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Vibrational Excitation of Nitrogen by Electron Impact*

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The vibrational excitation of nitrogen molecules by electrons in the energy range 1.5 to 4 ev is studied using a double electrostatic analyzer. The beam of essentially monoenergetic electrons (half-width about 0.06 ev) is produced by the first analyzer and is crossed by a molecular beam of N_2 in the collision chamber. The energy distribution of forward scattered electrons is analyzed in the second electrostatic analyzer. Peaks resulting from those electrons which have lost discrete amounts of energy in exciting vibrational levels up to $v=8$ are observed. The energy dependence of the cross section for vibrational excitation to $v=2, 3, 4, 5, 6, 7, 8$ is obtained and pronounced structure is observed. The experiment is consistent with the hypothesis that the vibrational excitation in N_2 around 2.3 ev proceeds via a temporary negative ion.

THE vibrational excitation of nitrogen molecules by electron impact has been studied recently using two types of experiments. Haas,[1] using a swarm experiment of the Maier–Leibnitz type, has found evidence for a large inelastic cross section below the first electronically excited level in N_2 and has attributed it to vibrational excitation of N_2. Using an electron beam technique (trapped-electron method),[2] we have confirmed the existence of a large inelastic cross section in N_2 with an onset at about 1.5 ev and a peak at 2.3 ev, and obtained indirect evidence for the excitation of a number of vibrational states.

The experiment described below has been undertaken in order to resolve the vibrational levels excited by electron impact and to investigate further the temporary negative-ion state in N_2. The experiment consists of crossing a "monenergetic" electron beam with a molecular beam. The energy distribution of the electrons scattered in the forward direction is studied by means of an electrostatic analyzer.

I. DOUBLE ELECTROSTATIC ANALYZER

The apparatus used for these studies consists of two identical, 127-degree electrostatic analyzers separated by a collision chamber, in which the electrons are crossed with a molecular beam of N_2. The electrostatic analyzers incorporate most of the features suggested by Marmet and Kerwin.[3] Figure 1 shows a schematic diagram of the apparatus. A thoria-coated iridium filament ribbon emits electrons which travel into the first electrostatic analyzer. Two cylindrical grids, $4A$ and $4B$, deflect the electrons and focus them on the exit slit. The "unwanted" electrons are collected on the "absorber shield," S_1. Thus, an essentially monoenergetic electron beam emerges at the exit of the first analyzer. The electrons are then accelerated into the collision chamber, 5, which consists of a cylindrical grid and a concentric ion collector ring. A molecular beam, originating in a 3-mm diam tube close to the cylindrical grid, crosses the path of the electrons. The energy distribution of the electrons scattered in the forward direction is analyzed by the second electrostatic analyzer. After passage through the second analyzer, the electrons are collected on a highly insulated and shielded electron collector and measured with a vibrating reed electrometer.

The second analyzer is identical to the first one except that the electrode, S_3, is added. This electrode collects the primary electron beam when the second analyzer is "tuned" to an energy loss process. It is important to minimize that portion of the primary electron beam reaching the electron collector by multiple reflections. The electrode, S_3, aids in preventing reflected primary electrons from reaching the electron collector.

Those parts of the tube which are nearest to the electron beam are gold plated; the absorber shields and the electron collector are electrolytically coated with platinum black in order to reduce the secondary emission of electrons. The platinum black replaces, in this instrument, the "electron velvet" suggested by Marmet

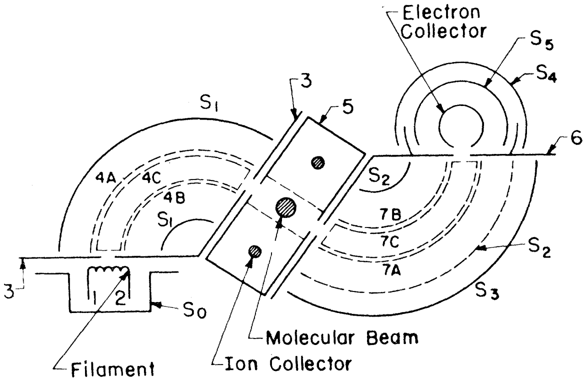

FIG. 1. Schematic diagram of the double electrostatic analyzer. Electrons are emitted by the filament, deflected by the cylindrical grids ($4A$ and $4B$) with radii of 1.0 and 1.5 cm, respectively, injected into the collision chamber 5, and analyzed by sweeping the voltage between electrodes 6 and 3. S_1, S_2, S_3, S_4, S_5 are shields to collect unwanted electrons; $4C$ and $7C$ are top and bottom grids. Typical operating voltages between the electrodes indicated: $(4A-4B)=1.2$v; $(7A-7B)=1.2$v; (Fil$-3)=1.4$v; $(F\text{-}S_1)=20$v; $(F\text{-}S_2)=(F\text{-}S_3)=20$v. The electron collector is grounded. All slits are 0.5×4 mm.

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[1] R. Haas, Z. Physik **148**, 177 (1957).

[2] G. J. Schulz, Phys. Rev. **116**, 1141 (1959).

[3] P. Marmet and L. Kerwin, Can. J. Phys. **38**, 787 (1960). The author wishes to acknowledge a stimulating discussion with P. Marmet and L. Kerwin regarding the problems involved in building an electrostatic analyzer.

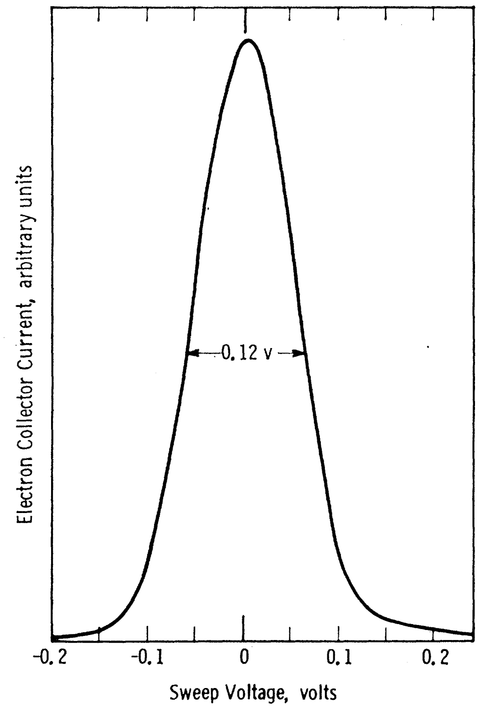

FIG. 2. Typical vacuum characteristics of double electrostatic analyzer.

and Kerwin. The tube is connected to a high-speed vacuum system with a calculated speed of about 130 liters/sec. The effective pressure in the molecular beam is about 100 times the background pressure and is determined from the positive-ion current reaching the ion collector and the known cross section for N_2^+. The vacuum system utilizes a forepump, booster pump, diffusion pump (300 liters/sec), and a liquid air trap. The tube is baked at 320°C and a residual pressure of 10^{-9} mm Hg is achieved. The gas is admitted to the vacuum system from a small pressurized tank of high-purity N_2.

The electrostatic analyzer can be operated with many sets of applied potentials such that one can obtain either high resolution or, by sacrificing resolution, high electron currents. In the experiments to be discussed, both electron analyzers are usually "tuned" to pass electrons of approximately 1.5 ev energy. The electron current reaching the collision chamber is about 10^{-8} amps. Although the dimensions of the electrostatic analyzer are nominally identical to those of Marmet and Kerwin's instrument, the voltages applied to the electrodes are different for optimum operation. The difference probably results from the different contact potentials and minor differences in the geometry. The caption of Fig. 1 gives a set of typical operating voltages as well as the dimensions of the instrument.

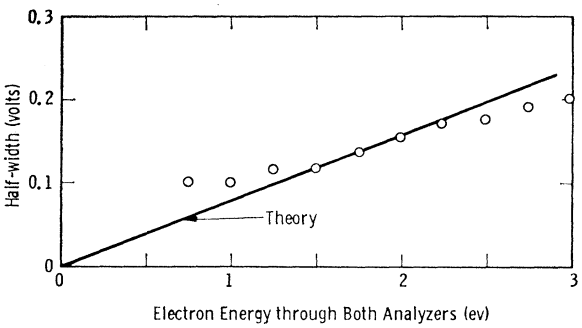

FIG. 3. Half-width of electron energy distribution for electrons passing through both analyzers at the same energy. The half-width of electrons going through one analyzer is assumed to be half of the value indicated.

The voltages applied to the tube are obtained from batteries. The voltage difference for the deflector screens are applied symmetrically about the potential of the respective 127° segment (electrodes 3 and 6, respectively). The accelerating voltage between the two segments can be swept by a motor driven helipot and the collector current vs accelerating voltage can be plotted on an X–Y recorder; a typical curve obtained after bakeout and before the surfaces have been exposed to nitrogen is shown in Fig. 2. The curve shows that the half-width of the energy distribution of the electrons going through both analyzers is about 0.12 ev, for the particular conditions chosen. Thus it can be estimated that the half-width of the energy spread of the electrons going through one analyzer is approximately 0.06 ev. Figure 3 shows a plot of the measured half-width as a function of energy through the analyzers. In this experi-

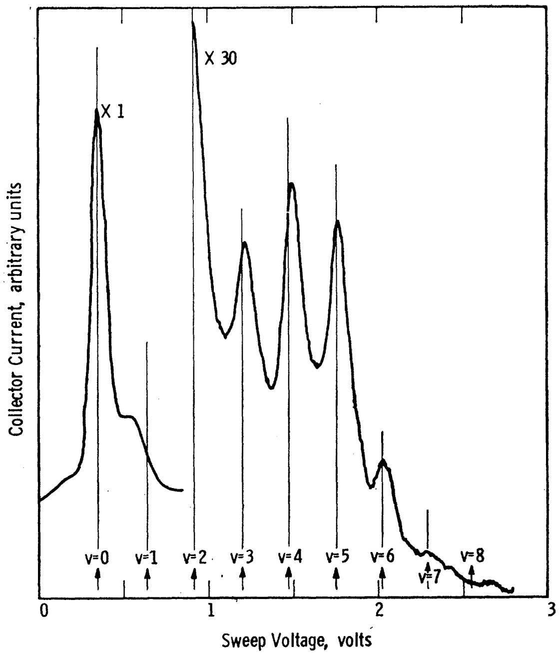

FIG. 4. Energy spectrum of forward scattered electron at an incident electron energy of 2.4 ev.

ment both analyzers were "tuned" to the same energy. It should be noted that the half-width through just one analyzer is taken to be half of the values given in Fig. 3. The line marked "theory" is double the computed half-width for each analyzer given[4] by $2(V_{\frac{1}{2}}/V)=(S+\frac{4}{3}r_0\alpha^2)/r_0$. Here, $V_{\frac{1}{2}}$ is the half-width, V is the electron energy, S is the slit width, r_0 is the mean radius, and α is the acceptance angle.

After the tube has been exposed to nitrogen, the vacuum characteristics are altered by the appearance of a satellite peak, spaced about 0.25 v away from the main peak (see Fig. 4 and 5). This condition prevents us from making meaningful measurements within about 0.3 ev of the primary peak.[5]

II. RESULTS

Figures 4 and 5 shows reproductions of typical traces obtained on the X–Y recorder. The collector current is plotted against sweep voltage (potential difference between electrodes 3 and 6 in Fig. 1) for electron energies in the collision chamber of 2.4 and 2.6 ev. A number of distinct peaks are evident. The largest, marked $v=0$, is due to the primary electron beam going through both sections. The magnitude of this peak is attenuated by elastic scattering in the collision chamber. This peak serves as a voltage reference since these electrons have

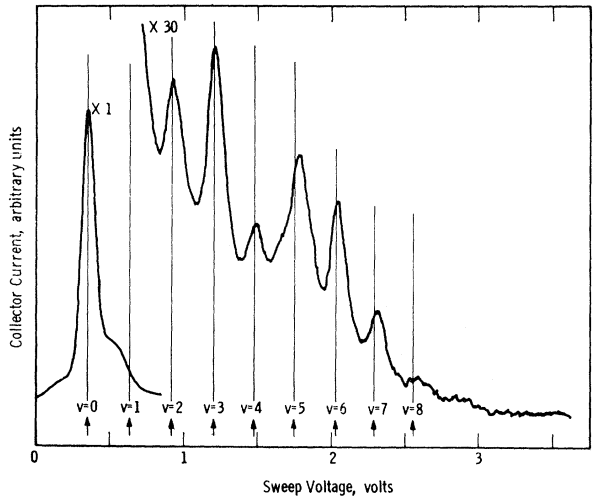

FIG. 5. Energy spectrum of forward scattered electrons at an incident electron energy of 2.6 ev.

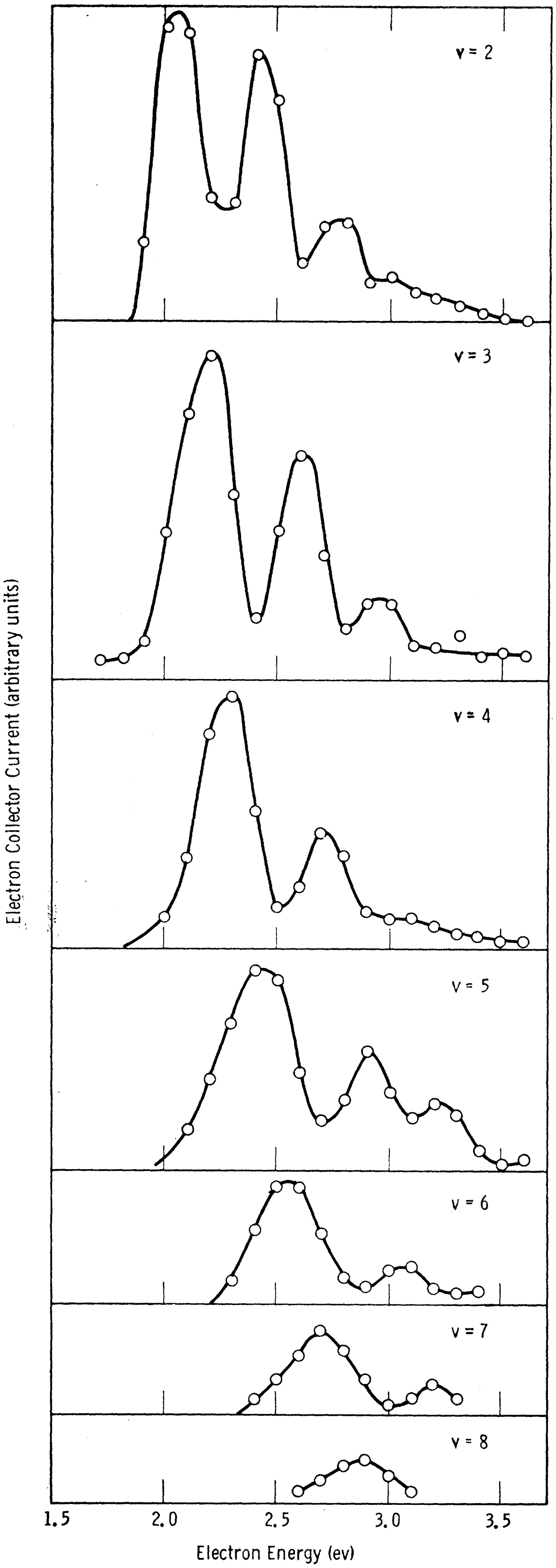

FIG. 6. Energy dependence of cross section to various vibrational states. The cross sections are plotted on the same relative scale; the absolute scale is arbitrary.

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[4] P. Marmet, Doctoral thesis, Universite Laval, Quebec, June, 1960 (unpublished).

[5] It is believed that this satellite peak results from vibrational excitation of nitrogen molecules adsorbed on the surface of one of the slits of the instrument. Only the first vibrational level seems to be excited in this process.

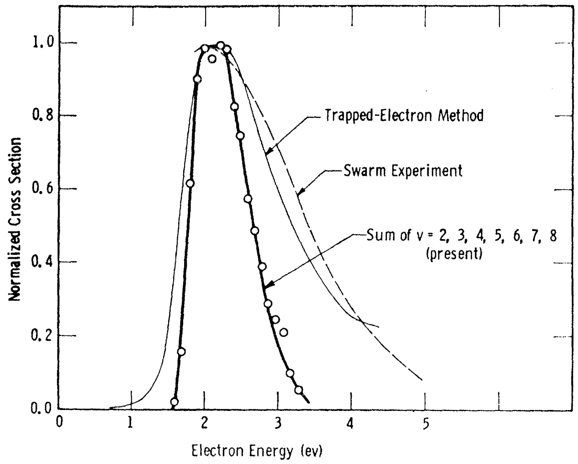

FIG. 7. Comparison of previous experiments with the present experiment. The curve marked "swarm experiment" has been obtained by Haas in a Maier–Leibnitz type experiment; the curve labeled "trapped-electron method" has been obtained by the author using an electron beam technique. The points are the sums of all the curves of Fig. 6, normalized to unity at the peak.

lost zero energy in the collision chamber.[6] The vertical line marked $v=0$ is drawn to coincide with this peak and then the lines marked $v=1$, 2, 3, etc. are drawn at the energies of the known vibrational levels of N_2.[7] The peaks at $v=1$ to 8 correspond to electrons which have excited particular vibrational levels. The intensity of energy loss peaks except that near $v=1$ are proportional to the gas density. The peak near $v=1$ is almost independent of gas density and is believed to be caused by surface effects in the instrument. The agreement between the expected position of the peaks for $v=2$ to $v=8$ and the experimentally observed positions of the peaks is good. It should be noted that the structure shown in Figs. 4 and 5 can be observed only when the incident electron energy is in the range from about 1.8 to 3 ev, the peak of the cross section for the excitation of the temporary negative ion state discussed below. From curves such as Figs. 4 and 5 taken at different energies of incident electrons, one can obtain the energy dependence of the cross section for excitation of various vibrational levels. These curves are shown in Fig. 6 for $v=2$, 3, 4, 5, 6, 7, 8. If one accepts the model of the temporary negative ion state, then the sum of the various vibrational cross section should be the cross section for excitation of the temporary negative ion state. Figure 7 shows the sum of the cross sections for $v=2$ to $v=8$ plotted against electron energy. Results of two previous experiments are also shown. The three curves are normalized to unity at the peak of the cross section. No shift in energy scale is necessary. The present result leads to a narrower curve; this may be due to the narrower energy distribution obtained in the present experiment or may be due to the absence of the state $v=1$ in the summation. As mentioned previously, it is not possible to obtain data on the $v=1$ state in the present experiment.

III. DISCUSSION

The present experiment confirms the large inelastic process in N_2 for electrons with energies around 2.3 ev and shows that vibrational levels of the nitrogen molecule, up to $v=8$, are excited. Also, the experimental data can be interpreted in terms of the hypothesis, previously advanced,[2,8] involving one or more temporary negative-ion states. On this model, a temporary negative ion is excited by an incoming electron, The lifetime of this state against autodetachment is assumed to be short; the temporary negative ion decays to various vibrational levels of the neutral nitrogen molecule and the electron is given off. The overlap integral between the wave function of the temporary negative-ion state and the respective vibrational states, together with the competition between the various channels of decay, has to be considered for interpreting the variation of cross sections of Fig. 6. Assuming that the lifetime of the temporary negative ion is short with respect to the vibration time, the transition "up" and "down" takes place with little change in internuclear separation of the molecule, within the Franck–Condon region.

The experimental results reported in this paper refer to the forward (zero degree) scattering. Recently, an apparatus has been completed which analyzes electrons scattered in a small solid angle around 60°. The results obtained at 60° for $v=2$ to $v=8$ are almost identical to those reported for 0° in the present paper. However, the results for $v=1$ and $v=0$ (elastic scattering at 60°) are not complete and will be reported at a later date.

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[6] The position of this peak on the voltage axis is determined by the relative values of energy to which the first and second analyzer are tuned.

[7] G. Herzberg, *Molecular Spectra and Molecular Structure*, (D. van Nostrand Company, Princeton, New Jersey, 1950).

[8] G. J. Schulz, J. Chem. Phys. **34**, 1778 (1961).