboratory study aiming at excitation cross sections much more difficult than appreciated in a number of previous studies. Among the earlier cross-section studies were few with photoelectric (linear) detection, and the earlier data show a considerable scatter. This has been traced back (by McNeal and Clark[36]) as being partly due to photometry problems. More often than not the spectral resolution used in those studies was clearly insufficient, leading to either unnoticed contamination of atomic features with molecular ones,[27,40] or not covering the whole band, the excitation cross section of which was to be studied.[36]

Although in a number of cases measured emission cross sections were believed to relate to individual production cross sections, that is not likely to be indisputable in the light of the present and some other experiments. For example, Ajello *et al.*[71] in a recent crossed-beam study (in which the effects of particle density are negligible) of electron excitation of N_2 required moderately high spectral resolution (comparable to our survey spectra) in order to disentangle vibrational perturbation effects and to achieve cross section measurements in the VUV. Furthermore, a cautionary example might be the recently found necessity to change by about a factor of 2[72,73] the benchmark reference data for electron excitation cross sections (which had been used for almost three decades).

To pursue the original goal of proper cross-section measurements, one has to work at gas pressures much lower than accessible here, with consequently much lower signal, for which very fast detection systems are demanded. High spectral resolution as employed in the present work is essential; the present investigation clearly points to problems of spectroscopic resolution in almost all of the earlier studies. Simple approximations can, of course, be made on the basis of data with poorer spectral resolution, but the present study defines systematic errors which are likely to occur in such an approach.

We deduce from our pressure studies of N_2 under H_3^+ ion impact the important role of electrons of various energies which are responsible for different excitation mechanisms. The modeling of the various molecular bands, however, a prerequisite for the proper interpretation of cross-section data, so far is insufficiently treated by theory. In the one case for which such a model exists, it permitted us to determine a rotational temperature on the basis of the best-resolved molecular band spectra obtained from a gas target under ion bombardment yet.

Very high spectral resolution can also clarify effects which hitherto had gone unnoticed: the kinematic broadening of the N II lines points to the production of this excited atomic ion by dissociation of highly excited molecular ions. The direct observation of decay chains in the N^+ residuals from the breakup of N_2^+ molecules proves the intermediate states to be more highly excited than hitherto deduced from translational energy spectroscopy studies of reaction products after inner-shell ionization, and confirms conclusions drawn from one of the electron-excitation studies.[17]

In contrast to the present data on N_2 our studies of O_2 under ion irradiation[74] show emissions from both neutral and ionized atoms. Linewidth measurements on those lines are planned to find out whether the same processes are present in that case or whether the different molecular and atomic structure leads to different reaction channels.

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[*] Presently on leave of absence at Harvard College Observatory, Mail Stop 50, 60 Garden Street, Cambridge, MA 02138.

[†] Present address: Department of Physics, California Institute of Technology, Pasadena, CA 91125.

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