

## Energy Migration and Isotopic Effects in Irradiated Solids at Low Temperature\*

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Energy migration to impurity molecules of hydrogen and methane trapped in solid matrices of argon and krypton at low temperature is shown to occur. The solid containing the impurity molecules in minute quantities was irradiated at 4.2°K with  $\gamma$  rays from  $\text{Co}^{60}$ , and the free radicals produced by dissociation of impurity molecules were measured from the intensity of their electron spin resonance signals. For concentrations of 0.001 mole fraction of  $\text{CD}_4$  in Ar or Kr, over 500 times as many molecules of  $\text{CD}_4$  were dissociated as would be expected from the same quantity of pure  $\text{CD}_4$  given the same exposure dose. It is concluded that the dissociation of the dilute impurity is produced almost wholly by the energy absorbed by the matrix and transferred to the impurity molecules. In the mixed isotopic species— $\text{HCD}_3$ ,  $\text{H}_2\text{CD}_2$ , and  $\text{H}_3\text{CD}$ —it is shown from the relative strength of the ESR signals of H and D atoms that the C-H bond has about 5 times greater probability of being broken by the migrating energy than has a given C-D in the same molecule. This large isotopic effect is attributed to the more rapid escape of H over D from the parent molecule within the lattice.

### INTRODUCTION

A PRELIMINARY publication<sup>1</sup> reported evidence from electron spin resonance for energy migration in argon and krypton at 4.2°K. The production of hydrogen atoms and methyl radicals by  $\gamma$ -irradiation of methane in concentrations of  $10^{-4}$  trapped in argon or krypton matrices was found to be as much as 500 times that which could be expected from the radiation directly intercepted by the methane from the cobalt-60 source used to irradiate the samples. A similar, abnormally large production of H atoms from small concentrations of  $\text{H}_2$  in these matrices was observed. For these low concentrations the production of free radicals appeared to result almost wholly from the  $\gamma$ -ray energy intercepted by the argon or krypton matrices and transferred to the impurity molecules. Further details on these phenomena are reported here. A study of isotopic substitution,<sup>2</sup> D for H, was undertaken in the search for additional information about the form in which this energy migrates and about the mechanism of its coupling to the impurity molecules.

### EXPERIMENTAL PROCEDURES

The cryostat, the ESR spectrometer, and the irradiation source, together with the procedures of their use, are those already described by Rexroad and Gordy.<sup>3</sup> The sensitivity of the spectrometer was approximately  $5 \times 10^{18}$  spins for a signal-to-noise ratio of unity. Measurements were made at the *K*-band frequency of 23 kMc/sec. The only procedures and methods to be de-

scribed here are those particular to this series of measurements.

The argon and krypton used were of research grade chemicals, obtained from the Matheson Chemical Company. Mass spectra analysis showed that the argon had an impurity concentration of less than 0.001 mole % and the krypton less than 0.005 mole %. The deuterated methanes were obtained from Merck, Sharp, and Dohme of Canada, Ltd. The isotopic concentration of each species was above 98%. All the samples used consisted of gases which froze above 77°K, except for nitrogen, either mixtures of two or three gases, or their reasonably pure form. This allowed a consistency and ease of handling that was important in this work.

The procedure was as follows: First the wave guide was attached to a vacuum system and was pumped out; the pump was closed off; then measured pressures of gases were let into the system or part of the system, all the relevant volumes of which were known, and were allowed to mix for times varying from a few minutes to an hour. Next, the sample was frozen into the cavity, either at 77°K while the wave guide was still attached to the system, or with the wave guide closed off and removed from the vacuum system, and the cavity was inserted directly into the liquid helium. In the former case, after the sample was frozen at 77°K the wave guide was closed off, removed from the system and inserted into the helium bath. The difference in the two procedures was for convenience in handling different concentrations of gaseous mixtures.

After the wave guide containing the sample had been placed in the flask filled with liquid helium, the whole assembly was taken to the radiation source and was lowered into the radiation chamber by means of a suitable pulley and wire arrangement. At the time of the experiment the radiation source contained  $\text{Co}^{60}$  which gave off  $\gamma$  rays of 1.17 and 1.33 MeV. The source had an exposure dose rate of 4000 R/min.

The amount of energy absorbed by the sample was calculated in this manner. The  $\gamma$  rays from the cobalt

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<sup>1</sup> W. V. Bouldin, R. A. Patten, and W. Gordy, *Phys. Rev. Letters* **9**, 98 (1962).

<sup>2</sup> A report of the effects of isotopic substitution has been given at a meeting of the American Physical Society. See W. Bouldin and W. Gordy, *Bull. Am. Phys. Soc.* **7**, 271 (1962).

<sup>3</sup> H. N. Rexroad and W. Gordy, *Phys. Rev.* **125**, 242 (1962).

source were approximately 1 MeV. In this energy region, for the elements used (C, D, and Kr), Compton scattering is the overwhelmingly predominant effect of the  $\gamma$  rays. The pertinent feature of this scattering is the amount of energy given to the secondary electrons. By interpolation from tables compiled at the National Bureau of Standards<sup>4</sup> the total Compton mass attenuation coefficients  $(\sigma/\rho)_\tau$  were obtained. These are the sum of the scattering and the absorption coefficients. Since the ratios of the two have been calculated,<sup>5</sup> the "true" mass absorption coefficients can be found. From the known rate decay of  $\text{Co}^{60}$  and the previously calibrated source the exposure dose rate at the time of the experiment was found to be 4000 R/min. The absorbed dose in air  $D_0$  is

$$D_0 = I(\sigma/\rho)_0,$$

where  $I$  is the incident intensity and  $(\sigma/\rho)_0$  is the mass absorption coefficient for air. Since the incident intensity can be calculated from known constants in terms of roentgens per minute, the dosage for any substance is

$$D_x = 5.47 \times 10^{13} R(\sigma/\rho)_x / (\sigma/\rho)_0 \text{ eV/(g-min)},$$

where  $D_x$  is the absorbed dose,  $R$  is roentgens per minute and  $(\sigma/\rho)_0$  is the mass absorption coefficient. Absorption coefficients for the methane samples and the mixtures with the matrices are calculated from relative weights of the constituents multiplied by the individual mass absorption coefficients.

For each run, known amounts of sample and matrix were frozen into the cavity and were irradiated at 4.2°K for periods of increasing duration between observations of the spectra. The gain control immediately preceding the recorder was calibrated so that its relation to signal height on the spectral trace was known. Thus, the relative strengths of separate signals could be measured. Because the radiation times are cumulative from point to point, the times given correspond to the total time of radiation. This conclusion is valid since no decay of the resonance signal is seen over a period of several hours so long as the sample remains at helium temperatures. The spin resonance signal was measured by its height on the recorder, averaged over several determinations. The validity of this simple procedure rests on the fact that the linewidths and shapes for concentrations up to 0.1 mole fraction remained nearly the same.

For total time of radiation up to about 20 min, the signal doubled approximately with doubled amounts of radiation. As expected, particularly for the lowest concentrations, the signal began to level off for longer radiation times as there were fewer methane molecules available for the radiation to modify. This is shown in

<sup>4</sup> G. W. Grodstein, Natl. Bur. Std. Circ. (U.S.) No. 583 (1957), p. 23.

<sup>5</sup> C. M. Davisson and R. D. Evans, Rev. Mod. Phys. 24, 79 (1952).

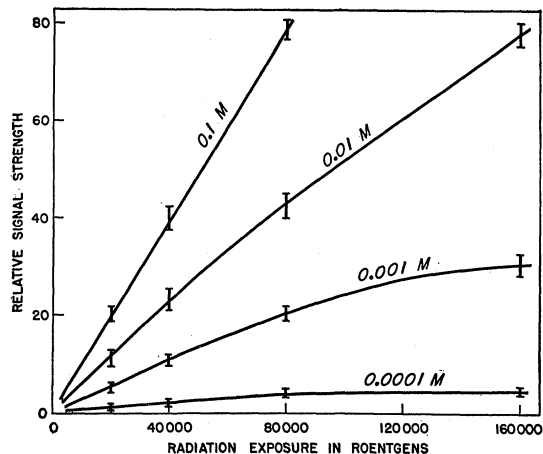


FIG. 1. Signal strengths of the electron spin resonance of D atoms as a function of  $\gamma$ -ray dosages for various concentrations of  $\text{CD}_4$  in krypton at 4.2°K.

the lower curves of Fig. 1. These facts lead to confidence in the direct proportionality of the resonance signal strength to the number of radicals present for a given concentration. Proportionality between concentrations depends on the relative sensitivity of the spectrometer from run to run. By careful tuning, sensitivity could be optimized to about the same maximum each time. In all cases, the magnetic field modulation was the same, and both klystron power and the power on the bolometer were kept approximately the same for all the runs in a series. From the projected leveling off points of the curves for different concentrations it can be assumed that the sensitivity stayed approximately constant.

Except for one case, different methods of freezing the gas mixtures had no detectable effect on the strengths or shapes of the curves for signal versus radiation time. For the 0.1 mole fraction of  $\text{CD}_4$  mixture, freezing first at liquid-air temperature gave lower signal strengths than did freezing directly at 4.2°K. Thus, for this concentration the freezing out of the krypton did not trap the  $\text{CD}_4$  molecules completely, as it did for the lower concentrations. The curves were therefore computed for the process of direct freezing at helium temperatures. Each concentration was run at least twice; some, as many as five times. The spread in the data is shown by vertical lines on the signal-versus-dosage curves of Fig. 1. The results were the same for different mixing times.

#### ENERGY MIGRATION IN SOLID KRYPTON AND ARGON AT LOW TEMPERATURE

Tables I and II show evidence for energy migration in the krypton matrix at low temperature and for transfer of the energy to  $\text{CD}_4$  molecules trapped in the lattice. To understand this evidence, one should consider the nature of the  $G$  values. The  $G$  value is defined as the number of free radicals produced by 100 eV of ab-

TABLE I. Free radicals (D atoms) produced from CD<sub>4</sub> in krypton matrix for an exposure dose of 40 000 R.

Mole fraction of CD <sub>4</sub> in matrix	Dose absorbed <sup>a</sup> in (eV/g) × 10 <sup>-16</sup>	Radicals per gram of CD <sub>4</sub> +Kr × 10 <sup>-18</sup>	Radicals per gram of CD <sub>4</sub> × 10 <sup>-18</sup>
1.0 (pure CD <sub>4</sub> )	2.15	4	4
0.09	2.08	2.7	30
0.01	2.08	2.0	200
0.001	2.08	1.0	1000
0.0001	2.10	0.22	2200

<sup>a</sup> By Kr matrix + CD<sub>4</sub> sample.

sorbed energy. This definition is explicit, but an ambiguity arises when one attempts to define the energy absorbed by the sample, which is here considered as the CD<sub>4</sub> exclusive of the krypton matrix. This energy might be taken as (1) the combined energy absorbed from the cobalt source by the matrix and the sample together or as (2) the energy which would be absorbed by the same amount of sample without the matrix. Condition (1) assumes that all the energy originally absorbed by the matrix is effectively transferred to the CD<sub>4</sub> sample. Condition (2) assumes that there is no transfer of the energy from the matrix to the sample or vice versa, i.e., only the energy which would be absorbed from the Co<sup>60</sup> source by the isolated sample produces the radicals. If complete transfer, condition (1), were to hold, the energy absorbed by the sample with constant dosage would remain essentially constant as the sample concentration was decreased. Until the sample approached depletion, a condition avoided in the data of Tables I and II, the number of free radicals produced would also remain approximately constant. Thus, if condition (1) were to hold, the *G* values calculated in this way would have the approximately constant value of 1.9 observed for the pure CD<sub>4</sub>. Likewise, if condition (2) were to hold, the *G* values calculated with only the energy directly absorbed by the sample from the Co<sup>60</sup> source should have the constant value of 1.9, whatever the concentration.

From Table II it is seen that the *G* values calculated

TABLE II. Apparent *G* factors and percentage of total energy employed for dissociation of CD<sub>4</sub> which is transferred from the Kr matrix. Calculated from data in Table I.

Mole fraction of CD <sub>4</sub> in matrix	Apparent <i>G</i> factor		% CD <sub>4</sub> energy from Kr matrix <sup>c</sup>
	Rad. per 100 eV <sup>a</sup>	Rad. per 100 eV <sup>b</sup>	
1.0 (pure CD <sub>4</sub> )	1.9	1.9	0
0.09	1.3	14	86
0.01	1	95	98
0.001	0.5	500	99.6
0.0001	0.1	1000	99.8

<sup>a</sup> Of total  $\gamma$ -ray energy absorbed by CD<sub>4</sub>+Kr matrix.

<sup>b</sup> Of only that energy absorbed directly by CD<sub>4</sub> from Co<sup>60</sup> source, on assumption of no energy transfer from Kr.

<sup>c</sup> Percentage of the total energy used for dissociation of CD<sub>4</sub> which is absorbed from the Kr matrix.

from the observed numbers of free radicals with the assumption of condition (1) decrease with concentration of the sample from 1.9 for pure CD<sub>4</sub> to 0.1 for a CD<sub>4</sub> concentration of 0.0001 M. The decrease shows that the transfer of energy from the matrix to the sample is not complete. This is not a surprising result, for certainly one would expect that some of the energy would be dissipated in the matrix and that some would be lost to the outside world.

The surprising evidence is the absurdly large *G* values which are obtained for the lower concentrations on the assumption that the observed free radicals are produced only by the energy intercepted by the sample, condition (2) (see column 3 of Table II). For example, 100 eV of absorbed energy obviously cannot dissociate 1000 CD<sub>4</sub> molecules whose bond strength individually is 4.4 eV. Instead of maintaining the constant value of 1.9 expected for no energy transfer, the *G* values calculated with assumed condition (2) increase to 1000 for the concentration of 0.0001 mole fraction. For the highest concentrations, solid CD<sub>4</sub> and 0.09 mole fraction of CD<sub>4</sub>, the estimates of the relative number of radicals present are more difficult to make than for the more dilute solutions, because of changes in line shape and width. However, the *G* value for solid CD<sub>4</sub>, 1.9, is a reasonable one which agrees fairly well with other determinations.<sup>6</sup> Even if the absolute values of these yields are incorrect by a large factor, the relative values, particularly those for the lower concentrations, would remain the same. Thus, the increase in yield with decreasing concentration must result from energy which is absorbed by the krypton matrix and transferred to the CD<sub>4</sub>.

From these results it is possible to calculate the percentage of the total energy required for production of the free radicals which is obtained by the CD<sub>4</sub> from the krypton matrix. These percentages for the various concentrations are listed in the last column of Table II. They are calculated with the assumption that 52.5 eV is required for dissociation of a CD<sub>4</sub> into CD<sub>3</sub> and D radicals in the matrix as well as in the pure solid CD<sub>4</sub>. Although not exact, this assumption should certainly hold to a good approximation. From examination of the column it is evident that for concentrations of 0.001 mole fraction and lower, more than 99% of the energy for the dissociation is absorbed by the krypton matrix and transferred to the CD<sub>4</sub>.

Argon was also studied as a matrix material. The argon matrix showed energy transfer like that of the krypton matrix although the argon employed unfortunately contained an unknown amount of CH<sub>4</sub> which made the results less reliable. Measurements were made on the H atoms and the CH<sub>3</sub> radicals from the impurity CH<sub>4</sub> in the argon sample. Then one part in one thousand of CD<sub>4</sub> was added to the argon. The yields of D and

<sup>6</sup> L. A. Wall, D. W. Brown, and R. E. Florin, *J. Phys. Chem.* **63**, 1762 (1959).

CD<sub>3</sub> radicals obtained were comparable to those for the same CD<sub>4</sub> concentration in krypton; the reduction in yields of the H and CH<sub>3</sub> radicals show that approximately ten times less CH<sub>4</sub> was dissociated than when CD<sub>4</sub> was not present. This quenching of the CH<sub>4</sub> dissociation by the more abundant CD<sub>4</sub> molecules provides another kind of evidence for energy migration and transfer. It indicates that excitations moving through the matrix are partially depleted on the more abundant CD<sub>4</sub> and thus have less probability of dissociating the CH<sub>4</sub>.

Nitrogen was investigated both as a matrix and as a sample. One part in one thousand of CD<sub>4</sub> was embedded in a nitrogen matrix and irradiated at 4.2°K. In this case the molecular nitrogen itself dissociated, giving the previously observed ESR of irradiated solid nitrogen,<sup>7</sup> with no signals caused by CD<sub>4</sub> dissociation. Nitrogen, then, is not a suitable matrix for dissociating energy transfer to CD<sub>4</sub>. When N<sub>2</sub> was used as a dilute sample (0.001 mole fraction) in a krypton matrix, the nitrogen spectra were not observed for radiation dosage up to 400 000 R. This result should not be interpreted as evidence against migration of energy in the krypton matrix. Perhaps the migrating excitation did not effectively couple with the N<sub>2</sub> or perhaps it was not of sufficient energy to dissociate the N<sub>2</sub>. The N-atom spectrum has been observed in a  $\gamma$ -irradiated frozen inert gas matrix, but with low yields.<sup>6</sup> Probably a longer radiation time would have made possible the observation of the N-atom spectrum.

Studies inferring intermolecular energy transfer have been made in several fields by different methods. Fluorescence quenching effects were among the earlier experiments. Chemical analysis of end products of radiolysis has also been used. Electron spin resonance studies of free radicals have recently given evidence of intermolecular energy transfer in several systems, particularly irradiated proteins<sup>8</sup> in which the electron spin density was found to show up only on certain groups such as the cystine or glycine constituents. Buben *et al.*<sup>9</sup> have observed scavenging effects of benzene on the yield of free radicals in the radiolysis of polyethylene, similar to earlier work on fluorescence quenching. Kallman *et al.*<sup>10</sup> were able to infer energy transfer from benzene to CCl<sub>4</sub> from radical yield results, while Wall, Brown, and Florin<sup>6</sup> obtained ESR signals from impurity H atoms in  $\gamma$ -irradiated solid deuterium which they mentioned as evidence for transfer of energy in

solid hydrogen. Rexroad and Gordy found ESR signals comparable in strength to those of the D atoms in  $\gamma$ -irradiated D<sub>2</sub>O at 4.2°K when the H isotopic concentration in the sample was less than 1%. They interpreted this surprising result as indicating energy transfer in ice at low temperature.

Other ESR studies on systems similar to those in the present work, CH<sub>4</sub> and CD<sub>4</sub> in rare-gas matrices, were done under conditions that would make energy migration difficult or impossible to detect. Florin, Brown, and Wall<sup>11</sup> irradiated CH<sub>4</sub> in a xenon matrix at 77°K, but they computed yields only over a limited range of concentrations, 0.23 to 0.69 mole fraction of CH<sub>4</sub>. Cochran<sup>12</sup> deposited CD<sub>4</sub> and argon at 4.2°K and irradiated the mixture with an ultraviolet source. Lines due to CD<sub>3</sub> and D were observed, but no yields were reported. Deposition of the products of a rf discharge in CH<sub>4</sub> deposited at 4.2°K would not, of course, show energy transfer.

#### POSSIBLE MECHANISMS FOR THE ENERGY MIGRATION

The energy migration and transfer found here can be explained in terms of concepts earlier advanced by James Franck and his associates. Franck and Teller<sup>13</sup> were the first to discuss the role of exciton migration in photochemical processes. More recent theories such as those of Simpson and Peterson,<sup>14</sup> of Magee<sup>15</sup> and of Forster<sup>16</sup> have been of a more quantitative nature, but, as Forster states, "All later work on excitation transfer may be traced back to the qualitative statements made in the early paper" (of Franck and Teller). In that early paper excitation transfer is considered as caused by the resonance between identical units, such as molecules or unit cells in a crystal, which allows the excitation energy to proceed by a radiationless transfer from one "cell" to the other. The rate of transfer depends on the strength of the coupling between cells. Two extreme cases can arise. For weak coupling, which corresponds to slow transfer of excitation relative to the period of vibration of the molecule, the molecular aggregate system under consideration should be treated as composed of individual molecules which pass their excitation energy from one to the next. In the strong coupling case, where the energy transfer is rapid as compared to the vibration frequency, the excitation

<sup>7</sup> T. Cole, J. T. Harding, J. R. Pellam, and D. M. Yost, *J. Chem. Phys.* **27**, 593 (1957).

<sup>8</sup> W. Gordy, W. B. Ard, and H. Shields, *Proc. Natl. Acad. Sci. U. S. A.* **41**, 983 (1955); F. Patten and W. Gordy, *Proc. Natl. Acad. Sci. U. S. A.* **46**, 1137 (1960).

<sup>9</sup> N. Ya. Buben, I. I. Chkheidze, A. T. Koritzky, Yu. N. Molin, V. N. Shamshev, and V. V. Voevodsky, in *Fifth International Symposium on Free Radicals* (Almqvist and Wiksell, Stockholm, Sweden, 1961), paper No. 46.

<sup>10</sup> H. Kallmann, W. Riedl, and N. Wotherspoon, in *Fifth International Symposium on Free Radicals* (Almqvist and Wiksell, Stockholm, Sweden, 1961), paper No. 29.

<sup>11</sup> R. E. Florin, D. W. Brown, and L. A. Wall, in *Fifth International Symposium on Free Radicals* (Almqvist and Wiksell, Stockholm, Sweden, 1961), paper No. 18.

<sup>12</sup> E. L. Cochran, V. A. Bowers, S. N. Foner, and C. K. Jen, *Phys. Rev. Letters* **2**, 43 (1959).

<sup>13</sup> J. Franck and E. Teller, *J. Chem. Phys.* **6**, 861 (1938).

<sup>14</sup> W. T. Simpson and D. L. Peterson, *J. Chem. Phys.* **26**, 588 (1957).

<sup>15</sup> J. L. Magee, in *Comparative Effects of Radiation*, edited by M. Burton, J. S. Kirby-Smith, and J. L. Magee (John Wiley & Sons, Inc., New York, 1960), Chap. 7.

<sup>16</sup> Th. Forster, in *Comparative Effects of Radiation*, edited by M. Burton, J. S. Kirby-Smith, and J. L. Magee (John Wiley & Sons, Inc., New York, 1960), Chap. 13.

spreads rapidly, and the assembly—or perhaps domains in the assembly—may be treated as a giant molecule. In either situation the excitation can be “localized” by a process such as molecular dissociation, if certain conditions are met. For example, units of the system that are transferring an excitation must resonate in some degree with the unit to be acted upon. If there is weak resonance, the excitation may be degraded by thermalization or radiation into its ground state and thus may disappear before it can react. For very strong coupling, the excitation may pass right through the site of reaction before the dissociation process can take place.

In the present work, excitation of the matrix and sample is due primarily to the stopping of energetic secondary electrons. This stopping leaves a “path” of atoms of the matrix in excited electronic states, including ionization. Excitations may leave this path, transferring the energy from one atom of the matrix to the next, probably through strong coupling. However, the coupling of the migrating excitations to the impurity or methane units is probably weak or intermediate in strength.

An observation that may have some bearing on this problem is the work of Schnepf and Dressler,<sup>17</sup> who observed absorption spectra in solid xenon, krypton, and argon. They found absorption bands in krypton, 300  $\text{cm}^{-1}$  wide, at 80 390  $\text{cm}^{-1}$  corresponding to energies of 9.9 and 10.1 eV. These absorptions were identified as belonging to the atomic levels  $4p5s$ , which were shifted 420 and 910  $\text{cm}^{-1}$  in the solid. The dissociation energy of  $\text{CH}_4$  into  $\text{CH}_3$  and H is approximately 4.4 eV,<sup>18</sup> and  $\text{CD}_4$  differs essentially only by the zero-point energy difference, about 0.131 eV, whereas the dissociation energy of  $\text{N}_2$  is 9.756 eV.<sup>18,19</sup> If the excitation that is migrating through the lattice is an excited electronic state of krypton, it should be able to dissociate either  $\text{CD}_4$  or  $\text{CH}_4$ , but probably not  $\text{N}_2$ . Since they are held in a “cell” of krypton atoms, additional energy is needed to allow the fragments to move away from one another. The excess of available energy over that needed for dissociation is smaller for  $\text{CD}_4$ , a fact which may explain the low yield of N atoms. Another possibility is that the energy migrates as an ionized hole in the Kr lattice. Thus the relative ionization potentials of the krypton,  $\text{N}_2$ , and  $\text{CD}_4$  are of interest. They are, respectively, 14.0, 15.6, and 13.2 eV.<sup>19</sup> If the transfer is a charge migration from one krypton atom to the next and then to a solute molecule ( $\text{CD}_4$  or  $\text{N}_2$ ), the krypton ionization energy would not be great enough to ionize the  $\text{N}_2$ , but would suffice for  $\text{CD}_4$ . This condition also offers a possible explanation of the low yields of N atoms. Obviously, further studies

need to be made on different matrices and samples to substantiate this idea. Charge-transfer processes in photosynthesis have also been proposed and discussed.<sup>20</sup>

#### ISOTOPIC EFFECTS

For the study of isotopic effects on the dissociation of bonds in methane, 0.001 M solutions of the samples in both krypton and argon matrices were examined. The  $\gamma$ -ray dosages were below the point where effects of saturation or of depletion of the sample become noticeable. For these concentrations, as the last column of Table II shows, dissociation of the bonds seems to be produced predominantly by energy migrating in the matrix, presumably in the form of excitons or as ionized holes in the lattice. For comparison, pure samples of the mixed isotopic species were also examined at low temperature.

The top curve of Fig. 2 shows a tracing of the ESR spectrum of  $\text{CH}_3\text{D}$  in concentration of 0.001 mole fraction in krypton, with irradiation dosage of the order of  $2.5 \times 10^{19}$  eV/g. A similar spectrum appeared when argon was used as the matrix. The lower curve of Fig. 2 represents corresponding tracings for  $\text{CH}_2\text{D}_2$ . A triplet of triplets is observed in the central portion of the spectrum for  $\text{CH}_3\text{D}$ . This can be attributed to the  $\text{CH}_2\text{D}$  radical, for which a triplet is expected from the equivalent coupling of the two protons, each line of which is further split into triplets by the deuterium coupling. For a  $\text{CHD}_2$  radical, a doublet of quintuplets is expected. These two configurations are observed in the spectra of irradiated  $\text{CH}_3\text{D}$  and  $\text{CH}_2\text{D}_2$ . The  $\text{CHD}_3$  sample gives the spectrum of the  $\text{CD}_3$  radical. Relative intensities of the weak lines within the central portion

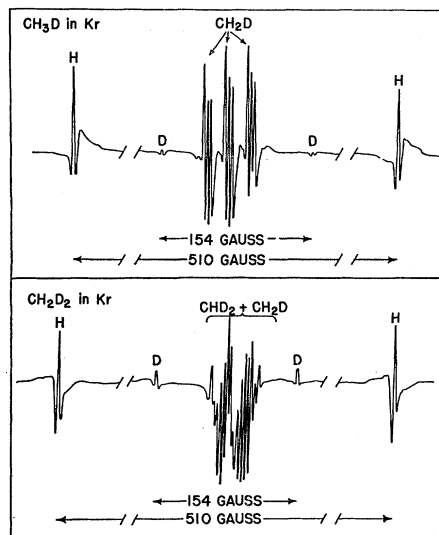


FIG. 2. Electron spin resonance signals of free radicals produced by a  $\gamma$ -ray dosage of 40 000 R on 0.001 mole fraction of  $\text{CH}_3\text{D}$  (upper tracing) and  $\text{CH}_2\text{D}_2$  (lower tracing) in krypton at 4.2°K.

<sup>17</sup> O. Schnepf and K. Dressler, *J. Chem. Phys.* **33**, 49 (1960).  
<sup>18</sup> T. L. Cottrell, *The Strengths of Chemical Bonds* (Butterworths Scientific Publications, Ltd., London, 1954), Chap. 9.  
<sup>19</sup> F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press, Inc., New York, 1957), Appendix.

<sup>20</sup> M. Calvin, *Rev. Mod. Phys.* **31**, 147 (1959).

TABLE III. Isotope effect in the production of H and D atoms by irradiation of deuterated methanes (in various matrices at 4.2°K).

Matrix	Sample	Mole fraction of sample	Observed intensity ratio	Expected intensity ratio	(H/D) <sup>a</sup>
Kr	CH <sub>3</sub> D	0.001	30.5	9/2	6.7
Kr	CH <sub>2</sub> D <sub>2</sub>	0.001	8.0	3/2	5.3
Kr	CHD <sub>3</sub>	0.001	3.2	1/2	6.4
A	CH <sub>3</sub> D	0.001	23.0	9/2	5.1
A	CH <sub>2</sub> D <sub>2</sub>	0.001	6.8	3/2	4.5
A	CHD <sub>3</sub>	0.001	2.5	1/2	5.0
...	CH <sub>3</sub> D	1.0	21.5	9/2	4.8
...	CH <sub>2</sub> D <sub>2</sub>	1.0	5.9	3/2	3.9
...	CHD <sub>3</sub>	1.0	2.2	1/2	4.4
CH <sub>4</sub>	CD <sub>4</sub>	0.5	8.3	3/2	5.4
Kr	CH <sub>4</sub> +CD <sub>4</sub>	0.002 <sup>b</sup>	2.7	3/2	1.8

<sup>a</sup> Ratio of observed to expected intensity.

<sup>b</sup> Total. CD<sub>4</sub> and CH<sub>4</sub> are present in equal concentrations, 0.001 mole fraction.

will be considered in the discussion of satellite lines. In each of the spectra, the H-atom doublet, with a splitting of about 500 G, and the outer components of the D-atom triplet are observed. The spectra are compressed to show the H-atom doublet. The middle line of the deuterium triplet is obscured by the central resonance. From these spectra, it is obvious that H atoms are more readily dissociated from the molecules than are D atoms. Relative intensities of the H and D lines for the lowest field were compared to give the relative numbers of H and D atoms produced by the irradiation from the partially deuterated methanes in the krypton and argon matrices as well as in the pure, solid forms. Spectra were obtained from irradiated samples of the pure solids, also for an equimolar mixture of pure CH<sub>4</sub> and CD<sub>4</sub>, and for equal concentrations of the two (0.001 mole fraction) in a krypton matrix.

The results of the spectral observations are collated in Table III. Each value given in the table represents an average of five to ten spectral recordings. The observed intensity ratios were measured from the heights of the lines. This simple procedure is justified by the similar line widths and shapes for H and D lines. Expected intensity ratios are calculated from the relative numbers of H and D atoms in the methane molecule multiplied by the relative number of lines (3 to 2) in the two spectra.

Comparisons of the observed intensity ratios to the expected intensity ratios are given in the last column of Table III. This comparative ratio (called henceforth H/D) is a measure of the isotopic effect on the production of free radicals by irradiation of these deuteromethanes. It gives an indication of the relative probability of breakage of C-H and C-D bonds by irradiation of the samples under the specified conditions. The H/D ratios were found to be insensitive to changes in microwave power over a range of 0.5 to 5 mW. Neither did radiation dosage affect these ratios over a range of 6 to 24 eV/g $\times 10^{18}$ . In addition to the

large H/D ratios obtained for the partially deuterated species and unequal mixtures of pure CH<sub>4</sub> and CD<sub>4</sub>, there are smaller but definite differences which depend on the kind of matrix employed. The H/D ratios are higher for the krypton lattice than for the argon lattice and higher for argon than for pure methane. These effects are shown diagrammatically in Fig. 3. This indicates that the barrier to escape from the parent molecule changes from one matrix to another. If the barrier height is assumed to be measured by the H/D ratio, it is higher in krypton than in argon or in the pure solid methane.

Another interesting trend is the relatively higher H/D ratio for CH<sub>3</sub>D than for CH<sub>2</sub>D<sub>2</sub>, about 13 to 26% in the various matrices. Also, CD<sub>3</sub>H has a higher H/D than does CH<sub>2</sub>D<sub>2</sub>, but the effect is slightly smaller. This smaller isotopic effect in CH<sub>2</sub>D<sub>2</sub> than in the other two partially deuterated methanes depends on the molecule itself rather than the lattice, since it is consistent from matrix to matrix. These differences probably result from the difference in vibrational modes of each species.

When pure CH<sub>4</sub> and CD<sub>4</sub> are irradiated in an equimolar mixture, the H/D is 5.4, or about the same magnitude as that for H<sub>2</sub>CD<sub>2</sub> in the krypton lattice. When, however, equimolar concentrations of CH<sub>4</sub> are in dilute solution in krypton at 4.2°K, an H/D of only 1.8 is obtained (see Table III). Explanation of this remarkable difference is attempted below. For the partially deuterated methanes in the various lattices, an isotopic effect is obtained which is due both to the nature of the lattice and the nature of the molecule.

Isotopic effects have been observed previously in mass spectra. Bauer and Beach<sup>21</sup> observed isotopic effects on the dissociation of H<sub>2</sub> and D<sub>2</sub> by electron impact. Stevenson and Wagner<sup>22</sup> discussed these effects in terms of the greater amplitudes of oscillation of the higher isotopic species of these diatomic molecules. This results in greater numbers of the lighter species

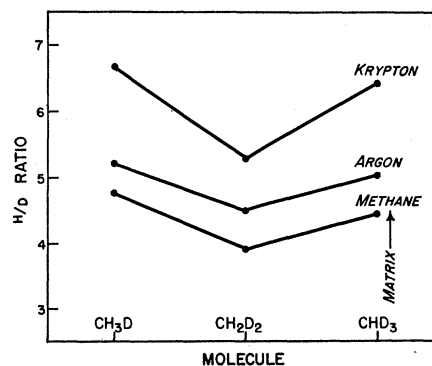


Fig. 3. Diagram showing influence of matrix material and of molecular type on the isotopic effects observed.

<sup>21</sup> N. Bauer and J. Y. Beach, J. Chem. Phys. 15, 150 (1947).

<sup>22</sup> D. P. Stevenson and C. D. Wagner, J. Chem. Phys. 19, 11 (1959).

having internuclear distances such that Franck-Condon transitions to energy levels above the dissociation limit may take place. Dibeler and Mohler<sup>23</sup> found isotopic effects in the molecular beam mass spectra of partially deuterated methanes. They found H/D ratios of 2.6 times the *a priori* probability for CH<sub>3</sub>D, 2.5 for CH<sub>2</sub>D<sub>2</sub>, and 1.6 for CHD<sub>3</sub>. Jesse and Platzman<sup>24</sup> have found an isotopic effect for the gaseous state in the probability of ionization of a hydrocarbon molecule by transfer of energy from a metastable noble gas element. A higher ionization probability was found for the deuterated form than for the normal hydrocarbon.

Mention has already been made of the pronounced isotopic effect found earlier in this laboratory for irradiated D<sub>2</sub>O with an HDO impurity.<sup>3</sup> Jen *et al.*<sup>25</sup> observed complicated ESR spectra when they deposited the products of an rf discharge in partially deuterated methanes at 4.2°K. They stated that the lines observed could be attributed to the various isotopic forms of the methyl radical. They did not report an isotopic effect, however, presumably because the composition of the mixture was unknown, but also possibly because of the manner in which the radicals were generated.

#### POSSIBLE MECHANISMS FOR OBSERVED ISOTOPIC EFFECTS

Qualitatively, the large H/D ratios observed here can be explained in terms of a shorter escape time of an H than of a D atom from the parent molecule within the lattice. Only one atom per molecule can escape to form the observed free radicals, an H or a D, whichever is first. If the excitation energy which causes the dissociation is adequate to dissociate either the C—H or the C—D, the relative escape rates of the H and D should be the determining factor in the relative probability of dissociation of C—H and C—D bonds. In a free molecule of a gas, the relative escape times should be closely related to the relative bond-stretching, vibrational frequency, which is approximately twice as great for the C—H as for the C—D bond. It is interesting that the H/D ratios obtained for isolated molecules in molecular beams by Dibeler and Mohler<sup>23</sup> have an averaged value of approximately 2.

The large H/D ratios observed here, more than twice that for the free molecule, indicate that the relative escape rates of H to D are significantly higher for the solid state than for gases or molecular beams. This is reasonable since the average time required for dissociation in a solid depends not only on the bond vibrational frequency but also on the tunneling frequency of the H or D out of the lattice cage in which it is trapped with the parent molecule. If the atom does not escape rapidly from this cage, there will be a high probability of re-

formation of the bond. The uncertainties and complications inherent in the problem do not permit quantitative calculation of the relative escape time of H and D through the cage barriers. As in simpler barrier-tunneling phenomena, the frequency of the tunneling should depend exponentially upon the mass of the tunneling particle. Thus, the ratio of the tunneling rates of H and D may well be large enough to account for the observed higher H/D ratios in the solids over those for the isolated molecules. The significance of the cage effect in determining the H/D ratios is also evident in the difference in H/D ratios observed for different matrices (see Fig. 3).

From the Franck-Condon principle one might expect that a bond dissociation caused by either ionization or excitation of a methane would have a higher probability of dissociating a C—H than a C—D because the lighter, faster moving isotope would have a greater probability of reaching the escape distance while the molecule is in the excited electronic state, i.e., before the energy is lost through emission or in some way other than dissociation. Also, as indicated by Stevenson and Wagner,<sup>22</sup> the greater vibrational amplitude of the lighter isotope would enhance its probability of escape. These experimental results seem, however, to require that the methane molecules in the lattice, brought into an excited or ionized state by the migrating energy, remain in this state, on the average, for a sufficiently long time to dissociate either C—H or C—D. This is indicated by the relatively low H/D ratio, 1.8, for equal mixtures of CH<sub>4</sub> and CD<sub>4</sub> in dilute solution in krypton. For an excited CD<sub>4</sub> molecule isolated in the lattice, there is no competition from the C—H, and the CD<sub>4</sub> remains in the excited state until a C—D has a high probability of dissociation. In the equal mixtures of pure CH<sub>4</sub> and CD<sub>4</sub>, unlike the equal but dilute mixtures of these methanes in krypton, there is always a nearby CH<sub>4</sub> to which the energy of excitation of CD<sub>4</sub> might be transferred before the C—D has time to break. The H/D ratio for the pure (CD<sub>4</sub>+CH<sub>4</sub>) mixture, 5.4, is comparable to that, 5.3, for CH<sub>2</sub>D<sub>2</sub> in the krypton matrix, a condition which indicates that there is quick transfer of energy between the closely packed CD<sub>4</sub> and CH<sub>4</sub> molecules of the pure matrices. An excited CD<sub>4</sub> isolated in an argon or krypton matrix evidently cannot give the excitation energy back to the matrix nor otherwise release it in a time less than the mean time required for the C—D bond to become dissociated.

Because of the higher zero-point vibrational energy of the lighter isotope, about 0.13 eV, somewhat less energy should be required to remove the H than the D from the methane. Nevertheless, the H/D ratios for the equal mixtures of CH<sub>4</sub> and CD<sub>4</sub> trapped in the krypton matrix indicates that the energy which migrates in the krypton matrix is adequate for dissociating either the C—H or the C—D. The composite results thus support the postulate that the large isotopic effects found here are due mainly to the difference in time re-

<sup>23</sup> V. H. Dibeler and F. L. Mohler, *J. Res. Natl. Bur. Std.* **45**, 441 (1950).

<sup>24</sup> W. P. Jesse and R. L. Platzman, *Nature* **195**, 790 (1962).

<sup>25</sup> C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.* **112**, 1169 (1958).

quired for the escape of the H and D atoms from the parent molecule and out of their lattice cage, rather than to their difference in energy of dissociation *per se*.

The higher ionization probability found for deuterated hydrocarbons by Jesse and Platzman<sup>24</sup> was interpreted by them as caused by a more rapid dissociation or other atomic rearrangement in the lighter isotopic species which would compete with the ionization process. The phenomenon which they found for gases, in as much as it depends on the relative dissociation rates of the C-H and C-D bonds, is related in a general way to the isotopic effect for the solid state which is reported in the present study. The present experiment differs, however, in that it measures effects which depend on the competitive dissociation rates of C-H and C-D within the same molecule.

The energy migration and the isotopic effects observed in the present experiments are probably related closely to the phenomena found for deuterated ice at low temperature.<sup>3</sup> The hydrogen-bonded D<sub>2</sub>O molecules probably can be regarded as closely coupled units for a migration excitation in the Franck-Teller theory. The dissociation time of the D<sub>2</sub>O would be long as compared to the time each D<sub>2</sub>O molecule would remain in an excited state, and the excitation would move through the closely coupled D<sub>2</sub>O matrix in a manner similar to that postulated for the krypton and argon matrices. The H<sub>2</sub>O or HDO impurity molecules would have vibrational frequencies differing from those of D<sub>2</sub>O and would be less closely coupled to the excitation than would be the D<sub>2</sub>O units in the matrix. Like the CH<sub>4</sub> or CD<sub>4</sub> in the krypton matrix, the impurity molecules would receive the energy through intermediate or weak coupling and would become dissociated. In addition, one would expect from the isotopic effect that the H in HDO (which is by far the more abundant impurity) would have 5 times the probability of the D of being removed from a given HDO. Both of these effects combine to make the exceptionally large isotopic effect observed. For a small HDO impurity in an H<sub>2</sub>O matrix, these effects would act in opposition.

#### SATELLITE LINES

In the course of this work, a large number of weak lines were observed in addition to the main spectra. These lines occurred in all regions of the magnetic field sweep, from about 50 G below the low-field line for H atoms to about the same distance above the high-field line. Typical spectra are those for irradiated CH<sub>3</sub>D in argon and krypton matrices, shown in Fig. 4.

These satellite lines are approximately 50 to 200 times weaker than those in the main spectrum. Larger modulation amplitudes seemed to increase the signal-to-noise ratio for these weak lines. Also, the lines are symmetrical about a *g* factor of 2.00, only one side of which is shown in Fig. 4. For each line on the low-field side, there is a corresponding line on the high-field side.

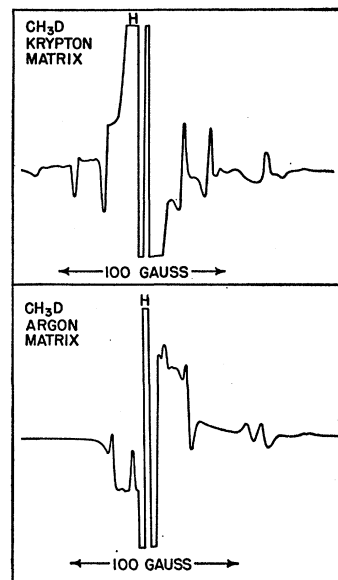


FIG. 4. Satellites of the lower field component of the H-atom doublet from  $\gamma$ -irradiated 0.001 mole fraction of CH<sub>3</sub>D in argon matrix (upper figure) and in krypton matrix (lower figure). The tracings were taken under high gain with samples having an exposure dosage of 480 000 R at 4.2°K.

There are consistent groups of lines around those for the H atom and for the D atom in each matrix, for each different molecule irradiated, but these are not always symmetrical about the position of the H and D lines. The satellites, although somewhat similar in form, do not have the same spacings in the two matrix materials, krypton and argon (see Fig. 4). A surprising feature is that satellite lines are observed 40 to 50 G outside the normal H-atom doublet. This doublet, of 504 G, indicates a spin density of unity in the 1s orbital of the H atom and arises from the well known Fermi contact interaction with the H nucleus. Further splitting by the Fermi contact interaction would not be expected if the possible, small, indirect spin-polarization effects in orbitals of neighboring H atoms are neglected. Thus the interaction which gives rise to the satellite components of the normally spaced (504 G) H doublet, if it is with atomic nuclei, must be of the direct dipole-dipole form rather than the Fermi contact interaction. Anisotropic, dipole-dipole interaction is also indicated by the shape of the satellite absorption.

For CH<sub>3</sub>D in the argon matrix, the only nuclear moments present other than those in the free radicals themselves are those of the undamaged CH<sub>3</sub>D molecules. The satellites symmetrical about the H components may arise from dipole-dipole interaction of the electron spin on H atoms with nuclei of undamaged CH<sub>3</sub>D molecules near which some H atoms would become trapped in the matrix. Because of possible multiple orientations in the magnetic field of the CH<sub>3</sub>D molecule relative to the H atom, this type of interaction would lead to a smeared-out, unresolved pattern. This pattern could, however, have bend points which would show up as peaks in the derivative curve similar to the observed ones. Probably the most stable position of the H atom near the methane would be the one in which its distance



from the three H atoms, or two H's and a D for CH<sub>3</sub>D, would be equal to the Van der Waals distance. In the argon matrix the separation of the satellite components is 24 G from the main H lines. The most favorable orientation of the CH<sub>3</sub> group of CH<sub>3</sub>D with the three H's coupled equally would require an internuclear separation of approximately 1.3 Å between the atomic H and each of the three CH<sub>3</sub> hydrogens to give such a

separation. This does not seem to be an unreasonable figure, although the satellite spacing is larger for the krypton matrix.

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## Disturbance of Phonon Distribution by Hot Electrons

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Calculations are made of the steady-state phonon distribution at low temperatures and high electric fields in a many-valley semiconductor, and numerical evaluation is carried out for *n*-germanium for which all parameters involved are known. It is concluded that the departure from thermal equilibrium will be significant for germanium samples in which the product of carrier concentration *n* and cross-dimension *L* is of the order of 10<sup>18</sup>/cm<sup>2</sup>, and will of course increase as the *nL* product increases beyond this value. The disturbed phonon distribution is found to be quite anisotropic. The relaxation time tensor and the mobility  $\mu$  in the presence of the disturbed distribution are calculated. It is found that, when the disturbance is not too large,  $\mu \propto (nL)^{-\frac{1}{2}}E^{-\frac{1}{2}}$ , where *E* is electric field intensity. This has been shown to agree with experimental data for *n*-Ge at 4°K. The question of whether these effects have been observed in *p*-Ge is discussed.

### I. INTRODUCTION

BECAUSE of the high rate of phonon generation by hot carriers, and the long lifetimes for acoustic phonons at low temperatures, it has been reasoned that significant deviations from the thermal equilibrium phonon distribution might be found at low temperatures.<sup>1-4</sup> Experimental evidence that such deviations do in fact occur in *n*-germanium has been obtained by Zylbersztejn.<sup>4</sup> It is the purpose of the present paper to further explore theoretically the hot-electron-caused disturbance of the phonon distribution in a many-valley semiconductor, and the effects it has on electron transport. Numerical evaluation will be carried out for the case of *n*-germanium.

### II. STEADY-STATE PHONON DISTRIBUTION

Consider the situation at 4°K in an *n*-germanium sample with saturation carrier concentration of the order of 10<sup>14</sup>/cm<sup>3</sup>. At low fields there are few free carriers, and no disturbance of the phonon distribution is ex-

pected. When the breakdown field is reached, carrier concentration increases rapidly. For a range of fields starting at about two to three times the breakdown field it is found typically,<sup>5</sup> in samples of small cross dimensions, that carrier concentration remains essentially constant, although at a value somewhat less than the saturation value. For fields at the beginning of this range, it is expected that the average energy of the electrons corresponds to a temperature of the order of 30°K since approximately this temperature is required to produce essentially complete thermal ionization of the impurities. At higher fields, when the average energy of the electrons corresponds to a temperature of about 70°K, optical phonon emission will become significant.<sup>6</sup> The calculations of this paper will apply to the range of fields in which carrier concentration is constant and scattering of the electrons is by intravalley acoustic lattice modes and, to a small extent, impurities.

Because the scattering is essentially elastic, whether or not the phonons have the thermal equilibrium distribution, the distribution function  $f^{(i)}$  of the carriers in the *i*th valley will take the form of a function of energy only,  $f_0^{(i)}(\mathcal{E})$ , plus a small drift term, in general not in the

<sup>1</sup> E. M. Conwell, V. J. Fowler, and J. Zucker, quarterly reports, Contract No. DA 36-039-SC-89174, U. S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey, 15 May 1962-15 May 1963 (unpublished).

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<sup>3</sup> H. Sato, J. Phys. Soc. Japan **18**, 55 (1963).

<sup>4</sup> A. Zylbersztejn and E. M. Conwell, Phys. Rev. Letters **11**, 417 (1963).

<sup>5</sup> See, for example, S. H. Koenig, R. D. Brown, III, and W. Schillinger, Phys. Rev. **128**, 1668 (1962).

<sup>6</sup> E. M. Conwell, Phys. Chem. Solids **8**, 234 (1959).