Formation of N_2^+ $B\,^2\Sigma_u^+$ and N_2 $C\,^3\Pi_u$ in collisions of H^+ and H with N_2†

John H. Birely
Chemistry and Physics Laboratory, The Aerospace Corporation, El Segundo, California 90045
(Received 25 February 1974)

The 200–500-nm radiation excited by collisions of beams of 1–25-keV H^+, D^+, H, and D with N_2 has been studied under thin-target conditions with a viewing geometry chosen to minimize polarization effects. For both ion and neutral impact, the N_2^+ ($B\,^2\Sigma_u^+$-$X\,^2\Sigma_g^+$) first negative ($1n$) bands are the most intense spectral features in this wavelength range. As expected from consideration of electron-spin conservation, the probability of excitation of the N_2 $C\,^3\Pi_u$-$B\,^3\Pi_g$ second positive ($2p$) bands by H or D impact greatly exceeds that for H^+ or D^+ bombardment. Relative emission cross sections for the (0, 0) bands of the $1n$ system at 391.4 nm and the $2p$ system at 337.1 nm were determined and made absolute via normalization to measurements reported at higher energies by previous workers. The relative vibrational population $P(v')$ for N_2 $C\,^3\Pi_u$ formed in 3–25-keV H and D impact is in good agreement with the prediction of a simple, Franck-Condon excitation mechanism; however, for N_2^+ $B\,^2\Sigma_u^+$ formed in collisions with 4–25-keV H and D, a dramatic enhancement in $P(v')$ for $v' > 0$ over the Franck-Condon values is observed at low projectile velocities. The higher-velocity onset and greater magnitude of this effect for H and D in comparison with that observed for H^+ and D^+ are in disagreement with the predictions of a modified Franck-Condon mechanism that allows for polarization of N_2 by the incident projectile. The measured values of $P(v')$ were used in conjunction with the (0, 0) band cross sections to derive total cross sections for formation of N_2^+ $B\,^2\Sigma_u^+$ and N_2 $C\,^3\Pi_u$. A maximum in the cross section for formation of N_2^+ $B\,^2\Sigma_u^+$ of 1.12×10^{-16} cm^2 at 10 keV was found for H^+ impact, while for H, the cross section for formation of this state rises steadily with increasing collision energy until reaching a nearly constant value of 3.4×10^{-17}cm^2 in the 15–25-keV range. The fraction of the total N_2^+ yield that is formed in the B state increases from about 0.03 to 0.08 in the energy range studied. For formation of N_2 $C\,^3\Pi_u$, the cross section has a maximum value of 2.2×10^{-17} cm^2 at 5 keV. At H-atom energies below 7 keV, exchange excitation of N_2 to the $C\,^3\Pi_u$ state is more probable than ionization to yield N_2^+ in the B state while, at higher energies, ionization to yield the B state is the more probable process. Comparison of our results with values calculated via the application of recently developed, semiempirical scaling relationships to electron impact cross-section data indicates that the latter approach yields a good prediction of the energy dependence and an acceptable prediction of the magnitude of the $C\,^3\Pi_u$ cross section for 1–100-keV H impact. The semiempirical approach also makes a good prediction of the cross section for formation of N_2^+ $B\,^2\Sigma_u^+$ in H^+ or H impact above 10 keV; however, primarily because of the lack of experimental data at lower energies, previous semiempirical predictions have overestimated the ionization contribution to the over-all N_2^+ $B\,^2\Sigma_u^+$ cross section.

I. INTRODUCTION

The interaction of precipitating protons with Earth's atmosphere results in the production of ions and electrons and in the emission of radiation. Most of the incoming particles at auroral altitudes have energies in the low-keV range, and, as a consequence of charge-changing collisions with ambient species, the majority of these are converted to atomic hydrogen. These fast neutral particles can undergo further collisions and, in many cases, collisions involving H atoms dominate the ionization and excitation processes.[1]

Heavy-particle collisions in the low-keV range present a formidable challenge to the theorist, and one of the factors that has limited the development of an adequate theoretical treatment of these events has been a lack of reliable experimental measurements. The availability of cross sections for H^+ and H collision processes will also aid in the refinement[2] of recently developed scaling laws[3] used to predict these quantities from electron impact measurements. In addition, it is anticipated that once cross sections are available for a number of stable target species, it will be possible to make useful estimates of cross sections for collisions of H and H^+ with unstable species, such as atomic oxygen, that are difficult to study in the laboratory.

References 1 and 4 review the substantial body of information on excitation of the (0, 0) band of the N_2^+ $B\,^2\Sigma_u^+$-$X\,^2\Sigma_g^+$ first negative ($1n$) system in high energy H^+ impact; however, below 25 keV, far less work has been carried out, and there exists a discrepancy between the energy dependence of the cross section determined by previous workers below 10 keV.[5-7] For H impact there has been only one previous study of excitation of the 1n (0, 0) band at energies less than 10 kev,[6] and no data are available below 10 keV for excitation of the (0, 0) band of the N_2 $C\,{}^3\Pi_u$-$B\,{}^3\Pi_g$ second positive (2p) system.

Previous studies of the excitation of vibrational levels of $N_2{}^+$ $B\,{}^2\Sigma_u^+$ with $v' > 0$ have been carried out primarily for impact of H^+ and other ions.[4,8] It has been found that interesting deviations[8,9] from the $N_2{}^+$ $B\,{}^2\Sigma_u^+$ vibrational distribution predicted from a simple Franck-Condon excitation mechanism occur at collision velocities $\lesssim 10^8$ cm/sec, which for a proton corresponds to a kinetic energy of 5 keV. Although it is of interest to see whether these same deviations occur in neutral particle impact and in nonionizing collisions, there have been no previous determinations of the vibrational distribution of $N_2{}^+$ $B\,{}^2\Sigma_u^+$ and N_2 $C\,{}^3\Pi_u$ produced in H-atom impact on N_2. Cross sections for H-atom excitation of 1n bands emitted from $N_2{}^+B\,{}^2\Sigma_u^+$ with both $v' = 0$ and 1 have, however, been reported at energies in the ranges 20–100 keV and 60–120 keV in Refs. 10 and 11, respectively.

In this paper cross sections are reported for excitation of the (0, 0) bands of the $N_2{}^+$ 1n and the N_2 2p systems by 1.5–25-keV protons and hydrogen atoms. From these results, cross sections for formation of the $v' = 0$ levels of the $B\,{}^2\Sigma_u^+$ state of $N_2{}^+$ and the $C\,{}^3\Pi_u$ state of N_2 have been determined. Vibrational distributions of $N_2{}^+$ $B\,{}^2\Sigma_u^+$ and $N_2\,C\,{}^3\Pi_u$ and over-all cross sections for formation of these states have been measured for impact of 1–25-keV H^+, D^+, H, and D.[12] The vibrational distribution of N_2 $C\,{}^3\Pi_u$ excited by either H or D is in good agreement over this energy range with that predicted using Franck-Condon factors for the $X\,{}^1\Sigma_g^+$-$C\,{}^3\Pi_u$ transition of an isolated nitrogen molecule; however, a dramatic enhancement of the relative vibrational population of $N_2{}^+$ $B\,{}^2\Sigma_u^+$ with $v' > 0$ is observed at low velocity for each of the projectiles. The onset of this effect occurs at higher velocity for H and D impact than for H^+ and D^+ bombardment. For a given projectile speed, the deviation from the Franck-Condon mechanism is more pronounced for the neutral projectiles than for ion impact.

We have used our data to assess the accuracy of cross sections for formation of $N_2{}^+$ $B\,{}^2\Sigma_u^+$ and $N_2\,C\,{}^3\Pi_u$ in hydrogen impact obtained by the application of scaling relationships to electron-impact cross sections for production of these states. The energy dependence of the results for the C state of N_2 are shown to be in remarkably good agreement with that of our measurements over the entire 15–25-keV interval. Above ~10 keV, the scaling approach also predicts well the energy dependence of the $N_2{}^+$ B state production cross section; however, the measured values decrease more rapidly than those predicted by the analytic model as the collision energy is reduced below this value.

II. EXPERIMENTAL

Figure 1 gives a schematic view of the apparatus employed in these studies. The techniques used to prepare and detect H^+ and H beams and bring them into collision with N_2 under thin-target conditions have been described in detail elsewhere.[13] A 1–5-keV H^+ beam is extracted from an rf ion source, mass analyzed, focused, and accelerated to a final energy as high as 25 keV. Charge-exchange neutralization was employed when an atomic hydrogen beam was required. The beam monitor was operated in either a Faraday cup mode to detect H^+ or in a secondary-electron-emission mode to detect H and H^+. In some of the experiments, deuterium was introduced into the rf ion source to produce a primary D^+ beam. The procedures used to prepare and detect D^+ and D beams were identical to those employed for H^+ and H, respectively. Nitrogen (Airco prepurified grade, stated purity 99.998%) was taken from a cylinder and used without further purification.

A. Spectroscopic arrangement

A portion of the light emitted along the beam track at a point 2.2 cm into the scattering chamber was focused onto the entrance slit of a step-scanning, 0.3-m monochromator with a 12.7-cm-focal-length lens. All of the transmitting elements in the optical system were fabricated from Spectrosil quartz or the equivalent. A 2.4-cm collimating diaphragm matched the *f* number of the lens to that

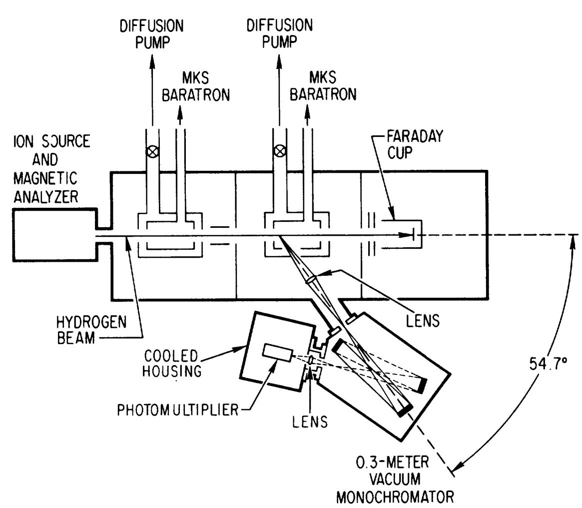

FIG. 1. Schematic diagram of the spectroscopic arrangement.

of the monochromator. The distance from the beam to the entrance slit was 50.8 cm, and the lens was nominally equidistant between them. Not shown in Fig. 1 is a light shield that prevented stray radiation from entering the optics. The monochromator viewed the interaction region in an optical orientation chosen to minimize the effects of polarization on the measurements.[14] In order to minimize the effects of polarization of electric dipole radiation, the observations were made with a nominal angle of 54.7° between the entrance optics and the projectile beam direction.

In order to minimize the effects of instrumental polarization on the cross section determinations, the monochromator was rotated so that the long axis of the entrance slit made an angle of 45° with respect to the plane containing the projectile beam and the entrance optical axis. During the cross-section measurements, the height of the slits was 1 cm, and equal entrance and exit slit widths were always employed. Some of the vibrational distribution measurements were performed with the long axis of the entrance slit in the plane of the projectile beam. In the latter configuration, the height of both slits was 2 cm.

The monochromator was equipped with a 2400-groove/mm plane grating blazed at 300 nm, giving a reciprocal dispersion of 1.33 nm/mm. Analyzed light emerging from the exit slit was focused onto the cathode of a photomultiplier. Survey spectra were obtained with an EMI 9558QB tube chilled to −25 °C, and cross-section measurements were performed with an EMI 6256S tube operated at −74 °C.

B. Relative spectral calibration

The relative spectral response of the detection system in the 210–471-nm interval was determined using the molecular-branching-ratio technique,[15,16] with $N_2^+\ B\,^2\Sigma_u^+$, $N_2\ C\,^3\Pi_u$, $CO^+\ B\,^2\Sigma^+$, and NO $A\,^2\Sigma^+$ as the emitting species. The total count rate $S_{v'v''}$ for the (v', v'') vibrational band emitted at wavelength $\lambda_{v'v''}$ by molecules making a transition from an upper electronic energy level (X_2, v') to a lower electronic energy level (X_1, v'') is given by

$$S_{v'v''} = GQ(\lambda_{v'v''})N_{v'}A_{v'v''} \ . \tag{1}$$

In this expression, G is a geometrical collection factor, $Q(\lambda_{v'v''})$ is the spectral response of the collection-detection system at wavelength $\lambda_{v'v''}$, $N_{v'}$ is the density of molecules in the (X_2, v') level, and $A_{v'v''}$ is the transition probability for the (v', v'') band. The relative values of $S_{v'v''}$ in a v'' progression are related to the relative values of the spectral response as

$$Q(\lambda_{v'v''_i})/Q(\lambda_{v'v''_j}) = (S_{v'v''_i}/S_{v'v''_j})(A_{v'v''_j}/A_{v'v''_i}) \ . \tag{2}$$

The transition probability is in turn defined as

$$A_{v'v''} = q_{v'v''}\nu^3_{v'v''}\, R_e^2(\bar{r}_{v'v''}) , \tag{3}$$

where $q_{v'v''}$ is the Franck-Condon factor, $\nu_{v'v''}$ is the wave number, $R_e(\bar{r}_{v'v''})$ is the electronic transition moment, and $\bar{r}_{v'v''}$ is the r centroid of the (v', v'') transition. Using Franck-Condon factors and r centroids given by Albritton *et al.*[17] and the electronic transition moment reported by Brown and Landshoff,[18] values of $A_{v'v''}$ for the N_2^+ 1n system were calculated.

For the N_2 2p system, Franck-Condon factors, obtained by numerical integration[19] over the RKR potential curves of Benesch *et al.*,[20] were used in conjunction with the transition moment of Keck *et al.*,[21] renormalized to reflect the results of Hesser,[22] to calculate transition probabilities.

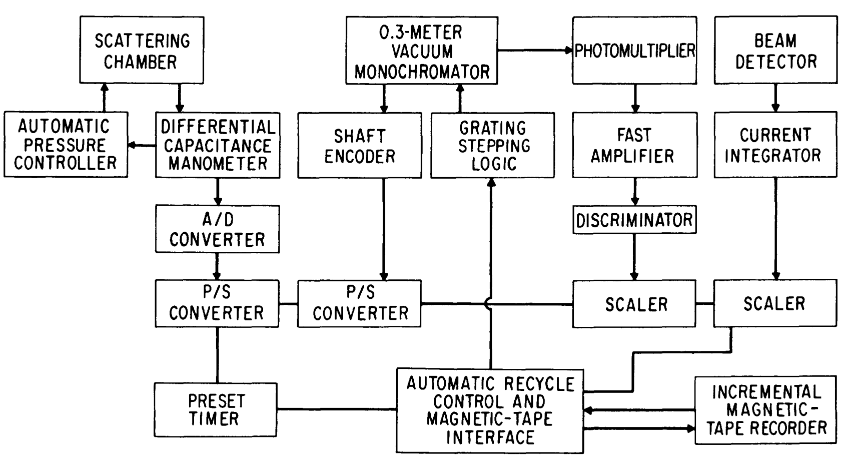

FIG. 2. Schematic diagram of the automatic data acquisition system.

Values of the transition probabilities[17] for the NO $A\,{}^2\Sigma^+$-$X\,{}^2\Pi$ γ-band system were taken from Poland and Broida.[23] Relative values of $A_{v'v''}$ for the CO^+ $\times B\,{}^2\Sigma^+$-$X\,{}^2\Sigma^+$ first negative (1*n*) system, calculated under the assumption of the independence of the electronic transition moment on r centroid from Franck-Condon factors obtained by numerical integration over RKR potential curves constructed using molecular constants for CO^+ given by Krupenie,[24] were kindly provided by Cartwright.[25] The range of wavelength over which this relative calibration was performed was 200–280 nm for NO γ, 200–270 nm for CO^+ 1*n*, 275–415 nm for N_2 2*p*, and 350–471 nm for the N_2^+ 1*n* system. Values of $S_{v'v''}$ were determined by integration of data obtained with the apparatus operated in the survey mode described below.

C. Data acquisition

A block diagram of the data acquisition system employed in these experiments is shown in Fig. 2. Beam currents were measured with a digital charge integrator, the output pulses from which were counted with a scaler. The dc output from the differential capacitance manometer connected to the scattering chamber was digitized with a digital voltmeter. Wavelengths were determined from the output of a shaft encoder that sensed the position of the grating to a least count of 0.025 nm. Output pulses from the photomultiplier were amplified with a 200-MHz amplifier and fed through a 200-MHz discriminator into a scaler. The digitized outputs from these devices were recorded on magnetic tape or punched paper tape for computer analysis and plotting.

III. RESULTS

Spectra in the 300–500-nm wavelength range excited in collisions of H^+ and H with N_2 are given in Fig. 3. These results were obtained in a *survey mode*, in which the grating was positioned at a fixed wavelength, and counting was carried out until a preset number of photons had been detected or a preset amount of time had elapsed. The grating was then advanced to the next wavelength in a step size small compared with the bandpass employed. In Fig. 3, the spectra have been corrected for drifts in the beam current, for the small fluctuation in pressure that occurred over the course of the scans, and for the variation of spectral sensitivity with wavelength.

For both H^+ and H impact, the N_2^+ 1*n* bands are the most intense spectral features, and in Fig. 3 the strong (0, 0) bands of this system have been truncated to allow the weaker bands to be displayed. As expected from consideration of electron spin conservation, the probability of excitation of the N_2 $C\,{}^3\Pi_u$-$B\,{}^3\Pi_g$ 2*p* bands by *H* impact greatly exceeds that for H^+ bombardment. Also observed are the weak, Doppler-shifted beta (H_β), gamma (H_γ) and delta (H_δ) Balmer lines of atomic hydrogen; however, the experimental configuration that we have employed is not suitable for measuring H_β, H_γ, or H_δ cross sections.[1] Except for the N_2 (2*p*) (2, 0) and (3, 1) bands at 279.7 and 296.2 nm that are excited by H impact, there are no prominent

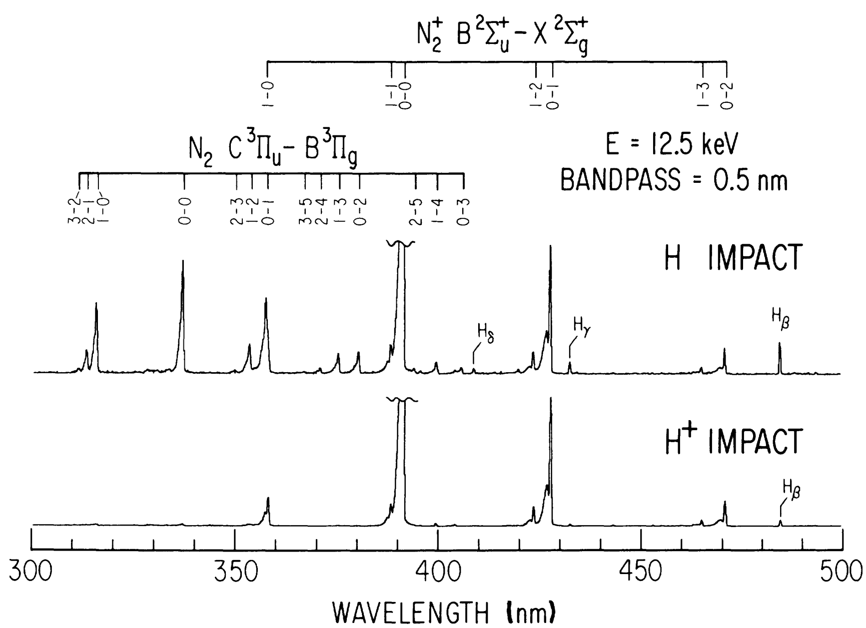

FIG. 3. Emission spectra in the 300–500-nm interval excited by impact of 12.5-keV H^+ and H on N_2: 0.5-nm bandwidth, 0.12-nm step size, EMI 9558QB photomultiplier.

emissions in the 200–300-nm range. For H-atom impact, weakly excited v'' progressions originating from $v'=0$ in the $N_2\ D\ ^3\Sigma_u^+ - B\ ^3\Pi_g$ fourth positive and $E\ ^3\Sigma_g^+ - A\ ^3\Sigma_u^+$ Herman-Kaplan systems are observed.

Prior to the determination of emission cross sections for N_2 and N_2^+ features, preliminary experiments were carried out to demonstrate that our results are free from potential systematic errors.[4] At several energies spanning the 1.5–25-keV range, the dependence of the count rate for the $1n$ (0, 0) and $2p$ (0, 0) bands on N_2 pressure was investigated to determine the scattering density below which one could ignore effects owing to contamination of the parent beam by charge-changing collisions or to excitation by secondary electrons released in ionization of N_2 and stripping of H. With the N_2 pressure maintained below that at which these effects are important, it was then demonstrated that the intensity in these two bands varied linearly with H^+ or H beam current. It was also demonstrated that the results for H-atom impact are independent of both the gas used to neutralize the H^+ beam and the strength of the electric field used to deflect unneutralized H^+ and quench metastable excited H atoms.

Cross section measurements were then carried out with the apparatus operating in the *integration mode*, in which the total number of counts $S_{v'v''}$ from the band of interest was determined by advancing the grating between counting intervals in wavelength steps equal to the bandpass of the monochromator. Small corrections (≲2%) for scattered light were made by scanning to adjacent wavelengths which were free of emission features and measuring the count rate under the same beam and scattering chamber conditions employed in the cross section measurement.

Figure 4 gives our determination of the cross sections $\sigma_p(391.4)$ and $\sigma_a(391.4)$ for emission of the 391.4-nm N_2^+ $1n$ (0, 0) band in H^+ and H impact, respectively. All of the cross sections reported in this paper have been made absolute by normalization to the values of $\sigma_p(391.4)$ reported by de Heer and Aarts[7] in the 10–25-keV range, as follows.

Equation (1) can be rewritten as

$$S_{v'v''} = (\omega_d l/4\pi) Q(\lambda_{v'v''}) I_b N_t\, \sigma(\lambda_{v'v''}) \quad (4)$$

In this expression, ω_d is the solid angle subtended by the detector, l is the length of beam track from which photons are detected, I_b is the beam flux in particles/sec, N_t is the number density of target particles, and $\sigma(\lambda_{v'v''})$ is the cross section for production of the (v', v'') transition. Using our measured value of S_{00}, I_{H^+}, and N_{N_2} in conjunction with the value of $\sigma_p(391.4)$ reported by de Heer and Aarts, the factor $\omega_d l Q(391.4)$ was determined. Cross sections for features at other wavelengths λ were then made absolute through the use of this factor and the appropriate value of the relative spectral response function $Q(\lambda)/Q(391.4)$ determined by the molecular branching ratio method.

Also shown in Fig. 4 are the relative results of McNeal and Clark[6] normalized to the work of de Heer and Aarts[7] in the 10–25-keV range. At impact energies below 5 keV, the discrepancy between the latter two determinations exceeds the sum of the stated relative errors in the respective works. The results of our determination of $\sigma_p(391.4)$ are seen to lie in between the results obtained in the previous studies; however, our values of $\sigma_a(391.4)$ are in excellent agreement over the entire 1–25-keV range with those reported by McNeal and Clark. Our results were obtained in the same atomic beam apparatus as was employed by McNeal and Clark, the major difference between the two experiments being their use of a photometer to isolate and detect the N_2^+ $1n$ (0, 0) band; however, a detailed comparison of the two experiments shows that a number of other modifications in equipment and procedure have been incorporated into our work that also yield improved accuracy (especially at low energy). Therefore,

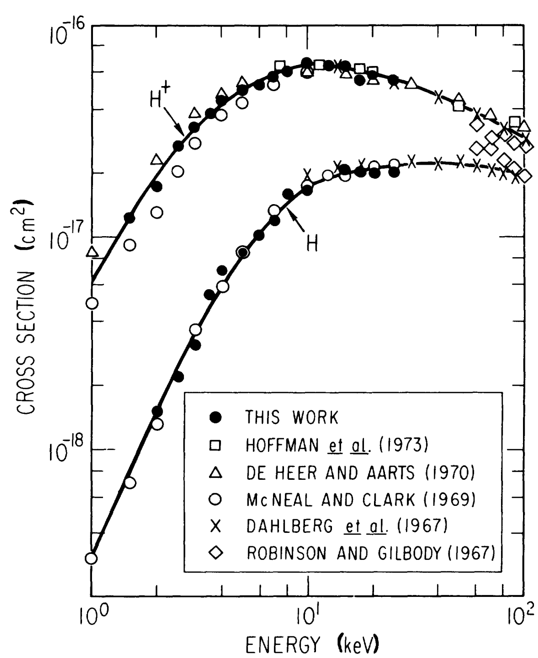

FIG. 4. Cross section for emission of the 391.4-nm $N_2^+\ B\ ^2\Sigma_u^+ - X\ ^2\Sigma_g^+$ (0, 0) band in collisions of 1–100-keV H^+ and H with N_2. Data are from Hoffman *et al.* (Ref. 26), de Heer and Aarts (Ref. 7), McNeal and Clark (Ref. 6), Dahlberg *et al.* (Ref. 10), and Robinson and Gilbody (Ref. 11).

the results for $\sigma(391.4)$ obtained in this work are considered to supercede those of Clark and McNeal. The agreement between the energy dependence of our results for $\sigma_p(391.4)$ and that of de Heer and Aarts is satisfactory, and it is suggested that the mean of our values and theirs be adopted at low energies.

Figure 5 gives our determination of $\sigma_a(337.1)$ for emission of the N_2 2*p* (0, 0) band at 337.1 nm. Attempts to measure the cross section $\sigma_p(337.1)$ for emission of this band by H^+ impact proved unsuccessful. Because of the very small value of this quantity, secondary effects were the dominant source of N_2 second positive emission at pressures high enough to see a significant signal in H^+ impact on N_2. Above 10 keV, where comparisons can be made, the agreement in magnitude of our results and the previous determination of Hoffman *et al.*[26] provides a useful test of the precision of the spectral calibrations in these two studies; however, the good agreement with the magnitude of $\sigma_a(337.1)$ reported by Dahlberg *et al.* is illusory, since the magnitude of $\sigma_p(391.4)$ from Ref. 27, to which they normalized their results, is in poor agreement with those in Fig. 4. Also, as discussed in Ref. 26, Dahlberg *et al.* did not take full account of the wavelength dependence of the sensitivity of their optical system.

The *relative* error in $\sigma_p(391.4)$ is estimated to be $\leq 7\%$ and includes contributions of $\leq 5\%$ from measurements of the beam current and photomultiplier counts and $\leq 2\%$ from nonlinearities in measurement of the N_2 pressure in the scattering chamber. Uncertainties in the secondary electron emission coefficient used to calculate the H beam flux introduce an additional relative error of about 10% in $\sigma_a(391.4)$. The largest source of error in the *absolute* value of the cross sections is the calibration of the photon detection system used in the work to which our results were normalized, although at low energies uncertainties in the energy of the parent beam could lead to errors in a rapidly changing cross section.

In applying Eq. (4), it is assumed that our results are unaffected by polarization, cascade, and collisional quenching effects.[4] The spectroscopic arrangement employed in the cross section measurements renders polarization effects unimportant. There are no known states of $N_2{}^+$ that populate the $B\,^2\Sigma_u^+$ state by cascade. Furthermore, the radiative lifetime of $N_2{}^+B\,^2\Sigma_u^+$ is about 6×10^{-8} sec,[28(a)] and, using the measured values of the cross section for collisional quenching of $N_2{}^+\ B\,^2\Sigma_u^+$ by N_2,[28] the time between quenching collisions at a pressure of 10^{-3} Torr is about 6×10^{-5} sec; therefore, the molecule will radiate very near its point of formation, and collisional quenching can be ignored.

Similar arguments based on measured values of the radiative lifetime of the *C* state of N_2,[28(a)] and the cross section for quenching of this state by N_2[29] can be used to demonstrate that collisional quenching of the N_2 2*p* system can be ignored under the conditions of our measurements. A small correction for population of $N_2\ C\,^3\Pi_u$ by cascade transitions[30] from the metastable $E\,^3\Sigma_g^+$ state is required; however, based on the very weak intensity of the

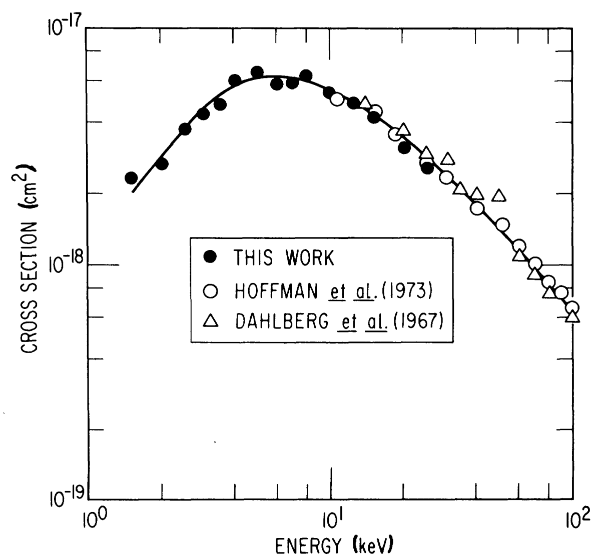

FIG. 5. Cross section for emission of the 337.1-nm $N_2\ C\,^3\Pi_u$–$B\,^3\Pi_g$ (0, 0) band in collisions of 2–100-keV H with N_2. Data are from Hoffman *et al.* (Ref. 26) and Dahlberg *et al.* (Ref. 10).

TABLE I. Cross sections in units of 10^{-17} cm² for formation of the $v'=0$ level of $N_2^+B\,^2\Sigma_u^+$ and $N_2\ C\,^3\Pi_u$ in collisions of 1.5–25-keV H^+ and H with N_2.

Energy (keV)	$N_2{}^+B\,^2\Sigma_u^+$ σ_p $(v'=0)$	$N_2{}^+B\,^2\Sigma_u^+$ σ_a $(v'=0)$	$N_2\ C\,^3\Pi_u$ σ_a $(v'=0)$
1.5	1.78	0.19	0.45
2.0	2.5	0.22	0.51
2.5	4.0	0.31	0.72
3.0	4.7	0.45	0.83
3.5	5.4	0.78	0.89
4.0	6.7	1.07	1.17
5.0	7.2	1.24	1.24
6.0	7.6	1.47	1.09
7.0	8.4	1.74	1.12
8.0	8.8	2.3	1.21
10.0	9.7	2.4	1.04
12.5	9.3	2.8	0.92
15	9.3	2.9	0.80
17.5	7.9	2.9	0.60
20	8.2	3.0	0.62
25	7.9	2.8	0.50

forbidden $E\,^3\Sigma_g^+$-$A\,^3\Sigma_u^+$ Herman-Kaplan bands observed here and the results of Freund,[31] this correction is estimated to be only a few percent.

Having demonstrated the absence of polarization, cascade, and collisional quenching effects, the cross section $\sigma(v')$ for formation of an electronically excited species in vibrational level v' can be calculated from the cross section $\sigma(\lambda_{v',v''})$ through the relationship

$$\sigma(v') = \sigma(\lambda_{v',v''})/R_{v'v''}\,, \tag{5}$$

where the branching ratio $R_{v'v''}$ is related to the transition probabilities as

$$R_{v'v''} = A_{v'v''}\Big/ \sum_v A_{v'v}\,. \tag{6}$$

Using transition probabilities discussed in Sec. II, the branching ratio R_{00} was calculated to be 0.70 and 0.52 for the 1*n* and 2*p* systems, respectively. These branching ratios and the data in Figs. 4 and 5 were used to calculate the cross sections $\sigma(v'=0)$ for collisional formation of the $v'=0$ levels of $N_2^+ \times B\,^2\Sigma_u^+$ and N_2 $C\,^3\Pi_u$ given in Table I.

The total cross sections $\sigma(B\,^2\Sigma_u^+)$ and $\sigma(C\,^3\Pi_u)$ for formation of N_2^+ in the B state and N_2 in the C state can be calculated from the values of $\sigma(v'=0)$ given in Table I if the relative vibrational probability $P(v'=0) = \sigma(v'=0)/\sum_v \sigma(v)$ for each of these states is known. For a number of excitation processes including heavy particle and electron impact,[8,32] the vibrational distribution within an electronically excited state can be accurately calculated as

$$P_{FC}(v') = q^{ex}_{v',0}\Big/\sum_v q^{ex}_{v,0}\,, \tag{7}$$

where $q^{ex}_{v',0}$ is the Franck-Condon factor for excitation of an isolated target molecule in its ground state with $v=0$ to the v' level of the excited state. This relationship has been shown to work well in predicting the N_2^+ B state vibrational distribution for ion impact at relative collision velocities above ~10^8 cm/sec; however, at lower velocities, deviations from this "isolated Franck-Condon" (IFC) distribution have been observed.[8,9,33]

In order to determine $\sigma(B\,^2\Sigma_u^+)$ and $\sigma(C\,^3\Pi_u)$, and to see if the isolated FC mechanism is also applicable to excitation in H and D impact, a determination of the vibrational population of N_2^+ $B\,^2\Sigma_u^+$ was carried out by integration of scans over the 415–430-nm $\Delta v = -1$ sequence of the 1*n* system with the spectrometer operating in the *survey mode*. Figure 6 indicates the typical changes that occur in this sequence as the projectile velocity is decreased and as a switch is made from ionic to neutral particle impact. For impact of all of the projectiles that we used, the intensity of the (1, 2)

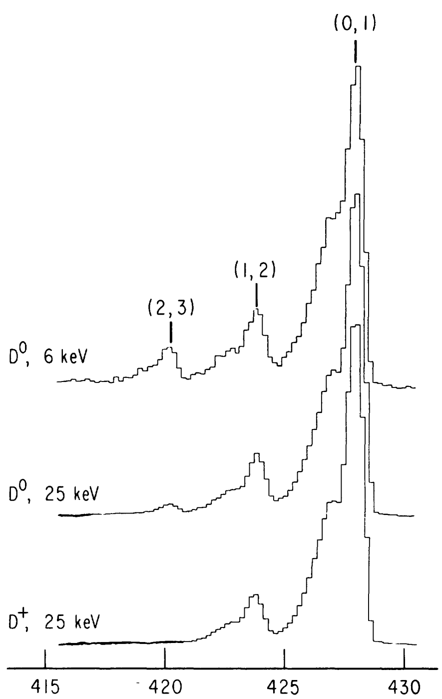

FIG. 6. Energy and projectile dependence of the $\Delta v = -1$ sequence of the N_2^+ $B\,^2\Sigma_u^+$-$X\,^2\Sigma_g^+$ first negative band system. The data were taken with 0.8-nm bandwidth and 0.25-nm step size, and the scans are normalized to equal heights of the (0, 1) band.

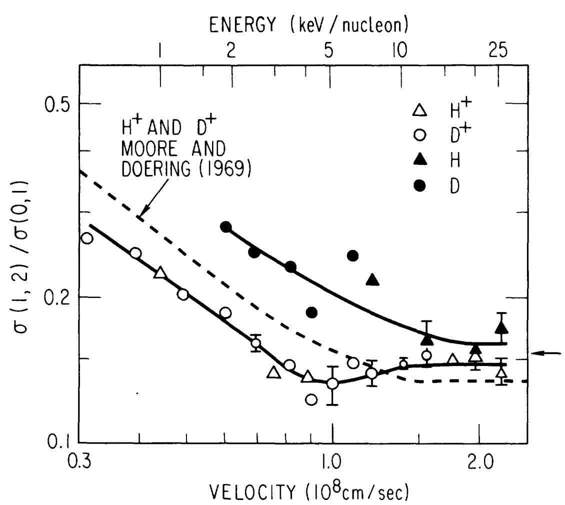

FIG. 7. Ratio of cross sections for excitation of the N_2^+ $B^2\Sigma_u^+ - X^2\Sigma_g^+$ (1, 2) and (0, 1) bands in collisions of 1–25-keV H^+, D^+, and H with N_2. Error bars indicate the standard deviation in the ratios for the relative velocities at which more than one determination was made. The arrow indicates the ratio calculated for a simple Franck-Condon mechanism as described in the text. Data for ion impact from Moore and Doering (Ref. 8) are shown by a dashed line.

TABLE II. Total cross sections in units of 10^{-17} cm^2 for formation of $N_2{}^+B\,^2\Sigma_u^+$ and $N_2\,C\,^3\Pi_u$ in collisions of 1.5–25-keV H^+ and H and N_2.

Energy (keV)	$N_2{}^+B\,^2\Sigma_u^+$ $P_p\ (v'=0)$	$\sigma_p\ (B\,^2\Sigma_u^+)$	$P_a\ (v'=0)$	$\sigma_a\ (B\,^2\Sigma_u^+)$	$N_2\,C\,^3\Pi_u$ $\sigma_a\ (C\,^3\Pi_u)$
1.5	0.83	2.2	0.64	0.30	0.88
2.0	0.84	3.0	0.67	0.33	1.00
2.5	0.84	4.8	0.71	0.44	1.41
3.0	0.86	5.5	0.73	0.62	1.63
3.5	0.86	6.3	0.74	1.05	1.75
4.0	0.87	7.7	0.76	1.41	2.3
5.0	0.87	8.3	0.77	1.61	2.4
6.0	0.87	8.7	0.78	1.88	2.1
7.0	0.87	9.7	0.79	2.2	2.2
8.0	0.87	10.1	0.80	2.9	2.4
10.0	0.86	11.2	0.82	2.9	2.0
12.5	0.86	10.8	0.83	3.4	1.80
15	0.86	10.8	0.84	3.5	1.57
17.5	0.86	9.2	0.84	3.5	1.18
20	0.86	9.5	0.85	3.5	1.22
25	0.86	9.2	0.85	3.3	0.98

band increases relative to that of the (0, 1) band as the relative velocity is decreased below a specified value; however, only for H and D impact does the intensity of the (2, 3) 1*n* band become significant. This shift in the relative intensities of the members of the $\Delta v=-1$ sequence is in direct contradiction to the prediction of the IFC mechanism.

Figure 7 gives the cross section ratios $\sigma(1,2)/\sigma(0,1)$ from which $P(v')$ for $N_2{}^+\ B\,^2\Sigma_u^+$ was determined. The solid symbols represent the first determination of this quantity for neutral hydrogen impact on N_2. These data are plotted as a function of relative velocity, since previous studies for ion impact have shown this to be the relevant scaling parameter. As a smooth curve can be drawn through the H and D points, this also appears to be a good scaling procedure for neutral particle impact. For the velocities at which more than one determination of $\sigma(1,2)/\sigma(0,1)$ was carried out, our results were reproducible to better than the absolute uncertainty (±20% at 3×10^7 cm/sec; ±10% at 2×10^8 cm/sec) in this ratio. At all energies, the value of the $\sigma(1,2)/\sigma(0,1)$ ratio for neutral impact exceeds that for ion impact; however, at the highest velocities studied in our apparatus, the magnitude of this ratio is in satisfactory agreement with the value of 0.154 calculated for the IFC mechanism. For ion impact, the magnitude and energy dependence of the enhancement of the ratio $\sigma(1,2)/\sigma(0,1)$ above the IFC value at collision velocities $\leq 10^8$ cm/sec are in acceptable agreement with the earlier work of Moore and Doering,[8] who quoted an absolute uncertainty of ≈ ±20% in their value of this ratio. Our results demonstrate that, for neutral particle impact, the onset of the enhancement of the relative values of $P(v')$ for $v'\geq 1$ occurs at a higher velocity and the enhancement is more pronounced than for ion impact.

The values of $P_p(v'=0)$ and $\sigma_p(B\,^2\Sigma_u^+)$ shown in Table II were determined from the data in Fig. 7 under the assumption that the population of $N_2{}^+$ $B^2\Sigma_u^+$ with $v'>1$ can be ignored for H^+ and D^+ impact. From our work and that of Moore and Doering, this

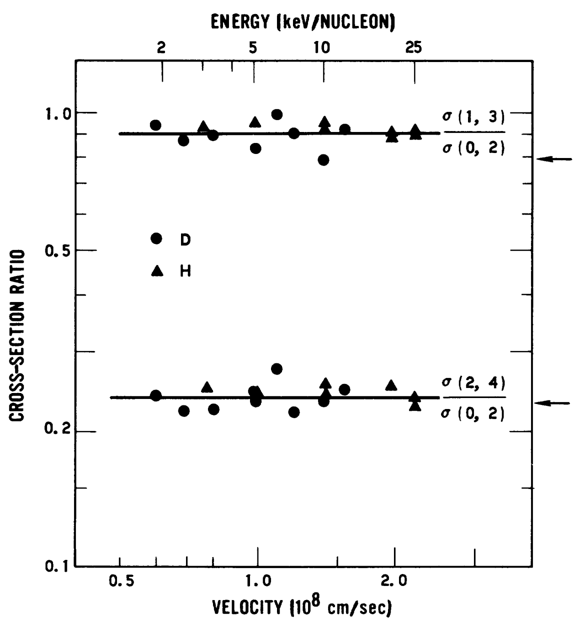

FIG. 8. Ratios of cross sections for excitation of the $N_2\ C\,^3\Pi_u$–$B\,^3\Pi_g$ (2, 4), (1, 3), and (0, 2) bands in collisions of 3–25-keV H and D with N_2. The arrows indicate the ratios calculated for a simple Franck-Condon mechanism as described in the text.

assumption is clearly justified; however, at the lower end of the velocity range employed in our experiments, the value of $\sigma(2,3)/\sigma(0,1)$ for D and H impact exceeds the IFC value of 2.3×10^{-3} by almost two orders of magnitude, and a small contribution for formation of N_2^+ $B\,^2\Sigma_u^+$ with $v'=2$ was included in the calculation of $P_a(v')$ and $\sigma_a(B\,^2\Sigma_u^+)$ given in Table II.

The vibrational distribution of N_2 $C\,^3\Pi_u$ formed in H and D impact was carried out by integration over the $\Delta v=-2$ sequence of the $2p$ system. Ratios of cross sections for excitation of members of this sequence are shown in Fig. 8. In contrast with our results for excitation of the $1n$ bands of the nitrogen molecule ion, these ratios for excitation of a neutral excited state were found to be constant over the entire velocity range studied. Values of $P(v')$ deduced from these results are compared with $P_{FC}(v')$ for the $2p$ system in Table III. The agreement between theory and experiment is seen to be excellent. From these measured values of $P(v')$, the values of $\sigma_a(C\,^3\Pi_u)$ given in Table II were calculated.

IV. DISCUSSION

In proton impact, N_2^+ $B\,^2\Sigma_u^+$ is formed by charge transfer,

$$H^+ + N_2 \rightarrow H + N_2^+\; B\,^2\Sigma_u^+ , \tag{8}$$

and by collisional ionization,

$$H^+ + N_2 \rightarrow H^+ + N_2^+\; B\,^2\Sigma_u^+ + e^- . \tag{9}$$

The hydrogen atom can also be left in an excited state in the electron capture process; but, with one exception,[34] experiments have provided no information on the distribution of electronic states of the H formed in (8). Wehrenberg and Clark have recently determined by coincidence techniques[35] that the fractional contribution of charge transfer excitation of N_2^+ $B\,^2\Sigma_u^+$, $v'=0$ is 0.6 at 60 keV, 0.8 at 30 keV, 0.9 at 10 keV, and >0.9 at lower energies.

In H impact, N_2^+ $B\,^2\Sigma_u^+$ is formed by impact ionization,

$$H + N_2 \rightarrow H + N_2^+\; B\,^2\Sigma_u^+ + e^- , \tag{10}$$

and electron capture,

$$H + N_2 \rightarrow H^- + N_2^+\; B\,^2\Sigma_u^+ . \tag{11}$$

There are no data to indicate the fate of the projectile in these collisions or the relative contributions of (10) and (11). The small value of the total cross section $\sigma_{0\bar{1}}$ for electron capture[36] by H relative to the total cross section for ionization of N_2 by H suggests, however, that (10) is the more important source of N_2^+ $B\,^2\Sigma_u^+$ in H impact. At energies above ~10 keV, $\sigma_a(391.4)$ is greater than $\sigma_{0\bar{1}}$.

Essentially all of the N_2 $2p$ radiation observed in our experiments is emitted by excited N_2 formed in the process

$$H + N_2 \rightarrow H + N_2\; C\,^3\Pi_u . \tag{12}$$

The configurations of the initial and final electronic states of nitrogen involved in processes (8)–(12) are

$$N_2\, X\,^1\Sigma_g^+ :\quad KK\; 2\sigma_g^2\; 2\sigma_u^2\; 1\Pi_u^4\; 3\sigma_g^2 ,$$

$$N_2\, C\,^3\Pi_u :\quad KK\; 2\sigma_g^2\; 2\sigma_u^1\; 1\Pi_u^4\; 3\sigma_g^2\; 1\Pi_g^1 ,$$

$$N_2^+\, B\,^2\Sigma_u^+ :\; KK\; 2\sigma_g^2\; 2\sigma_u^1\; 1\Pi_u^4\; 3\sigma_g^2 .$$

Both of the excited nitrogen species have a vacancy in the 18.76 eV[37] $2\sigma_u$ orbital. In the simplest description, N_2^+ in the B state is formed by removal of a $2\sigma_u$ electron. Actually, N_2^+ could also be formed via autoionization, but the measurements reported here cannot distinguish between these two mechanisms. N_2 in the C state is formed in an exchange process, the over-all result of which is the promotion of a $2\sigma_u$ electron to a $1\Pi_g$ orbital. The cross section for excitation of N_2 $C\,^3\Pi_u$ by atomic hydrogen peaks at a relative velocity of ~10^8 cm/sec, which is comparable to the classical speed of an electron in either the $2\sigma_u$ orbital of N_2 or the $1s$ orbital of H. The results in Table II show that, owing to the large cross section for process (8), $\sigma_p B\,^2\Sigma_u^+$ is always greater than $\sigma_a(B\,^2\Sigma_u^+)$ in the 1.5–25-keV interval, with the effect becoming more pronounced at low energies; however, using the results of Wehrenberg and Clark[35] for the ratio of cross sections for processes (8) and (9) in conjunction with the data in Table I, it can be shown that the cross section for production of N_2^+ $B\,^2\Sigma_u^+$, $v'=0$ by H impact is at least (40–50)% *greater* than the cross section for formation of this species by collisional ionization in proton impact (see below). From data on the over-all ionization cross section for N_2,[1] and from the observation that N_2^+ is the dominant secondary ion both for H^+ (Ref. 38) and H^0 [Refs. 38(b), 39, 40] impact, we find that the

TABLE III. Relative vibrational distribution of N_2 $C\,^3\Pi_u$ excited by H and D impact on N_2 in the energy range 2–25-keV/nucleon.

v'	$P(v')$ Measured	Franck-Condon
0	0.51 ± 0.03	0.55 ± 0.03
1	0.34 ± 0.03	0.31 ± 0.02
2	0.11 ± 0.01	0.11 ± 0.008
3	0.04 ± 0.01	0.03 ± 0.003

fraction of N_2^+ formed in the $B\,^2\Sigma_u^+$ state rises from about 0.03 at 1.5 keV to about 0.08 at 25 keV in both H^+ and H impact. For H-atom collisions at energies below about 7 keV, the probability of exchange excitation of a $2\sigma_u$ electron in N_2 to the $1\Pi_g$ orbital exceeds that for removal of a $2\sigma_u$ electron; however, at higher energies, the probability of formation of N_2^+ in the B state is greater than that for formation of N_2 in the C state.

As a consequence of the similarity in electronic structure of $N_2\ C\,^3\Pi_u$ and $N_2^+\ B\,^2\Sigma_u^+$ noted above, the difference in the success of the IFC mechanism in prediction of the vibrational distribution of these states is particularly intriguing. The deviation of $P(v')$ for $N_2^+\ B\,^2\Sigma_u^+$ formed in low velocity ion impact from the predictions of the IFC mechanism has been qualitatively[8] and semiquantitatively[9] described by application of the FC principle to the $N_2\ X\,^1\Sigma_g^+$ ground-state molecule that has been distorted by the presence of the projectile ion; however, our demonstration of an even more marked enhancement of the relative vibrational population of $N_2^+\ B\,^2\Sigma_u^+$ with $v' \geq 1$ in H impact is in direct contradiction to the prediction of this distorted Franck-Condon (DFC) mechanism, as was the earlier observation of a similar effect in rare-gas-atom impact on N_2.[40] Owing to the shorter range of the atom-molecule interaction, the DFC mechanism would predict that, if an enhancement in the relative population of levels with high v' owing to target polarization were to occur in an H and N_2 collision, it should occur at a lower velocity than in H^+ impact, and that the effect should be less pronounced. The independence of the vibrational distribution of $N_2\ C\,^3\Pi_u$ on H or D atom velocity is consistent with the prediction of the DFC mechanism; however, Moore and Doering found that the spin-allowed excitation of $N_2\ C\,^3\Pi_u$ in He^+ impact also is well predicted by the IFC mechanism. Furthermore, Moore has recently shown[41] that $P(v')$ for several neutral excited states of N_2 and CO excited by H^+, H_2^+, and N^+ at $2-7\times10^7$ cm/sec also can be adequately predicted from the IFC hypothesis.

Based on the systematics of the excitation processes observed to date, the following conclusions can be drawn:

(i) For formation of *neutral*, electronically excited species in either ion or neutral impact, the IFC mechanism is adequate for prediction of $P(v')$ at projectile speeds as low as 2×10^7 cm/sec.

(ii) For formation of *ionic*, electronically excited species in ion impact, the IFC mechanism successfully predicts $P(v')$ for projectile speeds $\geq 10^8$ cm/sec and the DFC mechanism can be used to describe the behavior of $P(v')$ at lower relative velocities.

(iii) For formation of $N_2^+\ B\,^2\Sigma_u^+$ in H or D impact, the IFC mechanism gives an adequate prediction of $P(v')$ at relative velocities in excess of 1.5×10^8 cm/sec; however, the enhancement of $P(v')$ for $v' \geq 1$ at lower projectiles is inconsistent with either the IFC or DFC mechanism.

A possible explanation of the observed velocity dependence of the $N_2^+\ B\,^2\Sigma_u^+$ vibrational distribution is the participation of an alternative excitation channel at lower projectile speeds. One attractive hypothesis is that N_2 is initially excited to a Rydberg state that subsequently autoionizes to form $N_2^+\ B\,^2\Sigma_u^+$. Measurements of photoelectron energy spectra have shown[42] that autoionization can play an important role in photoionization of N_2 and that the vibrational population of these states is substantially different from that predicted for direct IFC excitation. Pendleton and O'Neil have recently reported an enhancement in the relative values of $P(v')$ for $N_2^+\ B\,^2\Sigma_u^+$ formed in electron impact with $v' = 2$ and $v' = 3$ that they noted as possibly due to the occurrence of a mechanism other than a direct one.[43]

The availability of measurements of cross sections for excitation of $N_2\ C\,^3\Pi_u$ and $N_2^+\ B\,^2\Sigma_u^+$ allows us to make an evaluation of analytic formulas for these cross sections derived by Edgar, Miles, and Green[3(b)] using a procedure developed by Miller and Green.[3(a)] The latter authors have developed semiempirical rules, based on the systematics of data and on theoretical models, for prediction of H^+ and H ionization and excitation cross sections by scaling previously measured electron impact

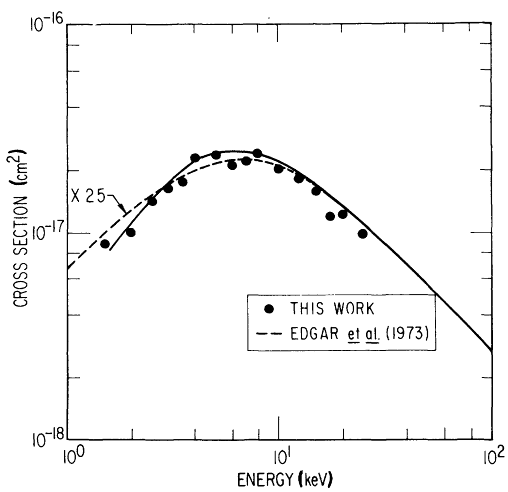

FIG. 9. Comparison of total cross section $\sigma_a(C\,^3\Pi_u)$ for formation of $N_2\ C\,^3\Pi_u$ in impact of 1–100-keV H atoms on N_2 (solid symbols) with values obtained by Edgar, Miles, and Green (solid line) using semiempirical scaling laws and electron impact data. The latter results have been multiplied by a factor of 2.5.

TABLE IV. Ionization and excitation cross-section parameters. Parameters for N_2 $B\,^2\Sigma_u^+$ are taken from Ref. 2 and those for N_2 $C\,^3\Pi_u$ are from Ref. 3b.

Process	W (eV)	ν	J (keV)	a (keV)	Ω
$H^+ + N_2 \to H^+ + N_2^+ B\,^2\Sigma_u^+ + e$	18.75	1.03	104.45	3.43	0.605
$H + N_2 \to H + N_2^+ B\,^2\Sigma_u^+ + e$	18.75	1.24	19.2	0.893	0.55
$H + N_2 \to H + N_2\, C\,^3\Pi_u$	10.1	1.00	6.39	0.082	1.00

cross sections. The basis for the scaling procedure is the demonstration that, in agreement with the Born approximation, at high energies the *total* ionization cross section for proton and electron impact become equal for equal velocity particles. At intermediate energies, the peak in the H^+ cross section occurs at a lower velocity and has a greater magnitude than that in electron impact. The systematics of these displacements were used by Miller and Green to prescribe a procedure for deriving the parameters in the cross section formula

$$\sigma(E) = \frac{\sigma_0 (Za)^{\Omega} (E - W)^{\nu}}{J^{\Omega+\nu} + E^{\Omega+\nu}}. \quad (13)$$

In this equation, E is the projectile energy, $\sigma_0 = 10^{-16}$ cm^2, Z is the number of electrons in the target, and W is the threshold energy. The parameters ν and Ω are related to the slope of a plot of σ vs E at low and high energy, respectively, whereas J and a depend upon the position and magnitude of the peak in the cross section as well as on ν and Ω.

Figure 9 compares the cross section $\sigma_a(C\,^3\Pi_u)$ derived by Edgar *et al.*[3(b)] from electron impact cross-section data with our cross sections measured for H impact on N_2. The values of the parameters used in Eq. (13) are given in Table IV. The shape of the analytic cross section curve for N_2 $C\,^3\Pi_u$ and the position of its maximum are in excellent agreement with those features of the measurements. Multiplication of the Edgar, Miles, and Green results by a factor of 2.5 makes the analytic curve and the experimental results nearly superimposable over the entire range 1.5–100 keV. Since these authors state that, at this stage of development, their results may be uncertain by a factor of 2, and since the absolute accuracy in $\sigma_a(C\,^3\Pi_u)$ is roughly 30%, the agreement between theory and experiment is acceptable.

Comparison of the semiempirical cross sections[3(b)] for N_2^+ $B\,^2\Sigma_u^+$ formation with our measured values for atomic hydrogen impact shows that, above 10 keV, the analytic formula does well in predicting both the magnitude and the energy dependence of the cross section $\sigma_a(B\,^2\Sigma_u^+)$; however, at lower energies, the measured values decrease much more rapidly than predicted by the formula as the projectile energy is reduced. For proton impact, the energy dependence of the semiempirical cross section $\sigma_{ip}(B\,^2\Sigma_u^+)$ for formation of N_2^+ $B\,^2\Sigma_u^+$ by collisional ionization in processes (9) predicted by Edgar *et al.*[3(b)] is in good agreement with that inferred[44] from the work of Wehrenberg and Clark. In this energy range, the calculated values of $\sigma_{ip}(B\,^2\Sigma_u^+)$ exceed the measurements by about a factor of 2; however, at lower energies, the values of $\sigma_{ip}(B\,^2\Sigma_u^+)$ inferred from the experiments decrease far more rapidly than those predicted by the theoretical treatment as the collision energy is reduced.

These discrepancies between theory and experiment are not unexpected. Since the kinetic energy of a proton or a hydrogen atom of velocity equal to that of an electron having the N_2^+ $B\,^2\Sigma_u^+$ threshold energy is 34 keV, simple velocity-equivalence scaling procedures cannot be employed to pre-

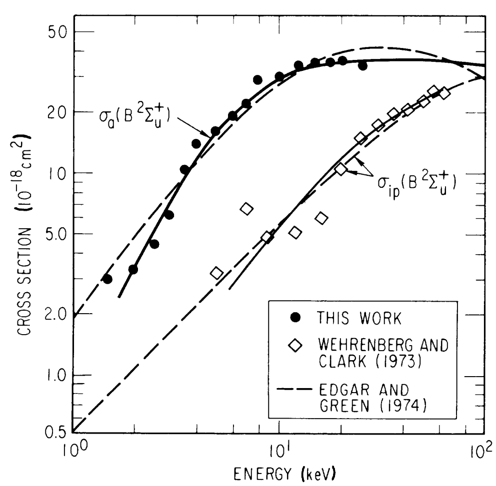

FIG. 10. Comparison of measured values of the total cross section $\sigma_a(B\,^2\Sigma_u^+)$ for formation of N_2^+ $B\,^2\Sigma_u^+$ in impact of 1–100-keV hydrogen atoms on N_2 with values calculated using the analytic formula of Edgar and Green (Ref. 2). Also shown are Wehrenberg and Clark's measurements (Ref. 35) and Edgar and Green's calculation of the cross section $\sigma_{ip}(B\,^2\Sigma_u^+)$ for the formation of $N_2^+ B\,^2\Sigma_u^+$ by proton impact ionization.

dict the low energy form of H^+ and H impact cross sections from electron impact data. Based on our results and those of Wehrenberg and Clark, Edgar and Green are revising the scaling procedure for calculation of N_2^+ $B^2\Sigma_u^+$ cross sections.[2] Figure 10 compares their preliminary results for $\sigma_a(B^2\Sigma_u^+)$ and $\sigma_{ip}(B^2\Sigma_u^+)$ with experimental determinations of these quantities. Table IV gives the revised values of $\nu, J, a,$ and Ω used in Eq. (13). It is anticipated that the systematics of cross section data for H^+ and H impact excitation of other states of N_2 and N_2^+ as well as for excitation of other target molecules currently under study will allow further refinements of the semiempirical scaling procedure in this energy regime.

ACKNOWLEDGMENT

It is a pleasure to thank P. A. Johnson for technical assistance in acquisition and analysis of the data, and Dr. K. C. Clark, Dr. B. C. Edgar, and Dr. A. E. S. Green for helpful discussions and communication of their results prior to publication. The continuing interest and advice of Dr. R. J. McNeal is gratefully acknowledged.

---

†Work conducted under U.S. Air Force Space and Missile Systems Organization (SAMSO) Contract No. F04701-73-C-0074.

[1]R. J. McNeal and J. H. Birely, Rev. Geophys. Space Phys. 11, 633 (1973).

[2]B. C. Edgar and A. E. S. Green (unpublished); B. C. Edgar (private communication).

[3](a) J. H. Miller and A. E. S. Green, Radiation Res. 54, 343 (1973); (b) B. C. Edgar, W. T. Miles, and A. E. S. Green, J. Geophys. Res. 78, 6595 (1973).

[4]E. W. Thomas, *Excitation in Heavy Particle Collisions* (Wiley, New York, 1972).

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

[6]R. J. McNeal and D. C. Clark, J. Geophys. Res. 74, 5065 (1969).

[7]F. J. de Heer and J. F. M. Aarts, Physica 48, 620 (1970).

[8]J. H. Moore, Jr., and J. P. Doering, Phys. Rev. 177, 218 (1969).

[9]M. Lipeles, J. Chem. Phys. 51, 1252 (1969).

[10]D. A. Dahlberg, D. K. Anderson, and I. E. Dayton, Phys. Rev. 164, 20 (1967).

[11]J. M. Robinson and H. B. Gilbody, Proc. Phys. Soc. Lond. 92, 589 (1967).

[12]Preliminary accounts of this work have been given by (a) J. H. Birely, in Proceedings of the Fourth International Symposium on Molecular Beams, Cannes, France, July, 1973 (unpublished); and (b) J. H. Birely, Bull. Am. Phys. Soc. 18, 1525 (1973).

[13]J. H. Birely and R. J. McNeal, J. Chem. Phys. 56, 2189 (1972).

[14]P. N. Clout and D. W. O. Heddle, J. Opt. Sci. Am. 59, 715 (1969).

[15](a) J. W. McConkey, J. Opt. Sci. Am. 59, 110 (1969); (b) J. F. M. Aarts and F. J. de Heer, J. Opt. Sci. Am. 58, 1666 (1968).

[16]M. J. Mumma, J. Opt. Sci. Am. 62, 1459 (1972).

[17]D. A. Albritton, A. Schmeltekopf, and R. N. Zare, *Diatomic Intensity Factors* (Harper and Row, New York, to be published).

[18]W. A. Brown and R. K. Landshoff, J. Quant. Spectrosc. Radiative Transfer 11, 1143 (1971).

[19]R. N. Zare, University of California Radiation Laboratory Report No. 10925, 1963 (unpublished).

[20]W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 142, 1227 (1965).

[21]J. C. Keck, R. A. Allen, and R. L. Taylor, J. Quant. Spectrosc. Radiative Transfer 3, 335 (1963).

[22]J. E. Hesser, J. Chem. Phys. 45, 2518 (1968).

[23]H. M. Poland and H. P. Broida, J. Quant. Spectrosc. Radiative Transfer 11, 1863 (1971).

[24]P. H. Krupenie, Natl. Stand. Ref. Data Ser.-NBS 5 (1966).

[25]D. C. Cartwright (unpublished).

[26]J. M. Hoffman, G. J. Lockwood, and G. H. Miller, Phys. Rev. A 7, 118 (1973).

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

[28](a) R. Anderson, At. Data 2, 227 (1971); (b) A. W. Johnson and R. G. Fowler, J. Chem. Phys. 53, 65 (1970); (c) K. B. Mitchell, J. Chem. Phys. 53, 1795 (1970); (d) F. J. Comes and F. Speier, Z. Naturforsch. 26A, 1998 (1971); (e) G. I. Mackay and R. E. March, Can. J. Chem. 50, 1 (1972).

[29]J. M. Calo and R. C. Axtmann, J. Chem. Phys. 54, 1332 (1971).

[30](a) T. G. Finn, J. F. M. Aarts, and J. P. Doering, J. Chem. Phys. 56, 5632 (1972); (b) L. Kurzweg, G. T. Egbert, and D. J. Burns, Phys. Rev. A 7, 1966 (1973).

[31]R. S. Freund, J. Chem. Phys. 50, 3734 (1969).

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

[33](a) L. Tomcho and M. J. Haugh, J. Chem. Phys. 56, 6089 (1972); (b) M. J. Haugh, J. Chem. Phys. 59, 37 (1973).

[34]S. J. Young, J. S. Murray, and J. R. Sheridan, Phys. Rev. 178, 40 (1969).

[35]P. J. Wehrenberg and K. C. Clark, Phys. Rev. A 8, 173 (1973).

[36](a) P. M. Stier and C. F. Barnett, Phys. Rev. 103, 895 (1956); (b) Ya. M. Fogel', V. A. Ankudinov, D. V. Pilipenko, and N. V. Topolia, Zh. Eksperim. i Teor. Fiz. 34, 579 (1958); [Sov. Phys.—JETP 7, 400 (1958)]; (c) D. V. Pilipenko and Ya. M. Fogel', Zh. Eksperim. i Teor. Fiz. 42, 936 (1962) [Sov. Phys.—JETP 15, 646 (1962)].

[37]G. R. Cook and P. H. Metzger, J. Chem. Phys. 41, 321 (1964).

[38](a) R. N. Il'in, V. V. Afrosimov, and N. V. Fedorenko, Zh. Eksperim. i Teor. Fiz. 36, 41 (1959) [Sov. Phys.—JETP 9, 29 (1959)]; (b) E. S. Solov'ev, R. N. Il'in, V. A. Oparin, and N. V. Fedorenko, Zh. Eksperim. i Teor. Fiz. 42, 659 (1962) [Sov. Phys.—JETP 15,

459 (1962)]; (c) R. Browning and H. B. Gilbody, J. Phys. B 1, 1149 (1968).

[39] D. V. Pilipenko and Ya. M. Fogel', Zh. Eksperim. i Teor. Fiz. 48, 404 (1965) [Sov. Phys.—JETP 21, 266 (1965)].

[40] V. A. Gusev, G. N. Polyakova, and Ya. M. Fogel', Zh. Eksperim. i Teor. Fiz. 55, 2128 (1968) [Sov. Phys.—JETP 28, 1126 (1969)].

[41] J. H. Moore, Jr., Phys. Rev. A 9, 2043 (1974).

[42] (a) J. L. Bahr, A. J. Blake, J. H. Carver, J. L. Gardner, and V. Kumar, J. Quant. Spectrosc. Radiative Transfer 11, 1839 (1971); (b) P. Natalis, J. Delwiche, and J. E. Collin, Chem. Phys. Lett. 13, 491 (1972).

[43] W. R. Pendleton, Jr. and R. R. O'Neil, J. Chem. Phys. 56, 6260 (1972).

[44] Experimental values of the cross section for proton impact ionization to yield the B state of N_2^+ in process (9) were calculated by taking the difference between $\sigma_p(391.4)$ and $\sigma_{10}(391.4)$ reported by Wehrenberg and Clark (Ref. 35), with the assumption made that the vibrational distribution of $N_2^+ \; B\,^2\Sigma_u$ formed in ionization was identical to the over-all distribution displayed in Table II.