Rotational Excitation in Ion-Molecule Collisions. II. H^+, D^+, He^+, Ne^+, H_2^+ and D_2^+, on N_2†

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A study was made of the rotational line intensities in the (0, 0) band of the N_2^+ first negative system produced by ion bombardment of N_2 at 130°K. H^+, D^+, He^+, Ne^+, H_2^+, and D_2^+ projectile ions at energies of 600 eV to 10 keV were used. The distribution of rotational energy in the upper state of the first negative system was found to deviate from a Boltzmann distribution for projectile ion velocities below 10^8 cm/sec. Excitation to high rotational states increased monotonically with decreasing projectile velocity. The band envelope of spectra excited by atomic ions displayed a characteristic shape different from that excited by the molecular ions. For atomic ion excitation the extent of excitation to high rotational levels appeared to be a function of projectile ion velocity only. The nature of the rotational transition probability function for the collision-induced excitation and the implication of rotational excitation to high states with respect to other types of experiments are discussed.

INTRODUCTION

In two previous papers,[1,2] we have reported the results of spectroscopic studies of rotational and vibrational energy distributions produced by ion-molecule collisions. Rotational excitation was investigated for the system $H_2^+ + N_2$ only, while vibrational excitation was studied for a number of atomic and molecular ions incident on N_2. In this paper we present the results of further investigations of rotational excitation using a variety of atomic and molecular projectile ions and an improved experimental technique involving the use of a 130°K N_2 gas target.

Our previous investigation of rotational excitation in the system $H_2^+ + N_2$[1] showed that the rotational states of the N_2^+ $B^2\Sigma_u^+$ state produced by H_2^+ projectiles with energies from 400 eV to 3 keV were not populated according to a Boltzmann energy distribution. The strong excitation to high rotational states which was found to occur under these conditions confused the experimental observations since the high-numbered rotational lines of the P branch in the N_2^+ first negative system overlap the R-branch lines whose intensities are used to determine the rotational energy distribution. We found, however, that the observed intensities of the R-branch lines could not be explained on the basis of a Boltzmann rotational energy distribution even when the effects of P-branch overlap were taken into account. The principal questions left unanswered by our previous work were the nature of the process which produces the non-Boltzmann rotational energy distributions in this system and the importance of such effects in other ion-molecule collisions.

In order to investigate the importance of these effects for other systems, a variety of projectile ions have been used in the present work. As we have noted previously,[1] non-Boltzmann energy distributions are often difficult to recognize, especially when the departure from a Boltzmann distribution is small. The results of other investigators[1] suggest that excitation to high rotational states occurs in a wide variety of ion-molecule collisions at low energies. We have therefore performed experiments using H^+, D^+, D_2^+, He^+ and Ne^+ incident on N_2 as well as some further experiments with H_2^+. Projectile ion energies from 600 eV to 10 keV were used. Attempts were made to use the other projectile ions such as N^+ and N_2^+ which are available from our apparatus; but the emission cross section for these ions was too small in this energy range to allow satisfactory spectra to be obtained.

In order to investigate the process which produces the observed energy distribution, we need to determine the probability of a particular rotational transition during the electronic transition from N_2 $X^1\Sigma_g^+$ to N_2^+ $B^2\Sigma_u^+$. Ideally, if only the lowest rotational state of the N_2 target were populated, the populations of the N_2^+ $B^2\Sigma_u^+$ rotational states calculated from the N_2^+ first negative system rotational line intensities would give the probability for rotational transitions directly. In practice, however, with a room-temperature N_2 gas target, the first 21 rotational states are significantly populated so that a large part of the emitted intensity observed experimentally up to the $K' = 21$ line of the R branch is simply due to the initial rotational energy distribution of the target molecule. This intensity obscures the processes of interest and complicates the data analysis. To improve the situation as much as possible, we have placed the N_2 target gas in a liquid-nitrogen-cooled collision chamber. As a result, only the first 11 rotational states of the target gas are measurably populated and a sig-

nificant simplification of the data results.

EXPERIMENTAL

The apparatus used for the production of the low-energy ion beams in these experiments has been previously described.[1] Briefly, it is a "multistage" device in which ions are withdrawn at a high voltage from a duoplasmatron ion source, magnetically mass analyzed, and focused and decelerated to the desired final energy. The ions then enter a liquid-nitrogen-cooled collision chamber which contains the target gas. The collision-chamber arrangement has also been described elsewhere.[3] Ion currents of 1 to 20 μA at energies of 600 eV to 10 keV were used for these experiments. The collision chamber is closely coupled to a 1.0 m Fastie-Ebert scanning monochromator. Light from the collision chamber which arrives at the monochromator exit slit is detected by a cooled EMR type 541D photomultiplier.

In a previous experiment[3] we have shown that 30–300 eV electrons incident upon N_2 in the cooled collision chamber produce N_2^+ first negative system emissions which correspond to a Boltzmann distribution of rotational energy at about 130°K. In order to demonstrate that there was no heating of the target gas by the ion beam, we took electron-excited spectra of the cooled gas while the ion beam was incident upon it. The collision chamber is arranged so that both the ion beam and an electron beam from an electron gun mounted behind the collision chamber may be used at the same time. Since the electron beam is much more intense than the ion beam and the cross section for excitation of the first negative system by electrons is greater than for excitation by ions, it is possible to observe the spectrum excited by electrons only by reducing the sensitivity of the optical system. The spectra obtained in this manner were identical to those obtained when only the electron beam was incident upon the target gas. Since the rotational temperature of the electron-excited spectra did not show any dependence upon electron current, we have assumed that the ambient temperature of the cooled gas was 130°K.

As has been discussed previously,[1] the R branch of the (0,0) N_2^+ first negative band at 3914 Å is overlapped by the folded over portion of the P branch. Each R-branch line, $R(K')$, is nearly exactly overlapped by the P-branch line, $P(K'+25)$. Furthermore, the rotational lines of the first negative system have a characteristic 2 : 1 intensity alternation: each even-numbered line is one-half as intense as its odd-numbered neighbors. Fortunately, in the (0,0) band, the R-branch lines corresponding to odd K' are overlapped by even K' lines of the P branch. As a result, the effect of overlap is only about one-quarter as great for the K'-odd lines of the R branch compared to the K'-even lines. For any odd K' line in the R branch, the intensity of the overlapping P-branch line is approximately equal to the intensity of $R(K'+25)$. On this basis, it is possible to estimate the effect of overlap on the spectra reported here. Except for $R(1)$, the relative intensity of the P-branch line overlapping any K'-odd R-branch line is less than 10%. $P(26)$ may be as much as 20% as intense as $R(1)$. The line intensity measurements reported here are accurate to about ± 20%. As a result we have reported only the intensities of the K'-odd lines of the R branch and have ignored the effect of overlap. Within the accuracy of these measurements the P-branch overlap has essentially no effect on the measured contours of the K'-odd lines.

RESULTS

Rotational line intensity measurements were made on the R branch of the (0,0) band of the N_2^+ first negative system excited by bombarding N_2 gas in the liquid-nitrogen-cooled collision chamber with H^+, D^+, H_2^+, D_2^+, He^+ and Ne^+ at energies of 600 eV to 10 keV. As each spectrum was taken, the target-gas pressure was maintained constant at 2 to 7 μHg. For each projectile and energy, two to five separate spectra were taken, and the measured intensities of the rotational lines were averaged. Preliminary examination of the spectra indicated that the band contour of the R branch had one characteristic shape for atomic ion excitation and a different shape for molecular ion excitation.

ATOMIC IONS

The line intensities in the spectra excited by atomic ion bombardment increased rapidly to a sharp maximum at $R(5)$. Beyond this point, as the line intensities decreased, it was found that for lines corresponding to upper-state rotational levels which were essentially unpopulated in the thermal distribution at 130°K ($K'>11$), the line intensities decreased exponentially with increasing K'. Within experimental error for $K'>11$, $\ln I$ varied linearly with K'. For this reason the spectral line intensity measurements are plotted as $\ln I$ versus K' in Fig. 1. The shape of the band contour which would arise from a Boltzmann distribution of rotational energy in the upper state is also shown. It was found that for projectile ion laboratory velocities in excess of about 10^8 cm/sec and for electron excitation, the measured band contours agreed with the theoretical Boltzmann contour. Below 10^8 cm/sec, the linear portion of the high K' region of the experimental band contours deviated most noticeably from the thermal band contour.

For each atomic projectile at each energy, the slope of the linear portion of the $\ln I$ versus K' curve was estimated. The slopes could be determined with an accuracy of about ±30%. It was found that within experimental error the slope of the linear portion of the experimental results was a function of the projectile ion laboratory velocity without regard for the chemical nature of the ion. The slope increased monotonically with decreasing projectile ion velocity. This result is presented in Fig. 2.

MOLECULAR IONS

At high energies, the spectra excited by H_2^+ are quite similar to the thermal spectrum. However, with decreasing energy the intensity maximum of the band contour becomes broader and moves toward higher K' values. The intensity of the lines which originate in rotational levels which are essentially unpopulated in the ground-state Boltzmann distribution also appear to decrease exponentially with increasing K'. Figure 3 presents measured line intensities as $\ln I$ versus K' for spectra excited by H_2^+ at energies of 1 keV to 10 keV. Also shown in Fig. 3 are the results of measurements of spectra excited by 1 keV D_2^+. The D_2^+ excited spectra have the same characteristic shape as the H_2^+ excited spectra at the same energy, but the slope of the linear section of the $\ln I$ versus K' plot is greater for the spectra excited by the slower D_2^+ ion.

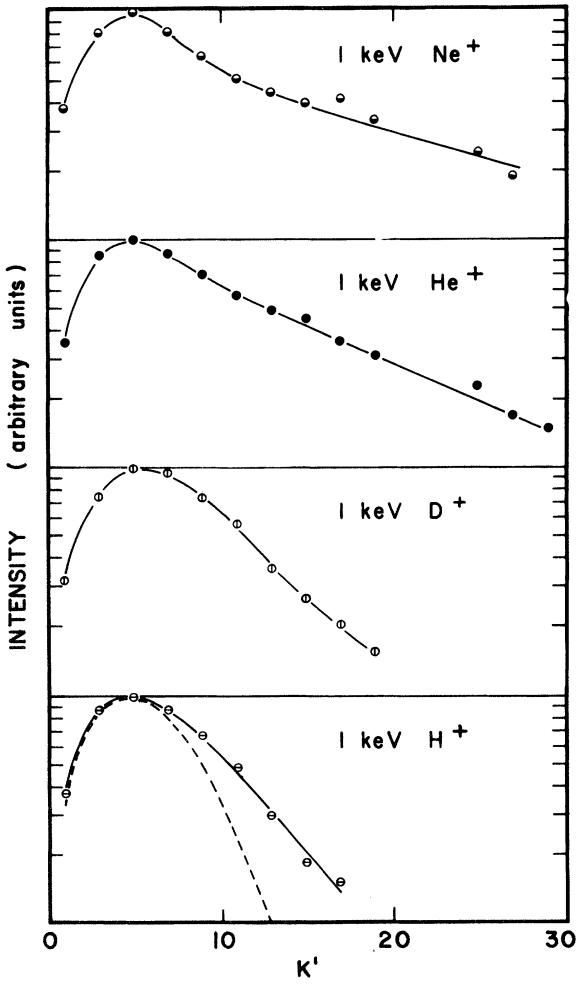

FIG. 1. Typical $\ln I$ versus K' plots of the odd K' rotational lines of the (0, 0) band of the N_2^+ first negative system produced by 1 keV H^+, D^+, He^+, and Ne^+ on N_2 at 130°K. The dashed line is the $\ln I$ versus K' contour which arises from a Boltzmann distribution of rotational energy in the upper state of the first negative system as determined in electron excitation.

CONCLUSIONS

The data presented here indicate that for projectile ion laboratory velocities in excess of about 10^8 cm/sec, the population of rotational states can be well described by a Boltzmann distribution. Below 10^8 cm/sec the population of high rotational quantum-number states increases above that given by a Boltzmann distribution and the deviation from a Boltzmann distribution increases with decreasing projectile ion velocity. The results of these experiments do not allow us to distinguish whether the interactions which produce the observed excitation are charge transfer collisions or ionization collisions. However, results such as those of Sheridan *et al.*[4] suggest that in this energy range the charge-exchange cross section is about an order of magnitude larger than the ionization cross section, while the cross section for excitation of N_2^+ in the $B\,^2\Sigma_u^+$ state is nearly as large as the total ionization cross section. Moreover, the Doppler shift results of Doering[5] for 10 keV N_2^+ on N_2 showed that most of the radiation in this collision came from the target molecule. We therefore feel that the excitation we observe is associated with the charge transfer collision, although a sharp distinction is probably impossible in these cases.

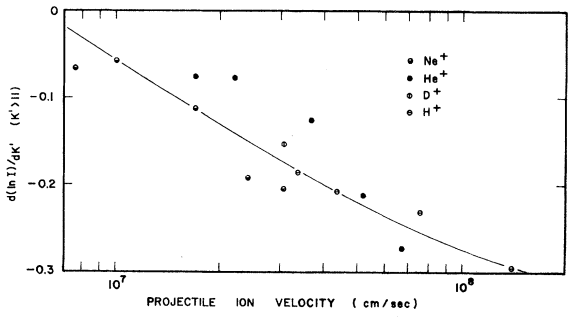

FIG. 2. The slope of the high K' ($K' > 11$) portion of the $\ln I$ versus K' curves for the atomic ion-excited spectra versus projectile ion laboratory velocity.

Within the accuracy of these experiments it was found that the high K' portion of the $\ln I$ versus K' plot was linear. We have taken the slope of this linear part of the tail of the $\ln I$ versus K' curve as a measure of the extent of excitation to high K' rotational levels. In relation to our previous study of vibrational excitation in the first negative system, it is significant that the energy distribution becomes non-Boltzmann when the projectile ion velocity decreases below 10^8 cm/sec. It was found that below 10^8 cm/sec the population of the vibrational levels in the $B^2\Sigma$ state of N_2^+ produced in ion-molecule collisions deviates from that predicted by the Franck-Condon principle. It appears that both of these results arise because the ion-molecule collision becomes of sufficient duration below 10^8 cm/sec that the vibrational and rotational wave functions are significantly perturbed giving rise to corresponding changes in vibrational and rotational transition probabilities. In this light, the differences between the band envelopes observed for molecular ion and atomic ion excitation are probably due to the anisotropic field of the molecular ion as compared to that of the atomic ion.

At high projectile ion velocities, the excited-state rotational energy distribution reflects the rotational energy distribution of the target molecules before collision. For slow collisions the probability increases for transitions with $\Delta K = \pm 3, \pm 5, \pm 7, \ldots (\Delta K = 0, \pm 2, \pm 4, \ldots$ being strongly forbidden by the symmetric-antisymmetric selection rule[6]). Our results indicate that the probability of a transition with $|\Delta K| > 1$ decreases exponentially with increasing ΔK. The rate of this exponential decrease is a function of the duration of the collision. An unsuccessful attempt was made to mathematically synthesize the observed spectra using a model involving only an exponentially decreasing probability for transitions with $|\Delta K| > 1$. The difficulty was apparently that the transition probability is a function of K as well as ΔK since the intensity of the first few lines closely approximates a thermal distribution. The form of the functional dependence on K could not be uniquely extracted from the data. The dependence of the transition probability on K is particularly evident in the molecular ion-excited spectra. The displacement of the intensity maximum toward higher K' indicates that the probability of transitions with large ΔK increases with increasing K.

These results indicate that certain commonly used experimental techniques may be of questionable value in the spectroscopic study of emissions arising from low-energy ion-molecule collisions. In the measurement of emission cross sections, the intensity of radiation passed by an interference filter centered on a single band is measured as a function of the exciting ion's energy. Our results

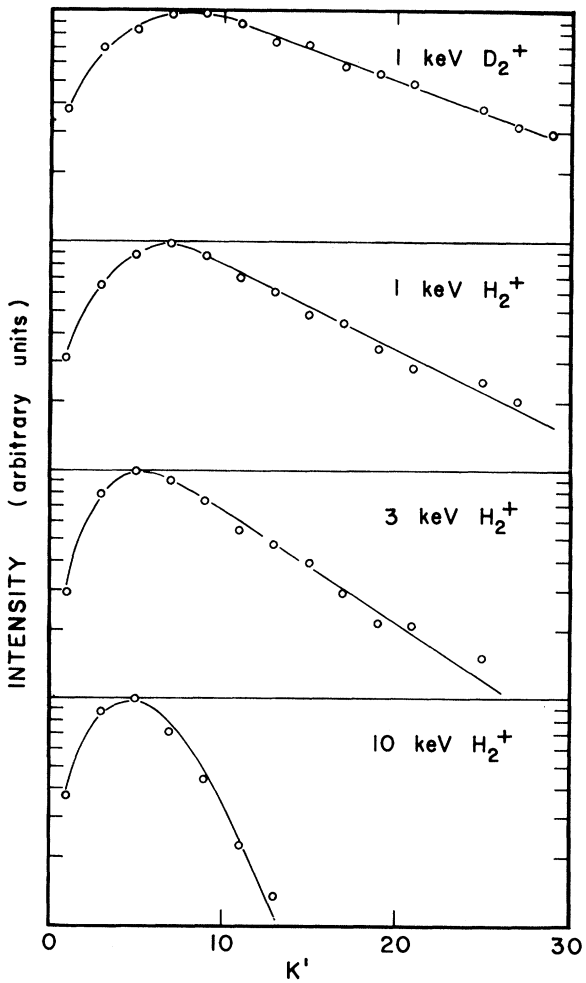

FIG. 3. Typical $\ln I$ versus K' plots of the odd K' rotational lines of the (0, 0) band of the N_2^+ first negative system produced by H_2^+ and D_2^+ bombardment of N_2 at 130°K.

indicate that at low velocities, the envelope of a band becomes broader as the population of rotational states extends to higher levels. As a result, the fraction of the total band intensity passed by a filter may decrease with decreasing ion energy since an increasing amount of the radiation in the band may fall outside the filter's bandpass.

In many cases, measured line intensities of band contours of the N_2^+ first negative system have been used to infer "rotational temperatures." Since the concept of rotational temperature requires that the emitting molecules have their rotational levels populated according to a Boltzmann distribution, our results indicate that for exciting ion velocities below 10^8 cm/sec and pressures less than about 10 μHg, such "temperatures" are meaningless. For example, our Figs. 1 and 2 indicate that auroral protons with energies below a few kilovolts will produce N_2^+ $B^2\Sigma_u^+$ state rotational energy distributions which are different

from a Boltzmann distribution. On the other hand, meaningful rotational temperatures can certainly be obtained if the gas is excited by electrons or high-energy ions.

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Delayed-Coincidence Study of $O^+ + Ar$ Collisions at 50–200 keV*

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Delayed-coincidence techniques have provided measurements of the distributions in values of Q, the energy transferred to inelastic processes, during $O^+ + Ar$ collisions at 50–200 keV. As a function of decreasing r_0, the distance of closest approach of the colliding particles, the average values $\overline{Q}$ of the Q distributions increase rapidly. At 50 keV, for example, $\overline{Q}$ increases from 142 eV at r_0 of 0.26 Å to 707 eV at 0.07 Å. For fixed r_0 the $\overline{Q}$ values increase with bombarding energy and lie 150–200 eV higher at 200 keV. The Q distributions for r_0 between 0.11 and 0.20 Å consist of two overlapping symmetrical distributions. Although one of these two distributions lies as much as 215 eV above the other, measurements of the average charges of the oxygen ions after their collisions show that none of the extra energy goes into ionization of the beam particles. These distributions occur over the range of r_0 where penetration of the argon L electron shell is expected; differential cross sections for scattering of the oxygen ions also show structure in this region. The qualitative behavior of the Q distributions agrees generally with theoretical expectations. However, the energy differences between the centers of the two overlapping distributions do not agree with simple theoretical predictions, which also do not forecast the observed variation of these differences with r_0.

I. INTRODUCTION

During close-encounter atomic collisions the electron shells of the collision partners interpenetrate deeply. The phenomena associated with interpenetration of electron shells are complex; thorough experimental studies of them were rare until the development of delayed-coincidence techniques within the last six years. These techniques, by allowing experimenters to examine both atomic collision partners after their interaction, have made it possible to study close-encounter collisions in more detail than earlier, conventional methods could provide. First reported by Afrosimov, Gordeev, Panov, and Federenko[1,2] and, independently, by Kessel and Everhart,[3] results of experiments[1–6] using these techniques have prompted increased interest in the theory of interpenetrating-shell phenomena. These theoretical efforts[7–12] have produced a qualitative understanding of the general features of close-encounter atomic interactions; in fact, some quantitative theoretical predictions have found empirical verification. However, so many details of the phenomena remain inadequately explored and poorly understood that further investi-