Cross Sections for the Formation of Excited States in a Nitrogen Target by the Impact of 0.15- to 1.0-MeV Protons*

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Protons in the energy range 0.15–1.0 MeV were incident on a molecular nitrogen target and the resulting emission was analyzed spectroscopically. Absolute measurements were made of the intensity of certain spectral lines. Cross sections are presented for the emission of two prominent lines of singly ionized atoms and for nine lines from the N_2^+ first positive band system. Cross sections for the population of the $v'=0$ and $v'=1$ vibrational levels of the $B\ ^2\Sigma$ excited state of N_2^+ are obtained from the emission functions. In the present work, the proportion of N_2^+ ions formed in the excited state remains almost independent of impact energy, indicating that the excited N_2^+ ions are produced by simultaneous ionization and excitation of the target. The measured relative populations of two vibrational levels in the N_2^+ ion are shown to be in good agreement with the ratios of the relevant overlap integrals. An investigation of the emission of the N_2 second positive system shows that it is mainly excited by secondary-electron impact, the cross section for proton impact excitation of the $C\ ^3\Pi$ state of the N_2 molecule being some three orders of magnitude less than that for electrons at the same impact velocity. This indicates the importance of spin conservation in governing the transitions which occur in collisional excitations by heavy-particle impact.

I. INTRODUCTION

THE present study of the excitation of molecular nitrogen by the impact of fast protons was undertaken with two objectives in mind. First, there is of course a need to provide information which will lead to the fundamental understanding of the processes involved. In the case of the heavier gases, no accurate quantum-mechanical predictions are available, and it is necessary to provide data which may stimulate and test the development of semiclassical theories which rely heavily on the availability of experimental data. Secondly, the information is of considerable importance to the diagnostics of phenomena occurring in the upper atmosphere of the earth and other planets. Although it is now believed that many of the auroral excitation phenomena are induced by primary and secondary electrons, incident protons undoubtedly do play a part.

The experimental apparatus used for this investigation has been described in detail elsewhere[1] and will be reviewed only briefly here. The ions are produced by a Van de Graaff accelerator equipped with an rf discharge type of source. A stabilization and analysis system defines the energy of the ion beam to within ± 2 keV at all energies from 0.15 to 1.00 MeV. The ions traverse the low-pressure gas cell target and the light emitted from the beam path is analyzed by a Jarrell Ash $\frac{1}{2}$-m Ebert spectrometer, fitted with photomultiplier detection. In order to reduce the effects of photomultiplier dark current, the light beam is mechanically chopped by a vibrating reed before entering the spectrometer, and the required signal is identified in the photomultiplier output by its specific frequency and phase. The optical detection efficiency of the system was calibrated quite simply by substituting a standard tungsten strip filament lamp of known emissive power for the experimental source of emission and measuring the signal produced by this known source at the wavelengths of interest. Single-collision conditions were maintained throughout, as evidenced by the linearity of emission with target-gas pressure up to 5×10^{-3} Torr.

In our previous work,[1] the pressure of the target gas was determined using a McLeod gauge. It has been shown that the McLeod gauge may give erroneous measurements of gas pressure due to the pumping effect of mercury streaming onto the cold trap.[2] In general, the effect is negligible for light gases such as helium and hydrogen, but must be considered for heavier gases such as nitrogen. The problem was eliminated by the use of a capacitance manometer, which is insensitive to the nature of the gas under investigation and does not exhibit the pumping error. It has been shown[3] that the calibration of such a device is quite accurate, but rather than rely on this characteristic being applicable to all models of the instrument, it was decided to calibrate the device frequently against a McLeod gauge using helium gas, for which the pumping error should be rather small. The present measurements are, therefore, free of any influence of the pumping error, unlike most of the published data with which comparisons are made.

The present work required the absolute calibration of the detection sensitivity of the system at wavelengths in the region 3000–4000 Å, where the emission from the standard lamp is exceedingly weak. A serious scattered-light problem was encountered due to a small proportion of the intense visible emission of the standard lamp reaching the exit slit of the spectrometer without dispersion. This problem was eliminated by the use of suitable filters of calibrated transmission.

When dealing with the quantitative analysis and detection of emission in the band system of a molecule,

* Work partially supported by the Controlled Thermonuclear Research Program of the U. S. Atomic Energy Commission.
[1] E. W. Thomas and G. D. Bent, Phys. Rev. **164**, 143 (1967).
[2] See, e.g., the review by P. H. Carr, Vacuum **14**, 37 (1964).
[3] N. G. Utterback and T. Griffith, Rev. Sci. Instr. **37**, 866 (1966).

it is necessary to ensure that the spectrometer slit widths are sufficiently broad to pass all of the rotational structure which might contribute an appreciable component to the total intensity of the transition between two vibrational levels. Most of the present data were taken with a spectrometer pass band of 16 Å, but improved resolution was necessary when dealing with the 3884, 3582, and 4236 Å lines in order to separate them from more intense neighboring transitions. In all cases, tests were made to ensure that all significant parts of the rotational structure were being detected.

It is convenient to define the cross section for the emission of a spectral line corresponding to the radiative decay of an excited state from level i to level j in terms of the photon emission per unit length of beam path J_{ij} (photons/sec cm), the target density n (particles/cc), and the incident beam current N (particles/sec):

$$\sigma_{ij}=J_{ij}(nN)^{-1}. \tag{1}$$

The cross section for the formation of the state i by direct collisional excitation may in turn be expressed as the difference between the sum of the cross sections for radiative decay to all levels below i and the population of the level i by cascade from higher levels k.

$$\sigma_i=\sum_j \sigma_{ij}-\sum_k \sigma_{ki}. \tag{2}$$

In a previous paper,[1] we have shown in a general manner how the emission cross section may be related to the transition probabilities for the radiative decays.

The major source of error in the present determination is the calibration of the detection sensitivity of the system using a tungsten strip filament lamp. There are certain possible systematic errors associated with the measurement of filament temperature, and the knowledge of the size of the filament and transmission of the window. In addition, there is a random error in ensuring good alignment and again in the measurement of filament temperature using an optical pyrometer. Furthermore, the problem of scattered light is more severe here than in our previous work,[1] since many of the transitions lie in the ultraviolet spectral regions, where the emissive power of the lamp is very low. Although day-to-day reproducibility of measurements of emission from the collision region was better than ±5%, it would be unrealistic to estimate the absolute accuracy of our data as better than ±25%. Because of the elimination of certain systematic errors associated with pressure measurement and detection sensitivity, the accuracy of the relative values of the various measurements should range from ±15% for emissions below 4200 Å to ±7% at higher wavelengths, where the scattered light is not a problem. The agreement of our previous data on the excitation of helium with theoretical predictions[4] gives us considerable confidence in our calibration procedures.

[4] E. W. Thomas, Phys. Rev. **164**, 151 (1967).

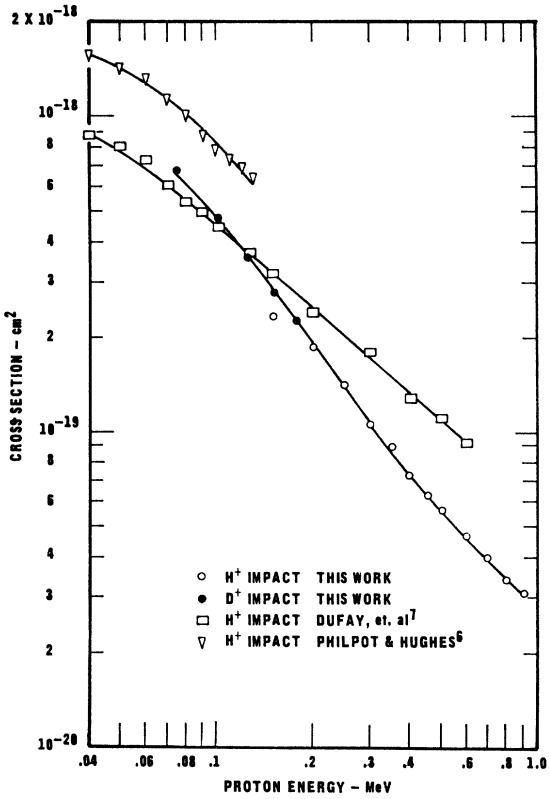

FIG. 1. Cross sections for the emission of the N II 5005Å and 5680 Å lines induced by the impact of protons and deuterons on a molecular nitrogen target. Since the cross sections for these two emissions are the same within random experimental error, the mean of the two has been plotted for the present work and also for the previously published data with which comparisons are made.

The present experiment essentially measures only the rate of emission of photons at an angle of 90° to the ion beam, and the cross sections were evaluated on the assumption that the emission is isotropic. The only factor which is likely to produce anisotropy in the emission is polarization of the radiation,[5] and this was briefly examined with the object of determining its influence on the present measurements. Our tests indicate that the emission in the first negative band system of the N_2^+ ion, which constitutes the bulk of the work reported here, had a polarization fraction of less than 6%. This would indicate that the difference between the cross sections determined on the assumption of isotropic emission and the true emission cross sections would be less than 3%. In the case of the N^+ emissions, it was difficult to determine the polarization due to the low light intensities, but it did not exceed 15%, thus indicating a maximum error of 7% in our measurements. No correction was made for this effect since it could not be determined accurately, and its influence was well within the accuracy limits of the cross-section determinations.

[5] J. Van Eck, F. J. DeHeer, and J. Kistemaker, Physica **28**, 1184 (1962).

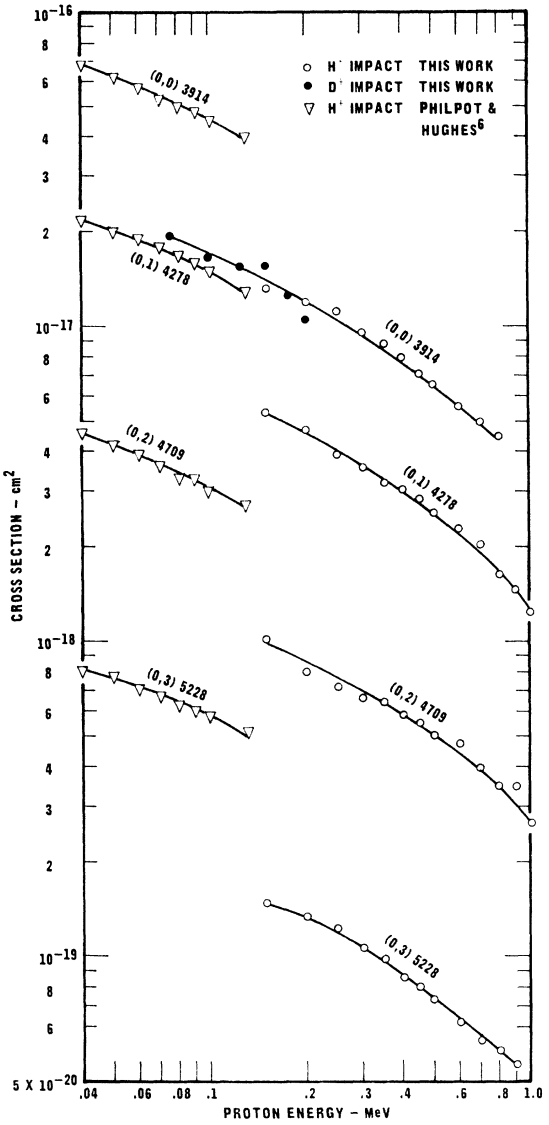

FIG. 2. Cross sections for the $v'=0$ progression emissions in the N_2^+ first negative band system, induced by the impact of protons on a molecular nitrogen target. $v'=0 \rightarrow v''=0$ (3914 Å); $v'=0 \rightarrow v''=1$ (4278 Å); $v'=0 \rightarrow v''=2$ (4709 Å); $v'=0 \rightarrow v''=3$ (5228 Å).

General theoretical considerations and previous work on the formation of excited states in a helium target[1] suggest that protons and deuterons at the same velocity of impact should exhibit the same cross sections for excitation of the target. This was again confirmed experimentally in the present work, and deuterons were used to extend the lower limit of velocity available from the accelerator for selected determinations.

In the spectral range 3000–6000 Å, for which the present equipment is reasonably sensitive, the most prominent feature of the emitted spectrum is a very intense N_2^+ first negative band system. Contributions from the second positive band system of the neutral molecule and from the singly charged atomic ion were also detected. Measurements have been made of certain emission functions from the N_2^+ and N^+ systems. An investigation of the emission from the N_2 system indicated that the principal process which causes the excitation of the neutral molecule involves secondary electrons produced by collisional ionization of the target.

II. EMISSION FROM THE N^+ ION

The emission functions of the 5005 and 5680 Å lines of this system were determined. The cross sections for these two emissions are the same within the random error of the determinations, and in Fig. 1 we show the mean of the two emission functions compared with the similar mean values from the work of Philpot and Hughes,[6] and that of Dufay *et al.*,[7] where again equality within random experimental error was demonstrated.

The fact that the energy dependences of the emission functions for the 5005 and 5680 Å lines are the same indicates that a common process leads to the formation of the relevant excited states. The wavelength tables of Moore[8] identify the 5680 Å line as the transition $3p\ ^3D \rightarrow 3s\ ^3P^0$. There is ambiguity in the identification of the 5005 Å transition since at least three multiplets produce emissions close to this wavelength, which could not be separated with the resolution available in the present experiment. Comparisons have been made between these emission functions and available data on ionization and on charge transfer in an attempt to decide which mechanism predominates in the formation of the N^+ ion in the excited state. However, there is insufficient correlation between the two types of data to allow any choice to be made.

III. N_2^+ FIRST NEGATIVE BAND EMISSION

Emission functions were measured for nine transitions in the $v'=0$ and $v'=1$ progressions of the first negative band system of the N_2^+ molecular ion ($B\ ^2\Sigma \rightarrow X\ ^2\Sigma$). In Fig. 2 are shown the cross sections for the emission of lines in the $v'=0 \rightarrow v''$ progression compared with the data of Philpot.[6] A fairly consistent difference of a factor of 2.5 between the two sets of data cannot be explained by pressure-measurement errors and is primarily due to a discrepancy in calibration. The emission cross sections in the $v'=1 \rightarrow v''$ progression are shown in Fig. 3. Measurement of the $v'=1 \rightarrow v''$ progression is hampered by the close proximity of fairly intense lines from the N_2 second positive system, requiring increased resolution and introducing the danger of cutting off a significant part of the rotational structure of the N_2^+ emission. We observe that the discrepancies between the data of Philpot and Hughes[6] and the present work

[6] J. L. Philpot and R. H. Hughes, Phys. Rev. **133**, A107 (1964).
[7] M. Dufay, J. Desesquelles, M. Druetta, and M. Eidelsberg, Ann. Geophysique **22**, 614 (1966). This work supersedes and in part changes a previous report: M. Dufay, M. Druetta, and M. Eidelsberg, Compt. Rend. **261**, 1635 (1965).
[8] C. E. Moore, National Bureau of Standards Technical Note No. 36, 1959 (unpublished).

are somewhat greater for this progression than for the $v'=0$ system, indicating perhaps inadequate assessment of overlap. In particular, the 3582 Å line, for which the discrepancy is largest, was not separated from the adjacent 3577 Å N_2 line in the work of Philpot and Hughes,[6] although an estimate of the overlap was made in the present measurements. It should be noted that the 3884 Å ($1 \rightarrow 1$) and 4236 Å ($1 \rightarrow 2$) emissions have cross sections which are the same, within the limits of the random error of the determinations, and we have therefore plotted the mean of the two functions, as did Philpot and Hughes.[6] Comparison may also be made with the work of Dufay *et al.*,[7] which for clarity was omitted from the diagrams presented here. In general, there is agreement in the energy dependence of the cross sections, but the magnitudes of the cross sections

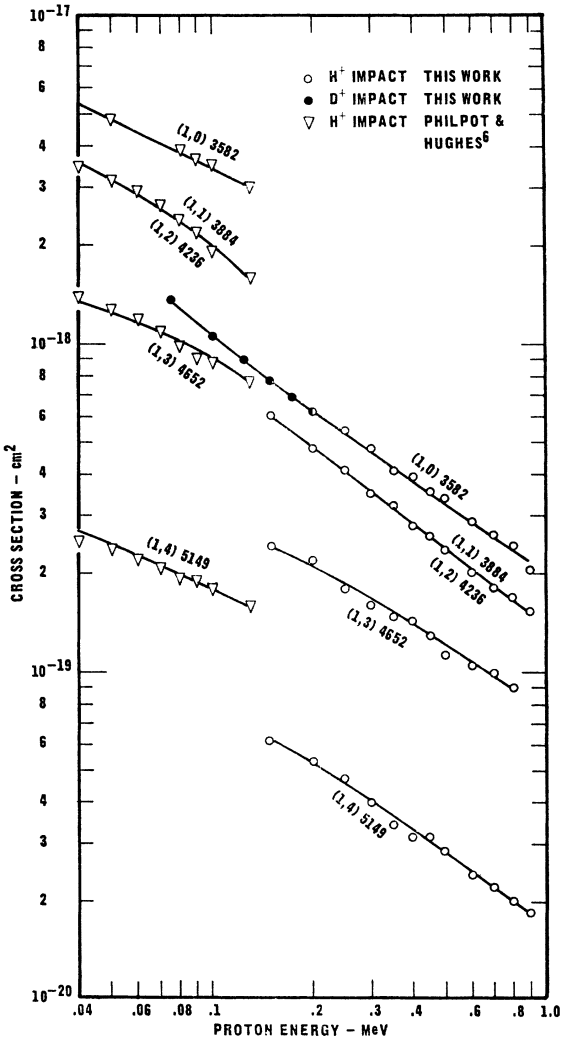

FIG. 3. Cross sections for the $v'=1$ progression emissions in the N_2^+ first negative band system, induced by the impact of protons on a molecular nitrogen target. $v'=1 \rightarrow v''=0$ (3582 Å); $v'=1 \rightarrow v''=1$ (3884 Å); $v'=1 \rightarrow v''=2$ (4236 Å); $v'=1 \rightarrow v''=3$ (4652 Å); $v'=1 \rightarrow v''=4$ (5149 Å).

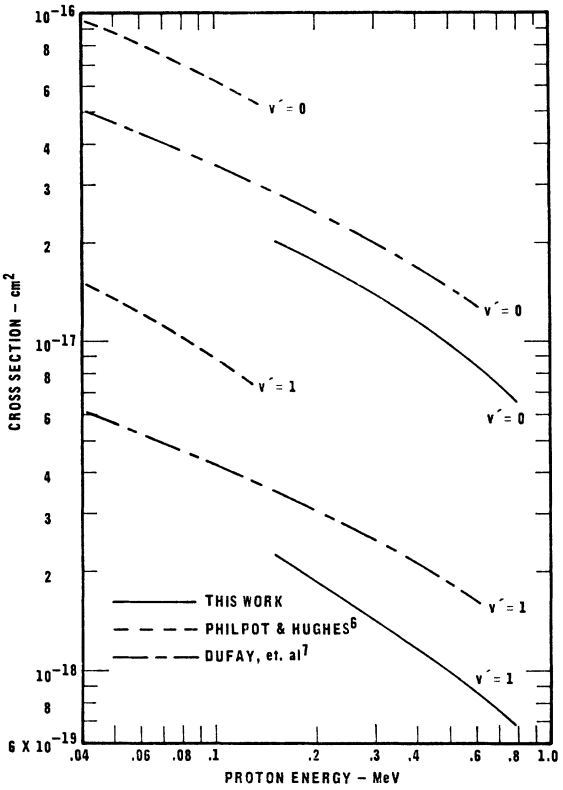

FIG. 4. Total cross sections for the population of the $v'=0$ and $v'=1$ vibrational levels of the $B\,^2\Sigma$ state of N_2^+.

quoted by Dufay *et al.* are higher than the present measurements by amounts ranging from 10% for transitions in the visible region to 100% for ultraviolet transitions. With one exception, the discrepancy is less than the sum of the experimental errors for the two determinations.

We obtain a total cross section for the population of the $v'=0$ and $v'=1$ vibrational levels of the $B\,^2\Sigma$ state of the molecular ion by summing the measured cross sections for emissive transitions from these levels, neglecting the v'' states above $v''=4$, which contribute very little to the total population cross section. These estimates are shown in Fig. 4, compared with the work by Philpot and Hughes,[6] and Dufay *et al.*[7] Herzberg[9] lists no transitions which could cause a cascade population of the $B\,^2\Sigma$ excited state, and we estimate the total cross section for exciting this state by summing the population cross sections of the $v'=0$ and $v'=1$ vibrational levels, contributions from higher v' states being assumed negligible. It is noticed that these population cross sections show a very similar energy dependence to the "gross ionization" cross sections measured by Hooper *et al.*,[10] which are essentially a sum of the cross

[9] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N. J., 1950).

[10] J. W. Hooper, D. S. Harmer, D. W. Martin, and E. W. McDaniel, Phys. Rev. 125, 2000 (1962).

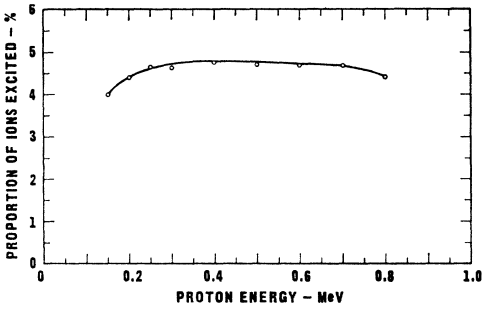

FIG. 5. Estimate of the proportion of the N_2^+ ions formed in the $B\,^2\Sigma$ excited state, as a function of energy.

sections for producing N_2^+ and N^+ ions. Solov'ev *et al.*[11] show that, at impact energies below 150 keV, approximately 80% of the positive ion production is N_2^+, and we may reasonably assume that Hooper's gross ionization cross section, measured at higher energies, represents primarily the formation of N_2^+. In Fig. 5 is plotted the ratio of the cross section for the formation of the N_2^+ ($B\,^2\Sigma$) excited state and the gross ionization cross section. Although the present estimates are admittedly approximate, we find that an almost constant proportion of approximately 4.7% of the N_2^+ ions are formed in the excited $B\,^2\Sigma$ state. Philpot and Hughes[6] also found that the proportion remained very constant from 20 to 130 keV although their estimate of 14% of the ions formed in the excited state is greater than in the present work. The difference between the two figures is due primarily to the difference in the measured excitation cross sections caused by the discrepancy in calibration. Also, in the lower-energy data,[6] it was possible to use a measurement of the N_2^+ production cross section rather than the composite gross ionization cross section that we employ here, which includes a small amount of N^+ production. We believe that the constancy of the ratio of excited-state population to ionization cross section indicates that, in the range of energy of the present work, the process leading to the formation of the excited states is simultaneous excitation and ionization.

$$H^+ + N_2 = H^+ + N_2^+(B\,^2\Sigma) + e. \tag{3}$$

Comparison of the excitation cross section with the available data on charge transfer[12] indicates not only a completely different energy dependency but also that the excitation cross section is greater than the total charge-transfer cross section at all energies above 300 keV. Charge transfer cannot be the primary mechanism for producing the N_2^+ excited state in the energy range of this experiment.

[11] E. S. Solov'ev, R. N. Il'in, V. A. Oparin, and N. V. Fedorenko, Zh. Eksperim. i Teor. Fiz. **42**, 659 (1962) [English transl.: Soviet Phys.—JETP **15**, 459 (1962)].

[12] C. F. Barnett and H. K. Reynolds, Phys. Rev. **109**, 355 (1958).

IV. TRANSITION PROBABILITIES IN THE FIRST NEGATIVE BAND

The probability of a transition from a vibrational level v' in an electronic state i to a level v'' of the electronic state j may be written in terms of the total eigenfunctions for the two states $\psi_{iv'}$ and $\psi_{jv''}$, and the electric transition moment M:

$$P_{iv',jv''} \sim \left| \int \psi_{iv'}^* M \psi_{jv''} d\tau \right|^2. \tag{4}$$

The integral is taken over the configuration space τ. Following Herzberg,[9] we may neglect the rotation of the molecule and write the total eigenfunction of the state as the product of ψ_e and ψ_v, the electronic and vibrational eigenfunctions. Furthermore, the electric moment M may be reduced into two components, one depending on the electrons, the other on the nuclei. The probability expression is then simplified to the following:

$$P_{iv',jv''} \sim \left| \int \psi_{v'} \psi_{v''} \, dR \int M_e \psi_{e'}^* \psi_{e''} d\tau_e \right|^2. \tag{5}$$

The integral over the vibrational wave functions depends only on the internuclear separation R and is called the "Franck-Condon factor or overlap integral." The second integral is taken over the volume space of the electron coordinates and is termed the electronic transition moment:

$$R^e_{ij} = \int M_e \psi_{e'}^* \psi_{e''} d\tau_e.$$

To a first approximation, this may be taken as varying slowly with internuclear separation R, and we may therefore replace R^e_{ij} by an average value $\bar{R}^e_{ij}$. Thus,

$$P_{iv',jv''} \sim \bar{R}^e{}_{ij}{}^2 \left| \int \psi_{v'} \psi_{v''} dR \right|^2. \tag{6}$$

We will examine the present data for both the process of excitation and the subsequent emission, to test available theoretical predictions of the electronic transition moment and Franck-Condon factors.

The first negative systems of the N_2^+ emission involve various vibrational transitions between the $B\,^2\Sigma$ and $X\,^2\Sigma$ electronic states. The intensity of the emission, expressed in photons emitted per second, will be given by

$$I_{v'v''} = K N_{v'} E_{v'v''}{}^3 \bar{R}^e{}_{ij}{}^2 \left| \int \psi_{v'} \psi_{v''} dR \right|^2, \tag{7}$$

where K is a constant dependent on the experimental geometry, $N_{v'}$ is the population of the level v', and $E_{v'v''}$ is the energy quantum of the $v' \rightarrow v''$ transition. Since the electronic transition moment $\bar{R}^e_{ij}$ is assumed to be

invariant with v' and v'' for the whole band, the ratio of intensities of any two lines will be equal to the ratio of the cubes of the frequencies of the emissions times the ratio of the Franck-Condon factors for the transitions. In Table I we show a comparison between various experimental and theoretical estimates of relative intensities, with the $0 \rightarrow 0$ and $1 \rightarrow 0$ transitions both taken as of unit intensity. Also shown are data from proton-impact experiments[6,13] similar to the present work, and from an electron-impact experiment.[14] The values calculated by Nicholls[15] involved the use of a Morse potential. Although the experimental values by Philpot and Hughes[6] agree well with the theoretical predictions by Nicholls,[15] the present work and the other more limited series of determinations using proton[13] and electron[14] impact experiments disagree appreciably from theory. It should be noted that the form of display used in Table I, where the $0 \rightarrow 0$ and $1 \rightarrow 0$ transitions are taken as unity, gives considerable weight to the measurements on these two transitions, which are likely to be least accurate both in the present work and in the other experimental determinations, since they lie in the near ultraviolet, where the calibration of the system is difficult. Neglecting these two transitions, the relative values of the remaining data are in rather better agreement.

In the process of collisional excitation, it may reasonably be assumed that the relative probability of forming any two particular states is fairly insensitive to small energy differences between the levels and will therefore be given by the ratio of the relevant probability functions $P_{iv',jv''}$. In this case, iv' refers to the initial state of the molecule before the collision, the $X\,^1\Sigma$ ($v=0$) level of N_2 and jv'' indicates the final state of the molecule after the collisions. In Fig. 4, we have shown the cross sections for the collisional population of the $v=0$ and $v=1$ levels of the $B\,^2\Sigma$ excited state of the N_2^+ ion. These values should be in the ratio of the vibrational overlap integrals for the transition from the N_2 ground state. The mean experimental value for the ratio of the populations of the $v=1$ and $v=0$ levels obtained from the present work is 0.10, which compares well with the value of 0.12 which can be obtained from the theoretical predictions of Nicholls.[15]

V. APPARENT ROTATIONAL TEMPERATURE OF THE N_2^+ ION

If the rotational levels of an excited state are populated according to the Boltzmann distribution, then it is possible to define a temperature applicable to the situation by studying the relative intensities of the rotational bands associated with a particular line in the first negative system. The technique is well known[9] and will not be discussed further here. The rotational structure associated with the $v'=0 \rightarrow v''=0$ (3914 Å) band was investigated with high spectral resolution and an apparent temperature of 310 ± 30°K observed. This is equal to ambient room temperature, within experimental error. Certainly, the excited N_2^+ ions are not in thermal equilibrium with their surroundings in this type of situation. Our observation indicates that the distribution among the rotational levels appropriate to the neutral target is unaffected by the collision process which simultaneously excites and ionizes the molecule. At the high velocities used in this experiment, the time during which the collision takes place is many orders of magnitude less than the time required for a transition between two rotational levels, and changes in the rotational distribution are therefore unlikely. Similar observations have previously been made by various workers.[6,13,16] A recent investigation by Polyakova *et al.*[17] using a mixed beam of protons and hydrogen atoms to excite a nitrogen target at 30-keV impact energy has disclosed a slight enhancement of the higher rotational levels. The present experiment was not sufficiently sensitive to allow measurements of sufficient accuracy to confirm the findings of Polyakova.

TABLE I. Comparison of the experimental and theoretical values of the relative intensities of emissions in the $0 \rightarrow v''$ and $1 \rightarrow v''$ progressions of the N_2^+ first negative band system. The intensities of the $0 \rightarrow 0$ and $1 \rightarrow 0$ transitions are taken as unity.

	Present work	Philpot and Hughes[a]	Sheridan and Clark[b]	Stewart[c]	Nicholls[d]
3914 Å $0 \rightarrow 0$	1	1	1	1	1
4278 Å $0 \rightarrow 1$	0.39	0.32	0.49	0.39	0.30
4709 Å $0 \rightarrow 2$	0.074	0.067	0.105	0.10	0.06
5228 Å $0 \rightarrow 3$	0.011	0.01			0.01
3582 Å $1 \rightarrow 0$	1	1			1
3884 Å $1 \rightarrow 1$	0.71	0.60			0.59
4236 Å $1 \rightarrow 2$	0.76	0.57			0.57
4652 Å $1 \rightarrow 3$	0.35	0.25			0.20
5149 Å $1 \rightarrow 4$	0.08	0.05			0.05

[a] Reference 6, experimental proton impact.
[b] Reference 13, experimental proton impact.
[c] Reference 14, experimental electron impact.
[d] Reference 15, theoretical.

VI. EMISSION FROM THE NEUTRAL MOLECULE

The only emission from the neutral nitrogen system observed in the present work is the second positive band system which involves the transition $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$.

[13] J. R. Sheridan and K. C. Clark, Phys. Rev. **140**, A1033 (1965).
[14] D. T. Stewart, Proc. Phys. Soc. (London) **A69**, 437 (1966).
[15] R. W. Nicholls, J. Res. Nat. Bur. Std. (U. S.) **65A**, 451 (1961).
[16] E. M. Reeves and R. W. Nicholls, Proc. Phys. Soc. (London) **78**, 588 (1961).
[17] G. N. Polyakova, V. I. Tatus', S. S. Strel'chenko, Ya M. Fogel, and V. M. Fridman, Zh. Eksperim. i Teor. Fiz. **50**, 1464 (1966) [English transl.: Soviet Phys.—JETP **23**, 973 (1966)].

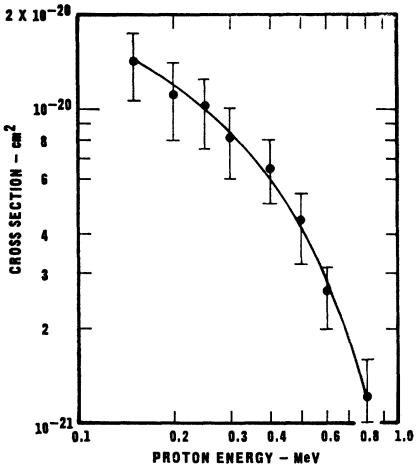

FIG. 6. Estimate of the cross section for the emission of the $0 \rightarrow 0$ transition of the N_2 second positive system, excited by direct proton impact. This cross section will be of the same order of magnitude and will exhibit the same energy dependence as the cross section for the formation of the $C\,^3\Pi_u$ state of N_2 by direct proton impact.

Since the N_2 ground state is a singlet level $X\,^1\Sigma_g^+$, the direct excitation of the $C\,^3\Pi_u$ state involves a change in multiplicity and violation of the Wigner spin-conservation law. It is of considerable interest to determine quite how important is the conservation-of-spin requirement when considering a relatively high-energy impact on a heavy complex structure such as the nitrogen molecule. Previous workers[18,19] find that the emission varies quadratically with target pressure, indicating that a secondary mechanism is responsible. Both electrons and neutral hydrogen atoms could excite the triplet state by an electron-exchange process. Carleton[18] considers that at 3-keV impact energy the principal secondary mechanism is the excitation of the nitrogen by neutral hydrogen atoms which were formed from the incident protons by a charge-exchange process in the cell itself. Hughes *et al.*[19] show that the principal secondary process at an impact energy of 200 keV is excitation by secondary electrons produced originally by the ionization of the target. These different explanations of the secondary processes are consistent with the energy dependence of the ionization and charge-transfer cross sections.

A brief investigation was carried out to test the postulates of Hughes *et al.*[19] and Carleton[18] at the somewhat higher energies available to the present experiment. The emission of the 3371 Å ($v'=0 \rightarrow v''=0$) line was investigated as a function of pressure at energies 150–800 keV. It was found that the variation of intensity with pressure p could always be represented by $J_{ij}=Ap+Bp^2$. We interpret the contribution which varied linearly with pressure to be the direct excitation of the level by proton impact:

$$H^+ + N_2 \rightarrow H^+ + N_2(C\,^3\Pi_u). \quad (8)$$

An estimate of the emission function of the 3371 Å line induced by the single mechanism described by Eq. (8) is shown in Fig. 6. Herzberg[9] lists no transitions which could cause a cascade population of the $C\,^3\Pi_u$ state, and therefore this emission function will be somewhat less than the total cross section for populating the $C\,^3\Pi_u$ state but will exhibit the same energy dependence. Because of the poor signal-to-noise ratio at low pressures, the random-error bars shown on the figure are large, and to these must be added an uncertainty of $\pm 50\%$ due to calibration difficulties at the low wavelength involved. We observe that the cross section drops quite rapidly with increasing energy. This emission cross section is a factor of about 10^3 less than that of the $v'=0 \rightarrow v''=0$ transition in the emission of the first negative system of the molecular ion. Stewart[14,20] shows that in electron impact, where exchange is possible, the cross sections for emitting the N_2^+ first negative and N_2 second positive systems are comparable. The present observation indicates the importance of spin conservation in governing the possible transitions which may take place. That part of the emission which varied quadratically with pressure was also measured absolutely and compared with the known cross sections for charge transfer and ionization. The mechanism of excitation by neutral-particle impact may be ruled out, since it would require a cross section some orders of magnitude greater than that for proton impact and increasing throughout our energy range. On the other hand, the mechanism of excitation by secondary electrons gives rise to more reasonable figures. Taking the gross ionization data of Hooper *et al.*[10] as giving a cross section for electron production and using the electron-impact-excitation cross section of Stewart and Gabathuler,[20] the emission may be explained both qualitatively and quantitatively if some 10% of the secondary electrons are produced with energies above the excitation threshold (11 eV). We conclude that the secondary electron impact is the predominant mechanism, in agreement with the general statements of Hughes *et al.*[19] and of Carleton.[18]

VII. CONCLUSION

Unlike the case of proton-impact excitation of helium that we have described in previous papers,[1,4] there are no theoretical treatments which can predict accurately the processes which will occur when high-energy protons are incident on a complicated molecular target such as nitrogen. It is therefore of considerable importance that the mechanisms which we have observed are in close qualitative accord with concepts that are normally associated with optical-emission phenomena. Applica-

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tion of the Franck-Condon principal to the well-known potential-energy curves[21] of the N_2 and N_2^+ systems suggests that the emission of the N_2^+ first negative and the N_2 second positive systems are the most likely results of the collisions. In electron impact, the cross sections are comparable.[14,20] However, for proton impact there is the additional consideration that the excitation of the $N_2(C\,^3\Pi_u)$ state is forbidden by the Wigner spin-conservation rule, and this is confirmed by our observation that the second positive band system of N_2 is only weakly excited by direct proton impact. Theoretical values of overlap integrals give a reasonable prediction of the relative population of the two vibrational levels of $N_2^+(B\,^2\Sigma)$ that we have investigated.

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Atomic Form Factor and Incoherent-Scattering Function of the Helium Atom*

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The atomic form factor and the incoherent-scattering function of the helium atom have been calculated from several wave functions of differing accuracies. The form factor calculated from the Hartree-Fock wave function is in very close agreement with that from the 20-term Hylleraas wave function for all values of the momentum transfer. For small momentum transfers (<3 atomic units), the incoherent-scattering function is sensitive to the wave function used, but it becomes insensitive for large momentum transfers. Correlated wave functions give values of the incoherent-scattering function, at small momentum transfers, approximately 5% lower than the Hartree-Fock wave function does. Consequences of the above results in the calculation of x-ray and electron-scattering cross sections are discussed.

I. INTRODUCTION

THE atomic form factor $F(K)$ and the incoherent-scattering function $S_{\rm inc}(K)$ for a neutral atom of atomic number Z are defined as follows:

$$F(K)=\sum_{j=1}^{Z}\langle\exp(i\mathbf{K}\cdot\mathbf{r}_j)\rangle, \tag{1}$$

$$S_{\rm inc}(K)=Z^{-1}\Big[\sum_{j,k=1}^{Z}\langle\exp[i\mathbf{K}\cdot(\mathbf{r}_j-\mathbf{r}_k)]\rangle-|F(K)|^2\Big], \tag{2}$$

where $\langle\ \rangle$ denotes an expectation value in the ground state, $\mathbf{K}h$ is the momentum transfer, and $\mathbf{r}_j$ the radial vector from the nucleus to the jth electron. Both $F(K)$ and $S_{\rm inc}(K)$ are even functions of K.

The functions $F(K)$ and $S_{\rm inc}(K)$ play important roles in the theory of scattering of x rays and electrons by atoms.[1–3] When the energy of an incident photon is much smaller than the rest energy mc^2 of an electron, the cross section $d\sigma_{\rm coh}$ for coherent scattering of the photon by an atom into the solid-angle element $d\Omega$ is

$$d\sigma_{\rm coh}=\tfrac{1}{2}r_0^2(1+\cos^2\theta)|F(K)|^2d\Omega, \tag{3}$$

where $r_0=e^2/mc^2$ is the classical electron radius, and θ, the angle between the initial and final momenta of the photon, is twice the Bragg angle. In Eq. (3), $I_{\rm Th}=\frac{1}{2}r_0^2(1+\cos^2\theta)$ is the Thomson cross section for scattering by a free electron, and we may interpret $|F(K)|^2$ as the effective number of atomic electrons contributing to the coherent scattering. In x-ray scattering, the variable $\sin(\theta/2)/\lambda=K/4\pi$ is commonly used in place of K, with λ the wavelength of the incident photon. The total incoherent-scattering cross section $d\sigma_{\rm inc}$ of x rays is[4]

$$d\sigma_{\rm inc}=I_{\rm Th}ZS_{\rm inc}(K)d\Omega. \tag{4}$$

Coherent and incoherent scattering of x rays correspond respectively to elastic and inelastic scattering of fast electrons. The differential cross section $d\sigma_{\rm el}$ for the elastic scattering of electrons by an atom, in the first Born approximation, is

$$d\sigma_{\rm el}=4a_0^2/(Ka_0)^4|Z-F(K)|^2d\Omega, \tag{5}$$

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[4] A relativistic correction is necessary for high-energy photons, particularly at large angles. In such cases, $I_{\rm Th}$ in Eq. (4) should be replaced by the Klein-Nishina cross section.