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ENHANCEMENT OF NEUTRAL-NEUTRAL IONIZATION PROCESSES BY INTERNAL EXCITATION ENERGY IN THE COLLIDING PARTICLES*

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Near-resonant charge transfer has been utilized for producing a fast (13 to 200 eV) neutral beam of excited nitrogen molecules (6-eV internal energy). The ionization cross section for $N_2^* + Ar$ collisions was measured with this excited beam over the center-of-mass kinetic energy range 12 to 120 eV, and was compared with the ionization cross section measured with a ground-state nitrogen molecular beam. The cross section for excited molecules was found to be 50 times that for ground-state molecules at 2 eV (center of mass) above the ionization-energy threshold involving ground-state molecules. The secondary-electron (or negative-ion) emission coefficient has also been measured for the excited N_2 molecules on a "dirty" gold surface. It was found to decrease rapidly with decreasing kinetic energy down to 25 eV (lab), but then appeared to approach 1×10^{-4} at the lower energies. In contrast, the coefficient for ground-state molecules continued to decrease rapidly toward zero with decreasing kinetic energy below 25 eV.

The apparatus for producing a ground-state nitrogen molecular beam has been previously described in detail.[1] It utilizes the production of nitrogen molecular ions by electron bombardment (22-eV electrons), electrostatic acceleration of the ions into a beam having the desired energy and trajectory, and their neutralization by charge transfer in a suitable gas. Nitrogen has normally been selected as the neutralizing gas because the resonant character of the interaction leads to production of fast ground-state neutrals with a large cross section at low energy. Hydrogen has also been employed, although it is not quite resonant and thus has a smaller charge-transfer cross section at the lowest energies. Hydrogen has the advantage that the energy available for excitation (center-of-mass energy) in $N_2^+ + H_2$ collisions is only 1/15 the beam energy, thus putting a limit on the internal excitation which might be present in the N_2 molecular beam.

For the excited beam discussed here, nitric oxide was used as the neutralizing gas (bar indicates the fast particle), i.e.,

$$\underline{N_2}^+ + NO \rightarrow \underline{N_2}^* + NO^+. \qquad (1)$$

The charge-transfer cross section for these reactants was measured to be about one-fourth that for N_2^+ in N_2 (i.e., about 9 Å^2 at 30 eV). Most significant was the observation that it appeared to increase with decreasing energy to below 20 eV suggesting that a resonant or near-resonant process was occurring. A plausible explanation can be found in the energy balance of Reaction (1). The N_2^+ has an ionization energy of 15.58 eV and the NO^+, 9.27 eV, a difference of 6.31 eV. This is very close to the energy of the metastable $A^3\Sigma(v=1)$ state of N_2. Reaction (1) would be essentially resonant if this were the excited state populated during the charge transfer. Capture into other states of the nitrogen molecule (except for other low-lying vibrational levels of the $A^3\Sigma$ state) would be significantly nonresonant. Furthermore, if other nearby electronic states were to be populated during the collision, some of these (such as the important $B^2\Pi$ state) would decay to the $A^3\Sigma$ level. Transitions from the N_2^+ to the $A^3\Sigma$ state of N_2 are compatible with the application of the Franck-Condon principle, and the spin-conservation rule is not violated. These considerations support the suggestion that the resultant fast-beam molecules were predominantly in the $A^3\Sigma$ state.[2]

The ionization cross section for N_2+Ar collisions was measured in the same manner described previously[3] for N_2+N_2 and N_2+O_2 collisions. The fast molecular beam traversed a low-pressure Ar gas target (10^{-4} Torr) between the guarded plates of a parallel-plate chamber. Negative charges arising from ionizing collisions were driven to the collector plate by the electrostatic field between the plates. Particular care was taken to exclude stray secondary electrons ejected by scattered beam molecules. Knowledge of the target number density, collector length, current of negative charges, and neutral beam intensity allowed a determination of the ionization cross section (more precisely, the total cross section for production of negative charges in N_2+Ar collisions). The target number density was determined from the target gas pressure.[4] Ideally, the neutral-beam intensity may be inferred from the current of slow ions produced in the charge-transfer cell, since each slow ion corresponds to a fast neutral molecule. In reality, some scattering occurs, and a small measured correction to the neutral beam intensity was applied.[1]

The threshold behavior of the measured ionization cross sections as functions of available (center-of-mass) interaction energy are shown in Fig. 1. Curve *A* depicts the results when N_2 or H_2 was employed as the neutralizing partner, and curve *B*, those obtained from charge transfer with NO. That excited molecular nitrogen was present in the latter case is proven by the data of curve *B* since ionization appeared at least 3 eV below the energy threshold for ground-state N_2+Ar ionizing interactions. Note that except in the immediate vicinity of threshold, curves *A* and *B* are separated on the energy axis by significantly more than 6 eV, indicating that internal energy is more efficient in producing ionization than kinetic energy for these collision participants.[5]

In Fig. 2, curve *A* shows the results obtained over a larger energy range when ground-state beam molecules were selected. Note that both cross section and available energy are here displayed on logarithmic scales. The abscissa values in this case represent kinetic energy in the center-of-mass system minus the minimum-ionization-energy threshold. Zero on this scale is therefore the energy threshold for production of ions.

Curve *B* shows the results obtained when the N_2^+ ions were neutralized in NO, thus corresponding to excited beam molecules. The abscissa scale is the same as for curve *A*, and the internal excitation energy is ignored. The "true" energy threshold (kinetic plus excitation) would therefore be −6.3 eV on this scale (assuming the N_2 $A^3\Sigma$ excitation energy). These same data are shown in curve *C*, where the energy scale is shifted by adding this excitation energy to the kinetic energy. Therefore, a zero abscissa value again corresponds to the energy threshold.

The method for measuring the secondary-electron (or negative-ion) emission coefficients from a surface has been described in detail earlier.[1] It consists simply of allowing the neutral N_2 beam to strike a negatively biased (3-V) gold plate. The current of negative charge leaving the plate is measured, and γ is defined as this cur-

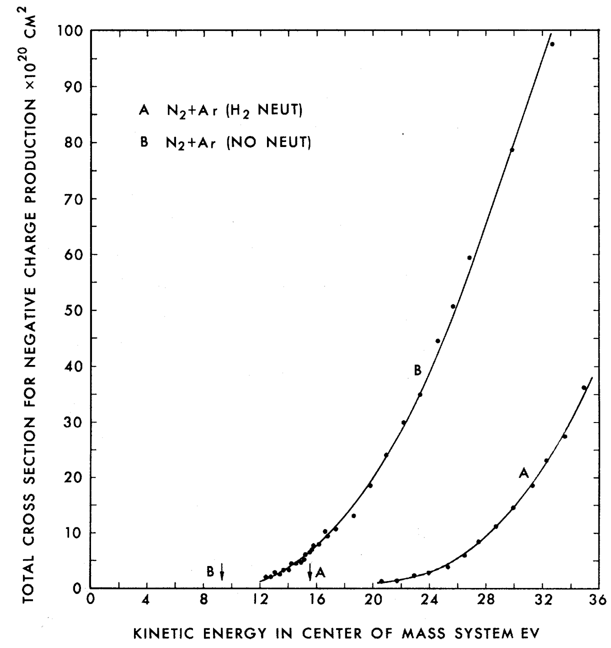

FIG. 1. Ionization cross sections as functions of kinetic energy in the center-of-mass system. Arrows indicate threshold corresponding to each curve.

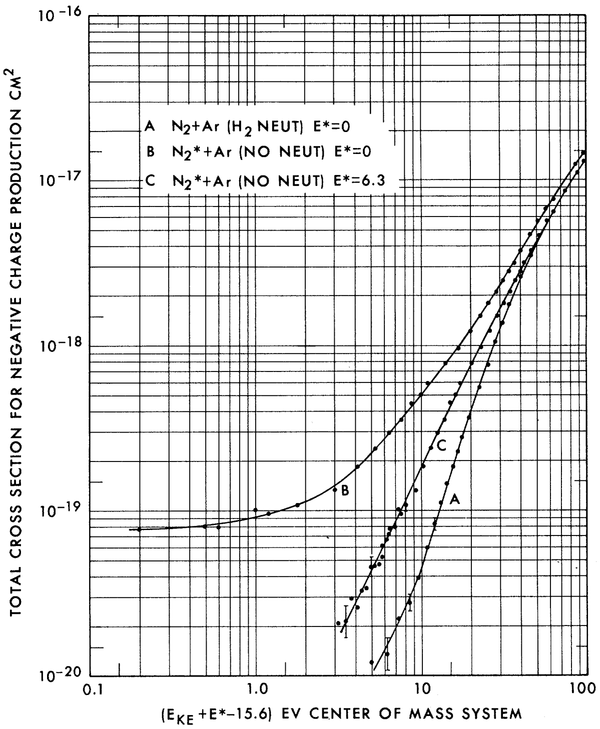

FIG. 2. Ionization cross sections as functions of available energy above threshold, curves *A* and *C*. Curve *B* shows effect of ignoring internal energy in the "excited" beam.

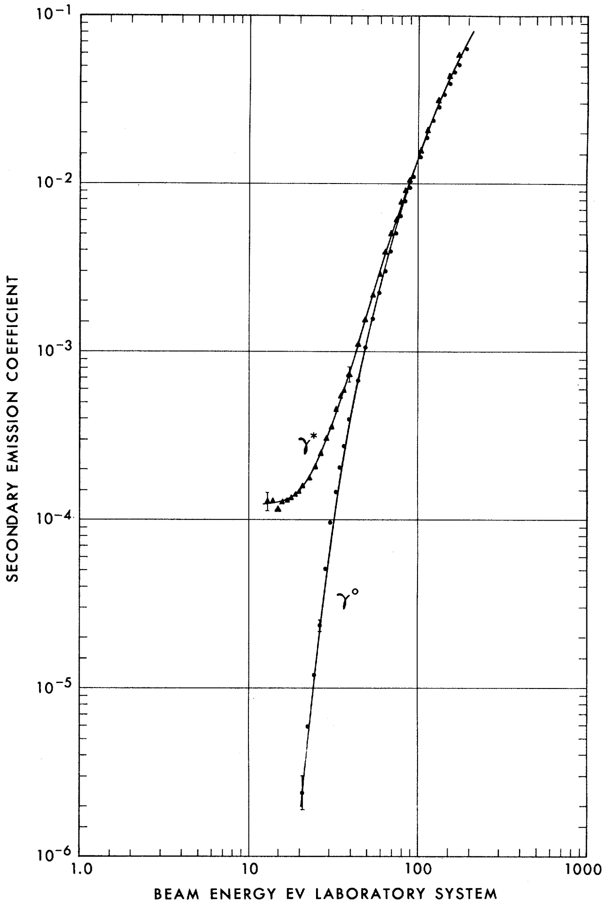

FIG. 3. Secondary-emission coefficients (number of negative electronic charges ejected per incident molecule) as functions of beam energy.

rent divided by the neutral beam intensity (i.e., the number of negative charges leaving the plate per incident neutral molecule).

Figure 3 shows the values obtained with the ground-state beam γ^0 and the excited-state beam γ^*. (Here again, neutralization with H_2 gave the same results as with N_2 within experimental error.) It may be seen that γ^0 and γ^* are nearly equal at high energy, but diverge below 25-eV beam energy. This result is not too surprising, since even at zero kinetic energy the excited molecules have energy available to liberate charge from the surface.[6] Conversely, ground-state particles must depend on their kinetic energy to eject charge, and therefore γ^0 falls rapidly to zero as the kinetic energy approaches zero.

Because neutralizing gas from the charge-transfer cell flooded the gold surface during these measurements, it was necessary to determine whether the excited-state results were correctly interpreted, or were merely due to this contamination of the bombarded gold surface. A second source of gas which simulated the charge-transfer cell was therefore directed at the surface. No measureable change in γ^0 was found when NO was directed at the surface during N_2 neutralization. Similarly, no change was found in γ^* when N_2 was directed at the surface during neutralization with NO. The gold surface was, nevertheless, not a "clean" surface, and these data for γ^0 and γ^* should not be considered in the light of fundamental gas-gold surface interactions.

The bars on the curves of Figs. 2 and 3 represent random uncertainties in the data. They are largest at low energy because of the small signal currents obtained, and decrease to less than ±10% at high energies. The largest potential systematic error arises from uncertainty in the neutral-beam intensity. Although the total neutral-beam intensity is believed to be known[1] within ±20%, the fraction of excited particles in the "excited" beam has not been measured. The data presented here have been reduced under the assumption that the "excited" beam consisted entirely of excited molecules. While it was argued that, on the basis of the almost resonant charge transfer, the excited $N_2\, A^3\Sigma$ should be highly preferred, the possibility that some ground-state N_2 molecules are produced cannot be eliminated. It should be noted, however, that corrections for this effect would make the excited-state ionization-cross-section and emission coefficient even larger.

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[1] N. G. Utterback and G. H. Miller, Rev. Sci. Instr. 32, 1102 (1961).

[2] These arguments contain the implicit assumption that the N_2^+ ions were in the ground state. In order to verify that excited N_2^+ ions did not dominate the results, the ionizing electron energy was varied from 18 to 24 eV in the charge-transfer cross-section measurement (35-eV ion beam) and from 19.5 to 24 eV in the ionization cross-section measurement (35-eV neutral excited beam). No change outside ±5 and ±10%, respectively, could be detected up to 22-eV electron energy. Above 22 eV, however, both cross sections increased markedly. This is interpreted as being due to the production of long-lived N_2^+ excited ions, which transfer charge with NO to produce highly excited metastable N_2 molecules.

[3] N. G. Utterback and G. H. Miller, Phys. Rev. 124, 1477 (1961), and 129, 219 (1963).

[4] N. G. Utterback and T. Griffith, Jr., Rev. Sci. Instr. 37, 866 (1966).

[5] This result has immediate practical importance in calculation of bulk ionization rates through integration of cross sections over velocity distributions. It has been shown (C. F. Hansen, private communication) that if this result holds generally, bulk ionization rates can be dominated by collision between excited particles even though relatively few of these are present. It would then be essential to know the cross sections for collisions between all the excited-state possibilities in order to calculate reliable reaction rates.

[6] H. D. Hagstrum, J. Appl. Phys. 31, 897 (1960).

ELECTRIC-FIELD-INDUCED PHASE CHANGE IN CHOLESTERIC LIQUID CRYSTALS

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Several workers[1-3] have reported the influence of electric fields upon the scattering of light by cholesteric liquid crystals. In this Letter, we wish to report a phase transition which was observed in cholesteric liquid crystals subjected to high dc electric fields. To our knowledge, a change of phase in these materials due to electric fields has not been previously identified.

Results were obtained as follows. A cholesteric liquid crystal was put between, and in contact with, tin-oxide-coated glass plates separated by 0.2 mm. The liquid-crystal materials were mixtures of cholesteryl chloride, nonanoate, and oleyl carbonate with typical proportions of 30, 56, and 14% by weight, respectively.[4] The normal appearance of the layer was that of a milky white, opalescent sheet from which light was diffusely scattered. When plane-polarized light was normally incident on the layer, it was impossible to extinguish the field of view with a linear analyzer. When an average electric field of $\approx 10^5$ V/cm was applied, the liquid crystal assumed a clear, colorless appearance. Normally incident, plane-polarized light now emerged plane-polarized and thus could be extinguished. However, the material was not optically isotropic. Plane-polarized light obliquely incident on the structure did not emerge plane-polarized, indicating that the film was acting as a birefringent material with an optic axis perpendicular to the surface of the film, i.e., parallel to the applied field.

The uniaxial character of the film and the sign of birefringence were determined in a second experiment using a Leitz Ortholux polarizing mi-

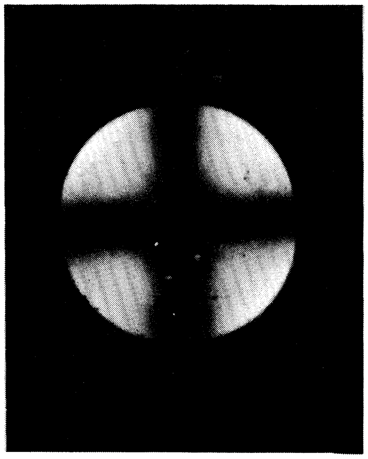

FIG. 1. Photograph of uniaxial conoscopic figure.