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Vibrational excitation in nonionizing ion-molecule collisions at $2-7\times10^7$ cm/sec†

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The vibrational-state population of electronically excited, neutral molecules produced by ion impact at $2-7\times10^7$ cm/sec has been determined by measuring the relative intensities of the vibrational components of electronic band systems observed in the energy-loss spectra of H^+, $H_2{}^+$, and N^+ scattered from N_2 and CO. The measured intensities agree with intensities which have been observed in optical and electron-impact spectra as well as with theoretical predictions based on the Franck-Condon principle. Previous reports of anomalous vibrational excitation of $N_2(a\,{}^1\Pi g)$ by proton impact are demonstrated to be the result of proton-impact excitation of N_2 to both the $a\,{}^1\Pi g$ and $w\,{}^1\Delta_u$ states.

I. INTRODUCTION

The applicability of the Franck-Condon principle to molecular electronic excitation in processes other than photon absorption has been a question of interest in the study of atomic- and electronic-collision physics and in investigations of the interaction of the solar wind with the planetary atmospheres. In the past, experimental measurements of vibrational-state populations resulting from electronic excitation by electron, ion, and neutral impact have been compared to theoretical Franck-Condon predictions. In general, it has been observed that experiment and theory diverge as the collision velocity decreases below 10^8 cm/sec. This region, where the Franck-Condon principle appears to fail, is the region where the collision velocity is about equal to, or less than, the velocity of the molecular-orbital electrons—the approach to near-adiabatic region.[1] This paper presents data obtained using the technique of energy-loss spectrometry to determine the vibrational energy distribution resulting from ion-impact-induced electronic excitation of molecules in the near-adiabatic region.

In the case of electron-impact excitation, Lassettre and his co-workers[2] have demonstrated that, for collision energies above 50 eV, the relative intensity of the vibrational components of electronic transitions appearing in electron energy-loss spectra are invariant with respect to scattering angle and energy. In addition, the relative intensities of the members of a vibrational progression agree with those observed in optical spectra and are generally proportional to the magnitudes of the corresponding Franck-Condon factors. More recently, Williams and Doering[3] have observed the relative intensities of vibrational progressions in electron energy-loss spectra to be invariant at impact energies down to within a few eV of threshold. Nevertheless, it must be realized that even at near-threshold energies, the collision velocity in these experiments exceeded 10^8 cm/sec.

In contrast to electron-impact work, most studies of ion-impact phenomena have been observations of the vibrational energy distribution in electronically excited molecular ions produced in charge-exchange or ionizing collisions of fast atomic ions with molecular targets.[4] Furthermore, most available data are for the excitation of the $B\,{}^2\Sigma_u^+$ state of $N_2{}^+$ by ion impact on N_2. Although this work is not completely self-consistent, there is ample evidence that, for charge-changing collisions at velocities in excess of 10^8 cm/sec, the vibrational energy distribution in the electronically excited products is in agreement with predictions based on calculated Franck-Condon factors. At lower collision velocities, vibrational distributions deviate dramatically from the Franck-Condon predictions. It has been suggested that the Franck-Condon principle is not violated in these collisions, but rather the principle must be applied to the molecular system after it has been distorted by the field of the approaching projectile.[4a, 5]

There is very little information on the vibrational excitation accompanying electronic excitation in nonionizing, ion-molecule collisions. From observations of the relative intensities of vibronic components of the N_2 second-positive emissions ($C\,{}^3\Pi_u \rightarrow B\,{}^3\Pi_g$) produced by H and He^+ impact on N_2, Moore and Doering[4a] determined the vibrational energy distribution of the $C\,{}^3\Pi_u$ state of N_2. The proton-induced spectra were probably the result of the interaction of secondary electrons with N_2, since a proton-impact-induced transition from the singlet ground state of N_2 to the triplet upper state of the second-positive system is strongly forbidden by the

Wigner spin rule. Excitation of N_2 to the $C\,^3\Pi_u$ state by He^+ impact is permitted[6] and their results indicate that ion-impact excitation of N_2 to the $C\,^3\Pi_u$ state, at collision velocities of (1–2) $\times 10^7$ cm/sec, results in a vibrational distribution which is in agreement with Franck-Condon predictions. In a later experiment, using an energy-loss technique, Moore and Doering observed the $a\,^1\Pi_g \leftarrow X\,^1\Sigma_g^+$ transition in N_2 as a result of proton impact at 3×10^7 cm/sec.[7] The high-energy tail of this band system appeared anomalously intense, and it was suggested that this was the result of excessive population of the high-lying vibrational levels of the upper ($a\,^1\Pi_g$) state. The work described in the present paper indicates that this anomalous intensity is the result of an underlying transition.

The vibrational excitation resulting from ionizing collisions of neutrals with molecules has been studies by Polyakova and her colleagues,[4b] and by Birely.[4g] They have determined the vibrational energy distribution in N_2^+ in the $B\,^2\Sigma_u^+$ state produced by collisions of rare-gas atoms and H atoms with N_2. The results of these experiments are similar to those of the charge-changing ion-molecule collisions in that unusual vibrational energy distributions resulted from collisions at velocities less than 10^8 cm/sec. On the other hand, Birely[4g] has determined that the relative intensities of the vibrational components of the N_2 second-positive system produced by H and D atom impact are invariant over the $(5-20)\times 10^7$ cm/sec collision velocity range.

The present paper reports the results of intensity measurements made on vibrational progressions observed in energy-loss spectra of H^+, H_2^+, and N^+ scattered, without charge-exchange, from N_2 and CO at velocities of (2–7) $\times 10^7$ cm/sec.

II. EXPERIMENTAL

The energy-loss spectrometer used in these experiments has been described previously.[8] In this apparatus a nearly monoenergetic beam of ions is passed through a gas at a few millitorr pressure. Ions scattered into a small cone centered at 0°, as well as unscattered ions, are collected by an analyzer in which their kinetic energy is measured with a resolution of about 0.17 eV full width at half-maximum.

For one of the processes investigated $[H^+ + N_2(X\,^1\Sigma_g^+) \rightarrow H^+ + N_2(a\,^1\Pi_g)]$ the total scattering cross section has previously been measured.[9] A knowledge of the scattered-ion intensity observed in the present, high-resolution experiment and this total cross section made it possible to determine that, in this case, about 50% of the inelastically scattered ions were being detected by the ion analyzer. The detected fraction of scattered ions included a sampling of scattering events at all angles because the detector was at 0°, and thus, able to observe relatively large angle scattering which occurred near the collision chamber entrance and exit. In any event, from previous work[9] it appears that there is very little momentum transfer in these collisions since all detectable scattering is strongly forward directed.

As can be seen in Figs. 1–4, the vibrational structure in the observed molecular band systems was only partially resolved. To aid in the determination of the relative intensities of the members of these vibronic progressions, a computer was employed to deconvolute the spectra. The resolution function of the instrument was taken to be the 0-eV peak in each spectrum. This choice was appropriate since the analyzer was set at 0°, and thus, the 0-eV peak was the energy profile of the unscattered beam. Each spectra and the corresponding resolution function were digitized and presented to the computer. In addition, since all of the observed features in the energy-loss spectra corresponded to known electronic transitions,[10–12] the expected position of each vibrational component was also given to the computer. The computer then synthesized a spectrum by placing a peak of the shape of the resolution function at each of these positions and summing them. This synthetic spectrum was compared

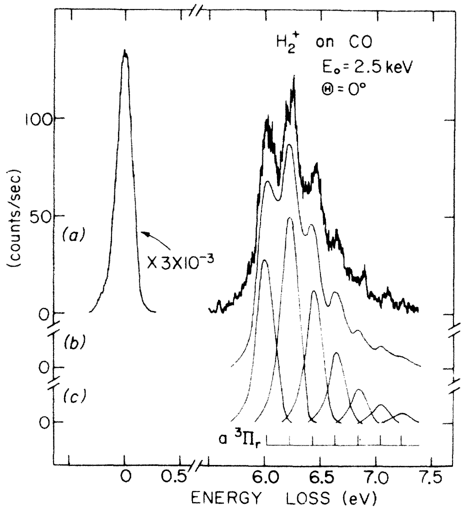

FIG. 1. (a) Energy-loss spectrum of 2.5-keV H_2^+ scattered from CO about 0° scattering angle. (b) Smoothed, computer-generated spectrum which best fits experimental spectrum. The spectrum was digitally analyzed at 0.02-eV intervals. (c) Deconvolution of synthetic spectrum into individual vibrational components.

to the real spectrum. By an iterative procedure, each peak height was then varied until the synthetic spectrum which best fit the real spectrum was found. The peak heights which gave this best fit were then taken to be proportional to the intensity of the vibrational components which made up the real spectrum.

In the fitting process two degrees of freedom were permitted. To account for the effects of rotational structure within each vibronic component, the resolution function was broadened by 8%. On the average, this broadening gave the best fit, although broadening factors of 0 to 15% were tried. Of all these broadening factors, none changed the final predicted intensities by more than a few percent.

It was also necessary to account for the uncertainty in the experimental energy-loss scale. To do this, the computer was permitted to displace the synthetic spectrum along the energy axis by as much as 0.2 eV as it attempted to find the best fit.

III. RESULTS

A. H_2^+ on CO

Excitation of CO to the $a\,^3\Pi$ state by ion impact is a particularly good case for studying vibrational excitation in electronic transitions, since the spacing between vibrational levels in this state is relatively large. In addition, the $a\,^3\Pi$ is the lowest-lying excited state of CO and transitions between the ground state and this state are not overlapped by other transitions. A typical energy-loss spectrum of 2.5-keV H_2^+ scattered from CO is shown in Fig. 1(a). This collision energy corresponds to a collision velocity of 4.9×10^7 cm/sec. Figure 1(b) is the computer-synthesized spectrum which best fits this experimental spectrum. The average rms deviation between synthetic and real spectra was 7.4%. The synthetic spectrum, deconvoluted into its vibrational components, is shown in Fig. 1(c).

The relative intensities of the first six vibrational components of the $a\,^3\Pi \leftarrow X\,^1\Sigma^+$ transition (the Cameron bands), determined from deconvoluted spectra, are given in Table I. The results of intensity measurements made on optical-absorption spectra[13] and electron-impact spectra[14] are given for comparison. The excellent agreement between the present results and the optical and electron-impact data indicate that, in this case, the vibrational population arising from electronic excitation by ion impact is in agreement with the Franck-Condon principle.

TABLE I. Relative intensities of the vibrational components of the $a\,^3\Pi \leftarrow X\,^1\Sigma^+$ transition in the energy-loss spectrum of 2.5-keV H_2^+ scattered from CO.

v'	Energy[a] (eV)	I	I_{cl}[b]	I_{opt}[c]
0	6.014	0.81 ± 0.03	0.84	0.83
1	6.225	1.00	1.00	1.00
2	6.430	0.68 ± 0.04	0.74	0.72
3	6.634	0.39 ± 0.05	0.39	0.37
4	6.839	0.18 ± 0.03		0.16
5	7.043	0.09 ± 0.02		0.07
6	7.229	0.05 ± 0.01		

[a] G. Herzberg (Ref. 10).

[b] Intensities from the electron-impact spectra of Skerbele *et al.* (Ref. 14).

[c] Intensities observed in optical-absorption spectra by Lawrence and Seitel (Ref. 13).

B. N^+ on CO

In order to observe the $a\,^3\Pi \leftarrow X\,^1\Sigma^+$ transition in CO, in a lower-velocity collision than that reported above, the H_2^+ projectile was replaced by N^+. Since the duoplasmatron ion source produces appreciable numbers of N^+ in both the ^3P ground state and the ^1D metastable state,[15] the Cameron bands appear at several places in the energy-loss spectrum. This transition occurs unoverlapped near 4 eV as a result of the process

$$N^+(^1D)+CO(X\,^1\Sigma^+)\rightarrow N^+(^3P)+CO(a\,^3\Pi).$$

In this case, low signal intensity prevented the

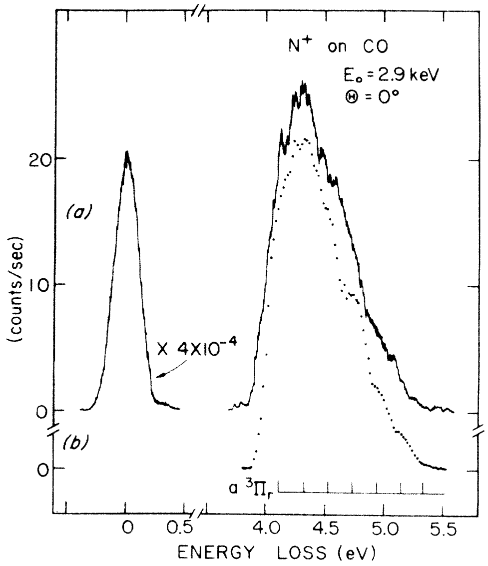

FIG. 2. (a) Energy-loss spectrum of 2.9-keV N^+ scattered from CO at 0°. (b) Computer-generated synthetic spectrum which best fits experimental spectrum. The spectrum was digitally analyzed at 0.02-eV intervals.

TABLE II. Relative intensities of the vibrational components of the $a\,{}^3\Pi \leftarrow X\,{}^1\Sigma^+$ transition in the energy-loss spectrum of 2.9-keV $N^+({}^1D)$ scattered from CO.

v'	Energy[a] (eV)	I	I_{el}[b]	I_{opt}[c]
0	4.11	0.83 ± 0.02	0.84	0.83
1	4.32	1.00	1.00	1.00
2	4.53	0.77 ± 0.04	0.74	0.72
3	4.73	0.48 ± 0.08	0.39	0.37
4	4.94	0.21 ± 0.05		0.16
5	5.14	0.09 ± 0.02		0.07

[a] Observed energy loss is the transition energy (Ref. 2) minus 1.90 eV from the ${}^1D \rightarrow {}^3P$ transition in N^+.

[b] Intensities from the electron-impact spectra of Skerbele *et al*. (Ref. 14).

[c] Intensities observed in optical-absorption spectra by Lawrence and Seitel (Ref. 13).

achievement of sufficient resolution to observe vibrational structure in the spectrum. In spite of this, the spectrum was digitally analyzed and these results are presented in Fig. 2 and Table II. The vibronic intensities determined by computer analysis must be regarded as uncertain in comparison with the H_2^+ – CO results; nevertheless, they are in reasonable agreement with the optical and electron-impact results.

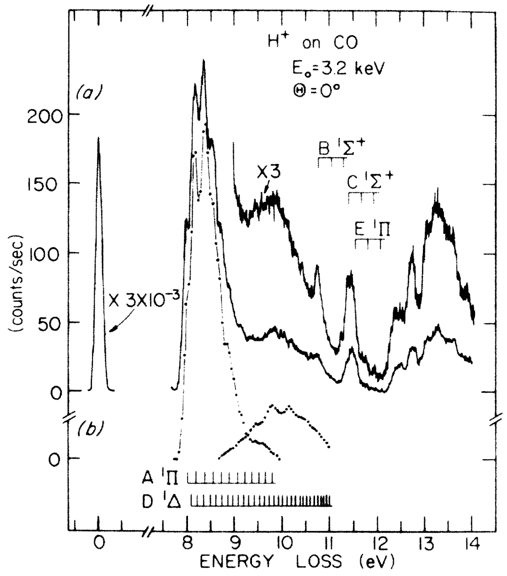

FIG. 3. (a) Energy-loss spectrum of 3.2-keV H^+ scattered at 0° from CO. (b) Computed resolution of the experimental spectrum into two band systems corresponding to the $A\,{}^1\Pi \leftarrow X\,{}^1\Sigma^+$ and $D\,{}^1\Delta \leftarrow X\,{}^1\Sigma^+$ transitions. The spectrum was digitally analyzed at 0.025-eV intervals. Only every other one of the digital points is represented.

TABLE III. Relative intensities of the vibrational components of the $A\,{}^1\Pi \leftarrow X\,{}^1\Sigma^+$ transition in the energy-loss spectrum of H^+ on CO which appears in Fig. 3.

v'	Energy[a] (eV)	I	I_{el}[b]	FC[c] factors
0	8.025	0.50	0.50	0.53
1	8.208	0.92	0.92	0.98
2	8.388	1.00	1.00	1.00
3	8.563	0.64	0.81	0.76
4	8.733	0.40	0.55	0.47
5	8.900	0.29	0.33	0.30
6	9.062	0.15	0.17	0.13
7	9.220	0.11	0.09	0.06
8	9.374	0.05	0.04	0.03

[a] G. Herzberg (Ref. 10).

[b] Intensities from the electron-impact spectra of Lassettre *et al*. (Ref. 2).

[c] Franck-Condon factors calculated by Tilford and Howard (Ref. 12).

C. H^+ on CO

The energy-loss spectrum of H^+ on CO shown in Fig. 3(a) is of interest because this collision system is isoelectronic with the $H^+ - N_2$ system, for which it has been suggested that excessive population of high vibrational levels accompanies the $a\,{}^1\Pi_g \leftarrow X\,{}^1\Sigma_g^+$ transition. In the CO spectrum, the band peaking at 8.4 eV corresponds to the

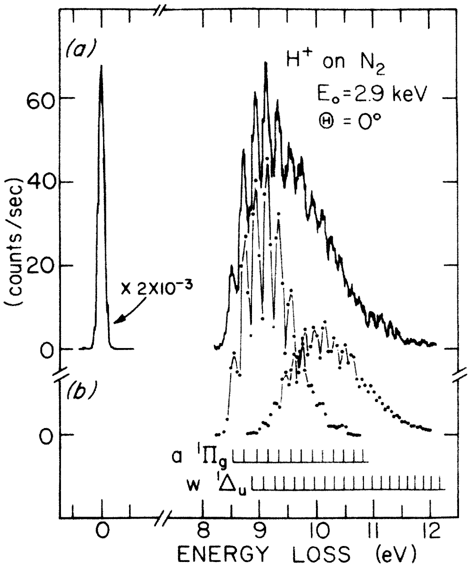

FIG. 4. (a) Energy-loss spectrum of 2.9-keV H^+ scattered at 0° from N_2. (b) Computed resolution of the experimental spectrum into two band systems corresponding to the $a\,{}^1\Pi_g \leftarrow X\,{}^1\Sigma_g^+$ and $w\,{}^1\Delta_u \leftarrow X\,{}^1\Sigma_g^+$ transitions. The spectrum was digitally analyzed at 0.025-eV intervals. Only every other one of the digital points is represented.

$A\,^1\Pi \leftarrow X\,^1\Sigma^+$ transition (the fourth positive bands) and the broad, structureless band peaking at about 10 eV is believed to be the $D\,^1\Delta \leftarrow X\,^1\Sigma^+$ transition.[11]

In the computerized deconvolution of the $A\,^1\Pi \leftarrow X\,^1\Sigma^+$ spectrum, the shape of the overlapping band system was taken to be the convolution of the vibrational components of the $D\,^1\Delta \leftarrow X\,^1\Sigma^+$ transition with energies as given by Tilford and Simmons[11] and intensities proportional to the calculated Franck-Condon factors of Tilford and Howard.[12] The total intensity of this band system was treated as a variable, but its shape and position relative to the $A\,^1\Pi \leftarrow X\,^1\Sigma^+$ bands was kept fixed. The computed resolution of the experimental spectrum into two band systems is shown in Fig. 3(b). The structure in the $D\,^1\Delta \leftarrow X\,^1\Sigma^+$ peak is an artifact of the digitation and extrapolation procedures. This difficulty occurred only when the vibrational spacing was much less than the half-width of the resolution function and was ignored in this case. The rms deviation, over the range 7.75–11.0 eV, between the experimental spectrum and the sum of the two computer-generated band systems is 3.0%. The relative intensities determined for the vibrational components of the $A\,^1\Pi \leftarrow X\,^1\Sigma^+$ transition in this spectrum are given in Table III, along with the intensities observed in the electron-impact spectrum[2] and the corresponding Franck-Condon factors.[12]

D. H^+ on N_2

The energy-loss spectrum of H^+ scattered from N_2 at 2.9 keV is shown in Fig. 4(a). The occurrence of the $a\,^1\Pi_g \leftarrow X\,^1\Sigma_g^+$ transition [the Lyman-Birge-Hopfield (LBH) system] in this collision is confirmed by the position and spacing of the first five vibrational components of the band which peaks at 9.2 eV. Because of the results of Sec. IIIC, it was assumed in the deconvolution procedure that the $w\,^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ transition underlay the LBH band system. The shape of this peak was taken to be the convolution of the vibrational components of the $w\,^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ transition with energies and intensities as determined by Tilford and Howard.[12] The resolution of the experimental spectrum into two band systems is shown in Fig. 4(b). The relative intensities of the LBH bands are those which gave the best fit to the experimental spectrum. In Table IV these intensities are compared to those observed in the electron-impact spectrum[2] and to computed Franck-Condon factors for the corresponding transitions.[16]

TABLE IV. Relative intensities[a] of the vibrational components of the $a\,^1\Pi_g \leftarrow X\,^1\Sigma_g^+$ transition in the energy-loss spectrum of 2.9-keV H^+ scattered from N_2.

v'	Energy[b] (eV)	I	I_{el}[c]	FC[d] factors
0	8.547	0.27	0.24	0.24
1	8.753	0.69	0.61	0.63
2	8.956	0.93	0.91	0.93
3	9.157	1.00	1.00	1.00
4	9.354	0.84	0.87	0.87
5	9.548	0.57	0.68	0.66
6	9.738	0.34	0.48	0.45
7	9.926	0.18	0.32	0.29
8	10.110	0.12	0.18	0.17

[a] Uncertainties (standard deviation): 0.03 for $v' < 3$ and 0.07 for $v' > 5$.

[b] G. Herzberg (Ref. 10).

[c] Intensities from the electron-impact spectra of Lassettre *et al*. (Ref. 2).

[d] Franck-Condon factors calculated by Benesch *et al*. (Ref. 16).

IV. DISCUSSION

For the four collision processes reported above, the total uncertainty in the measurements of vibrational-level populations is determined by the precision of the data (the standard deviation) and the deviation between the computer-generated spectra and the experimentally derived spectra. In general, this uncertainty has not exceeded 20%. Within experimental error, the vibrational populations observed in these nonionizing, ion-molecule collisions agree with populations which result from electronic excitation by electron impact and photon absorption. This is in sharp contrast to the electronic excitation which occurs in ionizing collisions between ions and molecules at collision velocities below 10^8 cm/sec. In the charge-changing collisions the populations of electronically excited molecular ions produced in collisions at 5×10^7 cm/sec have been observed to differ from Franck-Condon predictions by factors of 2 or more. There is at present no obvious reason for this remarkable difference.

ACKNOWLEDGMENTS

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