attributed in reference 1 to X_5-X_3 transitions is more reasonably assigned to the low-energy peak of the L_3'-L_3 transitions. The 4.52-eV peak in GaAs is ascribed to Γ_{25}'-Γ_{15} transitions and agrees well with a calculated value of 4.5 eV.[7] This peak is visible at room temperature in InSb (3.4 eV) and has previously been identified.[1] It is therefore reasonable to assign the corresponding peaks in InAs and GaSb to these transitions. The Γ_{25}' valence band in GaAs should have a splitting of 0.33 eV due to spin orbit interaction and it is possible that structure at 4.2 eV in Fig. 1 is associated with this mechanism. There is further evidence of this splitting from the peaks at 1.75 eV and 1.4 eV; the latter peak corresponds to the direct gap for GaAs. These two peaks can thus be assigned to Γ_{25}'-Γ_2' transitions. The cause of the rise in reflectivity at energies less than 1.5 eV is not clear, as the carrier concentration of the specimen (6×10^{17}/cc) is not sufficient to cause appreciable free carrier reflectivity at these energies. All previous work has associated the low-energy doublet (3.02 and 3.23 eV in GaAs at 80°K) with L_3'-L_1 transitions split by spin-orbit interaction of the valence band. Recent band structure calculations on germanium by Brust, Phillips, and Bassani[8] have shown the possibility that this peak in Ge is caused by Λ_3-Λ_1 transitions at the $\langle 0.17, 0.17, 0.17\rangle$ point of the Brillouin zone. According to the critical point theory,[9] reflectivity edges can occur wherever the condition

$$\nabla_k (E_{\vec{k}}^{c} - E_{\vec{k}}^{v}) = 0$$

is satisfied. Normally this occurs at zone edges when the gradients of the bands are zero, but the condition is also satisfied when both valence and conduction bands have the same gradient. The treatment of Brust et al. predicts that for Ge the reflectivity edges due to L_3'-L_1 transitions occur at slightly lower energies than Λ_3-Λ_1 and are much weaker. The general systematics indicate that the interpretation might also hold for GaAs. If this is true then the 3.0- and 3.2-eV peaks are due to Λ_3-Λ_1 transitions; the L_3'-L_1 transition should be responsible for the weak structure with thresholds near 2.2 and 2.5 eV. Approximately the same value of the spin-orbit splitting is observed for both Λ_3-Λ_1 and L_3'-L_1 transitions, which occur at quite different points in the Brillouin zone. This is in agreement with the germanium calculations of Kane[10] which show that the spin-orbit splitting (Δ_0) of the valence band at Γ reaches the L-point value of $\frac{2}{3}\Delta_0$ very near to the center of the Brillouin zone.

---

[1] H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters 8, 59 (1962).

[2] J. Tauc and A. Abraham, in Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961), p. 375.

[3] M. Cardona, Suppl. J. Appl. Phys. 32, 2151 (1961).

[4] M. Cardona and D. L. Greenaway, Phys. Rev. 125, 1291 (1962).

[5] W. Paul, J. Appl. Phys. 32, 2082 (1961).

[6] M. Aven, D. T. E. Marple, and B. Segall, Suppl. J. Appl. Phys. 32, 2261 (1961).

[7] D. L. Greenaway (to be published).

[8] D. Brust, J. C. Phillips, and F. Bassani, preceeding Letter [Phys. Rev. Letters 9, 94 (1962)].

[9] J. C. Phillips, Phys. Rev. 104, 1263 (1956).

[10] E. O. Kane, J. Phys. Chem. Solids 1, 82 (1956/57).

ENERGY MIGRATION AND TRANSFER IN SOLID ARGON AND KRYPTON AT LOW TEMPERATURES*

Walter V. Bouldin, Raymond A. Patten, and Walter Gordy
Department of Physics, Duke University, Durham, North Carolina

(Received July 5, 1962)

In the study of free radicals produced by γ irradiation of various substances trapped in an argon matrix at 4.2°K, we made the surprising observation that strong electron spin resonances (ESR) of H atoms and CH_3 radicals were produced from impurity concentrations of less than one part in 10^4 of CH_4 in the matrix with a moderate γ-ray dosage of 10^5 r. The same amount of CH_4 in the pure form, given the same dosage at 4.2°K, would not give a detectable signal with our spectrometer. It seems evident that a large portion of the γ-ray energy impinging on the argon matrix was being transferred to, and absorbed by, the slight CH_4 impurity. We found a similar effect for small concentrations of CH_4 in a krypton matrix. Because all samples of highest purity of argon which we could obtain had slight CH_4 impurity which gave H and CH_3 signals upon γ irradiation, we resorted to the

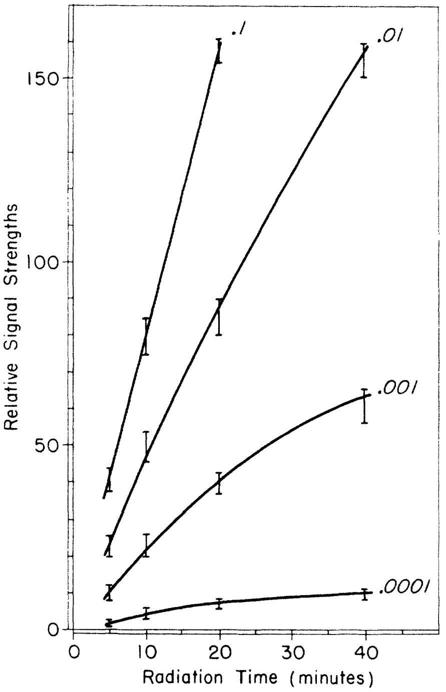

FIG. 1. Relative ESR signal strength of D atoms as a function of γ-ray dosage upon different mole fraction concentrations, 0.1 to 0.0001, of CD_4 in krypton at 4.2°K. The cobalt-60 γ-ray source gave 4000 roentgens per minute. The curves for the lower concentrations show saturation effects for the higher dosages caused by depletion of the CH_4 in the matrix.

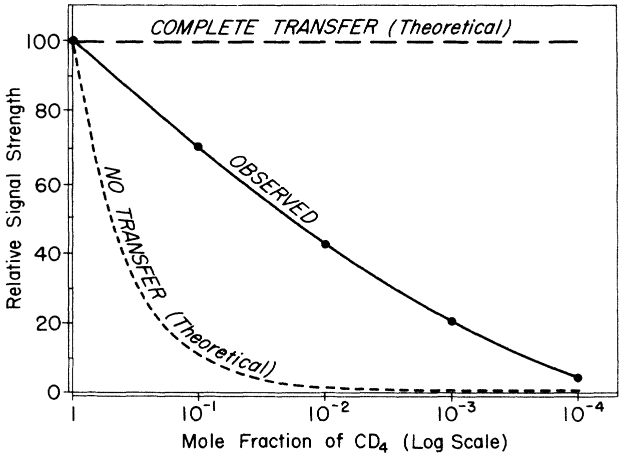

FIG. 2. Plot of the observed signal strengths of D atoms for different mole fractions of CD_4 in krypton at 4.2°K with the same dosage of 4×10^4 r. The relative signal strengths are normalized to give 100 for pure CD_4 (mole fraction 1). Theoretical curves show the variations in signal strength expected if there were complete transfer of the energy absorbed by the matrix to the CD_4 (top curve) and if there were no such energy transfer (bottom curve).

use of CD_4 to obtain a more quantitative test of this migration and transfer of energy from the argon or krypton matrix to impurity molecules.

Figure 1 shows the signal strengths of D atoms produced by different dosages and for different concentrations of CD_4 in krypton at 4.2°K. Signals of similar strength were obtained for the CD_3 radicals. The krypton samples, which were obtained from Matheson Chemical Company, had a mass spectral analysis indicating impurities of less than 5 parts in 10^5. The methods of irradiation and observation of the ESR are those described by Rexroad and Gordy.[1] Absolute calibration of spectrometer sensitivity at 4.2°K is difficult, and the actual number of free radicals produced is not measured with reliability. However, the relative numbers of free radicals produced in the samples of different concentration could be measured with reasonable accuracy over a wide range of concentrations.

Figure 2 compares the results at a constant dosage of 4×10^4 which is not sufficient to deplete the CD_4 molecules in the lowest concentration employed. The energy absorbed by the total sample ($Kr + CD_4$) remains approximately the same, 2.1×10^{18} eV/g, for the different concentrations. If no energy were transferred from the krypton matrix to the CD_4 molecules, the D or CD_3 signal strength for a given dosage should decrease in proportion to the decrease of CD_4 in the matrix, as indicated by the bottom curve. If all the energy intercepted by the matrix were transferred to the CD_4 molecules, the signal strength should remain the same as that of the pure CD_4. This behavior is indicated by the top (dashed) line of Fig. 2. The observed signal strengths follow the middle (solid) curve of Fig. 2. This comparison indicates considerable, but, of course, not complete, transfer of energy from the krypton to the CD_4. When the concentration of CD_4 molecules is only 1 in 10 000 in the sample, the observed signal strength is 500 times that expected for no energy transfer from the matrix. The G value, defined as the number of free radicals per 100 eV, is approximately 2 for the pure solid CD_4. The apparent G values for the solutions as calculated from the signal strengths on the assumption that no energy transfer occurs are absurdly high. For example, the apparent G value for a mole fraction of 10^{-4} is 1000. Since a minimum of 4.4 eV is required for breaking a C-D bond, certainly 100 eV 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 Wall[2] 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 energy[6] 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 energies[7] 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.

We have benefitted greatly from discussions of these problems with Professor James Franck.

---

*This research was supported by the U. S. Air Force Office of Scientific Research of the Air Research and Development Command.

[1] H. N. Rexroad and W. Gordy, Phys. Rev. 125, 242 (1962).

[2] R. E. Florin, D. W. Brown, and L. A. Wall, Fifth International Symposium on Free Radicals (Almquist and Wiksell, Stockholm, 1962), Paper No. 18.

[3] L. Cochran, V. A. Bowers, S. N. Foner, and C. K. Jen, Phys. Rev. Letters 2, 43 (1959).

[4] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. 112, 1169 (1958).

[5] J. Franck and E. Teller, J. Chem. Phys. 6, 861 (1938).

[6] T. L. Cottrell, The Strengths of Chemical Bonds (Butterworth's Scientific Publications, London, 1954), Chap. 9.

[7] F. H. Field and J. F. Franklin, Electron Impact Phenomena (Academic Press, Inc., New York, 1957), Appendix.

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

C. E. Fairchild and K. C. Clark
Department of Physics, University of Washington, Seattle, Washington

(Received June 21, 1962)

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 $\lambda = 1200$ Å is found to have an average oscillator strength $f = 1.2\times10^{-4}$. Absorption by the $3s\,^2P$-$(2p)^3\,^2D$ doublet at $\lambda = 1493$ Å and by the $3s\,^2P$-$(2p)^3\,^2P$ doublet at $\lambda = 1744$ Å, 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