Excitation of N_2^+ ions by collisions with rare-gas atoms[*]

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Collisions of 0.3–5-keV (4–20×10^6 cm/sec) N_2^+ ions with He and Ne targets have been studied by spectroscopic observation of the N_2^+ first-negative-emission spectrum. Vibrational excitation within the collisionally excited $X\,^2\Sigma_g^+ \rightarrow B\,^2\Sigma_u^+$ transition in N_2^+ was studied by a measurement of the relative band intensities of the $\Delta v = -1$ sequence of the first-negative system. Rotational excitation was examined by observation of the rotational line intensities of the (0,0) first-negative band ($\lambda = 3914$ Å). Although the N_2^+ ions used for these experiments were highly vibrationally and rotationally excited by the ion-source discharge, the initial-energy distribution could be inferred from the N_2^+ emission spectra produced by high-velocity ($v > 1.2 \times 10^7$ cm/sec) collisions. At these velocities, populations of vibrational levels in the upper state were independent of projectile-ion velocity and the rotational-energy distribution corresponded to a Boltzmann distribution at 3700 °K. At lower velocities, the population of high vibrational states increased with decreasing velocities and deviations from a Boltzmann distribution among rotational states were observed. Excitation to high rotational states increased monotonically with decreasing projectile-ion velocity. No differences in the rotational and vibrational excitation produced by He and Ne were observed. These results show that for some ion-molecule collisions there is vibrational and rotational excitation in the direct electronic excitation (non-charge-transfer) channel.

I. INTRODUCTION

Vibrational and rotational excitation accompanying electronic excitation produced by ion-molecule collisions is known to occur for a large variety of systems.[1] Most previous investigations of vibrational excitation have been concerned with excitation produced by various projectile ions on N_2,[1] CO,[2] HCl,[3] HBr,[3] N_2O,[4] and CS_2[4] via charge-transfer processes. For rotational excitation, N_2 has been the principal target molecule used.[1,5-7] The results of such investigations have shown, in general, that at high projectile-ion velocities, the vibrational-energy distribution of the collision products is well described by an application of the Franck-Condon principle to the excitation process and the rotational-energy distribution corresponds to a Boltzmann distribution at the ambient target-gas temperature. However, deviations occur for both rotational- and vibrational-energy distributions for low projectile-ion velocities.

Despite the large amount of previous work in this area, there have been few optical investigations to date in which excitation via the direct channel without charge transfer has been examined.[8] Most of the work on the direct excitation channels has been done with inelastic scattering experiments[1]; however, such experiments are useful only for vibrational excitation studies and are unable to study rotational excitation owing to lack of energy resolution. In the present work, we have examined the direct collisional excitation of N_2^+ ions in collisions with rare-gas atoms by observing the emis-

sions from the N_2^+ first-negative optical-emission system. The two target gases used were helium and neon. The reason for the use of these particular targets is that for most other gases, the charge-transfer–channel cross section is much larger than the cross section for the direct excitation channel so most collisions convert the N_2^+ projectile ions into fast neutral molecules. For helium and neon, however, the charge-transfer channel is quite endothermic ($\Delta E \sim 8$ and 5 eV for helium and neon, respectively) and the cross section for charge transfer is small. Other targets such as H_2 or CO_2 produced very little N_2^+ excitation.

The object of this investigation was to determine whether low-energy collisions produce rotational and vibrational excitation within electronic transitions in the direct excitation channel. In order to study such excitation, it is necessary to know the initial-energy distribution of the N_2^+ projectile ions. Ideally, projectile ions which are in their ground vibrational and rotational states should be used. In practice, however, the need for high-intensity ion beams requires the use of high-pressure discharge ion sources where the final electronic, vibrational, and rotational states of the molecular ions produced cannot be controlled. As a compromise to the ideal case mentioned above, we have used the optical emissions from the N_2^+ ion beam produced by excitation collisions of the various excited species in the ion beam with rare-gas targets at high velocities to infer the initial rotational- and vibrational-energy distributions. By lowering the projectile-ion velocity, we were

then able to investigate deviations from the initial-energy distributions as a function of projectile-ion velocity.

There have been few theoretical attempts to date to explain the observed excitation phenomena.[1] Liu[9] has suggested that rotational excitation occurs as a consequence of conservation of angular momentum in inelastic collisions. Lipeles[2(a)] suggested that vibrational excitation arises from the perturbing effects of the projectile-ion's electric field on the electronic structure of the target molecule. Although these theoretical models successfully explain the general features observed in some of the reactions studied to date, it is obvious that at very low velocities, specific effects become increasingly important. An understanding of the nature of these excitation phenomena obviously requires knowledge of the relative importance of such effects in the direct and charge-transfer channels since the collisions mechanisms and cross sections of the two channels are generally quite different.

In addition to the basic interest of the work at low projectile-ion velocities, we have also found that the determination of the energy distributions among rotational and vibrational states in an ion beam by observation of radiation produced by high-velocity collisions with a target gas is a most interesting technique which may find a wide variety of applications in experiments involving ion beams.

II. EXPERIMENTAL

The apparatus used in this investigation is very similar to the one used previously by Moore and Doering,[5] except for the mass analyzer which has been changed to a Wien filter.[10] The use of a Wien filter shortened the over-all length of the apparatus and reduced the ion-beam attenuation by the background gas.

The ions were produced by a duoplasmatron ion source,[11] extracted at high voltage, mass separated, and focused into the collision chamber which contained the target gas. Ion currents in the collision chamber ranged between 3 and 8 μA for energies of 300–5000 eV. The collision chamber was closely coupled to a 1.0-m Fastie-Ebert monochromator. The spectrometer slits were usually opened to provide a 1.5-Å bandpass for the vibrational band-intensity measurements and approximately 0.5 Å for the rotational line measurements. The experiments were done in the second order at a scan rate of 14 Å/min. The detector was an EMR type 541-E photomultiplier cooled to −40 °C. Pulses from the multiplier were amplified, discriminated, and fed to a Nicolet Instruments Inc. 1024-channel analyzer.

The $\Delta v = -1$ sequence of the first-negative sys-

tem was scanned over the range 4278–4150 Å. The rotational levels in the (0, 0) vibrational band were scanned over the range 3914–3760 Å. No corrections due to changes in the total optical sensitivity within a sequence of bands were required. The wavelength range for each experiment was scanned repeatedly until a useful signal-to-noise ratio was obtained. In no case was the number of scans less than seven and at the lowest velocities, 15–20 scans were usually summed because of low signal levels. By subdividing the 1024-channel memory of the analyzer into two halves, we were able to monitor the progress of each individual scan with the first half and then transfer the completed scan to the second half where the data were stored. This procedure ensured that all the runs which were included in the summation were acceptable, i.e., without either large fluctuations in the ion-beam intensity during the scan or large noise spikes from the photomultiplier.

The typical rotational spectrum represented in Fig. 3 shows that the even-odd 1:2 intensity alternation characteristic of the rotational lines of the first-negative system of N₂⁺ is not observed for low K' lines. Moore and Doering[5] have pointed out that in the (0, 0) band, this effect is caused by the overlap of an R-branch line with quantum number K' by the P-branch line originating in the (K' +25) upper rotational state. The measured line intensities were corrected for the contribution of P-branch lines using the calculated correction factors $D(K')$, given by Moore and Doering.[5] An empirical correction method, based on the fact that an even-K' R-branch line is overlapped by an odd-K' P-branch line and vice versa, was also applied. Assuming that the intensities of the overlapping lines are additive, the intensity of the odd-K' R-branch line, $I_R K'$, can be expressed by

$$I_R(K') = \tfrac{2}{3}[2I_t(K') - I_t(K' - 1)], \tag{1}$$

where $I_t(K')$ and $I_t(K' - 1)$ are the measured total intensities of the K' and (K' − 1) rotational lines. Both methods gave identical results, within experimental error.

The rotational spectra may be subject to misinterpretation if the N₂⁺$B\,^2\Sigma_u(v')$ ion undergoes appreciable rotational relaxation before emission. Estimates of the hard-sphere collision lifetimes of an N₂⁺ ion moving at velocities of 5×10^6 or 2×10^7 cm/sec at a pressure of 2 mtorr are ~8 $\times 10^{-7}$ and 2×10^{-7} sec, respectively. The radiative lifetime of the B state of N₂⁺ is about 6×10^{-8} sec.[12, 13] Thus, a N₂⁺ ion in the $B\,^2\Sigma_u^+$ state will hardly undergo one collision before radiating. Spectra taken at collision-chamber pressures between 0.5 and 5 mtorr did not show any significant changes in the distribution of rotational levels,

confirming that secondary collisions are insignificant at this pressure range.

The errors in the relative intensity measurements of the rotational lines in the (0,0) band arise from fluctuations in the ion beam during a run and from errors in the correction factors used to correct for overlap of P-branch lines on R-branch lines. The precision decreases with decreasing velocity and is estimated to be ±8% at the high velocities and ±15% at the lowest velocities.

The vibrational band spectra (Fig. 1) show that each vibrational band extends to high rotational levels. Since the vibrational bands in the $\Delta v = -1$ sequence have nearly identical structure, the ratio of integrated band intensities is equal to the ratio of the heights of the band heads. Therefore, intensity ratios were obtained from measurements of the heights of the band heads. The contribution of the high rotational level of the $[(v'), (v'+1)]$ vibrational band at the position of the $[(v'+1), (v'+2)]$ band head was estimated from the relative intensity of adjacent rotational levels and from the rotational-energy distributions in the (0,0) vibrational band. The overlap correction approaches a significant value for low velocities and was included in the reduction of the data.

The errors in the relative intensity measurements of the vibrational band heads arise from fluctuations in the ion beam and from the correction factors due to overlap of rotational levels of
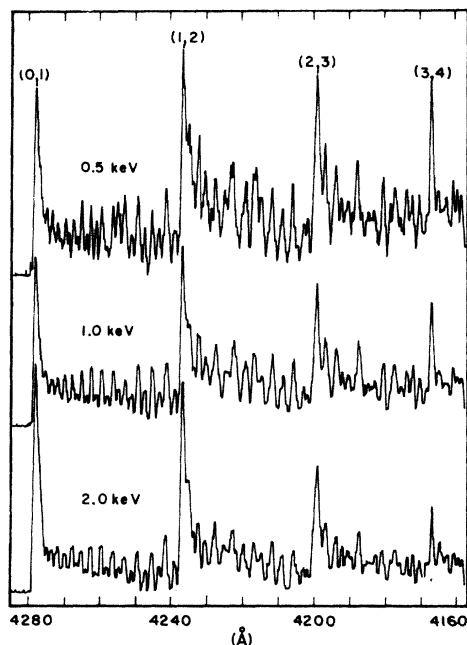
other vibrational levels in the same sequence. The precision is estimated at ±10%. The error in the relative population of the vibrational levels in the upper state is larger, especially for high vibrational levels, because of unfavorable Franck-Condon factors and varies between 15% and 30%. As these populations are used later in Eq. (4) for the derivation of the relative populations of vibrational levels in the ground state, the populations obtained by this method are accurate only to within 30%.

III. RESULTS

A detailed study was made of the relative band intensities of the $\Delta v = -1$ sequence of N_2^+ first-negative system ($B\,^2\Sigma_u^+ - X\,^2\Sigma_g^+$) excited by collisions with He and Ne over a projectile-ion velocity range of $(4-20) \times 10^6$ cm/sec. A typical spectrum is shown in Fig. 1. In Fig. 2 the experimentally determined intensity ratios: $I(1,2)/I(0,1)$, $I(2,3)/I(0,1)$, and $I(3,4)/I(0,1)$ are plotted against projectile-ion laboratory velocity. The relative populations of the vibrational levels in the upper state,
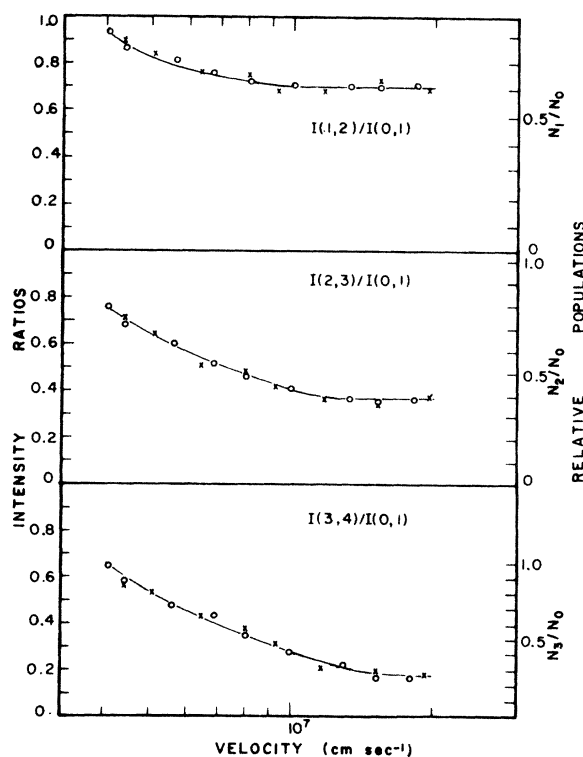

FIG. 1. Typical spectra of the N_2^+ first-negative system $\Delta v = -1$ sequence excited by collisions of 500-, 1000-, and 2000-eV N_2^+ ions with He.

FIG. 2. Intensity ratios $I(1,2)/I(0,1)$, $I(2,3)/I(0,1)$, $I(3,4)/I(0,1)$ vs laboratory projectile-ion velocity for the N_2^+ first-negative system emissions produced by He (O) and by Ne (x). The intensity ratios and relative populations of the upper vibrational states are given by the left- and right-hand axes, respectively.

$N_B(v')/N_B(0)$, have been obtained from the measured intensity ratios using calculated Franck-Condon factors for the $N_2^+(B\,^2\Sigma_u^+ \rightarrow X\,^2\Sigma_g^+)$ transition.[14]

The population of the v' vibrational level, $N_B(v')$, is given by

$$N_B(v') = \frac{KI(v', v'')\lambda^4_{v',v''}}{R\bar{e}^2(v', v'') \cdot q(v', v'')},\qquad(2)$$

where v'' is the vibrational level in the ground state, $\lambda_{v',v''}$ is the wavelength of the emission band head, $q(v', v'')$ is the Franck-Condon factor, $R\bar{e}(v', v'')$ is the average electronic transition moment for the transition, and K is a constant. Within a sequence, $R\bar{e}$ is nearly constant for a strong parallel band system such as the N_2^+ first-negative system.[15, 16] Hence, the population of the v' vibrational level relative to the zero vibrational level is

$$\frac{N_B(v')}{N_B(0)} = \frac{I(v', v'')\lambda^4_{v',v''}q(0, 1)}{I(0, 1)\lambda^4_{0,1}q(v', v'')}.\qquad(3)$$

The relative populations calculated from Eq. (3) are shown in Fig. 2. It is obvious that over the velocity range $(1.2-2.0)\times 10^7$ cm/sec the relative populations of the vibrational levels in the upper state are independent of velocity. However, as the projectile velocity is decreased below 1.2×10^7 cm/sec, the population of states with $v' > 0$ increases monotonically. No difference was found between the excitation produced by He and by Ne atoms.

The vibrational-energy distribution was also determined for collisions of N_2^+ with H_2 and CO_2 molecules. At high velocities, both molecules gave

rise to the same distributions as were observed with He and Ne. However, the excitation cross sections for reactions with H_2 and CO_2 were much smaller than those for Ne and He and the emission intensities were so small that the measurements could not be carried out at low velocities. Obviously, the charge-transfer channel is the predominant reaction channel in these cases, as is shown by the large attenuation of the primary ion beam and by the appearance of strong emission bands of CO_2^+ ions.

The observed relative populations of the vibrational levels in the $B\,^2\Sigma_u^+$ state are different from those expected for excitation of N_2^+ ions originally in the ground electronic and vibrational state. Using calculated Franck-Condon factors[14] for the excitation process

$$N_2^+\,X\,^2\Sigma_g^+\ (v=0) + He \rightarrow N_2^+\,B\,^2\Sigma_u^+\ (v=v') + He,$$
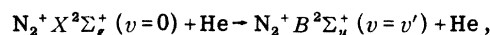
the relative populations in the upper state should be

$$N_B(0) : N_B(1) : N_B(2) : N_B(3) = 100 : 46 : 7 : 0.3,$$

as compared with the experimental values at an ion velocity of 2×10^7 cm/sec:

$$N_B(0) : N_B(1) : N_B(2) : N_B(3) = 100 : 61 : 39 : 25.$$

As shown below, the excitation process at this velocity is well described by the Franck-Condon principle. Thus, we conclude that the primary N_2^+ ion beam, produced by the duoplasmatron ion source must be highly excited.
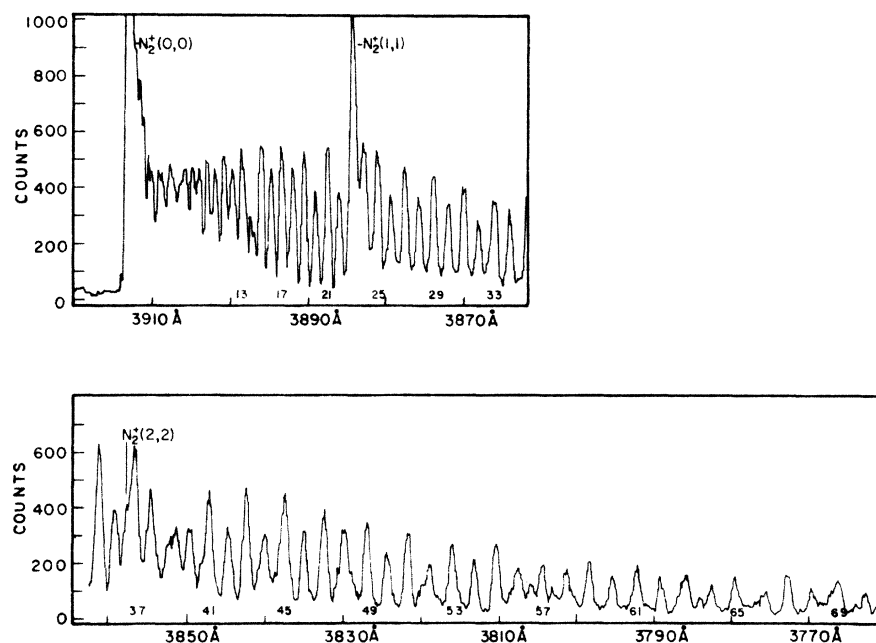
High-resolution spectra of the first-negative

FIG. 3. Typical spectra of the N_2^+ first-negative (0,0) band ($\lambda = 3914$ Å) excited by collisions of 2500-eV N_2^+ ions with Ne. The upper spectrum was taken with a spectrometer resolution of 0.5 Å, and the lower trace with a resolution of 1.5 Å.
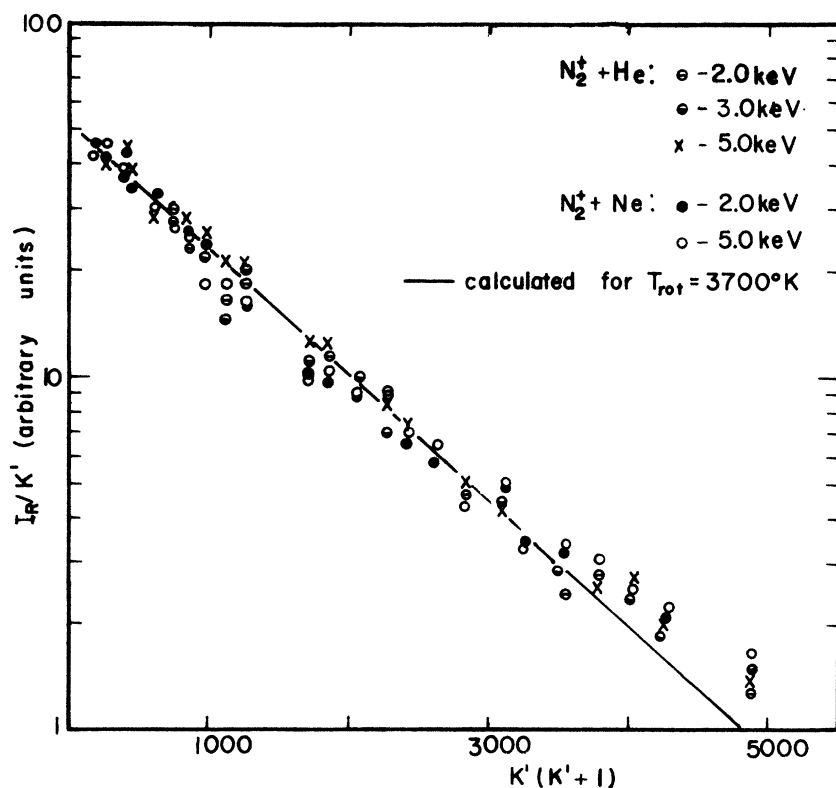
FIG. 4. Plot of $\ln(I_R/K')$ vs $K'(K' + 1)$ taken from spectra of the first-negative (0,0) band excited by collisions of 2.0-, 3.0-, and 5.0-keV N_2^+ ions with He and Ne. The measured intensities were corrected for overlap of P-branch lines (see text). The full line is the calculated curve for $T_{rot} = 3700$ °K.

(0,0) band ($\lambda = 3914$ Å) of N_2^+ produced by impact of N_2^+ ions upon He and Ne were taken in the energy range between 0.3 and 5 keV. The rare-gas pressure was maintained constant during each run at 1.5–2.5 mtorr. A typical spectrum is shown in Fig. 3. The intensity measurements were extended to $K' = 70$ and experimental plots of I_R/K' vs $K'(K' +1)$ were obtained. The measured intensities were corrected for overlap of P-branch lines as described above. Only odd-K' rotational lines were used as the error introduced by the overlap of the weak, even $(K' +25)$ P-branch lines is smaller than for the K'-even lines. Figure 4 shows a curve obtained from intensity measurements of spectra produced by excitation of 2.0-, 3.0-, and 5.0-keV N_2^+ ions by impact on He and Ne. The energy distribution among the rotational levels was velocity independent in this range and corresponded to a Boltzmann distribution of about 3700 °K rotational temperature.

The rotational-energy distribution in the upper state obtained at relative velocities lower than 1.2 $\times 10^7$ cm/sec deviated from a Boltzmann distribution and could not be ascribed to a single rotational temperature. The excitation of high rotational states increased with decreasing projectile-ion velocities and the intensity maximum of the band contour became broader and moved towards higher

K' values. Figure 5 shows measured line intensities in the form of $\ln I$ vs K' for spectra obtained at energies from 0.5 to 5 keV. Within the accuracy of these measurements, no difference exists between the excitation produced by He and Ne.

IV. DISCUSSION

A. Initial state of the N_2^+ ions

The initial state of excitation of the N_2^+ ions prior to collision must be known before any conclusions about the reaction mechanism can be drawn. Owing to the complexity of the ionization process in a discharge ion source, it is impossible to predict quantitatively the final energy distribution of the N_2^+ ions. However, we found that by combination of published data on the lifetimes of the electronic states of N_2^+ and measurements of the intensities of vibrational and rotational bands produced by excitation of N_2^+ ions to the $B^2\Sigma_u^+$ state by high-velocity collisions with rare-gas atoms, the composition of the reactant N_2^+ beam in the collision chamber could be inferred.

The fraction of the excited ions that will reach the collision chamber can be estimated from the lifetimes of $A^2\Pi_u$, $B^2\Sigma_u$, and $C^2\Sigma_u$ states and the delay between the formation of the ions and their arrival to the collision chamber. Ions formed ini-
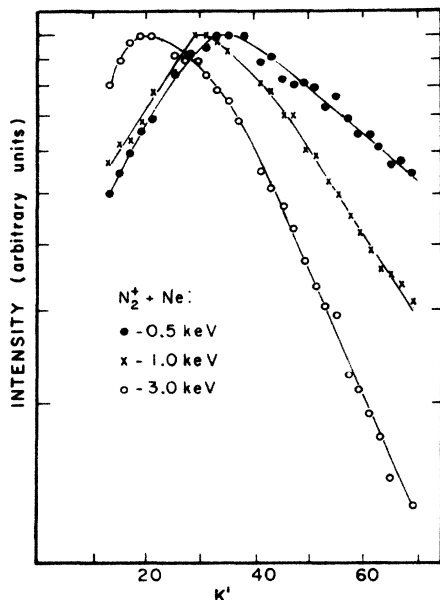
FIG. 5. Typical $\ln I$ vs K' plots of the odd-K' rotational lines of the (0,0) band of the N$_2$$^+$ first-negative system produced by collisions of 0.5-, 1.0-, and 3.0-keV N$_2$$^+$ ions with Ne. The intensities were not corrected for overlap of P-branch lines.

tially in the B and C states will undergo spontaneous radiative decay to the ground state before they reach the collision chamber; the lifetimes of these states are 6×10^{-8} sec [12, 13] and 1×10^{-7} sec,[17] respectively, whereas the time required for the ions to reach the collision chamber is longer than 10 μsec. The $A\,^2\Pi_u$ state of N$_2$$^+$ has a lifetime of 8–15 μsec, depending on the vibrational level.[18] Therefore, we expect that a fraction of the N$_2$$^+$$A\,^2\Pi_u$ ions will reach the collision chamber before decaying. The percentage of ions formed initially in the A state is estimated from electron-impact ionization cross sections to be between 13 and 50%.[18, 19] Photoionization experiments give values of 45–60%.[20] A fraction of these ions will decay either by spontaneous radiative transitions or by collisions with the neutral gas in the high-pressure ion source. The time required for 300–5000-eV ions to reach the collision chamber is 10–20 μsec. We estimate that the residence time of the ions in the ion source is at least this long (no attempt is made to force the ions through the exit aperture which acts merely as a leak[11]). If we assume that 50% of the ions are initially in the A state, then their fraction in the ion beam at the collision chamber is about 10–15%.

We have looked for emissions from the first-negative and the Meinel systems in the collision chamber with no target gas. No emission from the first-negative system could be detected, but there were some weak emissions from the Meinel system from which we estimated that ions in the A state constituted at most 20% of the ion beam.

The vibrational-energy distribution in the N$_2$$^+$ ground state can be estimated assuming that most of the $B\,^2\Sigma_u^+$ N$_2$$^+$ ions are produced in the collision chamber by collisions of N$_2$$^+$ ions in the ground electronic state with the rare-gas atoms.

The number of excited ions that are formed in the v' vibrational state, $N_B(v')$, is then given by

$$N_B(v') = \frac{F}{A(v')} \sum_{v''} N_X(v'') k_{XB}(v'', v'), \tag{4}$$

where $N_X(v'')$ is the number of molecules in the v'' level of the X state, $k_{XB}(v'', v')$ is the rate constant for producing the transition, $A(v')$ is the absolute transition probability, and F is a constant. In the velocity range where the relative populations of the vibrational levels in the B state are velocity independent (Fig. 2), we assume that the excitation rate constants k_{XB} are proportional to the Franck-Condon factors for the $X \rightarrow B$ transition. Therefore, $N_X(v'')$, the populations of the vibrational levels in the ground state, can be obtained from the measured emission intensities of the bands, using Eq. (2):

$$\frac{A(v')I(v', v'')(\lambda_{v',v''})^4}{q(v', v'')} = C \sum_{v''} N_X(v'') q(v'', v'), \tag{5}$$

where C is a constant.

The solution of the set of equations (5) with measured values of $I(v', v'')$ and $\lambda_{v',v''}$ and published values of q[14] and $A(v')$[21] gives the following relative vibrational populations, $N_X(v'')$, in the ground electronic state of N$_2$$^+$:

$$N_X(0) : N_X(1) : N_X(2) : N_X(3) = 100 : 60 : 26 : 17 : 11.$$

This distribution indicates, as expected, extensive vibrational excitation in the N$_2$$^+$ ions produced in the plasma ion source. We expect some vibrational excitation due to the high temperature prevailing in the ion source, but our results cannot be fitted to any single vibrational temperature. Therefore, we conclude that the final population of vibrational levels in the ground state is determined also by radiative decay from higher electronic states and by secondary reactions between the ions and the neutral gas in the ion source.

The measured intensity ratios were independent of the arc current, arc voltage, and pressure in the ion source. However, the vibrational energy distribution was altered when the N$_2$$^+$ ions were generated from a discharge in a mixture of N$_2$ and a rare gas. When a 80:20 mixture of He:N$_2$ was used, the vibrational-energy distribution in the ground-state N$_2$$^+$ ions was

$$N_X(0) : N_X(1) : N_X(2) : N_X(3) = 100 : 71 : 46 : 32 : 16 .$$

Here, we expect a large fraction of the N_2^+ ions to be produced by charge-transfer reactions with He^+, resulting in a different final vibrational-energy distribution as observed.

In order to derive the rotational-energy distribution in the ground state from the measured distribution in the upper electronic state, the rotational excitation produced in the collision must be known. At high energies ($E > 2000$ eV), we calculated the rotational excitation from angular-momentum-conservation considerations.

Liu[9] has shown that for a grazing ion-molecule collision at high energy, the change in angular momentum, ΔL, during the interaction is

$$\Delta L = b \Delta E (m/2E_L)^{1/2} , \tag{6}$$

where b is the impact parameter, ΔE is the kinetic energy lost during the collision, m is the mass of the projectile, and E_L is its initial laboratory energy. Since angular momentum must be conserved during the collision, the loss of angular momentum, ΔL, must be compensated by an increase in internal angular momentum of the reactants—in our case, in the N_2^+ molecular ion. The change in angular momentum calculated from Eq. (6) using $\Delta E = 3.2$ eV,[22] $E_L = 3$ keV, and $b = 2 \times 10^{-8}$ cm is $7\hbar$. If we assume that most of the excess angular momentum is carried away as rotation, then this value reflects the extent of the rotational excitation of the N_2^+ ion induced by collision. Assuming a Boltzmann distribution in the ground state,[23] we calculate that the rotational temperature in the ground state is about $1800\,^\circ$K. The above is an approximate result as the value of b in Eq. (6) is only an estimate. However, in view of the high plasma density in the duoplasmatron ion source, high rotational temperatures of the primary ions would be expected.

In summary, we conclude that most ($>80\%$) of the ions in the collision chamber are in the ground electronic state. However, these ions are highly excited, both vibrationally and rotationally and the extent of this excitation is characteristic of the conditions in the ion source.

B. Interaction of N_2^+ ions with He and Ne atoms

The experimental results presented in Sec. III show that at projectile-ion velocities higher than 1.2×10^7 cm/sec the vibrational-energy distribution in the upper state is velocity independent and the population of rotational states is well described by a Boltzmann distribution.

At these high velocities, the simplest model

which explains the results involves a grazing collision of the atom with the diatomic ion accompanied by an abrupt excitation stage due to conversion of translational to internal energy. The internuclear distance in the reactant ion remains constant during the interaction owing to the short duration of the collision. Hence, no vibrational excitation is expected in the product ion and the excitation process can be described by the Franck-Condon principle. Our conclusion is supported by results on charge-transfer reactions which show[1] that whenever deviations from the Franck-Condon factors are found, the vibrational-energy distribution is velocity dependent. This model, with minor variations, has been used successfully to explain the features observed in the high-energy collisional dissociation of H_2^{+}[25] and other diatomic ions.[26]

In contrast to the above results, the data below 1.2×10^7 cm/sec projectile-ion velocity show that the populations of high vibrational states increase with decreasing velocity and deviations from a Boltzmann distribution among rotational states are observed. This extensive excitation suggests that the N_2^+ projectile ion is perturbed during the collision.

It is interesting to compare the present results for the process $N_2^+(X^2\Sigma_g^+) + He \rightarrow N_2^+(B^2\Sigma_u^+) + He$ with data on the charge-transfer excitation process: $N_2(X^1\Sigma_g^+) + He^+ \rightarrow N_2^+(B^2\Sigma_u^+) + He$ which has been studied both by ourselves[27] and by Moore and Doering[28] in the velocity range $(0.5-7) \times 10^7$ cm/sec. In the latter case, excitation of high vibrational levels in the $N_2^+ B^2\Sigma_u^+$ state becomes important at He^+ ion velocities as high as 7×10^7 cm/sec and increases more rapidly with decreasing velocity than for the present case. Similar behavior has been observed in charge-transfer reactions of other projectile ions with N_2.[28]

The differences in the excitation produced in the charge-transfer and direct-excitation channels suggest that the perturbations of the neutral target N_2 molecule by the approaching ion in the charge-transfer channel are much stronger than the perturbations of the N_2^+ ion by the He target in the direct-excitation channel. In both cases, however, excitation effects become important when the perturbation is of long enough duration for the internuclear distance in the molecule or molecular ion to change significantly during the collision. In the charge-transfer channel, owing to the long range of the force exerted by the ion on the neutral molecule, vibrational excitation is observed at higher velocities than in the direct-excitation reaction.

The effective impact parameter of the reaction may also be important in determining the amount of excitation accompanying a specific process. For instance, in the charge-transfer reaction[29]

$$N_2^+(X\,^2\Sigma_g^+)+K \rightarrow N_2(C\,^3\Pi_u)+K^+, \qquad (7)$$
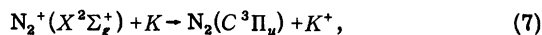
no excitation in the product $C\,^3\Pi_u$ state of N_2 is observed for velocities as low as 2×10^6 cm/sec. The cross section for this near-resonant charge-transfer reaction is large implying that the reaction occurs at quite large impact parameters. At such large distances, the vibrational states of the N_2^+ ion are hardly affected by the neutral atom. However, in the present experiment we have a case of a very endothermic process which apparently occurs at small impact parameters where the N_2^+ ion is significantly altered during the collision.

Nevertheless, the large differences in behavior of various reactions suggest that a general description of the excitation effects may not be valid. For instance, Moore has recently studied the electronic excitation of N_2 and CO by H^+, H_2^+, and N^+ ion in an inelastic scattering experiment.[30] In the projectile-ion velocity range $(2-7)\times10^7$ cm/sec he concluded that in contrast to the charge-transfer channel, there was no significant vibrational excitation during the collision and that the relative intensities of the vibrational bands agreed with predictions based on the relative Franck-Condon factors. Also, in charge-transfer reaction with triatomic molecules it was reported[4] that the populations of the vibrational levels in the product excited CS_2^+ and N_2O^+ ions agree with the predictions based on Franck-Condon factors at Ar^+ projectile-ion velocity of 1×10^7 cm/sec. On the other hand, we found[31] that the measured vibrational band intensities in the $CO_2^+(A\,^2\Pi_u)$ state excited by charge-transfer collisions between H_2^+ and CO_2 differed from those obtained by electron or photon impact and were velocity dependent at projectile-ion velocities lower than 4×10^7 cm/sec.

It appears, therefore, that specific effects in terms of the states involved in the transitions may determine the final state of excitation. Such factors may include the number and locations of crossing points between the potential-energy surfaces of the initial and final states as well as the instantaneous wave functions of the collision pair at the moment of interaction and their effect on the internuclear distance between the atoms of the molecule.

It is thus reasonable to assume that the excitation process occurs in two parts: in the adiabatic part of the collision the spring constant of the molecule is lowered by the interaction with the incoming particle. The electronic excitation reaction occurs during the shorter, diabatic part of the collision, within a certain range of impact parameters. No vibrational excitation is expected when the impact parameter for reaction is much larger than the range of internuclear distances within which the perturbation of the molecular energy levels is significant [i.e., reaction (7)]. However, the probability of excitation may be high when both ranges (for reaction and for perturbation) are comparable. The direct-excitation reaction described in this work falls into this last category.

V. CONCLUSIONS

The most interesting result of this investigation is the observation of extensive vibrational and rotational excitation in the direct-excitation channel of a low-velocity ion-molecule electronic excitation collision. This excitation was somewhat unexpected in a reaction between a molecular ion and a neutral atom as the molecular ion should be hardly affected by the weak field of the atom. However, our data, as well as the results of other investigators, suggest that at low velocities and small impact parameters the molecular ion may be significantly distorted during a strong-coupling collision and the specific details of the interaction determine the final state of the collision products.

Another aspect of this study which may prove to be useful in the further investigation of ion-molecule reactions is the use of optical emissions from ion beams produced by high-energy collisions to infer the initial energy distribution in the ions. In many ion-molecule reactions, the cross section depends strongly on the initial state of the reactant ion and, for this reason, it is desirable to know the excitation state of the ion as accurately as possible. We anticipate, therefore, that the method described here for the determination of the vibrational and rotational energy-level populations within an electronic state of the ion may find a wide application in the study of ion-molecule collisions.

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