Emission Spectra Excited by Electronic and Ionic Impact*

C. Y. FAN
Yerkes Observatory, University of Chicago, Williams Bay, Wisconsin
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This paper summarizes results of laboratory experiments on the optical emission of a rarefied air sample excited by the impact of electrons (10–8000 ev), protons (5–350 kev), and He^+ ions (10–450 kev). In the high-energy region, charged particles of different species but of the same velocity excite very much the same spectrum. In the low-energy region, on the other hand, the process of charge exchange plays such an important role that the spectra show marked characteristics of the species of the particles which cause the excitation. The relative band intensities of the negative system of N_2^+ and the relative intensities of the negative to the Meinel system of N_2^+ excited by low-energy particles depart notably from the prediction of the Franck-Condon principle. The importance of energy transfer in the process of charge exchange is discussed.

I. INTRODUCTION

SPECTROSCOPIC studies of the phenomena induced by the passage of a beam of energetic particles through air have been in progress at the Yerkes Observatory since 1952.[1–5] The program was initiated by Meinel with the purpose of investigating the fundamental processes involved in auroral excitation. Electrons, protons, and helium ions have been used as the primary particles. A monoenergetic beam of one of these species of particles, after being magnetically analyzed, was fired through a $\frac{1}{16}$-in. hole into an absorption chamber containing a rarefied air sample (Fig. 1). The optical emission induced in the air sample was then studied with a spectrograph, viewing through the side windows or through the end window to record the Doppler-shifted lines of the emission from the incident particles.

In our earlier experiments, the pressure of the absorption chamber was maintained in a range of 0.1–0.5 mm-Hg by a thin SiO window mounted on the entrance slit.[1,2] It then became apparent that the use of a window for the maintainance of a higher pressure of air had introduced intolerable distortions in the emission spectra. In the first place the emission spectra induced by the primary particles, which were the primary objective of the study, were obscured by the emission excited by large amounts of secondary electrons produced at the SiO window under the bombardment of the incident beams.[5] Furthermore, in the studies of the phenomena of charge exchange, since too high a pressure was used, the excited states of the incident particles produced through the process of electron exchange were largely destroyed by subsequent collisions with the target molecules.[4] These distortions had been one of the major factors making our earlier experimental results often as difficult to interpret as the upper atmospheric phenomena that the experiments were designed to elucidate.

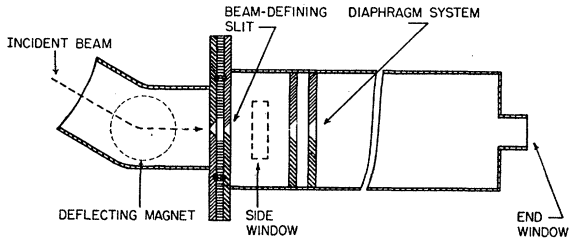


FIG. 1. Schematic diagram of the apparatus.

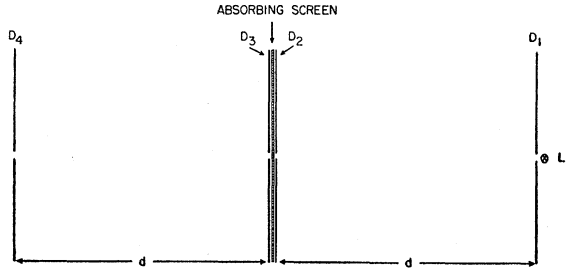


FIG. 2. Arrangement of diaphragm system for spectral calibration. (a) For the determination of the absorption coefficient of the absorbing screen, L represents the exit slit of a monochromator, and D_1, D_2, D_3, D_4 are the diaphragms of $\frac{1}{4}$-inch openings. (b) For the calibration of the spectrograph, L represents the standard lamp, D_4 is removed, and a rotating sector is placed behind D_3.

The experiments were repeated with the following changes: The air pressure was maintained in a range of 0.1–10 μ Hg by means of differential pumping. Precautions were also taken against the emission induced by the secondary electrons produced at the side wall of the absorption chamber by the primary particles. With these improvements, the emission spectra obtained begin to be understandable in accordance with general theories of electronic and ionic impact. In this paper, the results are qualitatively described and discussed.

II. APPARATUS AND CALIBRATION

The spectra were taken with an $f/0.65$ grating spectrograph (the B spectrograph) previously used at the

* The research reported in this paper has been supported in part by the Geophysics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command.

[1] A. B. Meinel and C. Y. Fan, Astrophys. J. **115**, 330 (1952).
[2] C. Y. Fan and A. B. Meinel, Astrophys. J. **118**, 205 (1953).
[3] C. Y. Fan, Astrophys. J. **119**, 294 (1954).
[4] C. Y. Fan, Astrophys. J. **112**, 350 (1955).
[5] C. Y. Fan, *The Airglow and Aurora*, edited by A. Dalgarno and E. Armstrong (Pergamon Press, London, 1956).

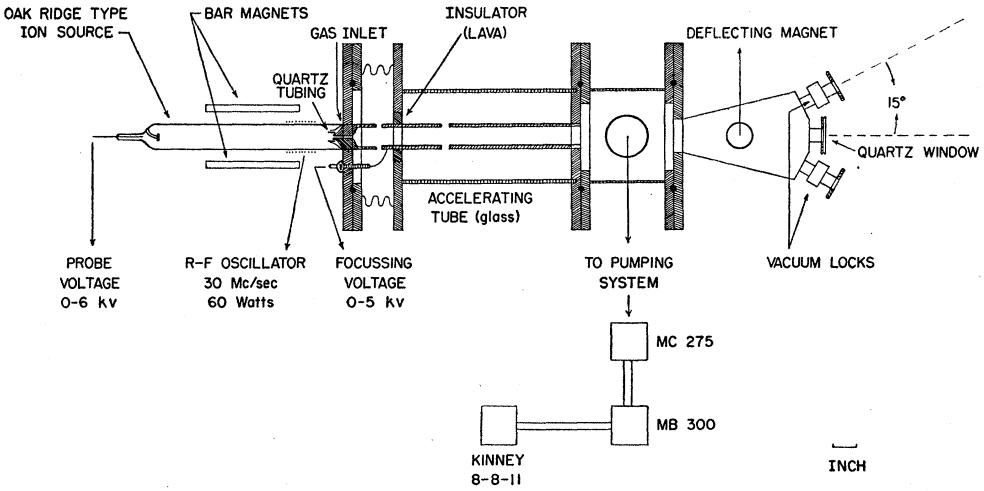


FIG. 3. Schematic diagram of the 30-kev linear accelerator.

McDonald Observatory for nebular spectra.[6] It provides a first order dispersion of 400 A/mm at H_γ and 350 A/mm at H_α. Eastman 103a-F(3) spectrographic films were used for the spectral range 3700–6800 A, and hypersensitized I-N films were used for the region of 6300–9000 A.

For the purpose of a spectral comparison the spectrograph was calibrated against a 25-watt standard lamp (2526°K) whose radiant energy in a band width of 50 A through a $\frac{1}{4}$-in. hole in a diaphragm in close contact with the lamp has been measured absolutely in the forward direction at six wavelengths, 3998 A, 4319 A, 4861 A, 5200 A, 5959 A, and 6563 A. The lamp was mounted at a distance d from a diffused absorber of known coefficient of absorption[7] (Fig. 2). The absorber itself was then regarded as a standard light source of variable intensity (by varying d). With the image of the absorber projected on the slit of the spectrograph, a set of spectra having intensities varied in steps by means of a fast rotating sector (50 rps) was taken. The microphotometer tracing of the set of spectra after being corrected for the nonlinear dispersion of the spectrograph, served as an absolute intensity scale for the particular geometrical position of the spectrograph. Several sets of the calibration curves were obtained for different lengths of exposures.

The experiments on the excitation by high-energy ions (40–500 kev) were done with the kevatron of The Enrico Fermi Institute for Nuclear Studies.[8] The experiments on the excitation by low-energy ions (5–30 kev) and by electrons (10–8000 ev) were done respectively with a 30-kev ion accelerator and an electron gun built at the Yerkes Observatory.

Figure 3 shows the schematic diagram of the ion accelerator. The ion source is of the Oak-Ridge type[9] but modified slightly to suit our own purpose. For instance, the channel tip of the base is a separate piece screwed on to the base so that a ruined one can be easily replaced. The positive electrode of the ion source is silver-soldered to a brass rod which is then soft-soldered to the copper-to-glass seal at the end of the ion source. For cleaning, the brass rod can be unsoldered and then the whole glass envelope can be dipped into cleaning solution. The solenoid described in the original paper of Moak *et al.*[9] was replaced by four bar magnets, and a magnetic coupling was used for the operation. The ion source yielded a beam current of protons or He^+ ions of several hundred microamperes.

Figure 4 shows the design of the electron gun. The shape of the cathode and the focusing electrodes was taken from the design of Ho and Moon.[10] Together with the filament (a 15-mil tungstun wire coated with emissive coating), they were rigidly attached to one part of the ground-glass joint to facilitate the replacement of the filament. It produced a collimated electron beam of 10 μa or higher for electrons of energies higher than 100 ev. For the acceleration of electrons of energy below 100 ev, electrons were first accelerated to 100 ev and then reduced to the desired value by applying a negative voltage before they entered the absorption chamber. A coaxial magnetic field of about 50 gauss was found to be necessary to prevent the spreading of the low-energy electrons. The magnetic coils were wound around the absorption chamber as indicated in Fig. 4.

III. EXPERIMENTAL RESULTS

Emission from Incident Particles

When low-energy protons and He^+ ions were used as exciting particles, Doppler-shifted hydrogen and helium

[6] T. Page, Astrophys. J. **108**, 157 (1948).
[7] The absorber was a piece of high-grade opal glass. The absorption coefficient of the glass was determined with a monochromator located at the position of the lamp L (Fig. 2) and a photocell. The ratio of the photocell current with the absorber mounted in position as indicated in Fig. 2 and the cell behind a diaphragm (D_4) identical with D_2 but at a distance d from it to the current with the cell mounted behind D_2 equals to the absorption coefficient at the wavelength, set by the monochromator.
[8] S. K. Allison, Rev. Sci. Instr. **19**, 291 (1948).
[9] Moak, Reese, and Good, Nucleonics **9**, 18 (1953).
[10] K. C. Ho and R. J. Moon, J. Appl. Phys. **24**, 1186 (1953).

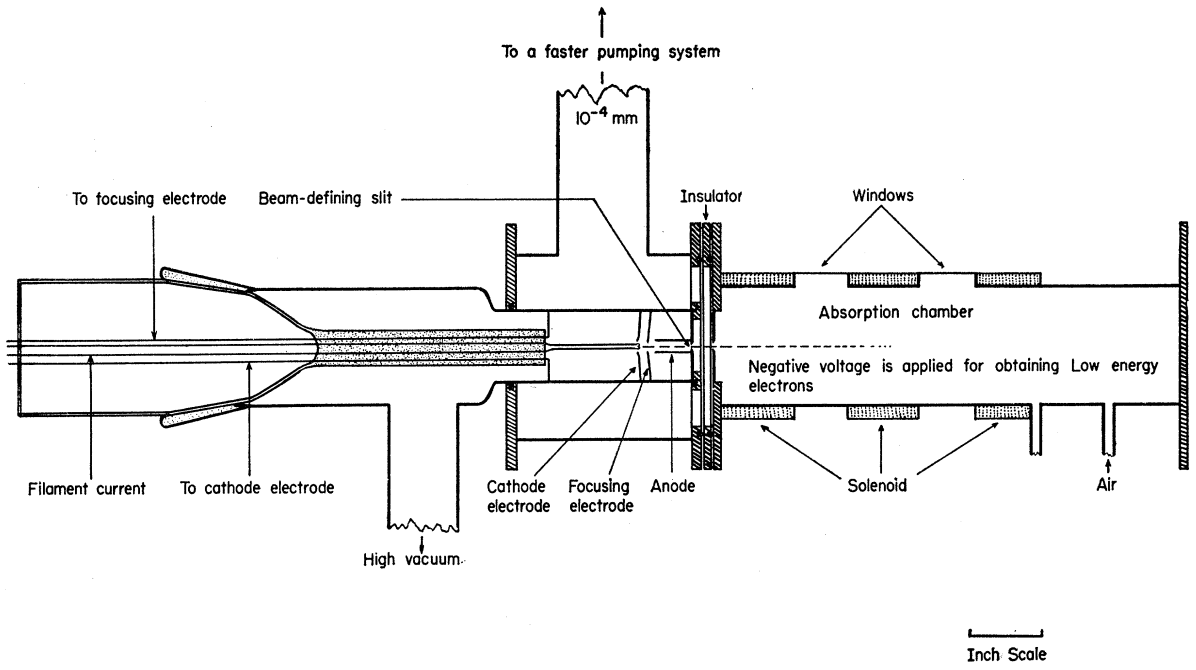


FIG. 4. Schematic diagram of the electron gun.

lines respectively could always be detected. These radiations were produced by the incident particles being excited by either capturing electrons from the air molecules directly into excited states or capturing electrons into the ground states but re-excited by subsequent collisions with air molecules.

The identification of the Balmer series in a proton induced spectrum and the 6678 A and 5876 A He I lines in a spectrum excited by 11-kev He^+ ions have been reported in our earlier publications.[2,4,5] Recently, in a spectrum excited by 196-kev He^+ ions, the 3889 A He I was identified. Figure 5 shows this spectrum in comparison with the two spectra obtained in the earlier experiments.

The detection of the emission from incident particles is of fundamental importance in the studies of auroral excitation since it is the only method which can be used to determine the relative abundances of the species of auroral particles. From the appearance of Doppler-shifted and merely broadened Balmer emission, a proton component of the primary auroral particles has been established beyond any doubt.[11,12] On the other hand, there is no conclusive evidence in the literature that helium lines have ever been observed. From Fig. 5, it appears that the 5876 A He I line is relatively unobscured and thus detectable.

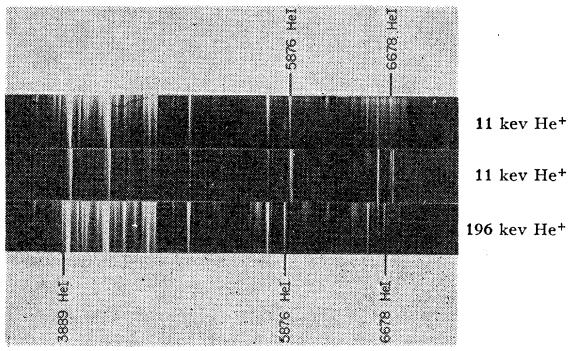


FIG. 5. Spectra excited by 11-kev and 196-kev He^+ ions respectively, showing Doppler-shifted He I lines.

Emission Excited by Means of Electron Exchange

The excitation of the first ($1PG$) and the second positive system ($2PG$) of N_2 from the ground state involves a change of multiplicity. Thus the emission can be produced only be either an N_2 molecule excited through the process of electron exchange:

$$\text{(a)}\quad N_2+e\rightarrow N_2(B\,^3\pi_g \text{ or } C\,^3\pi_u)+e,$$

or by an N_2^+ ion through the process of electron capture:

$$\text{(b)}\quad N_2^++e\rightarrow N_2(B\,^3\pi_g \text{ or } C\,^3\pi_u).$$

We assume that the contributions of the processes such as the association of N^+ and N^-, photoexcitation, etc., are negligible.

In laboratory experiments, process (b) can be eliminated by using a low air pressure (1 μ Hg or lower) in the absorption chamber. In this case, the N_2^+ ions would have their collisional mean free paths longer than the linear dimension of the chamber and so they would surely be neutralized after their collisions with the

[11] A. B. Meinel, Astrophys. J. **113**, 50 (1951).
[12] C. Y. Fan and D. H. Schulte, Astrophys. J. **120**, 563 (1954).

metallic wall of the chamber. Since the spectrograph was focused on the primary beam, the emission from the neutralization escaped detection.

A low pressure is also essential to avoid serious scattering of an incident beam towards the side wall of the absorption chamber. Under the bombardment of the primaries, a large amount of secondary electrons will be produced at the side wall and their induced emission often distorts the spectrum excited by the primary particles. It was found that a low pressure combined with a diaphragm system as indicated in Fig. 1, is quite efficient for the elimination of these undesired secondary electrons.

After these precautions have been taken, one can then demonstrate that reaction (a) is practically the only mechanism operating for the excitation of the $1PG$ and $2PG$ of N_2. This is shown in the three spectra of Fig. 6 which are excited by 23 ev, 500-ev electrons and 20-kev protons respectively. It is seen that $1PG$ and $2PG$ are practically the only emissions in the spectrum excited by 23-ev electrons, but their intensity is negligible compared to the negative system of N_2^+ in the spectra excited by 500-ev electrons and 20-kev protons. This illustrates the effect of the elimination of reaction (b) and the sensitive dependance of reaction (a) on the energy of the electrons as expected.

Energy Transfer in the Process of Electron Capture and the Relative Band Intensities of the Negative System of N_2^+ (ING)

The negative system of N_2^+ is excited by the following reaction:

$$\text{(c)}\quad N_2+X\rightarrow N_2^+(B\,^2\Sigma)+(X+e),$$

where X is an incident particle or a secondary electron. The contribution of direct excitation from the ground state of N_2^+ must be relatively unimportant.[2,13]

Reaction (c) can be a process of direct ionization or a process of electron capture, in which case the notation $(X+e)$ stands for the particle X having the electron in one of its bound states.

The process of a direct ionization by a *fast* particle can be treated as a reaction between an atomic electron and the impact particle. The nuclear charge plays an intrinsic role and the momentum transfer between the target nucleus and the impact particle can be neglected. On the other hand, when the reaction (c) is between a *slow* particle and a N_2 molecule, the momentum transfer could be a sizable amount should the incident particle be a heavy ion. The case is particularly clear in the process of electron capture which can be shown as follows:

Let M_1 and (M_2+m) be respectively the masses of the incident particle X and the target particle A, where m is the electronic mass. Before the electron transfer, X has a velocity u while A is assumed to be at rest. After the electron transfer, $(X+e)$ and A are scattered respectively with velocities v_1 and v_2 making angles θ_1 and θ_2 with the initial direction of incidence. Then, the conservation of momentum and energy require

$$M_1u=(M_1+m)v_1\cos\theta_1+M_2v_2\cos\theta_2, \tag{1}$$

$$0=(M_1+m)v_1\sin\theta_1-M_2v_2\sin\theta_2, \tag{2}$$

and

$$M_1u^2-2Q_2=(M_1+m)v_1^2+M_2v_2^2-2Q_1, \tag{3}$$

in which Q_1 and Q_2 are the binding energies of the electron in X and A, respectively. By eliminating θ_1 from (1) and (2) and then substituting the value of v_1 from (3), and neglecting m compared to M_1, we have

$$E_2-2\frac{(M_1M_2)^{\frac{1}{2}}}{M}E^{\frac{1}{2}}\cos\theta_2E_2^{\frac{1}{2}}-\frac{M_1}{M}(Q+\tfrac{1}{2}mu^2)=0, \tag{4}$$

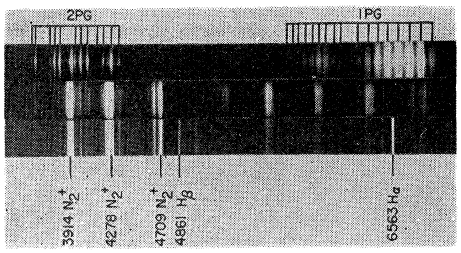
where $E_2=\frac{1}{2}M_2v_2^2$, $E=\frac{1}{2}M_1u^2$, $M=M_1+M_2+m$, and $Q=Q_1-Q_2$.

It is clear from (4) that E_2 cannot be zero except when Q is negative (endothermic reaction) and $u^2=-2Q/m$; then the energy transfer will be the same as in the case of elastic scattering. Otherwise, the value of E_2 which depends of course on θ_2, should be distinguished for the following two cases: namely, $Q+\frac{1}{2}mu^2<0$ and >0. In the former case, $\cos\theta_2$ must be less than $[-(Q/E+m/M_1)(M/M_2)]^{\frac{1}{2}}$ and thus E_2 has a minimum value

$$E_l=(M_1/M)\,|Q+\tfrac{1}{2}mu^2|. \tag{5}$$

In the latter case, θ_2 can be greater than $\pi/2$. However, to a high degree of approximation, the maximum value of θ_2 can be taken as $\pi/2$, and again, the minimum recoiling energy is given by (5). This is interpreted as the most probable energy transfer by the process of the charge exchange.

The energy transfer has very little effect on the structure of an atomic particle. However, in case of the target particle being a diatomic molecule, for instance an N_2, the energy transfer which is most likely unevenly divided among the two nitrogen atoms, will set up a forced vibration in the system. Consequently, the relative band intensities of the negative system of N_2^+ as excited by electron capture would be different from that excited by means of direct ionization. In other words,



23 ev electrons
500 ev electrons
20 kev protons

FIG. 6. Spectra excited by 23 ev, 500-ev electrons and 20-kev protons respectively. These spectra show the difference in intensities of the first ($1PG$) and the second positive ($2PG$) systems of N_2 excited by low-energy electrons compared with that excited by high-energy electrons and positive ions.

[13] D. R. Bates, Proc. Roy. Soc. (London) **A196**, 217 (1949).

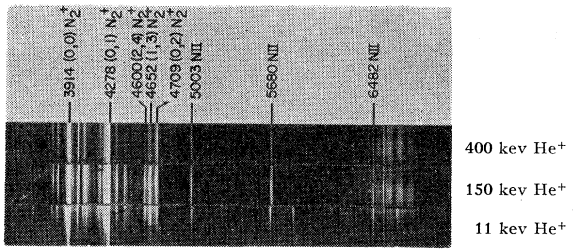


FIG. 7. Spectra excited by 400-, 150-, and 11-kev He^+ ions. These spectra show the variation of the relative intensities of λ4709(0,2), λ4652(1,3), and λ4600(2,4) bands of the negative system of N_2^+ with the energies of He^+ ions.

the band intensities are expected to vary with the energy of the exciting particles, reflecting the increasing importance of electron capture compared with direct ionization towards lower energies. Figure 7 which shows a set of He^+-induced spectra, seems to illustrate exactly the case.

A similar but less drastic variation also appears in proton-induced spectra. For the purpose of comparison, the relative intensities of λ4709 (0,2), λ4652 (1,3) and λ4600 (2,4) excited by low- and high-energy electrons, protons, and He^+ ions were measured and are listed in Table I. It is seen that the $\Delta v=2$ sequences excited by electrons and by high-energy ions of different species have almost the same relative intensities while those excited by low-energy ions have the bands of higher vibrational quantum number notably enhanced.

The less drastic intensity variation in the $\Delta v=2$ sequence in proton-induced spectra is presumably due to a smaller energy transfer in the process of electron capture by protons. Indeed, for a ground state capture, the value of Q is -5.2 ev, and so, for a 25-kev proton, E_l is only 0.56 ev. While for the case of excitation by 100-kev He^+ ions (captured into the ground state) Q is 5.7 ev and so $E_l=4.3$ ev.

The relative constancy of the intensity distribution in the electron-induced spectra is expected. Owing to the minuteness of the electronic mass, the momentum transfer from the incident particle to the target nuclei can be neglected and thus the intensity distribution should follow the prediction of the Franck-Condon principle.

Meinel System of N_2^+ and the First Negative System of O_2^+

From earlier experimental results, it was concluded that electrons are the only particles which can efficiently excite the Meinel system of N_2^+. This conclusion must now be revised.

It is perhaps interesting to see what can happen to the emission spectra when the absorption chamber is loaded with secondary electrons produced at the side wall or at a thin window as occurred in our earlier experiments. Figure 8 shows two spectra excited by 2-kev electrons

TABLE I. Relative intensities of the $\Delta v=2$ sequence of the negative system of N_2^+.

Exciting particles	Relative intensities λ4709(0,2)	λ4652(1,3)	λ4600(2,4)
Electrons (23 ev)	1	0.51	0.13
Protons (20 kev)	1	0.62	0.34
He^+ ions (150 kev)	1	1.0	0.50
Electrons (120 ev)	1	0.33	0.08
Protons (205 kev)	1	0.33	0.10
He^+ ions (450 kev)	1	0.39	0.21

with the image of the electron beam projected on the slit of the spectrograph. It is seen that the lateral intensity distribution of different systems is different. The 1*PG* and 2*PG* of N_2 have a uniform appearance, the first negative system of O_2^+ and the Meinel system are concentrated right in the path of the primary electron beam, while the lateral intensity of the negative system of N_2^+ is between these two extreme cases. These differences apparently reflect the differences in the excitation functions for these systems, namely, secondary (low-energy) electrons can excite with high efficiency 1*PG* and 2*PG* of N_2, but cannot do as well with the first

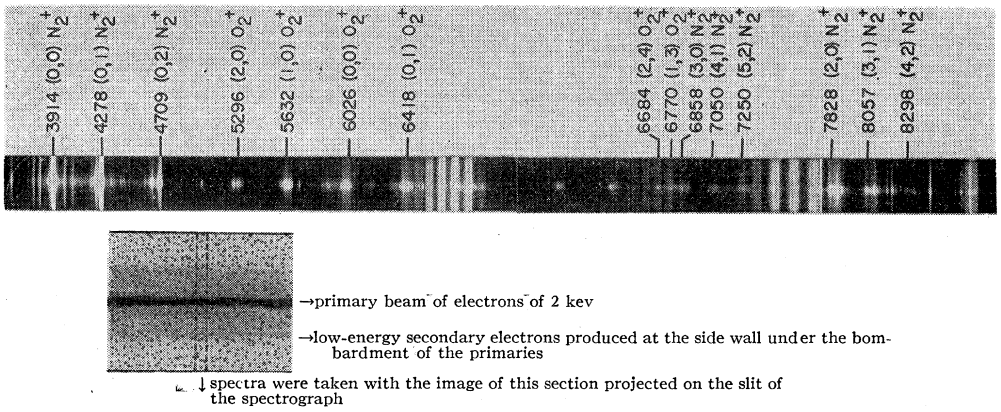


FIG. 8. Spectra excited by 2-kev electrons, showing the difference in the lateral distribution of intensities of different systems of molecular bands.

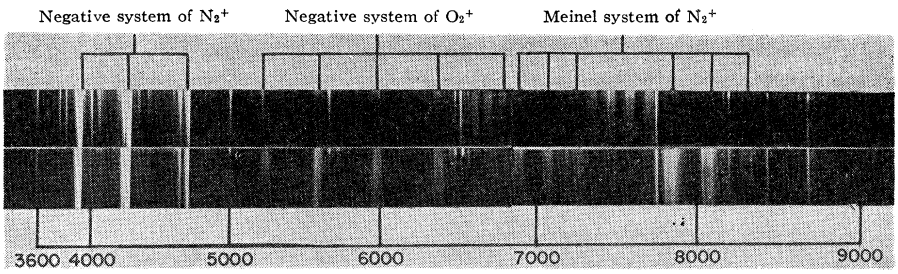


FIG. 9. Spectra excited by 20-kev and 300-kev protons respectively, showing the difference in intensities of the Meinel system of N_2^+.

negative system of O_2^+ and the Meinel system of N_2^+. Consequently, in an absorption chamber which is loaded with low-energy secondary electrons, the intensity of the O_2^+ and N_2^+ bands will be completely obscured by the intense first positive bands and are thus not detected. This also explains the failure of earlier efforts to produce the Meinel system in laboratories. Sayers first succeeded in producing the system with 220-ev electrons.[14]

It is interesting to note in Fig. 8 that by the apparent difference in lateral intensities, one can identify several bands of O_2^+ although they overlap in positions with the first positive bands. By the same method, we have identified two O_2^+ bands, λ6684(2,4), λ6770(1,3), which are not listed in the table by Singh and Lal.[15]

We have estimated the ratio of the excitation function of the negative system to the Meinel system of N_2^+ for different energies of electrons. It is almost constant for energies higher than about 35 ev. Toward lower energies, (25–35 ev), there is some indication that the ratio becomes higher. This brings the *average* energy of the auroral electron from 200 ev[3] down to about 30 ev in agreement with the estimation of Stewart *et al.*[16]

We have seen in Table I that high-energy particles react very much alike in excitations. This can also be inferred from the accuracy with which the Bethe-Bloch formula represents the observed stopping power of matter for energetic particles. The excitation of the Meinel system is also evidence of this general statement as is shown in Fig. 9.

Figure 9 shows two spectra excited by 20 kev and 300 kev protons, respectively. The ratio of the excitation function of the negative to the Meinel system is just about the same as that excited by electrons of a comparable velocity. This ratio is by far much higher in the spectrum excited by 20-kev protons. However, it is entirely unclear whether this is due to a negligible overlapping integral of the wave functions of the electron in the two bound states in the process of electron capture, or if the $^2\pi$ state of N_2^+ is perturbed by the energy transfer in the interaction with slow ions.

In conclusion, the present experiments indicate that in the high-energy region where the Born-approximation is valid, charged particles of different species but of the same velocity excite very much the same spectrum. Toward lower energies, on the other hand, the exchange of atomic electrons plays an increasingly important role in the process of inelastic collisions. The effects are so pronounced that the emission spectra begin to show the characteristics of the particles which do the excitation.

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to Dr. S. K. Allison for his interest in this work and for the use of the kevatron and the facilities of The Enrico Fermi Institute for Nuclear Studies.

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[15] N. L. Singh and L. Lal, Science and Culture (India) **9**, 89 (1943).
[16] Stewart, Gribbon, and Emeléus, Proc. Phys. Soc. (London) **A67**, 188 (1954).

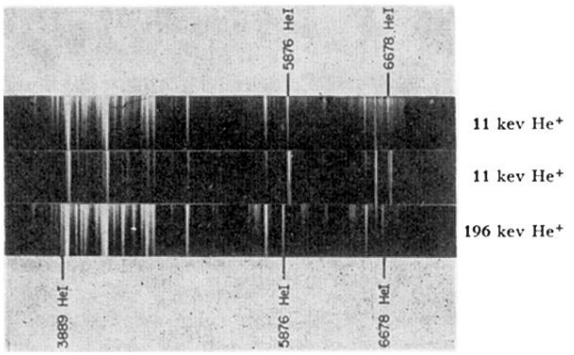
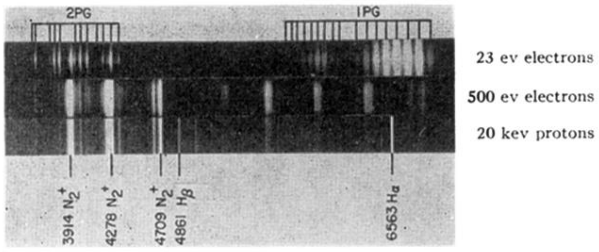


FIG. 5. Spectra excited by 11-kev and 196-kev He^+ ions respectively, showing Doppler-shifted He I lines.



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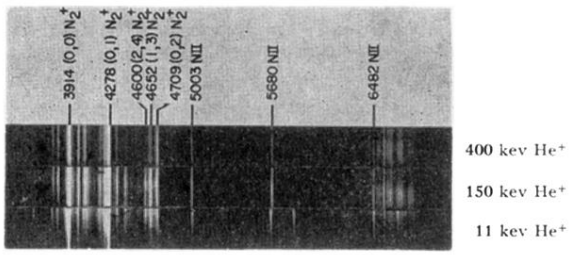

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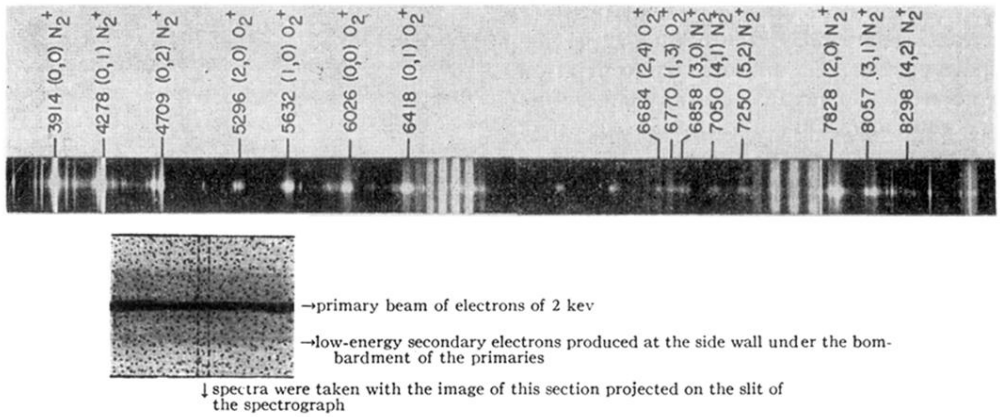

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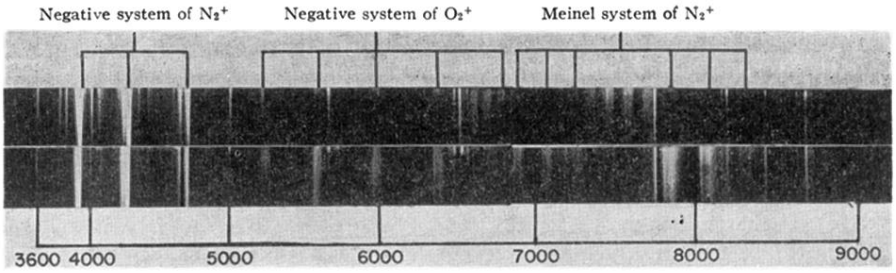

FIG. 9. Spectra excited by 20-kev and 300-kev protons respectively, showing the difference in intensities of the Meinel system of N_2^+.