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DETECTION OF VIBRATIONALLY EXCITED N_2 BY SUPERELASTIC ELECTRON IMPACT*

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We have observed electrons scattered superelastically from nitrogen molecules vibrationally excited by quenching collisions with optically excited rubidium atoms. Analysis of the energy gained by the electrons shows that in more than 10 % of the quenching collisions the highest energetically allowed vibrational state of N_2, $v=5$, is populated. The relative superelastic cross section for collisions between molecules in this state and electrons is measured and compared with that predicted by detailed balance.

In a superelastic collision, an electron colliding with an excited atom or molecule gains kinetic energy and leaves the atom or molecule in a lower energy state. This process has been studied with excited mercury[1] and more recently in excited rubidium.[2] In the present experiment, superelastic electrons are observed from collisions with vibrationally excited N_2 molecules in their ground electronic state. This technique should prove useful in the study of collisional processes involving vibrationally excited molecules, in particular homonuclear molecules, which are difficult to detect because of the absence of infrared emission.

In this experiment, vibrationally excited N_2 is produced by the quenching of optically excited Rb vapor. Rubidium resonance radiation is incident on a collision chamber containing Rb vapor and N_2. A fraction of the excited $Rb(^2P_{1/2,3/2})$ atoms produced by photon absorption collide with N_2 and are quenched with high efficiency.[3] As a result of the quenching, vibrationally excited N_2 is produced. A low-energy electron beam is passed through the collision chamber, and those electrons making superelastic collisions are analyzed. Preliminary information is obtained on the transfer of Rb electronic energy into vibrational energy of N_2.

The apparatus, which is shown in Fig. 1, has been previously described[1] and only a brief discussion is given here. Plates S_1 through S_5 form an electron gun which may be operated in the retarding-potential-difference mode.[4] Typical electron beam currents of 5×10^{-8} A with a resolution of 0.2 eV at half-maximum are used. The electron beam is collimated by a uniform axial magnetic field of 180 G. A retarding voltage may be applied to electrode S_7, to analyze the energy of the electrons. The electron current transmitted past the retarding plate is collected at EC and measured with a vibrating-reed electrometer.

The collision chamber is surrounded by a concentric quartz cylinder which admits Rb resonance radiation at 7800 and 7948 Å from three low-pressure Osram arc lamps positioned around the cylinder. The lamps are modified to include

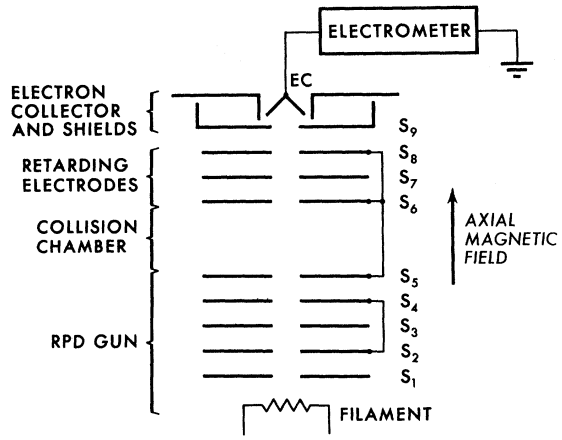

FIG. 1. Schematic diagram of the electron gun.

a cooling system which decreases the self-reversal of the resonance lines. Approximately 10^{18} photons per second of resonance light are delivered into the collision chamber. The tube and the side arm containing Rb are kept at a temperature such that the vapor pressure in the collision chamber is about 10^{-4} Torr. At this pressure all of the resonance light is absorbed. The nitrogen pressure is in the region of 10^{-2} Torr and is monitored by the fractional attenuation of the main electron beam.

With the proper retarding voltage applied to electrode S_7, the main electron beam and the elastically scattered electrons are reflected. Only the superelastic electrons arrive at the collector. With larger retarding voltages, the superelastic current decreases and eventually vanishes. The cutoff voltage measures the energy gained by the superelastic electrons. The dependence of superelastic current on retarding voltage is determined by the angles at which the superelastic electrons scatter. The magnetic field constrains the scattered electrons to spiral along the axis of the tube. The retarding field acts only against the component of velocity parallel to the axis. Therefore, at a given retarding voltage, the superelastic current is composed of all electrons scattered into a solid angle defined by the retarding voltage and the energy gained by the electrons. The dependence of the superelastic cross section on incident electron energy is obtained by varying the accelerating voltage of the main electron beam while keeping the relative retarding voltage fixed.

Because of the high-energy tail of the main electron beam, it is not possible in the present experiment to measure accurately superelastic current at retarding voltages less than 1.0 V. To have appreciable superelastic current at this retarding voltage, the scattering must take place from excited states higher than 1.2 eV above the ground state.

Since the energy levels of $Rb(^2P_{1/2,3/2})$ lie at 1.57 and 1.59 eV, respectively, quenching into vibrational levels of N_2 up to $v = 5$ at 1.41 eV is energetically allowed. However, because of the restriction mentioned above, it is only possible for us at present to observe superelastic transitions from the $v = 5$ level to the ground vibrational state of N_2. At the lowest retarding potential used, 1.0 V, there may be small contributions from electrons gaining 1.1 eV due to the transitions $v = 4 \rightarrow v = 0$ and $v = 5 \rightarrow v = 1$. These are not separable at present.

With Rb and N_2 in the collision chamber, superelastic electrons are expected from both excited species. The combined superelastic current as a function of energy is shown in Fig. 2 for a retarding voltage of 1.1 V. The energy scale is determined by a decrease in the transmitted beam current at the threshold for excitation to the first excited state of Rb. The energy calibration is accurate to 0.2 eV. In the absence of N_2, only excited Rb produces superelastic electrons. The approximate Rb contribution is shown as a broken line in Fig. 2. The remaining structure is due to the excited vibrational states of N_2.

The superelastic cross sections can be obtained from the excitation cross sections with the use of detailed balancing.[5] We have used recent excitation functions measured by Boness and Schulz[6] to calculate the relative cross section for superelastic impact with the $v = 5$ level, leaving the N_2 in its ground vibrational state. The result is shown in Fig. 3. The spacing between the peaks is in good agreement with our experimental data. The position is displaced by 0.15 eV which is within the accuracy of our calibration.

An additional measure of the maximum electron energy gained from collisions with excited N_2 is obtained by observing the combined Rb and N_2 superelastic cross sections with successively larger retarding voltages. The peaks due to N_2 vanish at a retarding voltage of 1.4 V, in agreement with the energy of the fifth vibrational level. Superelastic electrons from Rb continue to a retarding voltage of 1.6 V.

Based on our results, an estimate of the cross section for the quenching of excited Rb into the

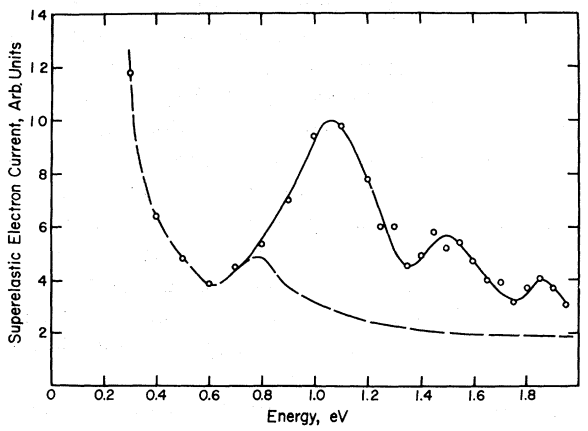

FIG. 2. Superelastic current from excited N_2 and Rb as a function of incident electron energy. The broken line shows the contribution from excited Rb.

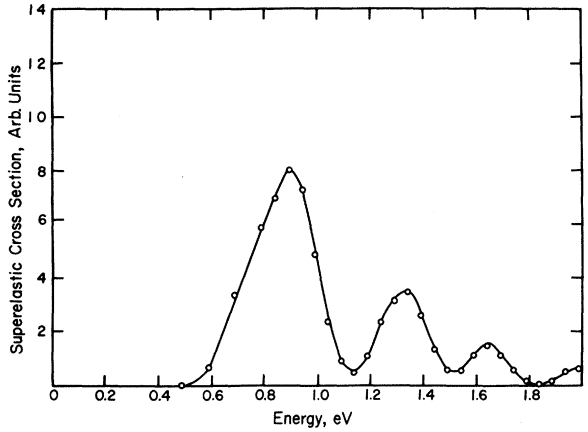

FIG. 3. The relative superelastic cross section for $v=5\rightarrow v=0$ in N_2 calculated from electron excitation data.

$v=5$ level of N_2 yields a value approximately equal to the total quenching cross section.[3] Because of the uncertainty in the distribution of excited rubidium atoms in the collision chamber, and to a lesser extent the uncertainty in the magnitudes of the Rb and N_2 superelastic cross sections, the estimate is reliable only to an order of magnitude. This result indicates that in not less than 10% of the quenching collisions, the Rb electronic energy is transferred into the $v=5$ vibrational level of N_2. Excitation to this level represents the maximum possible transfer of the available electronic energy into vibration. This is in contrast with the quenching of excited Hg by CO. Karl, Kruus, and Polanyi,[7] by direct observation of infrared emission from collisionally excited CO, measured the distribution of vibrationally excited states and showed that levels lying higher than half the available electronic energy of Hg are not excited. That is, every quenching collision transfers at least 2 eV into kinetic energy. It is also interesting to note that the total quenching cross sections of excited Rb and the other alkali metals[8] by N_2 are an order of magnitude larger than that of excited Hg by CO.

Information about the population distribution of remaining vibrational levels of N_2 will help to resolve the differences between the two quenching processes. Work along these lines with improved energy resolution is planned.

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RELATIONSHIP BETWEEN ELECTRIC FIELD STRENGTH AND HELIX PITCH IN INDUCED CHOLESTERIC-NEMATIC PHASE TRANSITIONS*

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A cholesteric-nematic phase transition can be induced by relatively weak electric fields, and the threshold field varies inversely with the pitch of the helix in corroboration of recent theoretical suggestions. The phase change is accompanied by a change in the activation energy for charge-carrier production and can easily be observed by both conductivity measurements and direct optical examination.

Recently Meyer[1] has presented a theory regarding the influence of electric and magnetic fields on the structure of cholesteric liquid crystals. He concludes that application of an electric field parallel to the helix axis should destroy the helical structure, and that the threshold field strength should be $F_C=(2\pi/Z_0)(k_{22}/\Delta\epsilon)^{1/2}$ where Z_0 denotes the pitch of the undisturbed helix, $\Delta\epsilon$ the anisotropy of the dielectric constant, and k_{22} the modulus of torsional strain. Wysocki, Adams, and Haas[2] have indeed observed a field-induced phase transition in a mixture of cholesteryl chloride, nonanoate, and oleyl carbonate at a field of $(3\text{-}4)\times10^5$ V cm^{-1}. They were unable to