Theoretical analysis of the vibrational population in the $N_2^+(B\,^2\Sigma_u^+)$ state produced in charge-transfer collisions of $He^+ + N_2(X\,^1\Sigma_g^+)$

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The vibrational distribution of the $B\,^2\Sigma_u^+$ state of N_2^+ produced in collisions of He^+ and $N_2(X\,^1\Sigma_g^+)$ is calculated using a simple moving-wave-packet model. The results agree very well with the experimental data over the entire accessible range of He^+ velocity $(10^5 - 10^8 \text{ cm/sec})$.

I. INTRODUCTION

Charge transfer between He^+ and N_2 is a well-studied process.[1] The total cross section has a value of ~ 100 Å^2 at thermal energy,[1(c)] and it falls to a value of ~ 5 Å^2 at kinetic energies of a few kilovolts.[1(b)] The $N_2^+(C\,^2\Sigma_u^+)$ state is nearly resonant in energy with He^+ and appears to be the major product channel at low energies[1(d),2]; at high energies a large number of N_2^+ states are populated.[3(a),3(b)] Only a small fraction of the N_2^+ is formed in the $B\,^2\Sigma_u^+$ state (typically 2% at thermal energies), but there is considerable evidence[1(d),3] that this state is produced directly in the He^+-N_2 collisions, rather than by cascade processes from higher states.

The vibrational distribution P_n of the $N_2^+(B)$ state has been determined over a wide range of collision energies by monitoring its fluorescence. For He^+ velocities above 10^8 cm/sec, the distribution matches the Franck-Condon factors for the $N_2(X\,^1\Sigma_g^+, v=0) \rightarrow N_2^+(B, v'=n)$ transition.[4] However, at thermal and intermediate energies P_n is considerably different from the Franck-Condon values and shows a strong energy dependence.[1(d),4,5] Govers et al.[1(d)] have shown that the thermal results can be fit well by Franck-Condon factors computed for the transition $N_2^\dagger(v=0) \rightarrow N_2^+(B)$, where $N_2^\dagger$ represents a ground-state molecule whose potential minimum has been shifted by $\Delta r \approx 0.10$ Å. This procedure does not work at intermediate energies, however, because the experimental distribution is broader than any set of Franck-Condon factors. The experimental values of P_n determined in three different laboratories[1(d)4,5] are shown in Fig. 1. Until now there has been no satisfactory explanation of the remarkable energy dependence of the vibrational distribution.

Recently, we have developed a moving-wave-packet model[6] to describe the molecular vibration in a nonadiabatic collision. In the model the vibrational degree of freedom is treated quantum mechanically, and all other coordinates are treated classically. The method has been applied with success to the quenching of Ar^* by N_2 (Ref. 7) and of Na^* by N_2 and CO.[6] In this paper we show that the model can explain the vibrational distribution of $N_2^+(B)$ produced in collisions of He^+ and N_2.

II. THEORY

The essence of the model is that the N_2 molecule is distorted by the approaching He^+, and consequently, vibrates before the charge transfer takes place. To simplify the calculations we assume the various states of N_2 and N_2^+ are harmonic oscillators with the same angular frequency ω_e. The various molecular parameters are summarized in Table I. We also assume that the oscillator is subject only to linear forces. The calculation involves the propagation of the initial vibrational wave packet forward through time as the collision occurs. The procedure is greatly simplified by the facts that the wave packet of a linearly forced harmonic oscillator evolves in time with no dispersion, and that the center of the wave packet obeys the classical equations of motion.[8] At any instant of time it is a simple matter to decompose the moving wave packet in terms of the stationary states of either the N_2 or N_2^+ molecule.

Accurate potential surfaces are not known for the He^+-N_2 system, but it is possible to make rea-
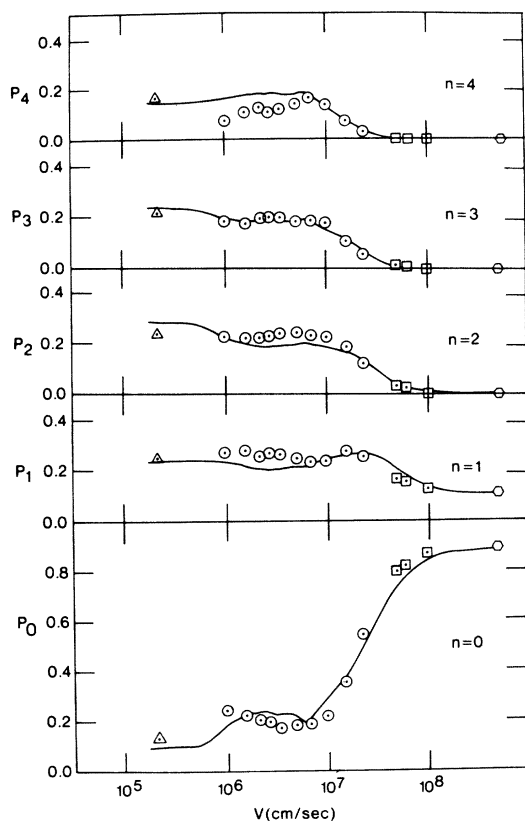
FIG. 1. Vibrational distributions $P_n(n=0,1,2,3,4)$ of the $B\,^2\Sigma_u^+$ state of N_2^+ produced in collisions of $He^+ + N_2$ as a function of relative velocity. The symbols are experimental data: triangles, Ref. 1(d); circles, Ref. 5; squares, Ref. 4. The hexagons are the Franck-Condon factors for the process $N_2(X,v=0)\rightarrow N_2^+(B,v'=n)$. The solid curve is the theoretical result from Eq. (2) averaged over all impact parameters and all allowed values of t_1.

sonable estimates of the features important to our analysis. The analysis of Dowek et al.[3(a)] shows that the $N_2^+(B)$ state is not formed via a direct curve crossing; this explains why the cross section

is small at all collision energies. Instead, the transition is a Demkov-Nikitin process, which can occur over a wide range of He^+-N_2 separations R. As discussed above, the thermal energy data[1(d)] indicates that the He^+ perturbs the N_2 molecule before the electron transfer occurs, causing an increase in the N_2 equilibrium distance r_e. Thus we assume the charge-transfer process can be written

$$He^+ + N_2(X,v=0)\rightarrow He^+ + N_2^\dagger$$

$$\rightarrow He + N_2^+(B,v'=n)\ .$$
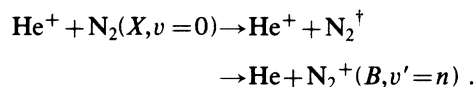
The increase in r_e, which produces the $N_2^\dagger$ molecule, is often referred to as the Lipeles shift.[9] The normal explanation of the shift is that the change in r_e increases the strength of the ion-induced dipole and (perhaps) the ion-quadrupole potential terms.[5] Consequently, the Lipeles shift is independent of the particular projectile ion at large R; this is the likely explanation of why the vibrational distributions of the $N_2^+(B)$ state produced by charge transfer with many ions are nearly identical at intermediate energies.[4,5] For the $He^+ + N_2$ system, however, the shift may also be affected by the interaction of the reactant state with the energy-resonant $He + N_2^+(C\,^2\Sigma_u^+)$ state. For the C state $r_e=1.263$ Å (Ref. 10) so any mixing of these two configurations will elongate the N_2. Whatever the explanation, however, the thermal data[1(d)] required us to assume the $r_e(N_2^\dagger)$ value given in Table I.

In the calculations we make the following assumptions. The He^+ follows a straight-line trajectory at constant velocity v. The change in r_e begins at $R=R_2$ (point A in Fig. 2), and r_e varies linearly in time until the full extension of $N_2^\dagger$ is reached at $R=R_1$ (point B). In general, the location $r(t)$ of the center of the vibrational wave packet can not keep pace with the change in r_e, and the $N_2^\dagger$ is produced with vibrational energy. We assume that charge transfer can occur at any

TABLE I. Molecular parameters for N_2.

State	r_e(Å)	Miscellaneous parameters
$N_2(X\,^1\Sigma_g^+)$	1.098[a]	$v_e=2389$ cm^{-1} [c]
$N_2^\dagger(X)$	1.175[b]	$k_e=147$ eV/Å^2
$N_2^+(B\,^2\Sigma_u^+)$	1.076[a]	$\Delta r = r_e(N_2^\dagger)-r_e(N_2)=0.077$ Å
		$\delta r = r_e(N_2^\dagger)-r_e(N_2^+)=0.099$ Å

[a]Reference 10. Note that $r_e(N_2^+)$ has been slightly from their value (1.074 Å) to give the proper Franck-Condon factors for our harmonic oscillator model.
[b]Chosen to give the best fit to the experimental data.
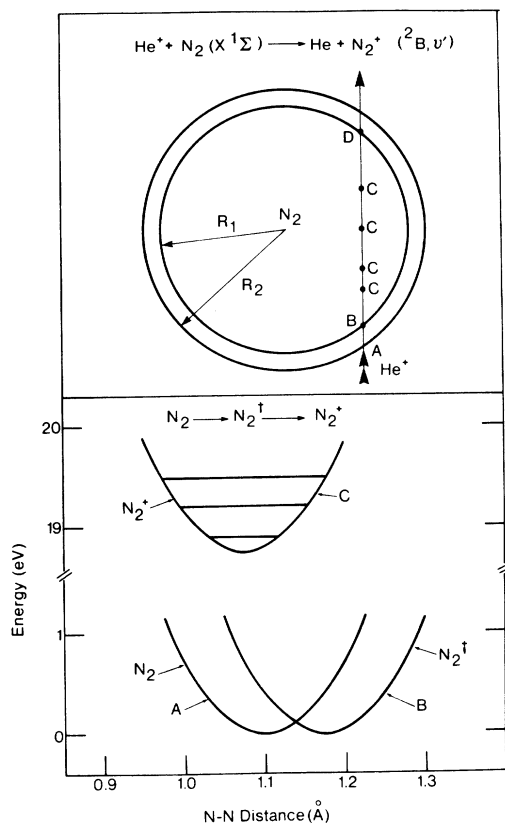[c]Taken as the geometric mean of v_e for the $N_2(X)$ and the $N_2^+(B)$ states.

FIG. 2. (Lower panel) harmonic oscillator representations of the potential-energy curves for the $N_2(X)$, $N_2^\dagger$, and $N_2^+(B)$ states. The molecular parameters are summarized in Table I. The vibrational levels for $n = 0$, 1, and 2 are shown for the $N_2^+(B)$ state. (Upper panel) schematic representation of the He^+-N_2 collision. The He^+ moves in a straight-line trajectory with constant velocity. When the He^+ reaches $R = R_2$ (point A) the N_2 molecule begins to stretch; when the He^+ reaches $R = R_1$ (point B) the stretching is complete, and the potential curve is that of $N_2^\dagger$. Charge transfer (indicated by various points C) can occur anywhere between points B and D.

point where $R \leq R_1$ (i.e., between points B and D in Fig. 2) with equal probability. Also, the transition from $He^+ + N_2^\dagger$ to $He + N_2^+(B)$ is sudden (Franck-Condon-like), so the values of $r(t)$ and $r'(t)$ on the new surface are identical to the values on the old surface at the instant of transition.

If the He^+ reaches point A at time $t = 0$, point B at time t_0, and the charge transfer occurs at time t_1 ($t_1 \geq t_0$), it is easy to solve for the motion of the wave packet on the $N_2^+(B)$ potential curve. The result for $t \geq t_1$ is given by $r(t) = r_e[N_2^+(B)]$ $+ T \sin(\omega_e t + \alpha)$, where the phase α is of no interest, and the amplitude T is given by

$$T^2 = (\delta r)^2 + (\Delta r/\phi)^2 \sin^2\phi$$
$$\quad - (2\Delta r \delta r/\phi)\sin\phi \cos(\omega_e t_1 - \phi) , \quad \text{(1a)}$$

$$\phi = \omega_e t_0/2 . \quad \text{(1b)}$$

The parameters δr and Δr are defiend in Table I. If the wave packet is decomposed in terms of the stationary states of $N_2^+(B)$, we obtain the vibrational distribution of the products

$$P_n = \epsilon^n \exp(-\epsilon)/n! , \quad \text{(2a)}$$

$$\epsilon = \epsilon(t_0, t_1) = \tfrac{1}{2} k_e T^2/\hbar\omega_e . \quad \text{(2b)}$$

Note that P_n equals the Franck-Condon factor $\langle 0 | n \rangle^2$ obtained for two identical harmonic oscillators whose minima are displaced by a distance T. Inspection of Fig. 2 shows that the result in Eq. (2) must be averaged over all impact parameters $0 \leq b \leq R_1$ and over all allowed values of t_1. We have carried out these averages numerically for velocities between 10^5 and 10^9 cm/sec for a wide range of R_1 and R_2 values. The results are sensitive to the value of $(R_2 - R_1)$, but not particularly dependent on R_1 and R_2 separately. The best agreement with experiments, shown in Fig. 1, was obtained for $R_1 = 4.07$ Å and $R_2 = 4.58$ Å.[11] In the experiments of Simonis[5] only levels $v' = 0-4$ were observed, so we have normalized the populations in these five states to one for all of the experiments as well as the theory.

III. DISCUSSION

Figure 1 shows that theory and experiment agree over the entire range of He^+ velocity. It is instructive to first consider the results in the low- and high-velocity limits. At thermal energies the transition from N_2 to $N_2^\dagger$ is slow ($t_0 \rightarrow \infty$), and the vibrational coordinate $r(t)$ follows the change in r_e adiabatically. Consequently, the product distribution P_n is given by the Franck-Condon factors for the transition $N_2^\dagger(v = 0) \rightarrow N_2^\dagger(B, v' = n)$. This can be seen from Eq. (1), where $T \rightarrow \delta r$ in the limit $t_0 \rightarrow \infty$. Thus, Eq. (2) gives the Franck-Condon factors directly. The result for P_n agrees with the interpretation by Govers et al.[1(d)] discussed earlier. By comparison, at very high velocities the shift in r_e still occurs (since this is determined by the electronic motion), but the wave packet does not have time to move before the charge transfer occurs. Consequently, P_n is given by the Franck-Condon factors for the transition $N_2(v = 0) \rightarrow$ $N_2^+(B, v' = n)$. This is confirmed by Eq. (1), since

$$T = \delta r - \Delta r = r_e(N_2) - r_e(N_2^+)$$

when $t_0 = t_1 = 0$, and Eq. (2) gives the appropriate Franck-Condon factors.

In the intermediate velocity range $(10^6 \leq v \leq 10^8$ cm/sec) the wave packet is no longer stationary before the charge transfer occurs. The wave-packet vibration acts to broaden the distributions obtained in the two limiting cases. The effect is particularly dramatic for $v \simeq 3 \times 10^7$ cm/sec (see Fig. 1), because for $v > 10^8$ cm/sec only $n = 0$ (89%) and $n = 1$ (11%) are populated, and the oscillation of the wave packet sharply reduces the amount of products produced in $n = 0$. For velocities between 10^6 and 10^7 cm/sec the distribution is quite broad. For example, at $v = 3 \times 10^6$ cm/sec each of the theoretical population falls between 18 and 24 %.

The model describes here should apply to a wide range of charge-transfer processes, with the under-standing that the parameters R_1, R_2, and $r_e(N_2^\dagger)$ will vary from system to system. We are presently applying the model to a variety of collision processes which produce the $N_2^+(B)$ product state.

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[11]Calculations by Simonis (Ref. 5) as well as unpublished *ab initio* computations by Gerard-Ain, Govers, Levy, and Millie suggest that significant perturbation of the N_2 by He^+ occurs only at smaller values of R than our "best" values. We have obtained curves very similar to those shown in Fig. 2 using smaller R values, provided that the difference $R_2 - R_1$ is kept at 0.5 Å. Since detailed potential curves are not available, we show only our best fit in Fig. 2.