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Vibration and Rotation of N_2^+ Excited by 10–65-keV Ions*

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Cross sections for excitation of the [$B(^2\Sigma_u^+)$ - $X(^2\Sigma_g^+)$] first negative bands of N_2^+ resulting from impact of H^+ , D^+ , He^+ , Ne^+ , and N^+ have been measured in the energy range 10–65 keV, and at pressures such that radiation occurs much sooner than subsequent collisions of the excited molecule. Intensity ratios of bands in this system and rotational distributions in the 3914-Å (0,0) and 4278-Å (0,1) bands have been directly measured and compared with those obtained from electron impact. Supplementary determinations of total charge-exchange cross sections have been made. Cross sections for excitation of Balmer alpha radiation in charge-exchange collisions of H^+ and D^+ with N_2 have been measured in the same energy range. Little or no increase of vibration occurs in H^+ , D^+ , and e^- impact, but a definite enhancement varying with ion velocity is produced by the heavier ions He^+ , Ne^+ , and N^+ . Rotation, however, remains in a thermal distribution at room temperature.

INTRODUCTION

It is known that in electron-collisional excitation of molecules the production of vibration can be described by the Franck-Condon principle with allowance for possible intermediate excited states. The distribution among rotational energy levels of the excited state is determined by requiring that the angular momentum remain unchanged in the collision. Experimental results^{1–5} agree with this description.

Theory does not specify the extent to which heavy-particle collisions enhance⁶ vibration and rotation at the energies where excitation of electronic transitions occurs. Some observations for the $B(^2\Sigma_u^+)$ - $X(^2\Sigma_g^+)$ first

negative bands of N_2^+ have already been reported. Carleton⁷ using 3-keV protons in N_2 , Roesler *et al.*⁸ using 10–30-keV protons and hydrogen atoms in N_2 , and Reeves and Nicholls⁹ using 0.5–1.5-MeV protons and H_3^+ in N_2 observed a Boltzmann distribution of rotational energies with a temperature equal to the gas temperature. Lowe and Ferguson¹⁰ found a Boltzmann distribution at about 3500°K when excitation was by 3-keV Li^+ . Smyth and Arnott¹ reported vibrational enhancement in the first negative system of N_2^+ excited by 5-keV canal rays from a Hg- N_2 discharge. Branscomb *et al.*¹¹ observed enhancement for the same system excited by 100-keV H^+ and H. Fan⁸ observed significant vibrational enhancement in this system when excited by 150-keV He^+ , and little or no enhancement when excitation was by electrons, protons, or higher energy He^+ . The results of Philpot and Hughes¹² for excitation of the

* This work was performed at the University of Washington and assisted by the U. S. Office of Naval Research and the National Science Foundation.

¹ H. D. Smyth and E. G. F. Arnott, *Phys. Rev.* **36**, 1023 (1930).

² G. O. Langstroth, *Proc. Roy. Soc. (London)* **A146**, 166 (1934).

³ C. Y. Fan, *Phys. Rev.* **103**, 1740 (1956).

⁴ L. Vegard, *Geofys. Publikasjoner Norske Videnskaps-Akad. i Oslo* **9**, No. 11 (1932).

⁵ L. M. Branscomb, *Phys. Rev.* **79**, 619 (1950).

⁶ The term "normal" will be used to refer to the population of vibrational levels predicted by the Franck-Condon principle and observed in the case of excitation by electrons. "Abnormal" or "enhanced" will refer to vibrational populations departing significantly from the latter.

⁷ N. P. Carleton, *Phys. Rev.* **107**, 110 (1957).

⁸ F. L. Roesler, C. Y. Fan, and J. W. Chamberlain, *J. Atmospheric Terrest. Phys.* **12**, 200 (1958).

⁹ E. M. Reeves and R. W. Nicholls, *Proc. Phys. Soc. (London)* **78**, 588 (1961).

¹⁰ R. P. Lowe and H. I. S. Ferguson, *Proc. Phys. Soc. (London)* **85**, 813 (1965).

¹¹ L. M. Branscomb, R. J. Shalek, and T. W. Bonner, *Trans. Amer. Geophys. Union* **35**, 107 (1954).

¹² J. L. Philpot and R. H. Hughes, *Phys. Rev.* **133**, A107 (1964).

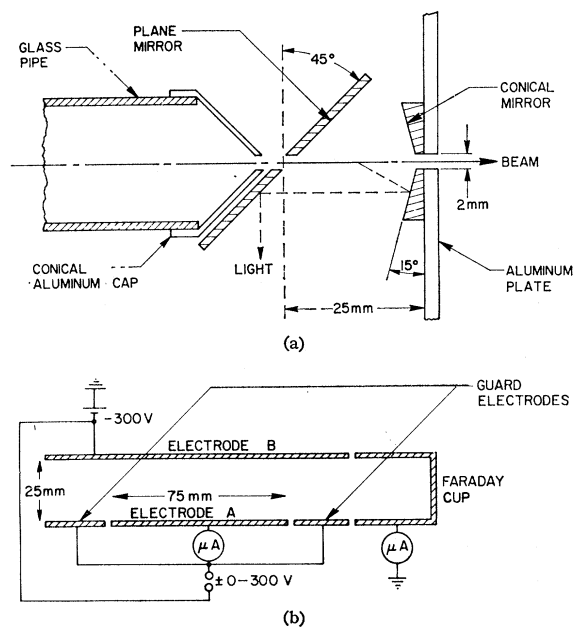


FIG. 1. Mirror arrangement and electrode system.

first negative system by 10- to 150-keV H^+ show no vibrational enhancement. The enhancement of internal motion in N_2^+ is also observable in upper-atmosphere auroral spectra under conditions of sunlit rays, local heating, or unilluminated red auroras generally associated with incoming hydrogen. The last-named occurrence has frequently been observed in Alaskan auroras¹³ as an increase in rotation together with a still greater increase in vibration.

To provide a fuller description, the present work extends the observational data for vibrational and rotational excitation by heavy particles to cover a variety of incident ions and a range of energies including the region where excitation by charge exchange is most probable. Specifically, relative band intensities in the N_2^+ first negative system excited by impact of 10–65-keV ions have been measured along with rotational intensity distributions in the 3914-Å (0,0) and 4278-Å (0,1) bands. Supplementary measurements have also been carried out, yielding total charge-exchange cross sections, cross sections for charge-exchange excitation of Balmer alpha radiation, and electron-impact data. From the above data, relative populations of the $v=1$ and $v=0$ levels of the $B^2\Sigma_u^+$ state of N_2^+ and the rotational temperatures resulting from ion impact are derived.

EXPERIMENTAL

A focused and mass-analyzed 0.01–0.5 μA ion beam of circular cross section was passed through a collision

region, containing N_2 at pressures near 10^{-3} Torr and the conical and plane mirrors shown in Fig. 1(a), and into a second region for electrical measurements. Light emitted either normal to or at an angle of 30° with respect to the beam axis was viewed through a glass window.¹⁴ The radiative lifetime for the band emission¹⁵ is so short ($\sim 6.6 \times 10^{-8}$ sec) that the emission region was visibly confined to that of the small-diameter (~ 2 mm) ion beam, and the target gas pressures were sufficiently low that the mean free path exceeded the total beam length in the collision chamber. Collisional relaxation of rotation and vibration was therefore considered to be negligible. This condition can be stated as an assumed upper limit on the ratio of the cross section for relaxation relative to that for neutral diffusion: for a 1-eV N_2^+ ion this requires a cross-section ratio of 300 or less at the pressure of 10^{-3} Torr, or an effective interaction distance no greater than 17 times that for diffusion. The rotational lifetime of a recoil ion at a given pressure would be limited by its speed if not by radiation, and the speed of a typical ion would be dependent on the type and energy of incident particle. No corresponding variation of rotational temperature was found under any of these conditions. Furthermore, the experiments of Lowe and Ferguson¹⁰ show that a high rotational temperature in N_2^+ , independent of beam current, is capable of persisting during the radiative lifetime at pressures 20 times greater than ours.

Two locally constructed spectrographs were used, a fast ($f/0.95$) transmission grating instrument having a slit-limited resolution of about 25 Å in first order and a crossed-grating echelle spectrograph operating at a resolution of 1 Å. In both cases, spectrograms were obtained on 16-mm Eastman 103a-F film with exposures of one and two hours. The spectral response of each system at these exposure times was determined with a G.E. calibrated incandescent lamp, and band intensities were obtained through integration of intensity curves. Absolute excitation cross sections were obtained by normalizing to the average of the values measured by Philpot and Hughes¹² and Sheridan, Oldenberg, and Carleton¹⁶ for proton excitation of the (0,0) band at 20 keV, where both results are in good agreement. Gas pressure in the collision chamber was measured with an ionization gauge and a thermocouple gauge, both calibrated against a McLeod gauge. Beam current was measured by using the entire collision chamber as a Faraday cup.

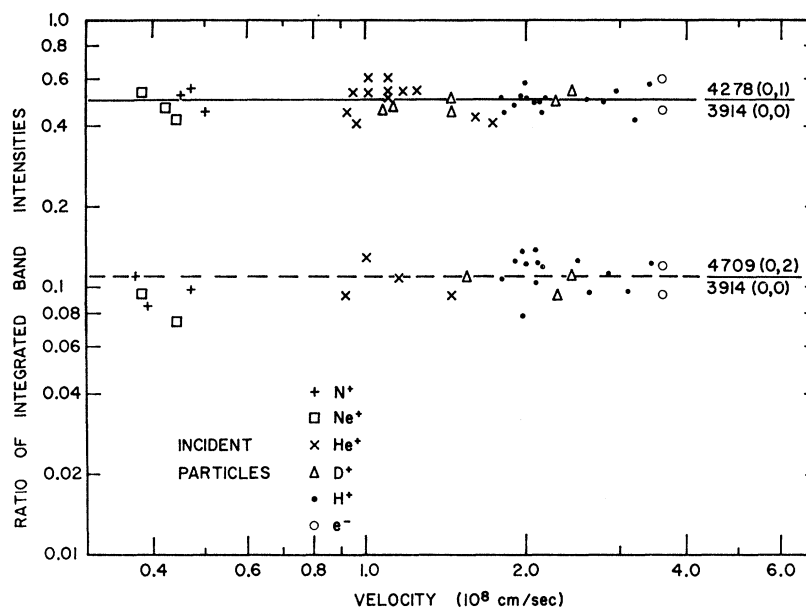
Measurements of total charge-exchange cross sections were made by collecting the slow ion current with the

¹⁴ Details of the apparatus and experimental procedure have been presented in a dissertation by J. R. Sheridan, University of Washington, 1964 (unpublished).

¹⁵ R. G. Bennett and F. W. Dalby, *J. Chem. Phys.* **31**, 434 (1959).

¹⁶ W. F. Sheridan, O. Oldenberg, and N. P. Carleton, *2nd International Conference on the Physics of Electronic and Atomic Collisions; Abstracts of Papers* (W. A. Benjamin and Company, Inc., New York, 1961), p. 159.

¹³ K. C. Clark and A. E. Belon, *J. Atmospheric Terrest. Phys.* **16**, 205 (1959).

FIG. 2. Branching ratios for the $v'=0$ progression.

electrode system shown in Fig. 1(b). The currents at the collector electrode A are

$$I^+ = I_s + I_i \quad (1)$$

and

$$I^- = I_s + I_i + I_e \quad (2)$$

when that electrode has a positive or negative polarity, respectively, with respect to electrode B. I_s is the current from secondary electrons from electrode B or A, respectively, I_i is the current from ionizing collisions in the reaction region, and I_e is the current from slow ions produced in the reaction region by charge-exchange collisions. The slow-ion current is then obtained by simple subtraction. Electrodes A and B and the guard electrodes are biased at $-300V$ with respect to ground to exclude secondary electrons produced at the entrance aperture or in the Faraday cup. The total cross section is then given by $Q_e = (I_e/I)nL$, where I is the beam current measured at the Faraday cup and properly corrected for beam degradation, n is the number density of target molecules, and L is the length of the reaction region.

CORRECTIONS FOR SPATIAL VARIATION IN EMITTER DENSITY

In this experiment a "thin" target was used to make multiple collisions negligible. The degradation of the ion beam due to charge-exchange collisions was given by

$$I(x) = I_0 \exp(-n\sigma_c x), \quad (3)$$

where I is the beam current at any point x , I_0 is the beam current entering the collision chamber, n is the density of target molecules, and σ_c is the total charge-exchange cross section. When the beam current was

corrected for degradation in this manner, the measured intensities of the lines and bands studied showed a linear dependence on beam current and target gas pressure, indicating that the spectral features resulted from single collisions of a beam particle with a target particle.

When excitation of beam particles is being measured, however, one must also be concerned about effects of emitter displacement if the mean distance travelled by excited beam particles is at least comparable to the distance from the observation region to the point of entrance into the collision chamber. This was the case in this experiment, since the excited hydrogen atoms produced in charge-exchange collisions were travelling at velocities of 10^8 cm/sec or more and the lifetimes for the $n=3$ states range from 5.4×10^{-9} to 1.6×10^{-7} sec. The requirement that a steady-state condition exist in the beam yields the equation,

$$\partial n^*/\partial t - v \partial n^*/\partial x = 0, \quad (4)$$

where n^* is the density of excited atoms in the beam and v is the velocity of the beam particles. Also, the net rate of production of excited atoms in the beam is

$$\partial n^*/\partial t = n v \sigma^* n^+ - n^* A, \quad (5)$$

where σ^* is the excitation cross section, n^+ is the density of ions in the beam, and A is the total radiative transition probability per unit time from the excited state to lower energy states. From Eq. (3), we have

$$n^+ = n_0^+ \exp(-n\sigma_c x), \quad (6)$$

where n_0^+ is the initial density of ions in the beam. The resulting differential equation is

$$n\sigma^* n_0^+ \exp(-n\sigma_c x) - (A/v)n^* - \partial n^*/\partial x = 0, \quad (7)$$

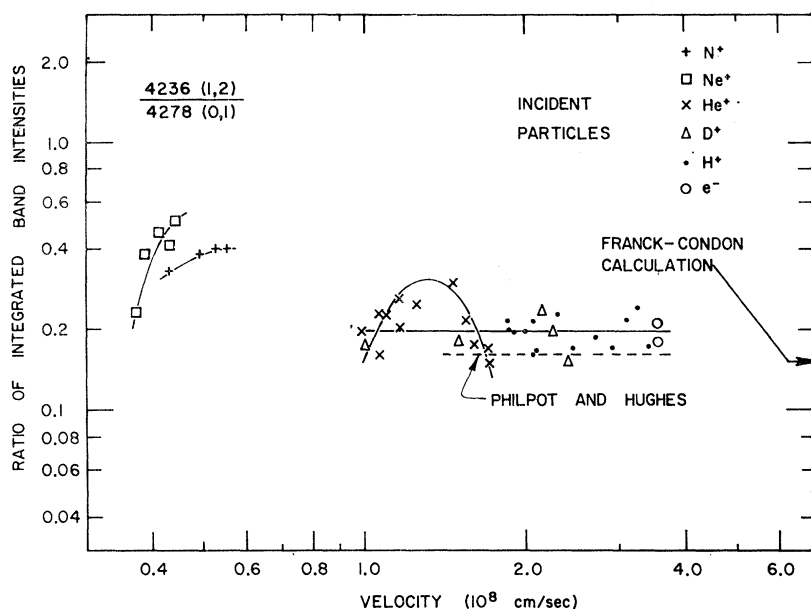


FIG. 3. Intensity ratios, $[4236 \text{ \AA} (1,2)] / [4278 \text{ \AA} (0,1)]$, for $\Delta v = 1$ bands.

whose solution is

$$n^* = [nm^+\sigma^*/(A/v - n\sigma_e)] [\exp(-n\sigma_e x) - \exp(-(A/v)x)]. \quad (8)$$

For $n\sigma_e \ll A/v$, this reduces to

$$n^* = (v/A)nm^+\sigma^*[1 - \exp(-(A/v)x)]. \quad (9)$$

The observed intensity of the radiation from the excited atoms in the beam is proportional to n^*A' where A' is the transition probability per unit time for the particular transition being observed. We can then write

$$\sigma^* \propto A/A' \frac{I_{\text{rel}}}{Ip[1 - \exp(-(A/v)x)]}, \quad (10)$$

where I_{rel} is the observed relative intensity and p is the pressure. In the case of Balmer alpha radiation, transitions from the $3S$, $3P$, and $3D$ levels are observed, and since a different correction applies to each of these levels, the total correction depends on their relative population. The corrections used here represent an extreme assumption that the levels are populated according to their statistical weight.¹⁷ The apparent cross section for exciting Balmer alpha radiation has been multiplied by factors varying from 2 to 5 for proton energies from 10 to 65 keV.

RESULTS

A. Band-Intensity Ratios

Measured ratios of integrated intensities for N_2^+ first negative bands excited by H^+ , D^+ , He^+ , Ne^+ ,

¹⁷ Work in progress by R. H. Hughes (informal communication) suggests that the correction will be less than that resulting from this assumed distribution. For example, if all excitation were into the P level, there would be essentially no correction needed.

N^+ , and e^- are shown in Figs. 2-4 as a function of the velocity of the incident particle. The branching ratios for the transitions originating in the $v=0$ level of the $B^2\Sigma_u^+$ state of N_2^+ are shown in Fig. 2 and illustrate that the observed relative transition probabilities are independent of the mode of excitation, as is to be expected. The branching ratios measured in this experiment are compared to the results of others in Table I.

The $4236 \text{ \AA} (1,2)/4278 \text{ \AA} (0,1)$ and $4652 \text{ \AA} (1,3)/4709 \text{ \AA} (0,2)$ band-intensity ratios are indicative of the relative population of the $v=1$ and $v=0$ vibrational

TABLE I. Relative intensities of the $v'=0$ progression in the N_2^+ first negative system.

Investigators	3914 \AA (0,0)	4278 \AA (0,1)	4709 \AA (0,2)	Method
Wallace and Nicholls ^a	1.0	0.32	0.063	Measured in N_2 negative glow
Stewart ^b	1.0	0.39	0.10	Measured using electron-impact excitation
Philpot and Hughes ^c	1.0	0.29	0.056	Measured using proton-impact excitation
Pillow ^d	1.0	0.31	0.099	Calculated
Herzberg ^e	1.0	0.34	0.48	Measured in N_2 discharge
Bates ^f	1.0	0.31	0.072	Calculated
This experiment	1.0	0.49	0.105	Measured using ion-impact excitation

^a L. V. Wallace and R. W. Nicholls, *J. Atmospheric Terrest. Phys.* **1**, 101 (1955).

^b D. T. Stewart, *Proc. Phys. Soc. (London)* **A69**, 437 (1956).

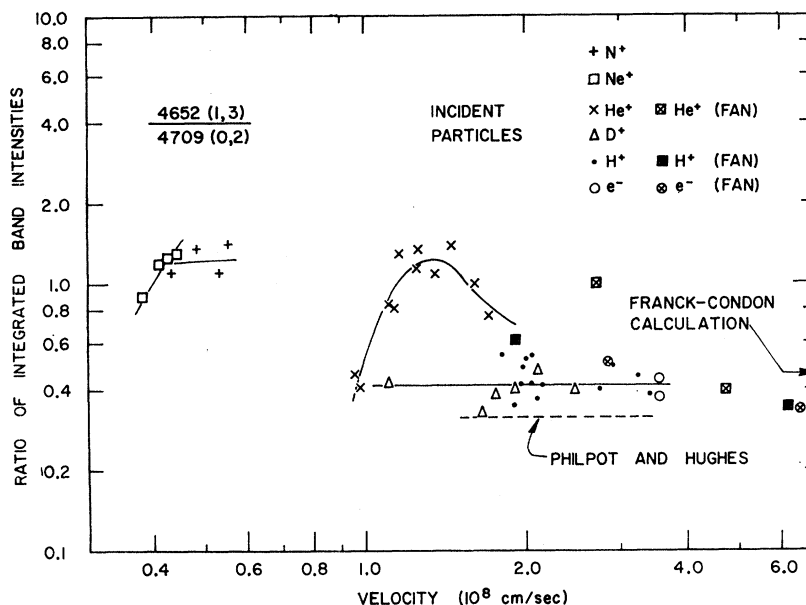
^c Reference 12.

^d M. E. Pillow, *Proc. Phys. Soc. (London)* **A64**, 772 (1951).

^e G. Herzberg, *Ann. Physik* **86**, 191 (1928).

^f D. R. Bates, *Monthly Notices Roy. Astron. Soc.* **112**, 614 (1952).

FIG. 4. Intensity ratios, $[4652 \text{ \AA} (1,3) / 4709 \text{ \AA} (0,2)]$, for $\Delta v=2$ bands.



levels of the $B^2\Sigma_u^+$ state of N_2^+ . Figures 3 and 4 show measured values for these intensity ratios as a function of velocity when excitation is by 10–65-keV ions or by electrons. The ratio of the intensities of any two bands in a system is given by

$$\frac{I_{ij}}{I_{kl}} = \frac{N_i}{N_k} \frac{A_{ij}}{A_{kl}} \frac{\lambda_{kl}}{\lambda_{ij}}, \quad (11)$$

where N_i is the population of the i th vibrational level of the upper state and I_{ij} , A_{ij} , and λ_{ij} are the intensity, transition probability per unit time, and wavelength, respectively, associated with the transition from the i th vibrational level of the upper electronic state to the j th vibrational level of the lower state. If the two upper vibrational levels i and k are excited from the lowest vibrational level of N_2 in accordance with the Franck-Condon principle, knowledge of the appropriate overlap integrals for the processes of excitation and emission permits calculation of the ratio I_{ij}/I_{kl} . These "normal" intensity ratios were calculated using Franck-Condon factors and transition probabilities given by Nicholls^{18,19} and are included in Figs. 3 and 4. Intensity ratios measured by Philpot and Hughes¹² for H^+ impact and by Fan⁸ for e^- , H^+ , and He^+ impact are also included in the same figures. The results of the present experiment show little or no vibrational enhancement when excitation is by e^- , H^+ , and D^+ and a definite enhancement, varying with velocity, when excitation is by He^+ , Ne^+ , and N^+ .

¹⁸ R. W. Nicholls, J. Atmospheric Terrest. Phys. **25**, 218 (1963).

¹⁹ R. W. Nicholls, J. Quant. Spectr. Radiative Transfer **2**, 433 (1963).

B. Rotation

If the population of the rotational levels of the excited state is distributed thermally (i.e., a Boltzmann distribution with allowance for statistical weights), the intensity of a rotational line in a first negative band is approximately proportional to²⁰ $(K'+K''+1) \exp[-hcB_v K'(K'+1)/kT]$, where K' and K'' are the quantum numbers for total angular momentum apart from spin of the upper and lower states, respectively, B_v is a constant for a given vibrational level, and T is the rotational temperature. A plot of $\ln[I_{\text{rel}}/(K'+K''+1)]$ versus $K'(K'+1)$ then gives a straight line of slope $-hcB_v/kT$. Figure 5(a) shows a typical plot of this type, indicating a thermal distribution of rotational populations and a temperature near 300°K. This thermal distribution was observed for all incident ions and velocities used and in both the (0,0) and (0,1) bands of the first negative system. Figure 5(b) shows the N_2^+ rotational temperatures measured in this manner for the various incident particles as a function of their velocity. In all cases the rotational temperature is equal to the laboratory temperature within a probable experimental error of $\pm 60^\circ\text{K}$.

C. Cross Sections for Exciting First Negative Bands

The measured cross sections for excitation of the (0,0) band of the first negative system are shown in Fig. 6. The apparent maxima in the He^+ , H^+ , and D^+ cross sections are in good agreement with the adiabatic maximum rule that the cross section is a maximum when $hv/a\Delta E \approx 1$, where v is the relative velocity of the

²⁰ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand, Inc., New York, 1950).

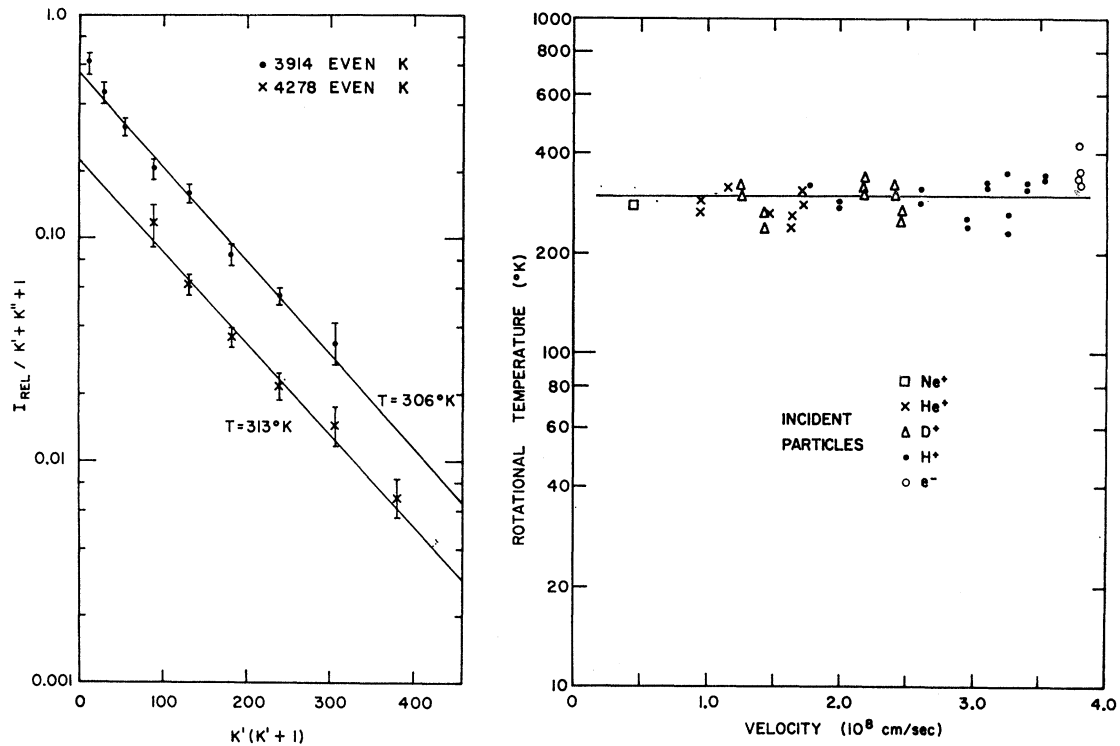


FIG. 5. Rotational temperatures in the (0,0) and (0,1) bands.

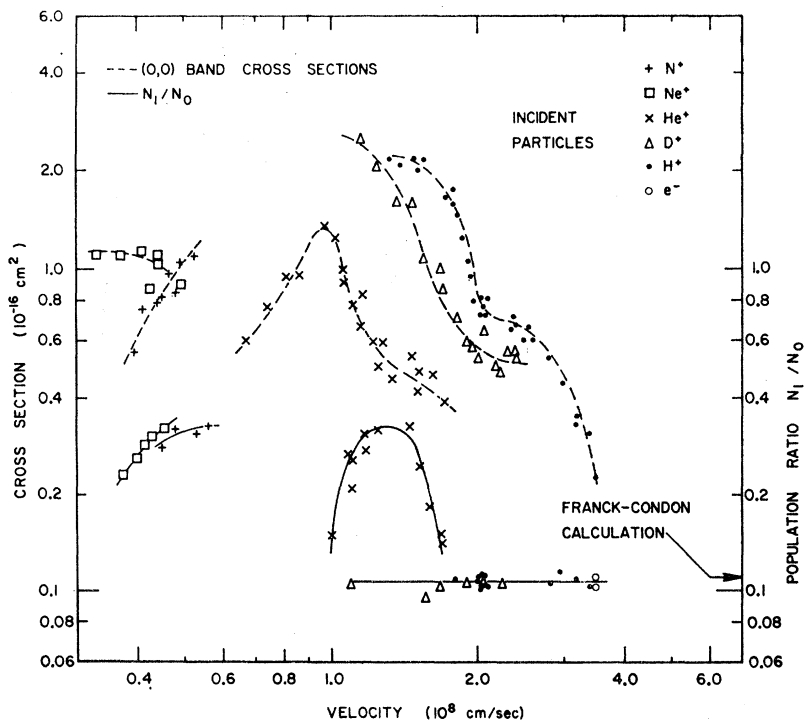


FIG. 6. N_2^+ vibrational enhancement and cross sections for the (0,0) band.

FIG. 7. Cross section for excitation of Balmer alpha radiation in charge-exchange collisions of H^+ and D^+ with N_2 .

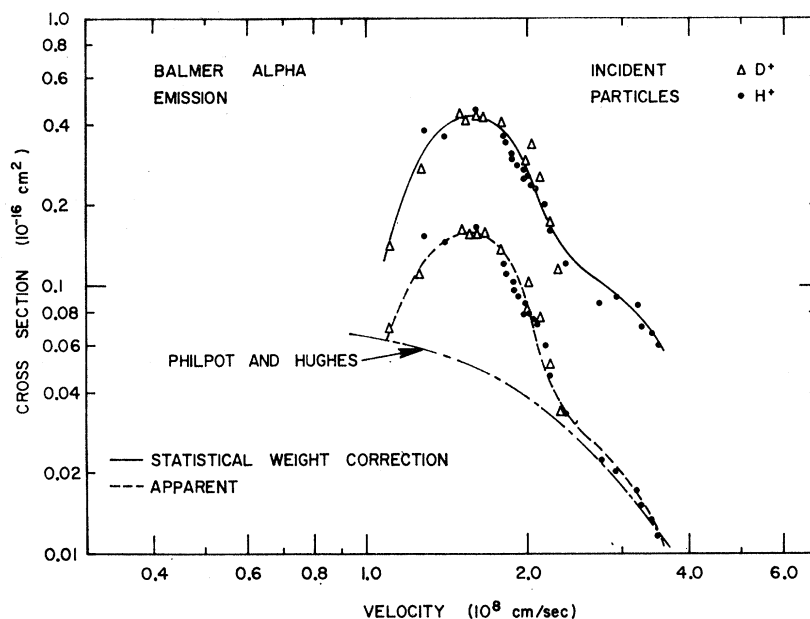
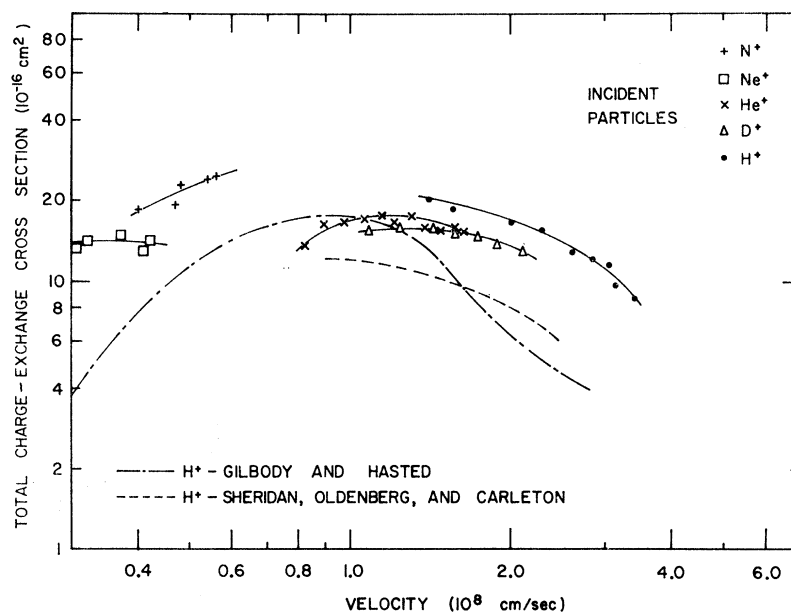


FIG. 8. Total charge-exchange cross sections.



colliding systems, a is the interaction distance (taken to be 8 \AA), and ΔE is the magnitude of the net change in internal energy of the systems during the collision. Although the cross sections for H^+ and D^+ impact show the same general shape, as expected, the latter appear to be roughly 30% smaller. Cross sections for the other bands of the first negative system may be obtained from the (0,0) band cross sections by using the smoothed values of the measured band ratios.

D. Relative Populations of Vibrational Levels

With Eq. (11) and the measured ratios of band intensities, the relative populations of the $v=1$ and

$v=0$ levels of the $B^2\Sigma_u^+$ state of N_2^+ excited by ion impact can be calculated. This relative population is shown in Fig. 6 along with the cross sections for excitation of the (0,0) band of N_2^+ . The ratios of the intensities of the (1,3) and (0,2) bands were used for the calculation of N_1/N_0 . The "normal" value of N_1/N_0 is shown on the figure for reference. This normal ratio, which is consistent with the observations by electron excitation, provides a base above which unusual vibration is evident.

The He^+ results indicate that the vibration enhancement is greatest near and somewhat above the velocity where the (0,0) band cross section is the largest. The

N^+ and Ne^+ results also show a definite enhancement of vibration, but measurements over a greater range of velocities are needed before any correlation with the charge-exchange reactions can be established.

E. Balmer Alpha Cross Sections

Cross sections for excitation of Balmer alpha radiation in charge-exchange collisions of H^+ and D^+ with N_2 are shown in Fig. 7. These values were obtained from intensity measurements of the Doppler-shifted Balmer alpha radiation with allowance for radiative lifetimes. Our uncorrected values agree well with those of Philpot and Hughes¹² except in the region of the maximum, where the cross section rises by a factor of about 3. Since the lifetime correction which must be applied to the data is quite strongly dependent on the particular geometry used, a direct comparison with the values of Philpot and Hughes is not justifiable.

F. Total Charge-Exchange Cross Sections

Electrical measurements of absolute cross sections for charge exchange of H^+ , D^+ , He^+ , Ne^+ , and N^+ with N_2 are plotted in Fig. 8 along with those of Sheridan, Oldenberg, and Carleton¹⁶ and Gilbody and Hasted¹ for charge exchange of H^+ and N_2 . Although the general shape of our comparable curve is the same as that of Sheridan, Oldenberg, and Carleton, our values are about a factor of 2 larger. Near the apparent maximum in the cross section, our measurements are in fairly good agreement with those of Gilbody and Hasted, but our curve falls less rapidly at higher velocities. The shape of the D^+ curve is the same as that for H^+ , and the D^+ cross section is again slightly smaller.

DISCUSSION

Several results stand out as guides to a partial explanation of the excitation of vibration and rotation in ion-impact collisions. Vibration is enhanced to various degrees for He^+ , Ne^+ , and N^+ , whereas there is no apparent enhancement of rotation. The vibrational enhancement is apparently greatest in the general range of velocities at which the cross sections for total charge exchange and charge exchange with excitation are largest. At very high and very low velocities of the ions

the distribution of vibrational populations apparently tends toward the normal values.

There exists no adequate theory to account in detail for the distribution of internal molecular motions in these collisions; certainly it is not justifiable to expect equal sharing of the kinetic energy among translation, vibration, and rotation. The adiabatic-maximum rule, if applied independently to the excitation of a vibrational level, leads to wide disagreement with experiment: Using a large impact parameter of $a=8 \text{ \AA}$, one would predict a maximum vibrational enhancement at velocities near $6 \times 10^6 \text{ cm/sec}$, which is less than 1/20 of that actually observed. Moreover, it is unlikely that excitation would avoid the more direct process and proceed via the upper ${}^2\Pi_g$ state of the Janin d'Incan system, terminating on the B state and producing vibration through overlap of Franck-Condon factors.

In analyzing some of the general kinetics of charge-exchange collisions, Fan³ has pointed out that part of the kinetic energy transferred to a molecular target could appear as vibration. If N_2^+ recoils at 90° to an incident 20-keV beam, its kinetic energy, if translational, would be about 1 eV when the incident ion is He^+ , Ne^+ , or N^+ , whereas in the case of H^+ and D^+ the transferred energy would be smaller by at least an order of magnitude. This compares to a 0.30-eV vibrational spacing. This same grouping of ions is here experimentally observed for enhancement of vibration. The absence of rotational enhancement, however, emphasizes that this simple analysis does not at all treat the details of internal motion.

An extreme example of avoidance of rotational excitation in the production of vibration is given by the collision of H^+ on H_2 specified by Korobkin and Slawsky,²² who have analyzed the adiabatic approach of a proton along the perpendicular bisector of the H_2 molecular axis. They show that when the proton is at a distance of 3 atomic radii, the molecular force constant is reduced to $\frac{1}{2}$ its normal value, whereas the equilibrium separation of the atoms has increased only 2%. The symmetry of their model precludes rotational effects. Even in noncentral collisions it can be suggested that fast incident ions may deliver a significant vibrational impulse through electron-cloud distortion, if enough kinetic energy is transferable, and yet show a considerable cancellation in the rotational impulse.

²¹ H. R. Gilbody and J. B. Hasted, Proc. Roy. Soc. (London) **A238**, 334 (1957).

²² I. Korobkin and Z. I. Slawsky, J. Chem. Phys. **37**, 226 (1962).