ANL-6769, 1963 (unpublished).

[6] M. Inokuti, Argonne National Laboratory Report No. ANL-7220, 1966 (unpublished).

[7] R. McCarroll, Proc. Phys. Soc. (London) A70, 460 (1957).

[8] L. M. Brown, Phys. Rev. 79, 297 (1950).

[9] K. Omidvar, Phys. Rev. 140, A38 (1965). See also Ref. 7.

[10] L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), Chap. 15.

[11] Ref. 2, p. 818.

[11a] J. D. Garcia, Phys. Rev. 177, 223 (1969). L. Vriens and M. Inokuti, private communication.

[12] M. Gryzinski, Phys. Rev. 115, 374 (1958).

[13] R. C. Stabler, Phys. Rev. 133, A1268 (1964).

[14] L. Vriens, Proc. Phys. Soc. (London) 89, 13 (1966).

[15] J. D. Garcia, Phys. Rev. 159, 39 (1967).

[16] R. Abrines, I. C. Percival, and N. A. Valentine, Proc. Phys. Soc. (London) 89, 515 (1966), give a statistical solution of the exact classical problem, but B_T is not specified in their work.

[17] These numbers with slightly different forms are given by Inokuti in Ref. 5, and they have been independently calculated and checked by the author.

[18] D. R. Bates and G. Griffing, Proc. Phys. Soc. (London) A66, 961 (1953). See also R. M. May, Phys. Letters 14, 98 (1965).

[19] G. Peach, Proc. Phys. Soc. (London) 85, 709 (1965).

PHYSICAL REVIEW VOLUME 177, NUMBER 1 5 JANUARY 1969

Vibrational Excitation in Ion-Molecule Collisions: H^+, $H_2{}^+$, He^+, N^+, Ne^+, and Electrons on N_2[†]

John H. Moore, Jr., and John P. Doering
Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

(Received 29 July 1968)

A study has been made of the relative band intensities of the $\Delta v = -1$ sequence of the $N_2{}^+$ first negative system excited by H^+, $H_2{}^+$, He^+, N^+, Ne^+, and electrons. Projectile ion laboratory velocities from 6×10^6 to 1.7×10^8 cm/sec (100 eV to 13.5 keV) were used. At ion velocities greater than 10^8 cm/sec, the relative band intensities were found to agree with those predicted by the Franck-Condon principle and found in excitation by 150-eV electrons. Below this velocity the relative population of higher ($v' > 0$) vibrational states increased monotonically. At the lowest velocity used, the populations of the $v' = 0$ and $v' = 1$ vibrational states of $N_2{}^+$ $B\,{}^2\Sigma_u{}^+$ were found to be equal within experimental error while the higher-state populations increased many orders of magnitude above those predicted by the Franck-Condon principle. The vibrational excitation was found to be solely dependent on the projectile ion's laboratory velocity and independent of its chemical identity. No vibrational excitation was observed in the N_2 second positive system excited under similar conditions. It is suggested that the excitation effects in the $N_2{}^+$ first negative system occur by a mechanism involving perturbation of the target molecule's vibrational wave functions by the projectile ion. Implications of these results for other collision studies as well as atmospheric phenomena are discussed.

INTRODUCTION

Experimental studies of vibrational excitation in ion-molecule collisions are of considerable importance since theory does not provide an adequate basis for the prediction of the vibrational energy distribution in the products of such interactions. The Franck-Condon principle, which is of great use in describing a wide variety of excitation and spectroscopic phenomena, is difficult to apply in the case of certain slow ion-molecule collisions where the molecular vibrational wave functions may be significantly distorted. This paper presents data we have obtained from experiments in which the products of collisions between a variety of atomic and molecular ions and N_2 have been studied spectroscopically to measure the vibrational energy distribution of the target after excitation.

It is known that in the case of electron excitation, the vibrational energy distribution of excited electronic states can certainly be well described by the Franck-Condon principle if the electron energy is greater than 100 eV.[1] In such a case, if the process involves excitation of a molecule which is initially in the ground electronic and vibrational states, $X(v''=0)$, to some excited electronic and vibrational state, $B(v'=i)$, the ratio of the population of the ith vibrational state of B to the population of the ground vibrational state of B is given by the ratio of the Franck-Condon factors for the two transitions $X(v''=0) \to B(v'=0)$ and $X(v''=0) \to B(v'=i)$:

$$N_i/N_0 = q_i^{X\to B}/q_0^{X\to B}. \tag{1}$$

If emissions are observed spectroscopically which correspond to transitions from state B to some lower electronic state A, the intensity of the emission band produced by the transition $B(v'=i) \rightarrow A(v''=i-\Delta v)$ is

$$I_{\mathrm{em}}(i,i-\Delta v)=K(N_i/\lambda^4_{i,\,i-\Delta v})\,|\bar{R}_e^{\,i,i-\Delta v}|^2\,q_{i,i-\Delta v}^{\;B\rightarrow A}\,, \tag{2}$$

where $\lambda_{i,\,i-\Delta v}$ is the wavelength of the emission, $q_{i,\,i-\Delta v}{}^{B\rightarrow A}$ is the Franck-Condon factor between states A and B, $\bar{R}_e{}^{i,\,i-\Delta v}$ is the average electronic transition moment for the transition, and K is a constant. Within a sequence ($\Delta v=\mathrm{const}$), $\bar{R}_e$ is nearly constant for a strong parallel band system such as the $N_2{}^+$ first negative system.[2,3] Hence, the ratio of the intensities of two bands in a sequence is

$$\frac{I(i,i-\Delta v)}{I(j,j-\Delta v)}=\frac{N_i}{N_j}\,\frac{q_{i,i-\Delta v}}{q_{j,j-\Delta v}}\left(\frac{\lambda_{j,j-\Delta v}}{\lambda_{i,i-\Delta v}}\right)^4 \tag{3}$$

This relation defines the "normal" intensity ratio as given by the Franck-Condon principle. A deviation of the intensity ratio from this normal value indicates an abnormal population of the vibrational states. N_i/N_0 would not be given by (1) if the target molecule were deformed in the collision so that the vibrational wave function was perturbed. In such a case, the Franck-Condon factors computed on the basis of the unperturbed wave functions would not apply, and abnormal relative band intensities would be observed.

Deviations from the normal, Franck-Condon, band-intensity ratios have been observed by a number of investigators who have found that in certain "slow" (projectile velocity $<10^8$ cm/sec) ion-molecule collisions the collision products are left in abnormally excited vibrational states. Abnormal vibrational band-intensity ratios have also occasionally been observed in auroral emissions suggesting an excitation mechanism involving slow ions.

Previous investigators have usually used nitrogen as a target molecule and have excited the gas with beams of ions. The vibrational energy distribution in the $\mathrm{N_2}^+\ B\,^2\Sigma$ and $\mathrm{N_2}\ C\,^3\pi$ states have been determined from spectroscopic studies of the $\mathrm{N_2}^+$ first negative and $\mathrm{N_2}$ second positive band systems. These two-band systems have been most extensively studied because of their ease of production and prominence in auroral emissions. Results of previous investigations have, however, not extended over a sufficient range of conditions to provide a complete picture of the process by which vibrational excitation occurs.

Several measurements have been made of the relative populations of the $v'=0$ and $v'=1$ levels of the $\mathrm{N_2}^+\ B\,^2\Sigma$ state excited by proton impact at energies above 10 keV. Philpot and Hughes[4] have bombarded nitrogen with 10–130-keV protons. Dufay *et al.*[5] extended these results to 0.6 MeV. Most recently Thomas *et al.*[6] studied the first negative system excited by 0.15–1.0-MeV protons. All of these results indicate that the ratio, N_i/N_0, is equal to that given by the ratio of the Franck-Condon factors connecting the N_2 ground state with the $N_2{}^+\ B\,^2\Sigma$ excited state. However, Fan[1] reported a normal band-intensity distribution in the first negative system excited by 450-keV He^+, 205-keV H^+, and 120-eV electrons but abnormal vibrational excitation by 150-keV He^+, 20-keV H^+, and 23-eV electrons.

Some experiments have been done with slower projectiles. Smyth and Arnott[7] report abnormal vibrational excitation in the $\mathrm{N_2}^+$ first negative and $\mathrm{N_2}$ second positive systems produced by 5-keV canal rays. Polyakova and Fogel'[8] found a normal intensity distribution in the first negative system for excitation by 30-keV H^+, 25-keV $\mathrm{H_2}^+$ and He^+, and 15-keV Ne^+. Sheridan and Clark's data[9] indicate some unusual vibrational enhancement in the first negative system excited by 15-keV Ne^+ and N^+ and about normal intensity ratios for 20 to 30-keV He^+, H^+, and D^+.

While it appears that protons with velocities greater than about 1.5×10^8 cm/sec (10 keV) do not produce any unusual vibrational enhancement in the first negative system, the effect of slower and heavier projectile ions is not clear. For this reason we wished to extend band-intensity measurements to the lowest-energy limits of our instrument. In this paper we present results of band-intensity measurements made on the first negative system and second positive system excited by H^+, $\mathrm{H_2}^+$, He^+, N^+, Ne^+, and electrons at energies of 100 eV to 13.5 keV.

EXPERIMENTAL

The apparatus used in this experiment has been described previously.[10] 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 by a Soa lens. The ions then enter a collision chamber which contains the target gas. Ion currents of 2 to 50 μA at energies of 100 eV to 13.5 keV were used for these experiments. The collision chamber is closely coupled to a 1.0-m Fastie-Ebert scanning monochromator. The relative transmission versus wavelength of the optical system was determined with a secondary standard which consisted of a MgO screen illuminated by a tungsten filament bulb powered by a regulated power supply. This secondary standard was calibrated against a tungsten-ribbon filament lamp that had been calibrated by the National Bureau of Standards. The total optical sensitivity varied less than 10% over the range 4140–4278 Å (the $\Delta v=-1$ sequence of the $\mathrm{N_2}^+$ first negative system) and changed by less than a factor of 3 over the range 3300–4800 Å. Since only band-envelope spectra were required, the spectrometer slits were opened to provide a 4–8 Å bandpass.

As we have described previously,[10] the $\mathrm{N_2}^+$ first negative system intensity was linear with pressure in our apparatus up to at least 20 μ. When making measurements, the relative intensity of each band was taken to be the height of the folded-over branch (the P branch in the case of the $\mathrm{N_2}^+$ first negative system) above the background. The background included some scattered light but consisted mostly of the unresolved rotational structure of overlapping bands. No attempt was made to obtain integrated band intensities. We have found previously[10] that excitation to high rotational states accompanies the production of the $B^2\Sigma$ state of N_2^+ by slow ion bombardment. This rotational excitation causes severe overlap of the P branch of each band on the corresponding R branch, and each band extends far enough into the violet to significantly overlap two or more of the shorter wavelength bands of the same sequence. Since each band head in a sequence contains about the same number of lines (23 in the first negative system), at the resolution used here the peak height of the band head is a good relative measure of the total band intensity.

RESULTS

A detailed study was made of the relative band intensities of the $\Delta v = -1$ sequence of the N_2^+ first negative system produced by bombarding nitrogen with H^+, H_2^+, He^+, N^+, Ne^+, and electrons over a range of projectile velocities from 6×10^6 to 1.7×10^8 cm/sec. The target gas pressure was maintained constant during each run at 2 to 6 μ. A typical set of spectra produced at several different projectile energies is illustrated in Fig. 1. The drastic change in the relative band intensities as a function of projectile ion energy is quite evident.

Spectra produced by each ion at energies from 100 eV to at least 10 keV were measured to determine the band-intensity ratios: $I(1,2)/I(0,1)$, $I(2,3)/I(0,1)$, $I(3,4)/I(0,1)$, and $I(0,1)/I(0,0)$. The last intensity ratio is the branching ratio and is given by

$$I(0,1)/I(0,0) = (A_{0,1}/A_{0,0})(\lambda_{0,0}/\lambda_{0,1}),$$

where $A_{i,j}$ is the transition probability for the

$$B^2\Sigma_u^+(v'=i) \rightarrow X^2\Sigma_g^+(v''=j)$$

transition of N_2^+. The branching ratio is a property of the emitting specie and is expected to be constant independent of the mode of excitation of the emitter. In these experiments, the branching ratio was found to be constant within experimental error over a wide range of excitation conditions (Fig. 2). $I(0,1)/I(0,0)$ was 0.31 ± 0.02 – in good agreement with previously reported experiments.[6] Using the transition probabilities computed by Pillow,[11] the theoretical branching ratio for these transitions is 0.31.

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 shown plotted against projectile ion laboratory velocity in Fig. 3. It is obvious that over the velocity range 6×10^6 to 1.7×10^8 cm/sec, the intensity ratios are functions solely of the ion velocity and, within experimental error, are independent of the nature of the projectile ion. As the projectile velocity is decreased below 10^8 cm/sec, the population of states with $v' > 0$ increases monotonically. Using Nicholl's computed values[12,13] for the

$$N_2\ X^1\Sigma_g^+ \rightarrow N_2^+\ B^2\Sigma_u^+$$

$$\text{and}\quad N_2^+\ B^2\Sigma_u^+ \rightarrow N_2^+\ X^2\Sigma_g^+$$

Franck-Condon factors, the predicted ratios for $I(1,2)/I(0,1)$, $I(2,3)/I(0,1)$, and $I(3,4)/I(0,1)$ are 0.138, 1.87×10^{-3}, and 2.01×10^{-5}, respectively. For the highest velocity projectile ions, the population of the $v' = 0$, 1, 2, and 3 upper vibrational states agrees with the distribution predicted by the computed Franck-Condon factors.

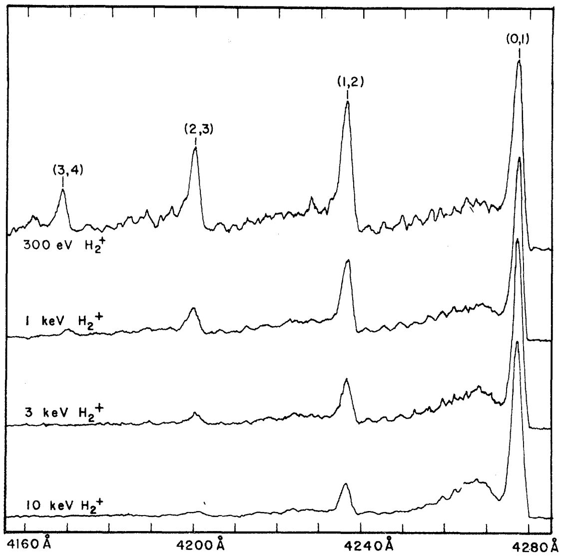

FIG. 1. Typical spectra of the N_2^+ first negative system $\Delta v = -1$ sequence excited by 300 eV, 1.0 keV, 3.0 keV, and 10.0-keV H_2^+ ions. The pressure in the collision chamber was 6 μ. The spectrometer slit width was 500 μ.

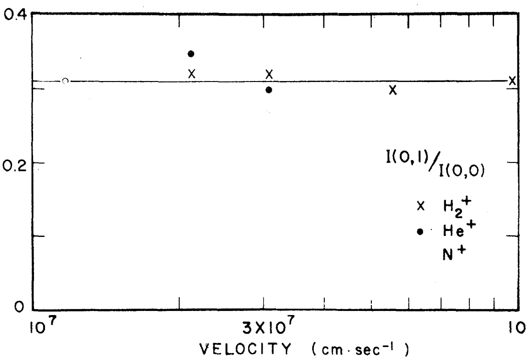

FIG. 2. The (0,1): (0,0) branching ratio of the N_2^+ first negative system measured from spectra excited by H_2^+, He^+, and N^+ at various laboratory velocities.

These theoretical values are indicated in Fig. 3 for comparison with the experimental data.

Spectra produced by 150-eV electrons on N_2 were also measured to determine the intensity ratios of the bands in the N_2^+ first negative system. The measured value of $I\,(1,2)/I(0,1)$ was 0.135 ± 0.01. This value is in excellent agreement with the theoretical value as well as with the measured value shown in Fig. 3 for excitation by ions with velocities greater than 10^8 cm/sec. The (2,3) and (3,4) bandheads were too weak to be detected in the electron-excited spectra so only an upper limit could be placed on the corresponding intensity ratios.

The N_2 second positive system was also investigated using the same conditions as for the N_2^+ first negative system. Spectra produced using H^+ and He^+ projectiles with velocities between 1.2×10^7 and 1.5×10^8 cm/sec were measured to determine the intensity ratio $I(1,3)/I(0,2)$. Within experimental error, this intensity ratio remained unchanged (Fig. 4). Because of the spin-selection rule, excitation of the upper state of the N_2 second positive system is not believed to proceed directly except in slow electron impact. These second positive system data are consistent with the idea that these emissions are produced largely by secondary electrons.

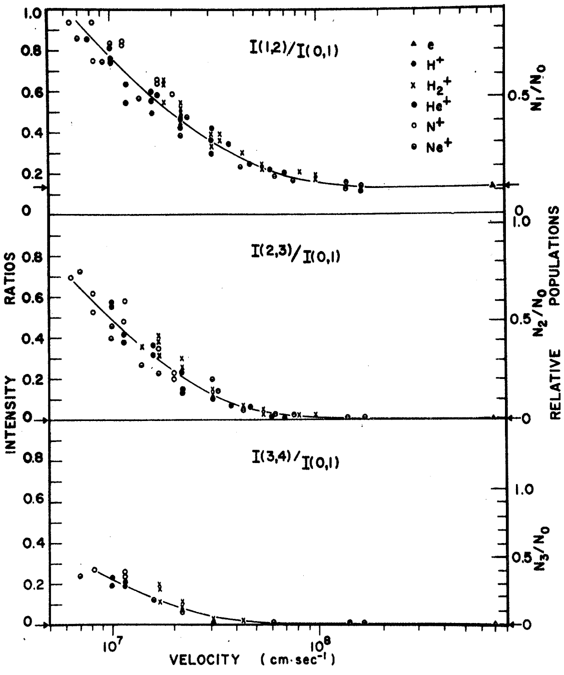

FIG. 3. Intensity ratios $I(1,2)/I(0,1)$, $I(2,3)/I(0,1)$, $I(3,4)/I(0,1)$ versus laboratory projectile ion velocity for the ${N_2}^+$ first negative system. The intensity ratios and relative populations of the upper vibrational states are given by the left- and right-hand axes, respectively. The relative populations were calculated using Eq. (3) and Nicholls's Franck-Condon factors (Ref. 13). The arrows on the vertical axes indicate the relative populations and corresponding intensity ratios predicted by the Franck-Condon principle.

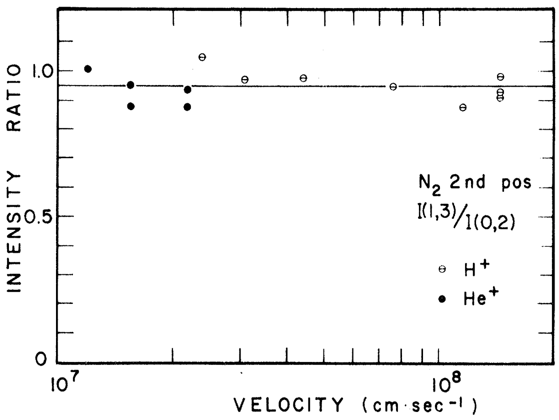

FIG. 4. Plot of the measured intensity ratio $I(1,3)/I(0,2)$ in the N_2 second positive system versus laboratory projectile ion velocity.

In all of the relative intensity measurements, the precision decreased with decreasing projectile ion energy. However, since the intensity ratios increased with decreasing energy, the relative precision remained constant at about ±15%. In many cases in Fig. 3, several measurements are presented for the same projectile ion velocity. These sets of measurements provide a direct indication of the reproducibility of the data. Since the calibration of the relative response of the optical system showed that only a small correction factor was needed to correct for the sensitivity variation over the range of the $\Delta v = -1$ sequence of the N_2^+ first negative system, we feel that the absolute accuracy of the data presented in Fig. 3 is of the order of ±20%. Although the $I(0,1)/I(0,0)$ branching-ratio measurement was considerably more precise, the larger correction factor necessary to reduce the data which arose because of the larger wavelength difference between the two emission bands caused the absolute accuracy of this measurement to be also in the range of ±20%.

CONCLUSIONS

The data we have presented here as well as most other available data show that for projectile ion laboratory velocities above about 10^8 cm/sec, the population of vibrational states in the products of ion-molecule collisions is constant and can be well described by the Franck-Condon principle. Below this velocity, however, the relative population of upper vibrational states increases monotonically. As has been suggested previously, it is possible for the electron cloud of the target molecule to be deformed in the field of a nearby projectile ion. This deformation of the electron cloud probably results in a perturbation of the vibrational wave function and a relaxation of the molecular force constant as has been discussed for collisions of H^+ with H_2 by Korobkin and Slawsky.[14] In spite of the vibrational perturbation, the transition may still be described by the Franck-Condon principle, but the calculations must be made using the deformed wave functions and not the unperturbed ones.

In this light, our results indicate that the extent of the perturbation increases as the projectile ion velocity decreases – that is, the perturbation increases as the time of interaction increases. For unperturbed wave functions, the Franck-Condon factors for the

$$N_2 X\,{}^1\Sigma(v=0) \to N_2^+ B\,{}^2\Sigma(v=0)$$

and $N_2 X\,{}^1\Sigma(v=0) \to N_2^+ B\,{}^2\Sigma(v=3)$

transitions differ by several orders of magnitude. At the lowest projectile ion velocities considered here, our data indicate that the vibrational wave functions have been altered sufficiently so that the probabilities for these two transitions are of the same order of magnitude.

Our results also indicate that the observed upper-state vibrational energy distribution is not a function of the nature of the projectile ion but solely a function of its laboratory velocity. This observation lends further support to the hypothesis that the observed vibrational energy distribution is produced by the deformation of the target molecule's electron cloud in the electric field of a nearby projectile ion.

In the measurement of emission cross sections, it is customary to present the (0, 0) band intensity as a function of the exciting ion's energy. Our results indicate that at low velocities, much of the emission in the N_2^+ first negative system is in the bands originating in vibrational states with $v' > 0$. As a result, the (0, 0) band-emission cross section may give a misleading idea of the total cross section for excitation of the $N_2^+ B\,{}^2\Sigma$ state. The observed drop in (0, 0) band-emission cross section at low energies[15,16] may be largely due to this effect of enhancement of higher vibrational state excitation rather than to an actual decrease in total excitation cross section for the $N_2^+ B\,{}^2\Sigma$ state.

In many cases, measured band-intensity ratios of the N_2^+ first negative system have been used to infer "vibrational temperatures." Our results indicate that such measurements should really be used to investigate the nature of the process which produced the excited state and that they contain little information about the temperature of the emitter. For example, relative band-intensity measurements of the first negative system in the aurora may be used to infer the velocity of the particles producing the emission. From measurements made during the great aurora of 10 February 1958, Clark and Belon[17] give average values for $I(1,3)/I(0,2)$ and $I(2,4)/I(0,2)$ of 1.3 and 0.6. Using the computed Franck-Condon factors of Nicholls[12,13] to determine N_1/N_0 and N_2/N_0, our data suggest that these intensity ratios would be produced by excitation by protons of velocities 1 and 2×10^7 cm/sec, respectively. The difference in these two velocities is probably caused by the accumulated effect of experimental errors. Such velocities correspond to excitation by 50–200-eV protons.

Our data on the N_2 second positive system do not show the vibrational enhancement that we observed for the N_2^+ first negative system. This is probably because of the indirect nature of the process which produces the second positive emissions. It is apparent that the relative band intensities of the second positive system would not provide useful information on the nature of the excitation process in the velocity range considered here.

Our experimental technique does not allow the direct production of the ground state of N_2^+ $(X\,{}^2\Sigma_g^+)$ to be studied. Available experimental data[6] indicate that for a variety of ions at different energies, the proportion of all charge-transfer collisions which result in the formation of an N_2^+ ion in the excited $B\,{}^2\Sigma$ state is generally between 1 and 10%. The effects we have observed, therefore, probably occur in less than 10% of the total number of ion-N_2 collisions. However, there seems to be no reason to expect that the same sort of vibrational enhancement will not occur for the production of N_2^+ in the ground electronic state. In view of the recent results of Schmeltekopf *et al.*[18,19] which have shown that the rates of certain atmospheric reactions are strongly dependent on the N_2 vibrational energy distribution, it is likely that the production of vibrational excitation by charge-transfer processes may be important in atmospheric processes.

[†] Work supported by a grant from the National Science Foundation.

[1] C. Y. Fan, Phys. Rev. 103, 1740 (1956).

[2] D. R. Bates, Proc. Roy. Soc. (London) 69A, 741 (1949).

[3] R. N. Zare, E. O. Larsson, and R. A. Berg, J. Mol. Spectr. 15, 117 (1965).

[4] J. L. Philpot and R. H. Hughes, Phys. Rev. 133, A107 (1964).

[5] M. Dufay, J. Desesquelles, M. Druetta, and M. Eidelsberg, Ann. Geophys. 22, 614 (1966).

[6] E. W. Thomas, G. D. Bent, and J. L. Edwards, Phys. Rev. 165, 32 (1968).

[7] H. D. Smyth and E. G. F. Arnott, Phys. Rev. 36, 1023 (1930).

[8] G. N. Polyakova and Ya. M. Fogel', Khim. Vys. Energ. 1, 103 (1967).

[9] J. R. Sheridan and K. C. Clark, Phys. Rev. 140, A1033 (1965).

[10] J. H. Moore, Jr., and J. P. Doering, Phys. Rev. 174, 178 (1968).

[11] M. E. Pillow, Proc. Phys. Soc. (London) A64, 772 (1951).

[12] R. W. Nicholls, J. Quant. Spectr. Radiative Transfer 2, 433 (1962).

[13] R. W. Nicholls, J. Res. Nat. Bur. Std. 65A, 451

(1961).

[14] I. Korobkin and Z. I. Slawsky, J. Chem. Phys. 37, 226 (1962).

[15] N. P. Carleton and T. R. Lawrence, Phys. Rev. 109, 1159 (1958).

[16] S. H. Neff and N. P. Carleton, Atomic Collision Processes, edited by M. R. C. McDowell (North-Holland Publishing Co., Amsterdam, 1964), p. 652.

[17] K. C. Clark and A. E. Belon, J. Atmospheric Terrest. Phys. 16, 205 (1959).

[18] A. L. Schmeltekopf, F. C. Fehsenfeld, G. I. Gilman, and E. E. Ferguson, Planetary Space Sci. 15, 401 (1967).

[19] A. L. Schmeltekopf, E. E. Ferguson, and F. C. Fehsenfeld, J. Chem. Phys. 48, 2966 (1968).

PHYSICAL REVIEW VOLUME 177, NUMBER 1 5 JANUARY 1969

Ejected Electron Distributions*

J. D. Garcia
Physics Department, University of Arizona, Tucson, Arizona 85721

(Received 29 July 1968)

Differential cross sections for production of secondary electrons in the ionization of atoms by charged-particle impact are examined in the classical binary-encounter approximation. General scalable expressions are given for both electron and heavy-charged-particle impact, and are compared with experimental and quantum treatments where possible. It is found that this formulation provides simple physical explanations of most features of ejected electron energy and velocity distributions. Proton-impact results are found to be in excellent agreement with experiment, and the electron-impact results converge to the Born results as expected.

I. INTRODUCTION

Previous work[1-5] has established that the classical binary-encounter approximation provides reasonable estimates of the total ionization cross sections of atoms and simple diatomic molecules, for almost all incident energies. This is not surprising, since the ionization process is one in which the correspondence principle can be applied.[6] Interest in the classical results is due in part to the ease of formulation, especially for systems such that even the Born approximation becomes intractable. Such a model, however, also enables us to extract more simply the physical explanations for the major features of the results,[2] if the model is quantitatively reliable.

The differential cross sections for secondary electron production provide a more sensitive test of the reliability and limitations of the classical binary-encounter approximation than do total cross sections. It is possible, for example, that the classical formulation approximates the total phase space reasonably, but does so by having fortuitous cancellations, so that the differentials would be incorrect. It is found, however, that at least the energy and speed distributions of the ejected electrons can be reasonably well predicted on this model.

In Sec. II, we present the formulation of the differential cross sections and discuss appropriate averages over bound electron properties. General, scalable expressions are obtained for both heavy particle and electron impact. Section III contains a comparison with existing experimental results. The discussion in Sec. IV includes some remarks on the application to general atomic systems. The proton results are found to be in good agreement with experiment. No experimental results are available for electron impact, but a comparison with Born results indicates the expected convergence for excited-state ionization.

II. ENERGY AND SPEED PROFILES

The binary-encounter approximation is based on the assumption that the dominant interaction is that between the incident charged particle and the atomic electrons.[1] It requires a knowledge of the differential cross section for the exchange of energy ΔE in the laboratory frame between the incident particle of mass m_1, charge Ze, and velocity $\vec{v}_1$, and the bound electron whose initial velocity is $\vec{v}_2$. The correct classical expression for this cross section, when averaged over all orientations of $\vec{v}_2$, for $m_1 \geqslant m_e$, is[7]

$$\frac{d\sigma^{\mathrm{eff}}}{d\Delta E} = \frac{\pi}{3}\,\frac{(Ze^2)^2}{(\Delta E)^3}\,\frac{3{v_2'}^2 + v_2^2}{v_1^2}\,, \quad 0 < \Delta E < b;$$

$$= \frac{\pi}{6}\,\frac{(Ze^2)^2}{(\Delta E)^3}\,\frac{(v_1 + v_1')^3 + (v_2 - v_2')^3}{v_1^2 v_2}\,,$$

$$b < \Delta E < a;$$