Rotational Excitation in Ion-Molecule Collisions: The System $H_2^+ + N_2$†

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A study has been made of the (0, 0) and (0, 1) bands of the N_2^+ first negative system excited by collisions between H_2^+ and N_2. H_2^+ projectile ion energies from 0.4 to 3.0 keV were used. An improved multistage apparatus produced sufficient ion current to allow the rotational lines up to $K'=50$ to be resolved and measured at all projectile ion energies. The energy distribution among rotational states was found to be grossly different from a Boltzmann distribution. The system could not be described by a single rotational temperature although the energy distribution among the high rotational states had a characteristic temperature in excess of 3000°K. The excitation of high rotational states was found to increase with decreasing projectile ion velocity. The effect of overlapping branches on the rotational line intensities was calculated and found to be an extremely important effect under these conditions. A review of previous experiments in the light of these data suggests that rotational excitation is a widespread phenomenon in ion-molecule collisions.

I. INTRODUCTION

Spectroscopic studies of rotational energy distributions produced by ion-molecule collisions have been carried out by a number of investigators.[1–10] The target molecule used in these studies has almost always been N_2. Aside from its importance in atmospheric processes, N_2 possesses no special qualifications for such studies other than spectroscopic convenience as the N_2^+ first negative band system in the near-ultraviolet spectral region is readily produced by electron or ion bombardment of N_2. Since the radiative lifetime of the $B\ ^2\Sigma_u^+$ state of N_2^+ is short compared with the time between gas-kinetic collisions at the pressures normally used, the rotational energy distribution of the collision products can be studied spectroscopically by analysis of the rotational structure lines in the first negative band system.

The results of previous investigations,[1-10] suggest that in certain ion-molecule collisions, energy is transferred from translation to rotation and elevated rotational temperatures are produced. The wide variety of results, however, allows no general statement to be made. In such cases as H^+, D^+, He^+, Ne^+, and N^+ projectiles incident on N_2 at energies from 3 to 65 keV, several investigators have reported[1,3,7] that the rotational line intensities followed a Boltzmann distribution and that the rotational temperature was equal to the ambient gas temperature. Elevated rotational temperatures with apparent conservation of the Boltzmann intensity distribution have been reported for 100-keV protons on N_2 by Branscomb *et al.*,[2] who estimated the rotational temperature to be between 700 and 1000°K, and Doering[5] who reported a rotational temperature of 475°K from 10-keV N_2^+ on N_2. In addition, Reeves and Nicholls,[4] and Lowe and Ferguson[6] carried out an investigation of 2–3-keV Li^+ ions on N_2 and found an apparent rotational temperature of 3500°K with conservation of the Boltzmann intensity distribution, although the data were complicated by overlap of the R-branch lines by P-branch lines of high rotational quantum number.

We have recently reported[10] the results of an investigation of 2–17-keV He^+, N_2^+, and Ar^+ ions on N_2. The relative line intensities followed a Boltzmann distribution within experimental error. The rotational temperature became equal to the ambient gas temperature at projectile ion velocities greater than 2×10^8 cm/sec and rose to 650°K at 1×10^7 cm/sec. This effect appeared to be approximately independent of the nature of the exciting ion.

On the other hand, deviations from the Boltzmann distribution have been recently reported for a number of ion-molecule systems by Polyakova *et al.*[8,9] These investigators bombarded N_2 with a large number of ions of energies from 5 to 30 keV. The results of these extremely precise measurements showed that for rotational lines with $K'<22$, the distribution of intensities was different from that of a Boltzmann distribution. The rotational temperature was not well defined in these cases.

Culp and Stair[11] have reported the results of a crossed-beam experiment in which N_2 was bombarded by electrons of energies from 19 to 300 eV. Below 100 eV, the rotational temperature was observed to be slightly elevated and small deviations from the Boltzmann distribution were observed.

The above results present a rather confused picture. As Polyakova *et al.*[8] have pointed out, few of the experiments reported were carried out with sufficiently high precision to detect small deviations from the Boltzmann distribution and slight elevations of the rotational temperature. Nevertheless, it is difficult to reconcile the 3500°K rotational temperature reported by Ferguson and Lowe[6] for 2–3-keV Li^+ ions, Carleton's thermal result for 3-keV H^+,[1] our 650°K results for 2-keV N_2^+ and Ar^+, and Polyakova *et al.*'s[8,9] results which showed deviations from the Boltzmann distribution at much higher projectile ion velocities.

For this reason, we wished to extend our measurements[10] to much lower projectile ion velocities, since it appeared that the rotational temperature was rising rapidly at a velocity of 1×10^7 cm/sec. We also felt that it was necessary to quantitatively clarify the situation with regard to P-branch overlap at high rotational temperatures, since this effect must be completely eliminated before conclusions can be drawn about departures from the Boltzmann distribution. Finally, it appeared to be quite important

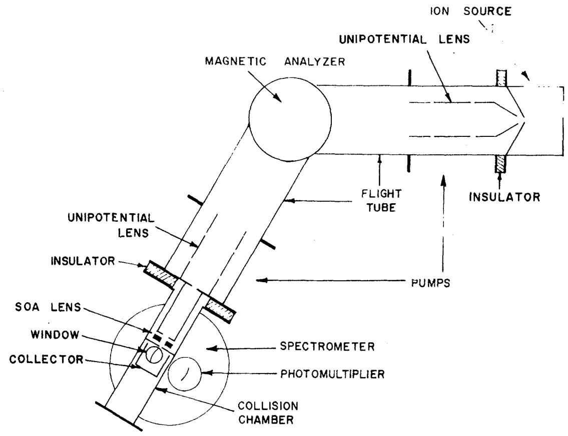

FIG. 1. Schematic diagram of the apparatus. The flight-tube section was maintained at −10 kV. The ion beam was decelerated with the SOA lens.

to measure the rotational lines of the R branch up to $K' = 50$ if possible, since an examination of the data presented by Lowe and Ferguson[6] leads to the conclusion that misleading results can be obtained if only the R-branch lines with $K' < 23$ are considered.

In this paper, we shall present results we have obtained for the system $H_2^+ + N_2$ at energies from 0.4 to 3.0 keV. This system appears to be particularly favorable for such studies since large H_2^+ ion currents are available from our apparatus and the emission cross section is large at low energies. Resolved spectra of the rotational lines of the (0, 0) and (0, 1) transitions of the N_2^+ first negative system were obtained at all energies, and the grossly perturbed intensity distribution could be studied with considerable accuracy. We regard this system as a favorable model for the development of techniques of analysis which can be extended to other systems.

II. EXPERIMENTAL

A simple ion-collision apparatus such as the one we have previously described[5] suffers from a severe loss of ion current at projectile ion energies less than 1 keV. The decrease in available current at low energies is due to space-charge effects which make it impossible to extract an intense ion beam from the source and convey it to the collision chamber. Since we required a beam current of the order of 10 μA at a few hundred eV final energy, we have constructed a multistage apparatus in which the ions are extracted from the source and conveyed through the apparatus at a high energy (10 keV) and then decelerated to the final energy as they enter the collision chamber.

A schematic diagram of the apparatus is shown in Fig. 1. Ions were produced in a conventional duoplasmatron ion source.[12] The use of an electron-bombardment ion source is an unfortunate necessity. All possible excited states of the projectile ion are undoubtedly produced in the source, and those whose radiative lifetimes exceed the flight time from the source to the collision chamber (a path of the order of 1 meter in length) will be used in the experiment. There appears, however, to be no other way to produce ion beams of the required intensity. Our results do not suggest that metastable H_2^+ molecules were present in sufficient numbers to influence the data, since there was no apparent variation of the results for different source conditions, but we cannot eliminate the possibility.

The source was maintained at a positive potential equal to the desired final ion energy. After leaving the source, the ions were accelerated into the flight tube which was maintained at −10 kV. The ion beam was focused through the 60° magnetic mass analyzer by two univoltage lenses, and then entered the deceleration region where the ions were focused into the collision chamber by a simple Soa lens designed from the data given Simpson and Kuyatt.[13] Ion currents of 5 to 50 μA were obtained at final energies from 100 to 3000 eV. The energy profile of the beam (which was independent of the final ion energy) was typically 35-eV full width at half-maximum (FWHM) as determined by a retarding-grid analyzer. The decelerated beam in the collision chamber was quite divergent with a full angle of divergence at 100 eV of approximately 90°. The Faraday-cup collector was arranged to collect the entire beam.

The flight tube was evacuated with two molecular sieve-trapped, 4-in. oil-diffusion pumps. One pump was in the region of the source and one in the region of the final lens system. Collision chamber pressure was measured with a Hastings type DV5M thermocouple gauge calibrated against an ion gauge.

Initial difficulty was experienced from electrons produced in the flight tube by stray ion bombardment of the walls. These electrons were accelerated ed to 10 keV as they passed through the ion-decelerating lens. To prevent these 10-keV electrons from entering the collision chamber, a magnet was placed above the Soa lens to deflect them away from the entrance aperture. This electron trap appeared to be completely effective since the negative current to the collision chamber could be entirely eliminated. Neither a weak electric nor a magnetic field in the collision chamber changed the appearance of the beam or the spectra produced.

Neutral particles produced by charge exchange of the beam with the background gas in the flight tube were also a source of difficulty under certain conditions. The presence of these high-energy neutrals in the beam entering the collision chamber could be detected by a bright luminous track in the center of the usual diffuse spray produced by the divergent slow-ion beam. By moving the entrance aperture in the horizontal plane, it was possible to exclude the core region containing the fast neutrals from the field of view of the spectrometer. Using this technique, we established that the spectrum of the luminous core was different from that of the surrounding spray. These fast neutrals were effectively eliminated by reducing the aperture diameter to 1.6 mm and keeping the collision chamber pressure below 10 μ.

In order to show that the N_2^+ first negative emission was produced only by the slow ions, several measurements were made of the total (0, 0) band intensity as a function of pressure at constant ion cur-

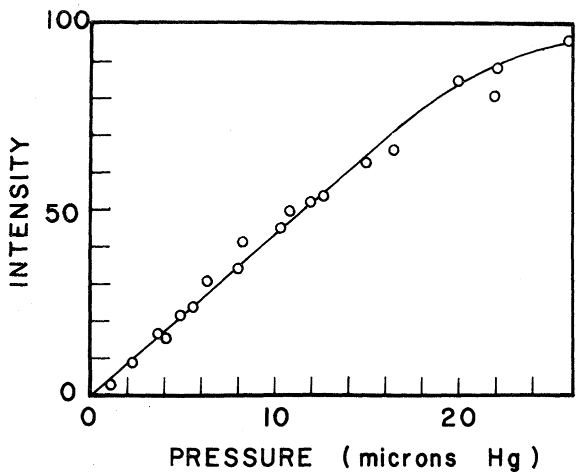

FIG. 2. Intensity of the N_2^+ first negative system (0, 0) band head (λ 3914 Å) versus collision-chamber pressure. The 1000-eV H_2^+ ion current was constant at 30 μA during these measurements.

rent. The intensity varied linearly with pressure up to at least 20 μ (Fig. 2). The data presented in this paper were all taken at pressures less than 10μ.

The spectra were taken with a 1.0-m Fastie-Ebert scanning monochromator. This instrument was especially designed to allow close coupling between the collision chamber and monochromator. The ion beam passed approximately 1.5 cm above the 5-cm-long curved entrance slit, so no optical system was necessary to relay the light from collision chamber to monochromator. The 10×10-cm Bausch and Lomb diffraction grating had 1200 grooves/mm and was blazed at 7500 Å in the first order. These experiments were done in the second order where the dispersion was 4 Å/mm. The bandpass with a typical 50-μ slit width was approximately 0.4 Å.

The detector was an EMR-type 541D photomultiplier cooled to −40°C. Pulses from the photomultiplier were discriminated and counted by a ratemeter coupled to a chart recorder. The photomultiplier dark current was less than 5 counts/sec at −40°C. During an experiment, the background level was set by the monochromator scattered light signal which was typically of the order of 10 counts/sec with a 50-μ slit. Most data were taken at a scan rate of 3.5 Å/min. A ratemeter time constant of 10 sec was normally used.

III. RESULTS AND DISCUSSIONS

Intensity Calculations

High-resolution spectra of the N_2^+ first negative (0, 0) band[14] indicate that the R-branch line corresponding to the upper rotational state with quantum number K' is closely overlapped by the P-branch line originating in the $(K'+25)$ upper rotational state. In the (0, 1) band, however, the R-branch line from state K' is overlapped by the $(K'+22)$ P-branch line. Lowe and Ferguson[6] have shown that for sufficiently high rotational temperatures, this overlap can cause the normally linear plot of $\ln[I/(K'+K''+1)]$ versus $K'(K'+1)$ (where I is the intensity of the K'th rotational line) to become nonlinear. Since the rotational temperature is extracted from the slope of this linear plot,[15] the effects of overlap must be removed before the temperature can be calculated.

Several plots of $\ln(I/K')$ versus $K'(K'+1)$ for the (0, 0) band, computed assuming simple addition of each R-branch line intensity to that of the overlapping P-branch line, are given in Fig. 3. For convenience, we plot $\ln(I/K')$ rather than $\ln[I/K'+K''+1)]$ as given by Herzberg.[15] Since $K''=(K'-1)$ for the R branch, the two quantities differ only by a constant factor of 2 which is not significant, since we are interested only in the relative intensities of the various rotational lines. These plots are also presented with the intensities of the K' even lines multiplied by 2 to eliminate the even-odd intensity alternation which arises from the different degeneracies of even and odd rotational states in this molecule.

The plot for T_{rot} = 300°K is a single straight line under these conditions. Note, however, that at a temperature of about 800°K, the overlap causes the curve to become nonlinear and to diverge into two lines of even and odd K' for low values of K'. Since the weaker K' even lines in the R branch are overlapped by the stronger K' odd lines from the

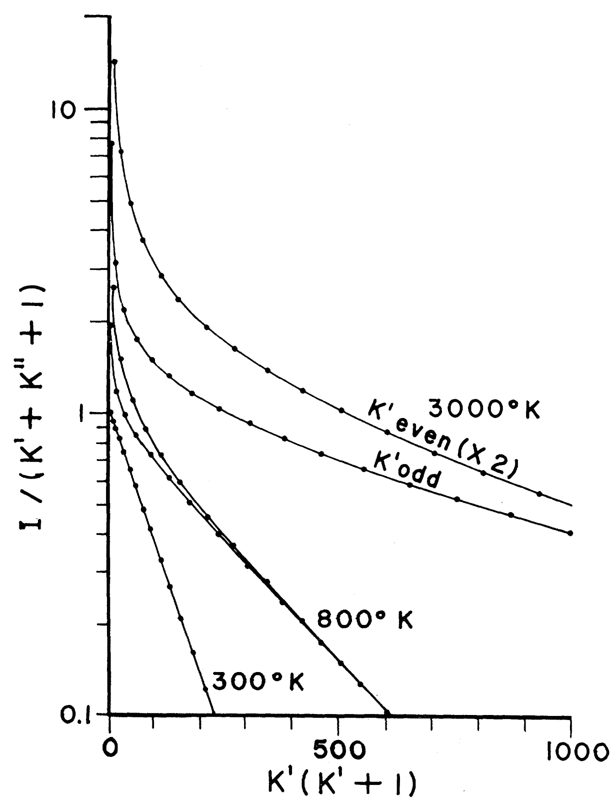

FIG. 3. Computed plot of $\ln(I/K')$ versus $K'(K'+1)$ at various rotational temperatures for the N_2^+ first negative (0,0) band. Intensities of points corresponding to K' even lines have been multiplied by 2.

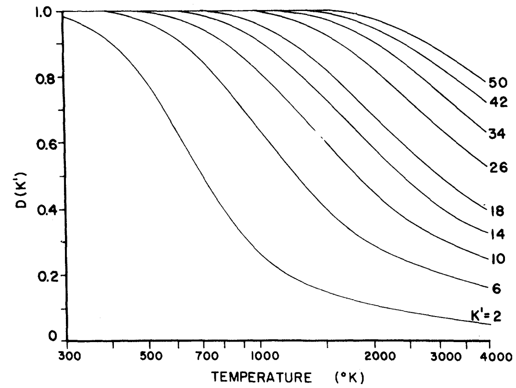

FIG. 4. Computed ratio of R-branch line intensity to total line intensity including P-branch overlap versus rotational temperature for N_2^+ first negative (0,0) band lines with even K'. These curves cannot be used for the (0, 1) band (see text).

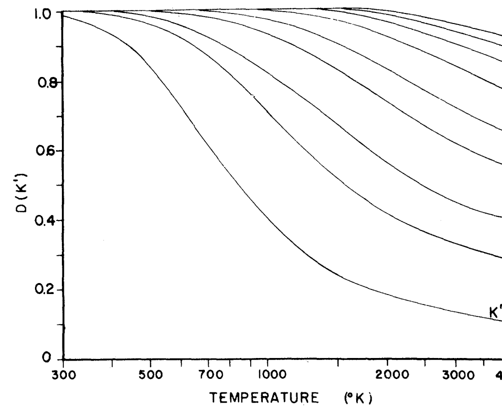

FIG. 5. Computed ratio of R-branch line intensity to total line intensity including P-branch overlap versus rotational temperature for N_2^+ first negative (0,0) band lines with odd K'. These curves cannot be used for the (0,1) band (see text).

P branch, the curve for $\ln[2I(K'-\text{even})/K']$ moves above the curve for $\ln[I(K'-\text{odd})/K']$ for low K' values. With increasing temperature, this effect becomes more pronounced, and at about 3000°K, the overlap becomes so severe that a measured spectrum of the (0,0) band will appear to have lost the even-odd intensity alternation up to about $K' = 23$.

The effect of the $(K'+25)$ P-branch line on the K' R-branch line is illustrated by the correction factor $D(K')$ which must be applied to the measured R-branch line intensity to give the actual intensity which is due to the R-branch line alone.

$$D(K')\, I_{\text{meas}}(K') = I_R(K').$$

Assuming that the intensities of the overlapping lines simply add,

$$D(K') = I_R(K')/I_R(K') + I_P(K'+25).$$

Plots of $D(K')$ versus temperature for even and odd K' are given in Figs. 4 and 5, respectively. Our calculations show, for example, that severe overlap occurs at a temperature of 500°K in the first few R-branch lines.

$H_2^+ + N_2$

A detailed study was made of the rotational structure of the (0, 0) band of the N_2^+ first negative system (λ 3914 Å) produced by H_2^+ on N_2. The nitrogen pressure was maintained constant during each run at 3–10 μ. A typical spectrum is shown in Fig. 6. Examination of this spectrum shows that the characteristic even-odd, 2 : 1 intensity alternation is not

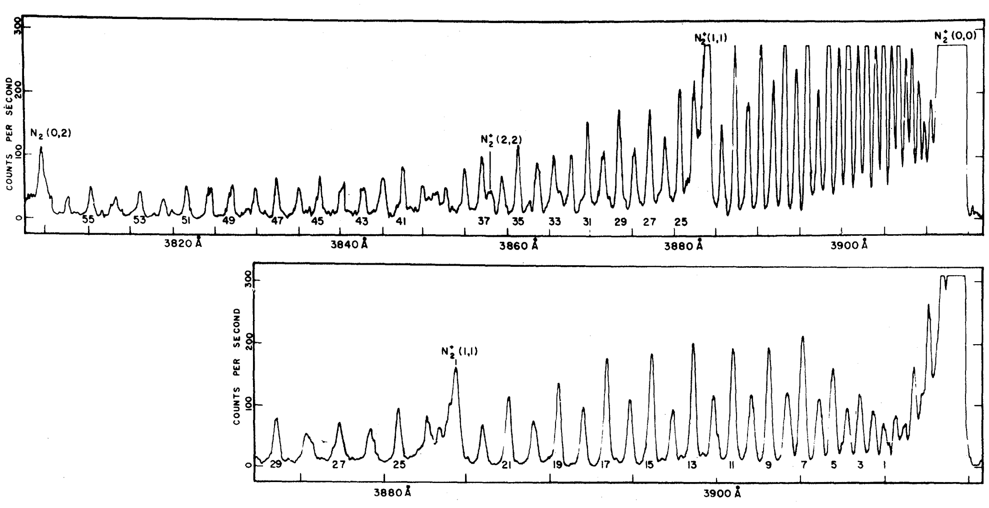

FIG. 6. Typical spectra of the N_2^+ first negative (0, 0) band (λ 3914 Å) excited by a 46-μA beam of 1000-eV H_2^+. The pressure in the collision chamber was 5.5 μ Hg. The upper spectrum was taken with a spectrometer-slit width of 70 μ, while the lower expanded trace was taken with a 30- μ slit. The effects of perturbations appear at K' =14 and K' =39 (see text).

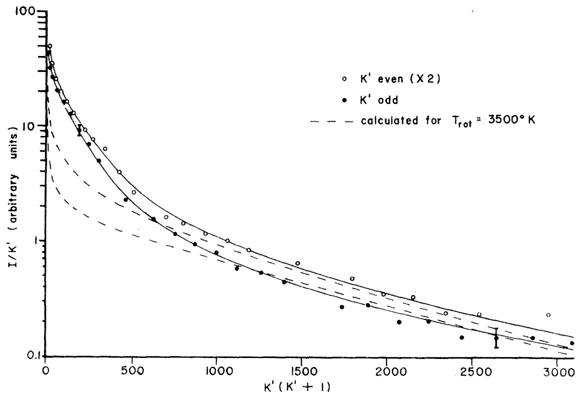

FIG. 7. Plot of $\ln(I/K')$ versus $K'(K'+1)$ taken from spectra of the N_2^+ first negative (0,0) band excited by 3.0-keV H_2^+. The intensities of the lines of even K' have been multiplied by 2. The calculated curve for $T_{rot} = 3500°K$ is included for comparison. The reproducibility of the data is indicated by the error bars at each end of the plot.

observed for high-K'-value lines. The analysis of the spectrum is complicated by the effects of perturbations of the rotational energy levels of the $N_2^+\ {}^2\Sigma_u^+$ state by the $A^2\pi_u$ state.[16] In the (0,0) band, the perturbation appears in the P and R branches near $K'=39$. Since the $K'=39$ P-branch line overlaps the $K'=14$ R-branch line, the intensities of lines near $K'=14$ and $K'=39$ in the spectrum presented in Fig. 6 appear anomalous. These perturbations make accurate measurement of line intensities impossible in these two regions.

Intensity measurements were extended to $K'=56$ and experimental plots of $\ln(I/K')$ versus $K'(K'+1)$ were obtained at a number of projectile-ion energies between 0.4 and 3.0 keV. Each of the plots presented here is derived from intensity measurements made on two to four separate spectra. Similar spectra of the (0, 1) band were also taken. Results obtained were entirely consistent with those from the (0, 0) band; but the more severe effects of the perturbations in this transition as well as the difference in overlap effects caused the data to be less useful for our purposes.

Figures 7 and 8 show plots of $\ln(I/K')$ versus $K'(K'+1)$ from measurements of spectra of the (0, 0) band produced by a 3.0- and 0.4-keV H_2^+ on N_2. The limiting slope at high values of $K'(K'+1)$ corresponds to a rotational temperature of 3500°K. Two smooth curves have been drawn through the experimental points for even and odd K'. As usual, the values for even K' have been multiplied by 2. The computed curve for $T_{rot} = 3500°K$ normalized to the high $K'(K'+1)$ end of the experimental curve is included for comparison.

From these plots, it can be seen that there is significant disagreement between the measured and computed curves. Perhaps the most important difference is the fact that the two experimental curves for even and odd K' are quite close together for small $K'(K'+1)$, indicating that the even-odd intensity alternation at low K' is only slightly disturbed. As mentioned above, the effect of overlap in the (0, 0) band is so severe that we expect the even-odd intensity alternation to be almost completely destroyed at small K' for a rotational temperature of 3500°. We found it to be impossible to reproduce the experimental curves using line intensities calculated assuming an upper rotational-state population consistent with a Boltzmann distribution characterized by a single rotational temperature.

The curvature of the experimental plots changes in a systematic manner as a function of projectile ion energy. However, the high $K'(K'+1)$ region maintains a relatively constant slope characteristic of $T_{rot} = 3500°K$. The data corresponding to the lowest projectile energy most nearly agree with the curve computed for 3500°K. As the ion energy increases, the curves agree within experimental error with the $K'>30$ region of the computed curve. The regular change in curvature as a function of the ion energy is illustrated in Fig. 9.

Since our data, as well as the available data from the literature, indicate that elevations in rotational temperature and deviations from the Boltzmann distribution are small at high energies, we conclude that the low-energy ions are responsible for the observed population of states with high K'. However, it is obvious that our total result could be produced by a mixed beam of two projectile particles. If the incident beam were a mixture of low-energy H_2^+ ions and 10-keV neutral H_2 molecules produced by charge transfer in the flight tube, the observed energy distribution would be expected to consist of a high-temperature component produced by the low-energy ions and a thermal component produced by ionizing collisions of the fast neutrals with N_2. Such a sum of two energy distributions could give the observed data. However, using the experimental arrangement described previously, which included the 1.6-mm-diameter collision chamber aperture, we have been unable to detect any dependence of the observed spectra on the pressure of gas in the collision

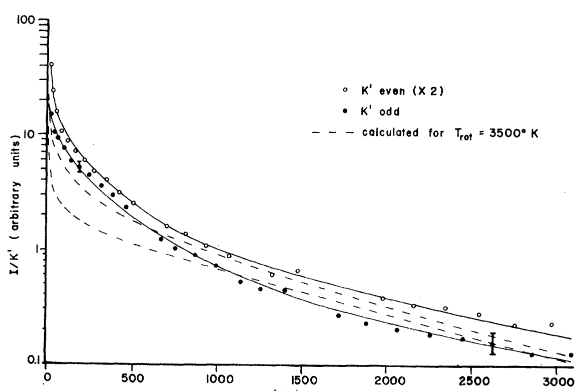

FIG. 8. Plot of $\ln(I/K')$ versus $K'(K'+1)$ taken from spectra of the N_2^+ first negative (0,0) band excited by 0.4-keV H_2^+. The intensities of the lines of even K' have been multiplied by 2. The calculated curve for $T_{rot} = 3500°K$ is included for comparison. The reproducibility of the data is indicated by the error bars at each end of the plot.

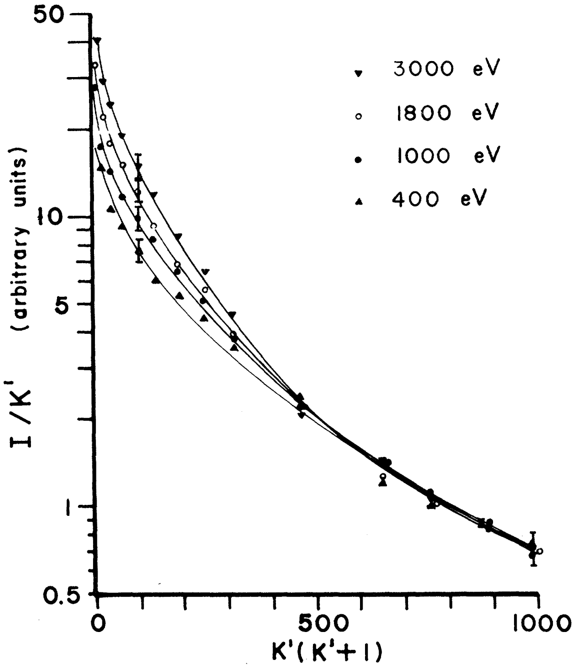

FIG. 9. Plots of $\ln(I/K')$ versus $K'(K'+1)$ taken from spectra of the N_2^+ first negative (0,0) band excited by 0.4-, 1.0-, 1.8-, and 3.0-keV H_2^+ on N_2. Only the lines with odd K' have been included. This figure illustrates the systematic change in curvature for low K' with projectile-ion energy. The curves have been normalized to coincide for $K'(K'+1) > 1000$. The reproducibility of the data is indicated by the error bars at each end of the plots.

chamber up to 20 μ. If fast neutral H_2 molecules were an important source of the observed emission, we would expect a strong dependence of the rotational energy distribution on collision-chamber pressure, since the gas leak from the collision chamber determines the pressure in the flight-tube region. The characteristic luminous core mentioned before was not present in these experiments. Furthermore, moving the entrance aperture of the collision chamber in the horizontal plane to exclude this region from the spectrometer's field of view produced no change in the observed spectrum. We are therefore forced to conclude that the entire rotational energy distribution is produced by slow ions. A single rotational temperature is not defined, since the Boltzmann distribution is not maintained.

IV. CONCLUSIONS

We believe that it is possible to reconcile the apparently divergent results of previous investigators using the data presented in this paper. Consider the resolved spectrum we have presented in Fig. 6. If this spectrum were taken under much poorer signal-to-noise conditions so that only the strong lines up to $K'=19$ could be measured, the result would be plots such as we have presented in Figs. 7 and 8 cut off at $K'(K'+1) = 380$. A straight line drawn through these first 19 points would have a slope corresponding to a rotational temperature of 300 to 500°K. Virtually all of the older data in the literature with the exception of the work of Lowe and Ferguson,[6] who successfully observed the high-temperature limiting slope for high K' $(K'+1)$ are of this type.

The data we have presented in Fig. 9 suggest that at H_2^+ projectile-ion energies greater than 3 keV, the curvature of the $\ln(I/K')$ versus $K'(K'+1)$ plot will become small for the low-K' region. This is consistent with the results of Polyakova *et al.*[9] who present extremely precise data for 5 to 30 keV H_2^+ on N_2. Since these investigators present their results up to $K'=21$ only, we can draw no conclusions about the relative population of the high rotational states in their experiments. Their results are, however, entirely consistent with ours.

Our results show that in all cases where departure from the Boltzmann energy distribution is suspected, the P-branch overlap must be eliminated before definite conclusions can be drawn. It is also essential to recognize the difference in overlap effects in the (0,0) and (0,1) bands. For the (0,0) band, if the energy distribution among the rotational states follows a Boltzmann distribution, the odd-even overlap of the P-branch on the R-branch lines will cause the 2 : 1 intensity ratio of even and odd rotational lines to be destroyed for small K' at high rotational temperatures. In the (0,1) band, however, the even-even and odd-odd overlap of the P branch on the R branch causes the 2: 1 intensity alternation to be approximately preserved at all rotational temperatures.

The effect of the overlapping branches in the (0, 0) band allows qualitative conclusions to be drawn about the energy distribution in experiments where poor signal-to-noise ratios prevent accurate measurement of the weak lines of high K'. As is shown in the calculated overlap correction factors (Figs. 4 and 5) the first few rotational lines of the R branch are extremely sensitive to elevations in the rotational temperature. If it is found experimentally that the even-odd intensity alternation is disturbed for the lines with $K'<5$, measurable P-branch overlap is present, indicating that the rotational temperature is greater than 300°K. In addition, any appreciable curvature in the plot of $\ln(I/K')$ versus $K'(K'+1)$ for the intense lines of $K'<20$ for either the (0,0) or (0,1) bands definitely indicates a significant population of high $(K'>25)$ rotational states. Any attempt to draw a straight line through such a curve to obtain an approximate rotational temperature can be highly misleading. An examination of $\ln(I/K')$ versus $K'(K'+1)$ plots published by previous investigators shows that in many cases the plots have appreciable curvature as well as disturbances of the even-odd intensity alternation at low K'. A number of these cases have been reported as thermal rotational energy distributions, although P-branch overlap was clearly present.

If the system is highly enough excited to allow a rough measurement of the lines with $K'>30$, the approximate rotational temperature can be estimated from the intensities of the lines in this region. An examination of the even-odd intensity alternation of the low-K' lines of the (0, 0) band can then reveal whether there is significant deviation from the Boltzmann distribution. The same sort of conclusions cannot be drawn from data on the (0, 1) band, since the intensity alternation is not a sensitive function of rotational temperature. For these reasons, we feel that the (0, 0) band is the most useful spectral feature for analysis of these systems.

To facilitate comparison of our data with those of previous investigators, we have presented our results in the traditional form of rotational-temperature plots. It is obvious, however, that the concept of "rotational temperature" is of little use in dealing with this system since non-equilibrium effects are extremely important. In order to unfold the data so that the actual rotational energy distribution can be determined, it will be necessary to quantitatively compute the *P*-branch overlap. Since the *P*-branch energy distribution is non-Boltzmann, the removal of overlap is a complicated problem. We prefer to defer this stage of the analysis until data have been accumulated on more systems with different projectile ions, at which time it may also be possible to make a more definite analysis of the energy conversion mechanism which gives rise to these effects. However, the data we have presented as well as the existing data in the literature show that the transfer of energy from translation to rotation in ion-molecule collisions is a widespread phenomenon exhibited by many systems.

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