

cannot produce 1000 free radicals from CD_4 . Thus, for dilute solutions the energy must be absorbed primarily by the Kr matrix and then transferred to the CD_4 .

Other ESR studies on systems similar to those in the present work, CH_4 and CD_4 in matrices of inert elements, were done under conditions that would make energy transfer difficult, or impossible, to detect. Florin, Brown, and Wall² irradiated CH_4 in an Xe matrix at 77°K, but they computed yields only over a limited range of concentrations (0.23 to 0.69 mole fraction of CH_4). Cochran *et al.*³ deposited CD_4 and argon at 4.2°K and irradiated the mixture with a uv source. Lines due to CD_3 and D were observed, but no yields were reported. Deposition of the products of an rf discharge in CH_4 , deposited at 4.2°K with an inert gas,⁴ would not, of course, show energy transfer.

The specific mechanism by which the energy migrates in the argon or krypton matrix is not known, but experiments are in progress which may give information on the process. It has already been found that H_2 behaves like CH_4 , but that N_2 does not. One possible mechanism is that of excitation transfer.⁵ The dissociation energy⁶ of CH_4 , 4.4 eV, is well below the excitation energy of krypton, 10 eV. So is that of N_2 , which is 7.4 eV. However, to displace an N atom from its position in the lattice would require more than the N_2 dissociation energy and more than that required to displace the lighter atoms, H or D. The first ionization energies⁷ of CH_4 , Kr, and N_2 are 13.2,

14.0, and 15.6 eV, respectively. Thus, an electron hole in the krypton could ionize the CH_4 or CD_4 , but not the N_2 . This suggests, but does not prove, that the dissociation is brought about through ionization of the molecule by energy which migrates as a positive charge or hole in the argon or krypton matrix. The ionization would presumably produce a CH_3 and an H^+ , but the H^+ would later capture an electron to become a hydrogen atom.

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OSCILLATOR STRENGTHS FOR THE $3s^4P-(2p)^3^4S$ TRANSITIONS IN ATOMIC NITROGEN*

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Oscillator strengths for the atomic-nitrogen resonance transitions are of interest in upper atmospheric and astrophysical processes, in afterglow studies, and as checks for calculations of approximate wave functions. A measurement of these f values is not simple because of the need for known atom concentrations and for intensity measurements in the extreme ultraviolet. Although these transitions have been observed in absorption photographically,¹ the results given here are the first oscillator-strength measurements reported. Of the resonance absorption lines from the ground and metastable states, the resolved $3s^4P-(2p)^3^4S$

triplet at $\lambda = 1200 \text{ \AA}$ is found to have an average oscillator strength $f = 1.2 \times 10^{-4}$. Absorption by the $3s^2P-(2p)^3^2D$ doublet at $\lambda = 1493 \text{ \AA}$ and by the $3s^2P-(2p)^3^2P$ doublet at $\lambda = 1744 \text{ \AA}$, which is generally less than 0.01 as strong as ground-state absorption, is easily measurable but does not yield f values because the populations of these states are not determined. Although the small value for \bar{f} will be seen not to be unrealistic, it is particularly desirable to outline the method by which it has been obtained.

Nitrogen atoms were produced in a pure nitrogen afterglow,² which flowed between a steady

source of Ni resonance radiation and a vacuum grating monochromator equipped with a photoelectric detector. The separate regions were isolated by thinly cleaved LiF windows. Before and after each absorption measurement the atom densities in the absorption cell were determined, using the standard technique³ of calibrated titration with nitric oxide in conjunction with the photometry of the afterglow emission. Nitric oxide added to an afterglow reacts very quickly with nitrogen atoms, giving N₂ and O; at titration the input flow of NO reduces the N concentration to an undetectable level and indicates the untitrated N density.

Pure line emission by N throughout the regions of interest was obtained from an electrodeless 2450-Mc/sec discharge in a mixture of 5 percent N₂ in 1 mm Hg of He. Resonance line absorption acts here not on a background continuum but on a background emission line. Therefore, observation does not depend critically on instrumental resolution, but a detailed treatment of the relative line shapes is instead required. Absorption of about 70 percent of the background line emission was produced at a maximum concentration of about 10¹⁵ cm⁻³, and the dependence of the absorption on atom density showed that Doppler broadening with partial self-reversal was predominant. Possible curves of fractional absorption vs linear absorption coefficient were obtained from IBM-709 calculations systematically covering a variety of line-shape parameters.⁴ A good fit to the experimental data was obtained by choosing a source temperature of 600°K and self-reversal of 60, 40, and 20 percent at 450°K for the resolved components of the triplet. The effective cell length of 10 cm and the linear absorption coefficients thus obtained give directly the oscillator strengths. These values, weighted as 3:2:1 in order of increasing wavelength, yield the average \bar{f} quoted above.

This value of \bar{f} , which is the result of several hundred absorption measurements covering a wide range of concentrations and many separate runs, is judged to have 40 percent precision. This estimate of reliability includes evaluation and experimental checks of possible systematic errors from flow measurements, titration (bracketed by measurements upstream and downstream from the

absorption cell), scattered light (less than 1 percent of line intensities), and inaccurate description of line shapes.

It is clear that the oscillator strength for this 2*p*-3*s* transition should be much smaller than for resonance transitions in the alkalis, because here the principal quantum number changes and *n* and *l* change in opposite directions. An estimate made using Hartree-Hartree⁵ numerical wave functions for the ground state and Slater-type⁶ orbitals for the upper state clearly demonstrates the lack of overlap in these wave functions, and its result of $\bar{f}=0.01$ was governed largely by the form of the tails. Bates⁷ has recently calculated *f* numbers for the somewhat similar 2*p*-3*d* transitions in N. It is to be expected that the *f* for the 2*p*-3*d* transition would be about an order of magnitude greater than that for the 2*p*-3*s*; comparison of the present measurement with Bates' calculations shows qualitative agreement with such a ratio.

Application of this resonance absorption technique has been made in the study of the persistence of metastable and ground-state atoms in normal nitrogen afterglows. It has also been found that their concentrations do not change appreciably throughout the so-called pink region⁸ of the fast-flowing afterglow.

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