to mean that the impurity moment is essentially a spin-only (no orbital contribution) magnetic moment. As noted above, our theory does not apply to the $g \approx 2$ case.

A few experiments have been performed on other rare-earth impurities in metals[24] and g values differing greatly from two (e.g., $g \approx 3$ to 9) have been observed. Our theory applies directly to this case. In particular, Burr and Orbach[24] have measured the linewidth of Er impurities in Mg from 2 to 4°K and found good agreement with the lowest-order Kubo-Tomita[1] theory. The Kondo temperature associated with Er impurities in Mg is thus presumably lower than 2°K.

Since iron-group impurities are in general expected to have higher Kondo temperatures than rare-earth impurities, it would be interesting to study the resonance of iron-group ions having $g \neq 2$ at low temperatures. For example, cobalt resonances at $g \approx 5$ have been observed[25] in $ScCo_2$ and YCo_2, but the linewidth increases as the temperature is lowered due to the strong Co-Co interactions. It would be interesting to try similar experiments on these compounds, but with all but a small fraction of the cobalt atoms replaced by another diamagnetic metallic atom. Also, other dilute alloys of paramagnetic ions having $g \neq 2$ will no doubt be found in the near future; should these ions have Kondo temperatures in a practically attainable temperature range, they will serve as a good test of our theory of the Kondo-like anomalies (3.17) and (3.24). It should also be noted [Eqs. (3.18) and (3.25)] that when $\omega_0 > T$, increasing the magnetic field tends to suppress the Kondo anomalies.

ACKNOWLEDGMENTS

I would like to thank A. Griffin and L. Dworin for stimulating conversations.

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Electron Spin Resonance of Free Radicals Formed from Group-IV and Group-V Hydrides in Inert Matrices at Low Temperature*

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The electron-spin-resonance spectra of molecular free radicals formed from the group-IV and group-V hydrides at 4.2°K in the xenon matrix have been observed and compared with those observed in krypton and other matrices. From these spectra, certain properties of the free radicals and certain matrix effects have been derived. Molecular free radicals formed by γ irradiation of a matrix containing PH_3 or AsH_3 are PH_2 and AsH_2, respectively. From analysis of the hyperfine structure, the P-bonding orbitals of PH_2 were found to have 20.6% $3s$ character in the Xe matrix, compared with 19% in the Kr matrix. Because of anisotropies in the coupling and in the g tensor the hyperfine structure of AsH_2 could not be measured. In the Xe matrix the average g is 2.0050 for PH_2, and 2.034 for AsH_2. No spectra could be observed for SbH_2, although evidence for dissociation of SbH_2 was indicated by the strong H-atom lines observed for a γ-irradiated sample of SbH_3 in the Xe matrix. Molecular free radicals formed by γ irradiation of the group-IV hydrides are CH_3, SiH_3, GeH_3, and SnH_3. The observed hyperfine structure caused by the isotopes ^{29}Si, ^{73}Ge, and $^{117,119}Sn$ indicate that the radicals SiH_3, GeH_3, and SnH_3 are not planar like CH_3, but are pyramidal in structure. Noticeable difference in the isotropic coupling of ^{29}Si for the Kr matrix, 240 G, and for the Xe matrix, 190 G, indicates strong interaction of the matrix with the SiH_3 radicals.

I. INTRODUCTION

Energy absorbed from a γ-ray source by a rare-gas matrix at low temperature is efficiently transferred[1] to dissociate certain simple molecules trapped in dilute solution in the matrix. This process provides an effective method for production of trapped atoms and simple molecular free radicals at isolated points in the inert matrix which can then be studied effectively with electron spin resonance (ESR).[2,3] For many substances this method is simpler to apply than the method of producing the free radicals in the gaseous state and then trapping[4] them at low temperatures. From this laboratory we have reported studies of radicals formed

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* This study was supported by the U.S. Air Force Office of Scientific Research, Grant No. AF-AFOSR-66-0493 A and by the Army Research Office (Durham), Grant No. DA-ARO-D 31-124-G731.

[1] W. V. Bouldin, R. A. Patten, and W. Gordy, Phys. Rev. Letters **9**, 98 (1962); W. V. Bouldin and W. Gordy, Phys. Rev. **135**, A806 (1964).

[2] R. L. Morehouse, J. J. Christiansen, and W. Gordy, J. Chem. Phys. **45**, 1747 (1966).

[3] R. L. Morehouse, J. J. Christiansen, and W. Gordy, J. Chem. Phys. **45**, 1751 (1966).

[4] F. J. Adrian, E. L. Cochran, and V. A. Bowers, Advan. Chem. Ser. **36**, 50 (1962).

from hydrides of group-IV and group-V elements trapped in a krypton matrix. In the present work we extend these studies to a xenon matrix. Interesting effects of the matrix material on the ESR spectra and on the formation of radicals are observed. In the companion paper, systematic effects of the matrix on the ESR spectra of the group-V atoms are treated in detail. In this paper the spectra of simple molecular free radicals are described.

II. EXPERIMENTAL METHOD

The instruments and experimental method are described in previous papers of this series.[1–3] The ESR spectra were observed at K-band frequency. The molecules from which the radicals were produced were trapped in the desired proportions (usually 2%) with the matrix elements directly within the microwave cavity which was itself contained in a low-temperature cryostat. The sample thus prepared was maintained at a temperature of 4.2°K while being irradiated directly through the walls of the cryostat and cavity with a 4000-C cobalt-60 γ-ray source. Dosages of the order of 2×10^6 were applied.

III. GROUP-V HYDRIDES

A. Dissociation Products of NH_3

Ammonia appears to be an exception to the simple hydrides which are readily dissociated by energy transferred from the irradiated rare-gas matrix. Although Foner *et al.*[5] detected H atoms and NH_2 radicals by uv irradiation of NH_3 in an argon matrix, it seems probable that the dissociation was produced by direct action of the uv on the NH_3 molecules rather than by energy absorbed by the matrix and transferred to the NH_3. Coope *et al.*[6] and Fischer *et al.*[7] have reported observations of the ESR of NH_2 radicals produced by uv photolysis of HN_3 in the rare-gas matrices at low temperature. Earlier efforts in this laboratory at dissociation of NH_3 by γ-ray dosage of 1×10^6 R on a krypton matrix containing a slight concentration of NH_3 were unsuccessful in that no resulting radicals were detectable.[2] Either the excitation energy migrating in the krypton matrix, which presumably is of the order of the lowest excitation energy of krypton, 10 eV, is insufficient to dissociate the NH_3, or this excitation energy is ineffectively coupled to the trapped NH_3 molecules.

Nevertheless, in the present study we were able to produce detectable free radicals from NH_3 in both krypton and xenon matrices at 4.2°K by subjecting the matrix containing 2% $^{15}NH_3$ to a γ-ray dosage of $(2.5–3.5)\times10^6$ R from a 4000-C cobalt-60 irradiation source. Figure 1 shows the ESR signals of the resulting free radicals. The signals are weaker by an order of magnitude than those obtained by similar dosage of a similar concentration of PH_3 which is dissociated by excitation energy which can migrate in the krypton or xenon matrices. Thus we conclude that the dissociation of the NH_3 is produced mainly by direct hits on the NH_3 by γ-ray quanta or by secondary electrons ejected from nearby atoms of the matrix.

To enhance the detectability of the weak signals of the radicals and to increase the resolvability of the hyperfine pattern, we have used a sample of $^{15}NH_3$ with the ^{15}N isotope highly concentrated. The ^{15}N nucleus has a spin of $I=\frac{1}{2}$ which causes a doublet splitting of all the components, whereas the ^{14}N nucleus has a spin $I=1$ which causes a more closely spaced triplet splitting of all components.

The ESR of the irradiation products (see top curve of Fig. 1) shows that NH_3 dissociates in two different ways in the krypton matrix to produce three kinds of radicals. One of the transformations is

$$NH_3 \rightarrow NH_2 + H,$$

and the other is

$$NH_3 \rightarrow N + 3H \quad \text{or} \quad N + H + H_2.$$

The two sharp outer components, which are spaced 508 G apart, arise from the H atoms; the two sharp central components, spaced 6.2 G apart, arise from the ^{15}N atoms. The $^{15}NH_2$ spectrum is partly obscured by the ^{15}N atomic doublet, but the two broad lines to the

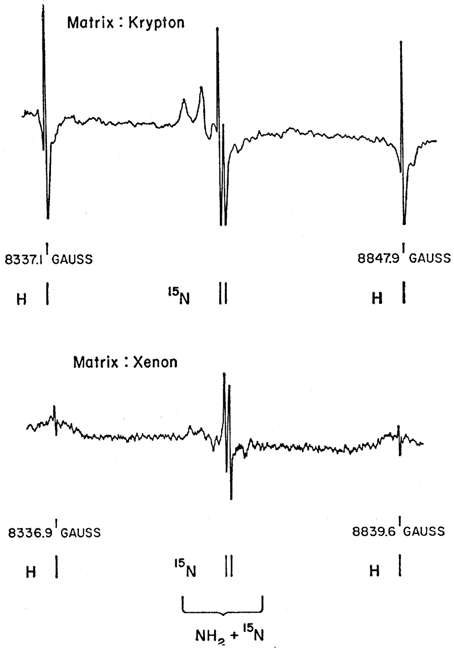

FIG. 1. ESR spectra of free radicals formed by γ-irradiation of 2% $^{15}NH_3$ in the Kr and Xe matrices at 4.2°K.

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[5] S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, Phys. Rev. Letters **1**, 91 (1958).

[6] J. A. R. Coope, J. B. Farmer, C. L. Gardner, and C. A. McDowell, J. Chem. Phys. **42**, 2628 (1965).

[7] P. H. H. Fischer, S. W. Charles, and C. A. McDowell, J. Chem. Phys. **46**, 2162 (1967).

left of the ^{15}N doublet and a partially resolved component to the right of this doublet are a part of the $^{15}NH_2$ spectrum. Theoretically, the hyperfine pattern of the $^{15}NH_2$ spectrum should consist of six components resulting from a triplet splitting by two equivalent hydrogen nuclei with $I=\frac{1}{2}$ and a further doubling of each of these components by the ^{15}N nucleus. Although there is uncertainty caused by the superposition of the atomic doublet, the NH_2 spectrum appears to be a quartet of intensity ratios 1:2:2:1 and component spacing of 24 G with $g_{av}=2.005$ at the center. Such a pattern would be expected if the ^{15}N splitting were near enough to the hydrogen splitting that the structure could be considered as arising from three equivalent nuclei with spins of $\frac{1}{2}$. However, this would require an ^{15}N coupling of the order of 20–24 G, whereas that expected from the earlier measurements on $^{14}NH_2$ is only 14.4 G. Because of this inconsistency and the incomplete resolution, we shall not attempt an analysis of this spectrum.

In the xenon matrix, the NH_3 breaks up predominantly in one way, producing N and H atoms. The spectra of the atoms are treated in the accompanying paper. It is interesting that the tendency for complete dissociation of NH_3 into atoms increases with the size of the matrix atoms, from argon to xenon, whereas PH_3 and AsH_3 described below show the opposite trend.

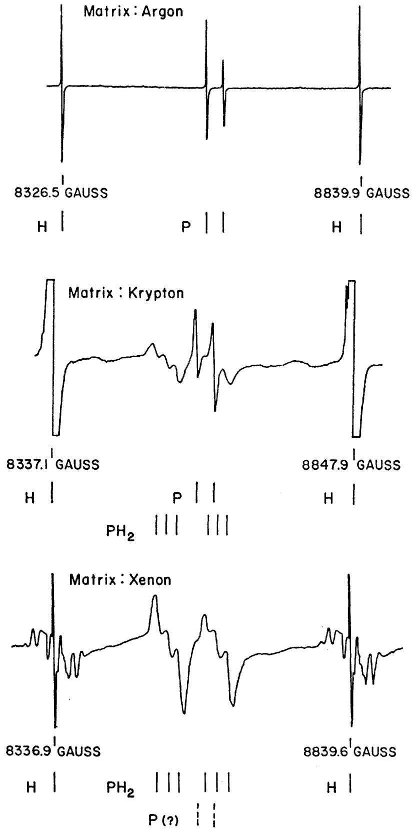

FIG. 2. ESR spectra of free radicals formed by γ-irradiation of rare-gas matrices containing 2% PH_3 at 4.2°K.

Morehouse *et al.*[2] have used the $^{14}NH_2$ coupling constants in the argon matrix to estimate the 2*s* bond orbital hybridization of the N and to estimate the bond angle of the radical. The good agreement of the calculated bond angle (103°) with the measured value (103°25′) given for the gaseous NH_2 radical by Dressler and Ramsey[8] supports the validity of their method of calculation which we shall apply to the PH_2 in the xenon matrix.

B. Dissociation Products of PH_3

Figure 2 demonstrates the different types of ESR spectra obtained by γ irradiation of a 2% molar concentration of PH_3 in the different rare-gas matrices—argon, krypton, and xenon at 4.2°K. In the argon matrix, spectra of only P and H atoms are obtained. The two outer lines are due to H atoms; the central doublet, to ^{31}P atoms. The unequal intensity of the two components of this doublet is due to effects of radiation saturation. Qualitatively, these results are in agreement with those of Adrian *et al.*,[4] who irradiated a sample of PH_3 in argon using uv from a mercury arc and obtained the spectra of P and H atoms only.

For purposes of comparison, we repeated the earlier observations[2] on γ-irradiated PH_3 in the krypton matrix. The results are in good agreement with the previous observations. They show that the PH_3 in the krypton matrix breaks up in two different ways:

$$PH_3 \rightarrow P+H_2+H \quad \text{or} \quad P+3H \qquad (1)$$

and

$$PH_3 \rightarrow PH_2+H \qquad (2)$$

to form PH_2 radicals as well as P and H atoms, with the signals from P atoms and PH_3 radicals of comparable strength. The ESR of the P atoms is treated in the following paper; that of PH_2 was analyzed in the earlier work.[2]

The bottom curve of Fig. 2 shows the ESR spectra obtained from PH_3 γ-irradiated in the xenon matrix. Here the predominant signals are from H atoms and PH_2 radicals, with only very weak signals which are attributed to P atoms. Evidently Eq. (2) represents the predominant reaction in the xenon matrix, whereas Eq. (1) is the only reaction observed in the argon matrix. These matrix effects on the manner of dissociation of the PH_3 are not fully understood, but they may result partly from the decrease of energy in the migrating exciton which causes the dissociation and partly from the increasing size of the vacancy site in which the PH_2 is trapped.

The observed *g* factors and isotropic nuclear couplings obtained for the PH_2 radicals are listed in Table I. These coupling constants are nearly the same in the krypton and xenon matrices.

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[8] K. Dressler and D. Ramsey, Phil. Trans. Roy. Soc. London **A251**, 533 (1959).

TABLE I. Hyperfine coupling constants and g factors for PH_2 and AsH_2.

Radical	Matrix	g_{av}	Isotropic nuclear coupling (in G)	
			A(H)	A(^{31}P)
PH_2	Kr	2.0087[a]	18[a]	80[a]
	Xe	2.0050 ±0.0010	17.0 ±1.0	81.79 ±0.50
AsH_2	Xe	2.034 ±0.020		

[a] Data of Ref. 2.

From the H and P nuclear coupling constants, Morehouse *et al.*[2] showed that the hybridization of the P bonding orbitals is 0.19 to 0.27. From the lower value, the bond angle was estimated to be 104°. The corresponding values for PH_2 in the xenon matrix, derived in a similar way, are $s_b = 0.206$ and $<HPH = 105°$. However, this calculation of the bond angle from the s hybridization may not be reliable because of possible contributions from the d orbital. It is seen that these values, unlike those for SiH_3 described below, do not differ significantly in the two matrices.

The triplet components caused by the couplings of the two equivalent protons of PH_2 have equal intensities in both krypton and xenon matrices, whereas a Gaussian distribution of the spin populations would indicate intensities in the ratio of 1:2:1. This equalization of intensity, which appears not to arise from effects of radiation saturation, was explained in the earlier paper[2] in terms of statistical weights of the allowed nuclear spin states of the ground rotational level, which is the one predominantly populated at 4.2°K.

C. AsH_2 Radicals

When we γ-irradiated a 2% solution of AsH_2 in a xenon matrix we obtained a relatively strong signal which can be attributed to AsH_2 radicals and only relatively weak signals attributable to As atoms. The signal of the AsH_2 radicals is indicated on the chart in Fig. 3. Unfortunately, the expected hyperfine structure could not be resolved. Because ^{75}As has a spin I of $\frac{3}{2}$, it will cause an anisotropic quartet splitting, each component of which will have a superimposed triplet splitting caused by the two equivalent hydrogens. Hence, 12 closely spaced components are to be expected. It is not surprising that the anisotropy in g and in the ^{75}As coupling would prevent resolution of this structure. The over-all width of the resonance is compatible with the expected spread of the unresolved hyperfine structure. The averaged g value (see Table I) is larger than that of PH_2. This difference in g_{av} is comparable with that for SiH_3 and GeH_3.

It is interesting that the hyperfine structure of the ^{75}As atoms is also unresolvable in the xenon matrix, although the over-all spread of the spectrum is the same as that for the resolved hyperfine structure of ^{75}As in the krypton matrix.

Only arsenic and hydrogen atoms were detected in the earlier work on γ-irradiated AsH_3 in a krypton matrix.[2] Subsequently, we received a private communication from Duxbury indicating that he and his co-workers[9] had produced and detected with optical-spectroscopy gaseous AsH_2 radicals by irradiation of AsH_3 and suggesting that our failure to produce the AsH_3 radicals must have been caused by the krypton matrix.

After we had observed the AsH_2 resonance in a xenon matrix we were able to identify a much weaker signal from AsH_2 radicals in a γ-irradiated 2% solution of AsH_3 in a krypton matrix (see Fig. 3). Nevertheless, the signals from ^{75}As atoms are much stronger in a krypton matrix. Signals were observed from H and As atoms only in a 2% solution of AsH_3 irradiated in an argon matrix (see Fig. 3).

From these results it can be concluded that the dissociation of AsH_3 in the three rare-gas matrices is similar to that of PH_3. Only atoms are formed in the argon matrix, whereas the dihydride radicals form in

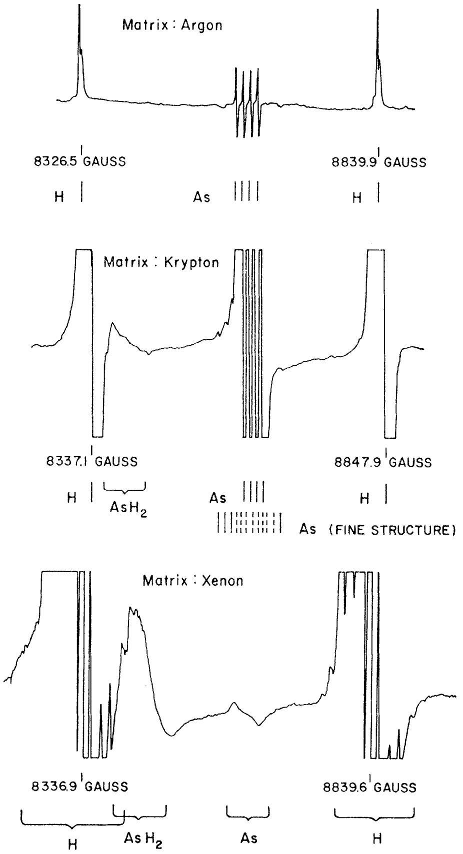

FIG. 3. ESR spectra of free radicals formed by γ-irradiation of rare-gas matrices containing 2% AsH_3 at 4.2°K.

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[9] R. N. Dixon, G. Duxbury, and H. M. Lamberton, Chem. Commun. **14**, 460 (1966).

Table II. Hyperfine coupling constants and g factors for CH_3, SiH_3, GeH_3, and SnH_3.

Radical	Matrix	g factor	Isotropic nuclear coupling (in G)	
			A(H)	
CH_3	Ar[a]	$g_{av}=2.00203\pm0.00008$	23.10 ± 0.07	
	Xe	$g_{av}=2.0020\pm0.0001$	22.97 ± 0.05	
			A(H)	$A(^{29}Si)$
SiH_3	Kr	$g_{\parallel}=2.003$[b] $g_{\perp}=2.007$	8.1 ± 0.5[b]	266[b]
	Xe	$g_{av}=2.003\pm0.001$		190
			A(H)	$A(^{73}Ge)$
GeH_3	Kr	$g_{\parallel}=2.003$[b] $g_{\perp}=2.017$	15 ± 2[b]	75 ± 3
	Xe	$g_{av}=2.0073\pm0.0010$		75 ± 3
			A(H)	$A(^{117,119}Sn)$
SnH_3	Kr	$g_{\parallel}=2.003$[b] $g_{\perp}=2.025$	26 ± 4[b]	
		$g_{av}=2.017\pm0.040$		380

[a] From C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. **112**, 1169 (1958). [b] From Ref. 3.

increasing numbers according to the increase in the size of substitutional sites of the matrix.

D. Stibine—SbH_3

Numerous experiments similar to those previously described were carried out for stibine, SbH_3, but no spectra assignable to any Sb or Sb–H_n species were detected. Evidence was obtained, however, that stibine is dissociated in xenon at 4.2°K.

Antimony has two stable isotopes with nuclear spins: 121 (57%) with $I=\frac{5}{2}$ and 123 (43%) with $I=\frac{7}{2}$. Thus, if atoms were formed during the irradiation, one would expect up to $6+8=14$ lines, probably with small hyperfine splittings. On the other hand, if SbH_2 were formed, it is harder to say what would be expected. Possibly this heavier radical would have a substantial g shift; if the hyperfine splittings are not resolved, a very broad line might result. During investigation of these possibilities, samples containing 2% stibine in krypton and xenon were γ-irradiated and studied at 4.2°K. Low modulations were used in the search for the Sb atom whereas high modulations were employed in the search for the possibly broad SbH_2 resonances. A wide range of microwave power was used for elimination of the possibility of saturation, and a region of magnetic field 2500 G on either side of the free-spin field was scanned. No resonances were found for stibine in the krypton matrix, but strong signals from H atoms with no other signals were observed for stibine in the xenon matrix. Work subsequent to the detection of the hydrogen lines seems to prove conclusively that they come from dissociated stibine. For example, a sample of the xenon used in these experiments was irradiated and studied in the spectrometer, but no hydrogen lines were found. Then another run was made on this sample of xenon with 2% stibine added. After the mixture had been frozen into the sample cell at 77°K, the cell was pumped for several minutes. Thus, any hydrogen that might have been generated by decomposition of the stibine during mixing and freezing was removed since it would not have frozen into the sample. (Even if it had frozen, at 77°K it would have quickly diffused through the solid and been removed.) Then the sample was irradiated and studied, and hydrogen lines were observed as before. These facts, plus the fact that no hydrogen lines were observed in the stibine-krypton system even when no such precautions were taken to exclude hydrogen, indicate that stibine does dissociate in the larger xenon matrix, and that the resulting fragments are trapped in the matrix, but only hydrogen lines are visible to the ESR spectrometer. This conclusion agrees with the recent evidence from optical spectra that gaseous SbH and SbH_2 can be formed.[10] Presumably, if the previously studied group-V radicals are any indication, the species most likely produced and trapped in xenon is SbH_2. It is possible that, for this radical, the spin-orbit coupling is so strong that the orbital angular momentum is not strongly quenched. If so, then the interaction between the matrix field and the orbital angular momentum could produce a magnetic anisotropy large enough to broaden the line beyond detection. It can be noted in this connection that the trend within the radicals studied here is consistent with such an explanation. The group-IV radical from the same row of the periodic chart as Sb, SnH_3, will be shown in a later section to be several hundred gauss wide. Furthermore, comparison of spectra presented here for PH_2 and AsH_2 as opposed to SiH_3 and GeH_3 shows that the spectra of group-V radicals tend to be broader than those of the group-IV radicals. Thus it is conceivable that the SbH_2 spectra could be broadened to the point where they would not be visible.

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[10] N. Basco and K. K. Yee, Spectroscopy Letters **1**, 13 (1968).

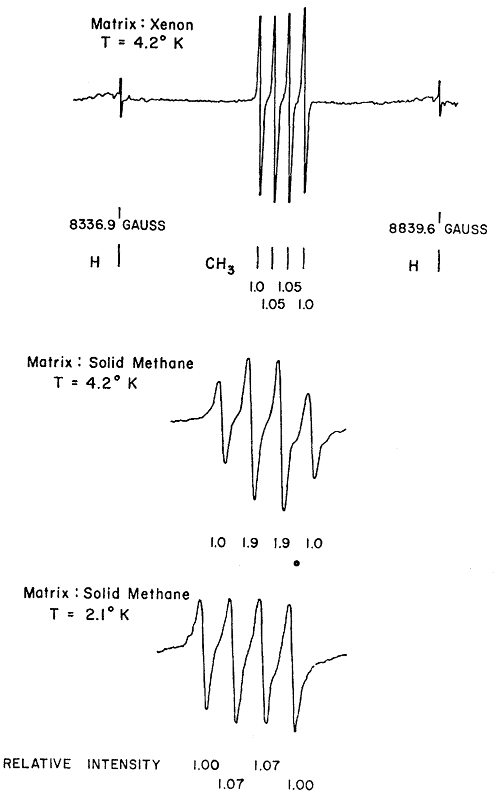

FIG. 4. Demonstration of the effects of temperature on the relative intensities of the hyperfine components in the ESR of trapped CH_3 radicals at low temperatures.

IV. GROUP-IV HYDRIDES

A. Methyl Radical—Restricted Rotation

The CH_3 radical has been most thoroughly investigated in earlier studies although it has not, so far as we know, been observed in a xenon matrix. We find the ESR spectral constants to be very nearly the same in xenon as in the argon matrix. See Table II for comparisons. In the present studies, we have found additional evidence for restricted rotation of the radicals from observation of the temperature effects in the relative intensities of the hyperfine component of the ESR.

Figure 4 shows the ESR spectra obtained by γ-irradiation of a xenon matrix containing 2% methane. The central quartet arises from methyl radicals; the outer lines arise from H atoms. As was earlier found in the krypton matrix,[3] the components of the quartet pattern of the CH_3 radicals in the xenon matrix have nearly equal intensities at 4.2°K, rather than the 1:3:3:1 intensity ratio expected from the Gaussian distribution of the three-spin orientation. In the earlier work[3] this was attributed to the symmetry of the over-all wave function in the lowest rotational state which requires that the acceptable nuclear spin function of the three identical hydrogens be a symmetric function. When $K=0$, the symmetric spin functions are represented by the contributions:

$$\psi_1=(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}), \tag{3}$$

$$\psi_2=(\tfrac{1}{2},\tfrac{1}{2},-\tfrac{1}{2})+(\tfrac{1}{2},-\tfrac{1}{2},\tfrac{1}{2})+(-\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}), \tag{4}$$

$$\psi_3=(\tfrac{1}{2},-\tfrac{1}{2},-\tfrac{1}{2})+(-\tfrac{1}{2},\tfrac{1}{2},-\tfrac{1}{2})+(-\tfrac{1}{2},-\tfrac{1}{2},\tfrac{1}{2}), \tag{5}$$

$$\psi_4=(-\tfrac{1}{2},-\tfrac{1}{2},-\tfrac{1}{2}), \tag{6}$$

where $M_I=\frac{1}{2}$ and $M_I=-\frac{1}{2}$ correspond to the two possible orientations of each proton spin in the external field. Each of the allowed functions, $\psi_1\cdots\psi_4$, corresponds to a separate hyperfine component, and hence all four components have equal weight, and the line intensities have the ratio 1:1:1:1 for this particular rotational state.

As the matrix is warmed above 4.2°K, higher rotational states are excited, and the intensities of the four components then approach the relative values 1:3:3:1 corresponding to the normal distribution of the spin alignments. In the krypton matrix[3] the components of CH_3 achieve the 1:3:3:1 intensity at 18°K, or higher.

Even at 4.2°K the ESR hyperfine components of CH_3 in the CH_4 matrix do not achieve equality although they do not have the normal ratio. However, we have shown that equality in intensity of the four components is approximately achieved when the temperature of the sample is reduced to 2.1°K. This effect is demonstrated in Fig. 4. In obtaining these spectra we took care that the power was sufficiently low that power saturation could not equalize the intensities. A very low Q cavity was employed, and the power level was held below 1 μW for the observations of Fig. 4; the power was held effectively lower for the bottom curve than for the middle one of the figure.

From the relative intensity of the components one can learn something about the relative energies of the radicals in the matrix. The relative populations of the various rotational levels are related by the Boltzmann expression

$$n_{N,K}/n_0=\exp(-E_{NK}/kT), \tag{7}$$

where $n_{N,K}$ is the population of the higher rotational state and n_0 that of the lowest. Because the orbital moment of the unpaired electron is thoroughly quenched by the strong chemical-bond forces (the value of g is almost exactly equal to that of the free-electron spin) we shall neglect the coupling of the spin with the molecular rotation for the low rotational states considered. Following Herzberg,[11] we use N as the quantum number for the rotational energy and reserve J for the sum $(N+S)$. The quantum number K has the usual significance in measurement of the component of the rotational momentum along the symmetry axis. If there were free, unrestricted rotation of the radicals in the solid, the moments of inertia of the radical measured by

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[11] G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1966), p. 87ff.

Herzberg and Shoosmith[12] from the optical spectra of the gas could be used for calculation of $E_{N,K}$. The radical is an oblate symmetric top for which

$$E_{NK}=BN(N+1)-(B-C)K^2. \qquad (8)$$

From the structure of the radical measured by Herzberg, $B=9.57$ cm^{-1} and $C=4.80$ cm^{-1}. The rotational energies of the first few levels and the fractional populations at $T=4.2$°K and $T=2.1$°K are calculated from these constants and are given in Table III. The population values in this table account for the essentially equal intensity of the four components for the radicals in a krypton or xenon matrix at 4.2°K. This interpretation of the equality requires that the effective values of B and C be roughtly the same in these matrices as in the free gas. Evidently there is little restriction of the rotation in these matrices.

When $K\neq 0$ and not a multiple of 3, the acceptable wave functions are linear combinations[13] of the spin functions for which one is up ($\frac{1}{2}$) and the other two are down ($-\frac{1}{2}$) or vice versa. The symmetric combinations $\uparrow\uparrow\uparrow$ and $\downarrow\downarrow\downarrow$ are not allowed. Therefore, the population of the $N=1$, $K=1$ state contributes only to the intensity of the two inside components of the quartet. For an equal population of the two lowest rotational levels, $N=0$, $K=0$ and $N=1$, $K=1$, with no other levels populated, the intensity ratio should be 1:2:2:1. Accounting for the observed intensity ratio 1:1.9:1.9:1 at 4.2°K in the CH_4 matrix would seem, therefore, to require a considerable lowering of the rotational levels through interaction of the CH_3 radicals with the CH_4 molecules of the matrix. The specific form of the restriction is not known, but it is evident that the effective values of B and C are both lowered. This is equivalent to saying that the effective moments of inertia I_b and I_c are increased through the restrictive interactions. This is not too surprising. What is more surprising is that the components could be reduced to nearly equal intensity by nothing more than a reduction of temperature from 4.2–2.1°K. The required change in population could not be achieved by this reduction in temperature alone without a marked increase in the effective B. Thus the restrictive interactions of the CH_4 matrix on the rotation must be significantly less at 2.1°K than at 4.2°K. From the limited information, we cannot estimate the effective values of B and C, but the observed intensity indicates that the $N=1$, $K=1$ level would be 5 cm^{-1}, or more, above the $N=0$ level at 2.1°K.

TABLE III. Calculated rotational energies and level populations for completely free rotation of CH_3 radicals at 4.2°K.

N	K	$E_{N,K}$ (cm^{-1})	$(n_{N,K}/n_0)$ ($T=4.2$°K)
0	0	0	1
1	1	14.4	0.0072
1	0	19.2	0.0011
2	2	38.3	0.0000

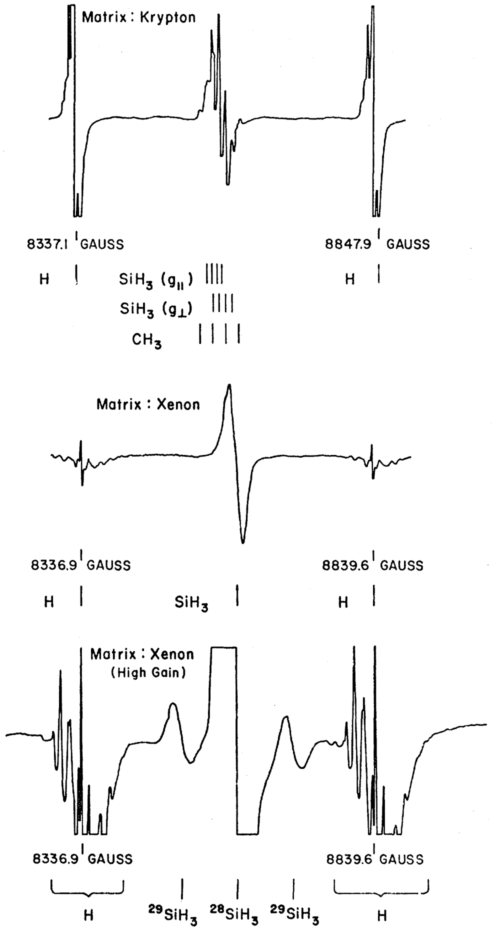

FIG. 5. ESR spectra of free radicals formed by γ-irradiation of rare-gas matrices containing 2% SiH_4 at 4.2°K.

There is another factor which could equalize the observed intensities even when there is significant population in excited rotational levels. The magnetic moment generated by the rotation might be sufficient to split the spin doublet so that the ESR would occur at such a different field value that the resonance would not be detectable in the excited rotational states. Only radicals in the ground rotational state having the equal intensity ratio would be detectable. Although this explanation of the equalization would still depend upon the assumption of discrete rotational states in the matrix, it would not necessarily require that the ground rotational state have the predominant population. This explanation would not account for the increased intensity ratios observed in the CH_3 at 4.2°K.

B. SiH_3 Radical

The most pronounced difference between effects of the xenon matrix and those of the krypton matrix was

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[12] G. Herzberg and J. Shoosmith, Can. J. Phys. **34**, 523 (1956).

[13] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Co., New York, 1955), p. 71.

TABLE IV. Structures of XH_3 radicals in the xenon matrix.

Radical	s character of bond orbitals	Bond angle α	Pyramidal angle[a] β
CH_3	0.333	120°	90° (planar)
SiH_3	0.285	113.5°	74°
GeH_3	0.295	115°	76.5°
SnH_3	0.31	117°	83°

[a] Angle between perpendicular height and an edge of pyramid.

observed for the SiH_3 radical. The xenon matrix smeared out the proton hyperfine structure of the ESR of the radical, which is well resolved in the krypton matrix (see Fig. 5). The spread of the unresolved resonance, however, is about that which would be caused by an unresolved hyperfine structure, the same as that in the krypton. Another effect of the xenon matrix is the averaging out of the anisotropy in g by random tumbling motions or rotations. The most notable difference is in the ^{29}Si splitting, which is 266 G in the krypton matrix and only 190 G in the xenon matrix (see Table II).

As was previously shown, the large ^{29}Si coupling indicates that the SiH_3 radical is pyramidal in structure rather than planar like CH_3. The coupling observed here will be used for calculation of the bond orbital hybridization and the HSiH angle for the radicals in the xenon matrix. If small but possible effects of other s orbitals are disregarded, the spin density of the $3s$ orbital on the Si can be calculated from the isotropic ^{29}Si coupling as

$$\rho_{3s} = a(^{29}\mathrm{Si})/A_{3s} = 0.158, \tag{9}$$

where $A_{3s} = 1206\mathrm{G}$ is the coupling of the $3s$ orbital[14] for $\rho_{3s} = 1$. The resulting value 0.158 is equal to the amount of $3s$ hybridization of the unpaired electron orbital s_u, if small corrections for spin-polarization effects of the bond are made. In the krypton matrix these effects can be shown from the observed proton coupling to cause at most a reduction of 0.014 in the estimated s_u. Since the proton splitting is not resolvable in the xenon matrix, we shall assume the same correction as that for the krypton matrix, $s_u = \rho_{3s} - 0.014 = 0.144$. Proper normalization of the $3s$ requires the hybridization of each of the bond orbitals, $s_b = 0.285$. With this value the bond angle θ can be calculated by use of the equation

$$\cos(\pi - \theta) = s_b/(1 - s_b). \tag{10}$$

These results are summarized in Table IV.

The pronounced difference of effects of the two matrices, krypton and xenon, on SiH_3 radicals is surprising, especially upon consideration of the much smaller difference of effects on GeH_3 radicals, described in the next section.

C. GeH_3 Radical

The proton hyperfine structure of the ESR of the GeH_3 radical, like that for SiH_3, is resolved in the krypton matrix but smeared out in the xenon matrix. Likewise, the anisotropy in g, which is detected in the krypton matrix, is not evident in the xenon matrix. The ESR signals obtained from a 2% sample of GeH_4 in xenon, γ-irradiated and observed at 4.2°K (see Fig. 6) is rather broad, but symmetrical. The lack of anisotropy in g can be explained on the basis of random tumbling or rotation which averages out this anisotropy. The g_{av} is that expected from an average of the $g_{\parallel}$ and $g_{\perp}$ values earlier obtained for GeH_3 in a krypton matrix.

The ^{73}Ge isotope with nuclear spin $I = \frac{9}{2}$ has a natural

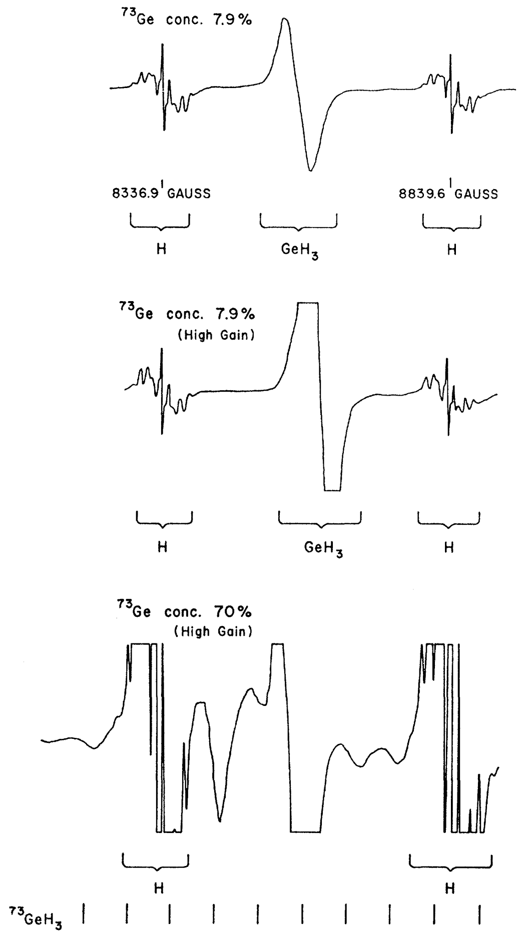

FIG. 6. ESR spectra of free radicals formed by γ-irradiation of rare-gas matrices containing 2% GeH_4 at 4.2°K.

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[14] J. R. Morton, Chem. Rev. **64**, 453 (1964).

abundance of 7.9%. Because its hyperfine structure is split into 10 components, it could not be detected without concentration of the isotopic sample. Earlier,[15] with a GeH_4 sample having a 70% concentration of the ^{73}Ge, we were able to measure the isotropic hyperfine coupling constant for GeH_3 radicals in the krypton matrix at 4.2°K. From this measurement we calculated the orbital hybridization and bond angles, using methods similar to those described for $^{29}SiH_3$. We have now made measurements on similarly concentrated samples in the xenon matrix. The observed ESR curve is shown in Fig. 6. The theoretical coupling constant for a 4s electron in the Ge atoms is $A_{4s}(^{73}\mathrm{Ge})=530$ G. The observed constant of ^{73}Ge in the $^{73}GeH_3$ radicals in the xenon matrix therefore indicates a 4s spin density of

$$\rho_{4s}=a(^{73}\mathrm{Ge})/A_{4s}(^{73}\mathrm{Ge})=0.14. \qquad (11)$$

To estimate the 4s hybridization in the unpaired electron orbital we subtract from this the amount of spin polarization of the 4s component in the three bonding orbitals estimated from the H coupling measured in the krypton. This is approximately 0.026. Thus the s character of the orbital of the unpaired electrons is $s_u=0.114$, and the 4s character of each bonding orbital is $s_u=0.295$. From this result the bond angle is found from Eq. (10) to be 115°. Comparison of the various constants for the two matrices is given in Table IV.

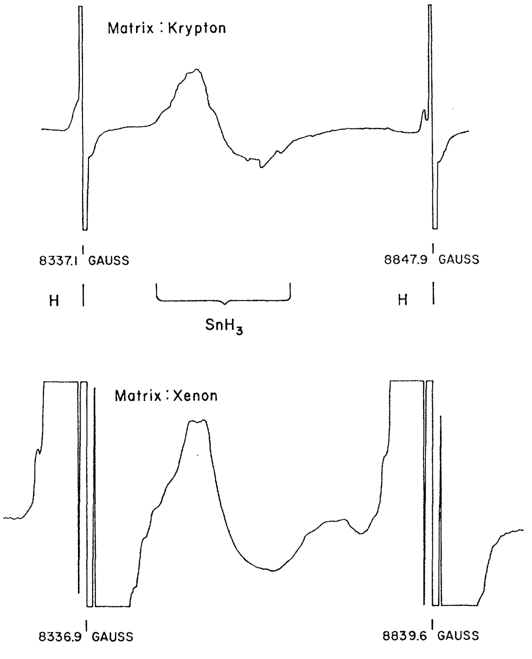

FIG. 7. ESR spectra of free radicals formed by γ-irradiation of rare-gas matrices containing 2% SnH_4 at 4.2°K.

D. SnH_3 Radical

The ESR of the SnH_3 radical in the xenon matrix is very similar to that in the krypton matrix; the proton hyperfine structure and the g factor are essentially the same in the two matrices at 4.2°K. Comparisons of the values are provided in Table II.

No hyperfine structure caused by the Sn nuclear moment was observed in the previous work. In the present work, we believe that we have detected a line which represents the combined absorption of the upper field hyperfine components of the two isotopes ^{117}Sn and ^{119}Sn, which have equivalent nuclear spins $I=\frac{1}{2}$ and nearly equal magnetic moments, $-0.99982\mu_N$ and $-1.04600\mu_N$, respectively. Because of the large anisotropy in their nuclear couplings and in g, the hyperfine structure of these two nuclei could not be separated. The absorption ascribed to the ^{117}Sn and ^{119}Sn isotopic species is indicated in Fig. 7. It has the strength, relative to that of the signal from the species with $I=0$, which would be expected for their relative abundance. The $I=0$ isotopes have a combined abundance of 83.5%; the combined abundance of ^{117}Sn and ^{119}Sn is 16.2%. Therefore, the observed hyperfine line should be 19.4% as strong as the principal SnH_3 signal. This is in agreement with the observations. The shape of the hyperfine line is, however, somewhat different from that of the principal line. All evidence of the proton splitting is smeared out by the large anisotropy in the Sn coupling because of the large p-orbital character of the unpaired electron orbital of the Sn. This is also true for the Si and Ge hyperfine components discussed above.

Unfortunately, the $^{117,119}Sn$ doublet splitting is such that the lower-field component—if our assignment is correct—would be obscured by the strong absorption of the lower-field hydrogen components. This makes impossible the identification of the absorption of the lower-field components and makes our assignment of the observed line somewhat uncertain until observation on concentrated isotopic species can be made. Nevertheless, we think that the expected relative intensity, the reasonable shape, and position of the line make the assignment highly probable. From the separation of the component from the principal signal we have obtained the tentative isotropic coupling constant of the $^{117,119}Sn$ isotope listed in Table II.

To use the observed Sn nuclear coupling for estimation of the 5s electron and the 5s hybridization in the orbital of the unpaired electron, we need the value of the coupling of the 5s electron in the atom. Since we were unable to find the value in the literature, we shall

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[15] G. S. Jackel, J. J. Christiansen, and W. Gordy, J. Chem. Phys. **47**, 4274 (1967).

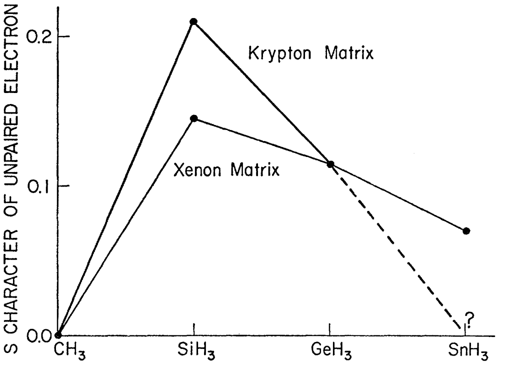

FIG. 8. Plots of the s character in the orbital of the unpaired electron in MH$_3$ radicals, evaluated from the hyperfine structure of their ESR spectra.

estimate it from the measured nuclear coupling[16] of the doubly ionized ^{115}In, 21900 Mc/sec or 7820 G. Indium is next to tin in the atomic table. Because of their close similarity we can assume in an approximate treatment that they have the same effective quantum number, n_0, relativistic corrections, etc., and can use the proportionality

$$\frac{A_{5s}}{A_{5s}'}=\frac{g_I Z_i Z_0^2}{g_I' Z_i' (Z_0')^2}, \qquad (12)$$

in which the primed values refer to $^{115}\mathrm{In}^{++}$ and the unprimed values refer to ^{117,119}Sn. The averaged nuclear g factor for ^{117}Sn and ^{119}Sn is $(g_I)_{\mathrm{av}}=2.046$. That for ^{115}In is $g_I'=1.220$. The effective nuclear charge in near the nucleus can be taken as the atomic number times e:

$$Z_i=50 \quad \text{and} \quad Z_s'=49.$$

For the estimation of the value of the effective charge in the outer region of the orbital, complete screening by the subvalence electron shells can be assumed, and nearly complete screening by the other electrons of the valence s, p shells. The two other electrons are missing in In^{++}, and thus $Z_0'=3$. From the effective screening of the valence shell electrons in Ge we estimate 0.16 as the screening by each of the three other valence shell electrons in Sn. Therefore, $Z_0=1+3(0.16)=1.48$. With these approximations, the averaged coupling of the 4s electron of ^{117,119}Sn is estimated to be

$$A_{5s}(^{117,119}\mathrm{Sn})\approx 0.416 A_{5s}(^{115}\mathrm{In}^{++})=3260\ \mathrm{G}. \qquad (13)$$

With this value and the observed coupling of 380 G we obtain

$$\rho_{5s}(\mathrm{Sn})=a_{5s}/A_{5s}=0.116. \qquad (14)$$

This spin density has a contribution from the bonding orbitals which can be estimated from the proton coupling to be $0.93(26)/502=0.048$, where the factor of 0.93 arises from the fact that the three bonding orbitals contain a total of only 93% of the 5s electronic character. The 5s hybridization of the orbital of the unpaired electron is thus estimated to be

$$s_u=\rho_{5s}-0.048=0.068. \qquad (15)$$

The 5s character of each of the three bonding orbitals is then $0.93/3=0.31$. From Eq. (10), the bond angle corresponding to this degree of hybridization is 117°.

E. Comparison of Results

Figure 8 provides a graphic comparison of the s hybridization of radicals of group-IV hydrides in xenon and krypton matrices. The CH$_3$ radical is known to have a planar structure with the unpaired electron in a pure p orbital with its symmetry axis perpendicular to the plane.[17] Although we have not measured the ^{13}C coupling in Kr and Xe matrices, the essentially equivalent proton hyperfine splitting suggests the same planar structure for the radical in the different matrices. Our results for the xenon matrix indicate some s character in the orbital of the unpaired electron in each of the three other MH$_3$ radicals. This hybridization is greatest for SiH$_3$ and decreases with the increasing size of the M atom. In contrast to the results in the xenon matrix, no evidence was found for Sn nuclear splitting in the Kr matrix. Possibly the splitting is too small to allow recognizable separation of the components from the signal of the more abundant isotopic species, $I=0$. An extension of the plot in Fig. 8 indicates that the unpaired electron is in an almost pure p orbital for SnH$_3$ in the krypton matrix. This could explain the absence of hyperfine splitting if the projection is valid.

A plausible explanation, advanced earlier, for the planar structure peculiar to CH$_3$ among the group-IV elements is the relative difference in electronegativities of the atoms. The electronegativity of C is greater than that for H, whereas that for Si, Ge, and Sn is less than that for H. Consequently, C will have a negative formal charge, whereas Si, Ge, and Sn will have positive formal charges as a result of ionic character in their bonds in the MH$_3$ radical. With a negative formal charge on the M atom, a greater electronic charge will be in the lower-energy s orbital when the unpaired electron is in a pure p orbital. On the other hand, a greater electronic charge will be in the s orbital with s hybridization of the unpaired electron orbital when the bond polarization puts a positive charge on the central atom.

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[16] H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958), translated from the German by E. E. Schneider, p. 136.

[17] Reference 11, p. 347.