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# Observation of vibrationally excited nitrogen with a simplified electron transmission apparatus

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# Observation of vibrationally excited nitrogen with a simplified electron transmission apparatus*

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A simple electron transmission apparatus is used to observe vibrationally excited $N_2$ in the first two vibrational levels. The method is based on the pronounced peaks appearing in the total electron scattering cross section in the range of energy 2–4 eV. Because of the wide spacing between these peaks, good energy resolution is not required and measurements can be performed without an electron monochromator.

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A variety of methods[1] have been devised for detection of vibrationally excited nitrogen molecules in the ground electronic state. The methods, in general, are complex and in many cases are useful only for $N_2(v=1)$. We have recently introduced[2] a technique suitable for detecting $N_2(v=0-4)$ based on the high-resolution electron transmission method.[3] Although this technique appears to us to be less formidable than most, it incorporates a highly monoenergetic electron beam. In this communication we point out that vibrationally excited $N_2$ can still be observed by electron transmission in a greatly simplified version of our apparatus which does not employ an electron monochromator.

The transmission method is based on detection of the pronounced oscillatory structure in the total scattering cross section of electrons from $N_2$ in the 2—5-eV region.[4] The structure is due to the formation of a temporary negative ion of $N_2$, the $N_2^-(^2\Pi_g)$ state, which has a lifetime of approximately $10^{-15}$ sec. The ion produces a resonant contribution to the scattering cross section with peaks at energies corresponding to the vibrational levels of the negative ion.[5] The lowest of the peaks is, therefore, characterized as a transition from $e+N_2(v=0)$ to $N_2^-(v'=0)$, the second peak as $e+N_2(v=0)$ to $N_2^-(v'=1)$, and so forth.

If vibrationally excited molecules in $v=1$ are present, the lowest transition will correspond to $e+N_2(v=1)$ to $N_2^-(v'=0)$, producing a peak in the effective total scattering cross section which lies below the lowest transition in the unexcited gas by 290 meV, the vibrational spacing in $N_2$. In a similar way, if $N_2(v=2)$ is present, the lowest peak will occur two $N_2$ vibrational quanta below that in the unexcited gas. These transitions are analogous to the "hot bands" found in optical spectroscopy.

The presence of the additional peaks in the total scattering cross section provides the basis for detecting vibrationally excited $N_2$ as we have indicated previously.[2] In particular, the wide spacing between the peaks suggested that high electron energy resolution might not be required and that a transmission experiment with a simple electron gun having no dispersive elements would suffice.

Before describing the components in more detail, we review briefly the principles of a transmission experiment. A beam of electrons with initial current $I_0$, collimated by an axial magnetic field, is passed through a cell of length $L$ containing a gas at density $N$ which has a total electron scattering cross section $Q$. After leaving the cell, the scattered electrons are rejected by retarding at an aperture following the cell. The unscattered or "transmitted" current, given by $I_0\exp(-NQL)$, is collected. To enhance the sharp variations in this signal which arise from the structure in the scattering cross section, we use the technique devised by Sanche and Schulz,[3] namely, we detect the derivative of the transmitted current with respect to energy. This is carried out by modulating the electron energy in the cell by applying a small sine wave voltage and detecting synchronously the ac component of the transmitted current.

Figure 1 illustrates the components of the simplified transmission apparatus. Electrons leaving a thoria-coated iridium filament $F$ are collimated by an axial magnetic field $B$ of approximately 150 G and are accelerated by electrode P1. Our only concession toward improving the energy spread of the electrons is to retard roughly one-half of the current at P2 and P3 resulting in an asymmetric energy distribution with a FWHM of about 200 meV.

A crossed beam geometry, rather than a static gas cell, is used to minimize contact of the vibrationally excited gas with metal walls. The molecular beam formed by effusion from the sampling slit is intersected at

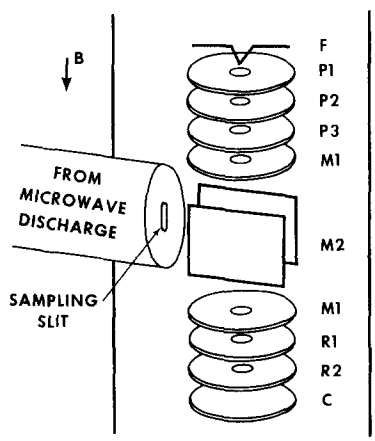


FIG. 1. Schematic diagram of the transmission apparatus.

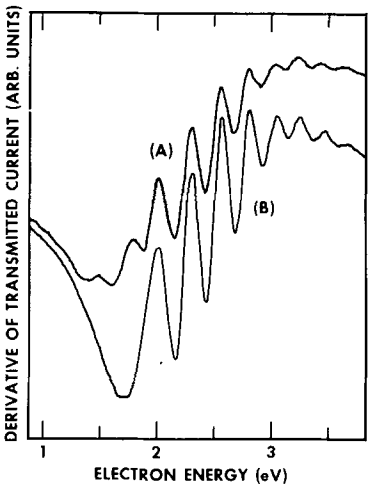


FIG. 2. Derivative of the current transmitted through $N_2$ as a function of electron energy. In curve (B), the $N_2$ is in the ground vibrational state. In curve (A), the $N_2$ has been passed through a microwave discharge. The additional peaks in the spectrum indicate the presence of $N_2$ in $v=1$ and 2.

right angles by the electron beam. The collision region is defined by the electron-beam entrance and exit plates M1 and by two plates M2 parallel to the plane of the gas and electron beams. The energy modulating voltage is applied to the latter plates. After leaving the collision region, the scattered portion of the electron beam is rejected by retarding at plates R1 and R2. The unscattered portion of the current is collected at electrode C.

As in our previous test of the transmission method, a microwave discharge in rapidly flowing $N_2$ was employed as a source of vibrationally excited molecules. In the discharge region, pressures of typically 6 Torr were used with the excited gas reaching the sampling slit in approximately 10 msec.

Figure 2 illustrates sample spectra taken with the microwave discharge on [curve (A)] and off [curve (B)]. In this figure, the derivative of the transmitted current is plotted as a function of the electron impact energy. To indicate the signal-to-noise ratio, these spectra were each taken in less than $1\frac{1}{2}$ min using a time constant of 100 msec in the synchronous detector. The electron beam current was $\sim 2\times10^{-8}$ A and a microwave discharge power of 100 W was used.

In the undischarged $N_2$, the structured nature of the scattering cross section is clearly visible even with the broad electron energy distribution used here. The formation of eight vibrational levels of $N_2^-$ is evident over the range from 2 to 3.8 eV. With the discharge active, two additional features are apparent below 2 eV. The lower peak indicates the presence of $N_2(v=2)$ by the transition to $N_2^-(v'=0)$. The next peak contains contributions from both $e+N_2(v=2)$ to $N_2^-(v'=1)$ and $e+N_2$ $(v=1)$ to $N_2^-(v'=0)$.

The transmission method in its present form provides a simple and rapid means for observing vibrationally excited $N_2$. To put measurements such as these on a quantative basis, we require the relative scattering cross sections from each vibrationally excited level of $N_2$ proceeding through the formation of $N_2^-$.[6] These cross sections may be computed using the semi-empirical model of Birtwistle and Herzenberg.[7] The calculations are being carried out by Dubé and Herzenberg[8] by fitting to recent data of Wong and Schulz[9] for vibrational excitation from the ground state of $N_2$. A preliminary comparison of the calculated transmission spectrum for $N_2(v=0)$ shows excellent agreement with the experimental data. A detailed account of the transmission method and the unfolding procedure for determination of the fraction of $N_2$ in vibrationally excited levels is in preparation.

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[1]Many of the methods are listed in S.J. Young and K.P. Horn, J. Chem. Phys. **57**, 4835 (1972).
[2]J.A. Michejda and P.D. Burrow, *IX International Conference on the Physics of Electronic and Atomic Collisions* (University of Washington Press, Seattle, 1975), p. 949.
[3]L. Sanche and G.J. Schulz, Phys. Rev. A **5**, 1672 (1972).
[4]G.J. Schulz, Rev. Mod. Phys. **45**, 423 (1973).
[5]Strictly speaking, $N_2^-(^2\Pi_g)$ possesses only "quasivibrational" levels since its average lifetime is somewhat less than the period of vibration. Reference 7 contains a discussion of the characteristics of the resonance peaks as they appear in the cross section.
[6]If the $N_2^-$ negative ion were long lived with respect to its vibrational period, the interpretation of the transmission data would be greatly simplified since we would require only the relative Franck-Condon factors for transitions between $N_2(v)$ and $N_2^-(v')$.
[7]D.T. Birtwistle and A. Herzenberg, J. Phys. B **4**, 53 (1971).
[8]L. Dubé and Z. Herzenberg (private communication).
[9]S.F. Wong and G.J. Schulz (unpublished).