Matrix isolation spectroscopy in methane. Isotropic ESR spectrum of HC1 7O

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The isotropic electron spin resonance (ESR) spectrum of HC^{17}O has been observed in methane at 20 K (prepared by photolysis of HI in CH$_4$ containing 1% of ^{17}O enriched CO), and the isotropic oxygen hyperfine splitting determined [a_0(HCO) $= -15.1$ G]. Isotropic spectra of HO$_2$ (prepared similarly with O$_2$ replacing CO) and NO$_2$ in methane were also observed. Superhyperfine interactions in the ESR spectrum of H atoms in CH$_4$ indicate H is trapped in the octahedral interstitial site of the matrix. "Forbidden" proton spin-flip transitions in the ESR spectrum of CH$_3$ in methane indicate it is trapped at a substitutional site in the matrix.

I. INTRODUCTION

Matrix isolation spectroscopy is an invaluable method for investigating the structure and photochemistry of reactive intermediates such as free radicals, triplets, etc. One very frequent complication in the electron spin resonance (ESR) spectroscopy of matrix isolated polyatomic free radicals is that one observes a so-called powder ESR spectrum resulting from the superposition of orientation-dependent spectra from an ensemble of randomly oriented radicals.[1] Although powder ESR spectra usually can be analyzed to obtain the magnetic constants of the radical, there are cases where it is either helpful or essential to have the isotropic spectrum, i.e., the spectrum of the radical rotating fast enough to average out the anisotropic part of its magnetic Hamiltonian.

Work by Bhattachayra, Wang, and Willard has indicated that the formyl radical (HCO), and perhaps also the perhydroxyl radical (HO$_2$), exhibit isotropic ESR spectra in methane at temperatures only slightly above 4 K,[2] which indicates methane could be a useful matrix for certain ESR investigations if superhyperfine interactions with the methane protons did not produce excessive line broadening. We have confirmed their results for HCO and HO$_2$, which radicals, along with NO$_2$, have well resolved isotropic ESR spectra in methane at some temperatures in the 10–20 K range, and have used the exceptionally strong HCO spectrum to determine its isotropic ^{17}O hyperfine splitting.

Also interesting are the spectra of the H atom and the CH$_3$ radical in this matrix, where the superhyperfine interactions of the H atom with the CH$_4$ protons indicate it is located in an interstitial site, while the CH$_3$ spectrum contains "forbidden" spin-flip transitions of protons on adjacent CH$_4$ molecules which indicate it is in a substitutional site.

II. EXPERIMENTAL

The matrix depositions used the simple apparatus shown in Fig. 1. After filling the sample bulb with the desired gas mixture, the apparatus was removed from the vacuum line, and the matrix formed by rapid condensation of the gaseous mixture into a 4 mm o.d. fused silica ESR tube cooled to 10 K in an Air Products Helitran helium flow-through cryostat equipped with a temperature controller. The condensing gas mixture passed through a narrow (1 mm i.d.) tube located inside the ESR tube, which minimized deposition of the sample in regions of the ESR tube outside the ESR cavity.

The samples were optically irradiated *in situ* through the slotted port in the back of the Varian rectangular ESR cavity, and the ESR spectra were taken on a home-built *X*-band ESR spectrometer.

The CO(g) sample enriched to 38% in C^{17}O was obtained from Isotec, Inc. In use, a small amount of this isotopically enriched CO corresponding to 1% of the sample was admitted into the sample bulb through a 1 cm^3 calibrated volume attached to this bulb via a stopcock (not shown in Fig. 1).

III. RESULTS AND DISCUSSION

A. Isotropic ESR spectra

The isotropic ESR spectra of HCO/HC^{17}O, HO$_2$, and NO$_2$ in methane at 20, 14, and 20 K, respectively, are shown in Figs. 2, 3, and 4. These spectra, which we next discuss individually, are all sufficiently well resolved to determine their isotropic magnetic constants, including the previously unknown ^{17}O hyperfine splitting in HCO.

A general point of interest is that all the radicals observed here in the methane matrix, including the hydrogen atom, have quite short relaxation times for radicals in a low temperature matrix, as indicated by the fact that they can be observed at relatively high microwave powers ($\sim$ tens of milliwatts) without excessive line broadening. This property, which may be due to efficient
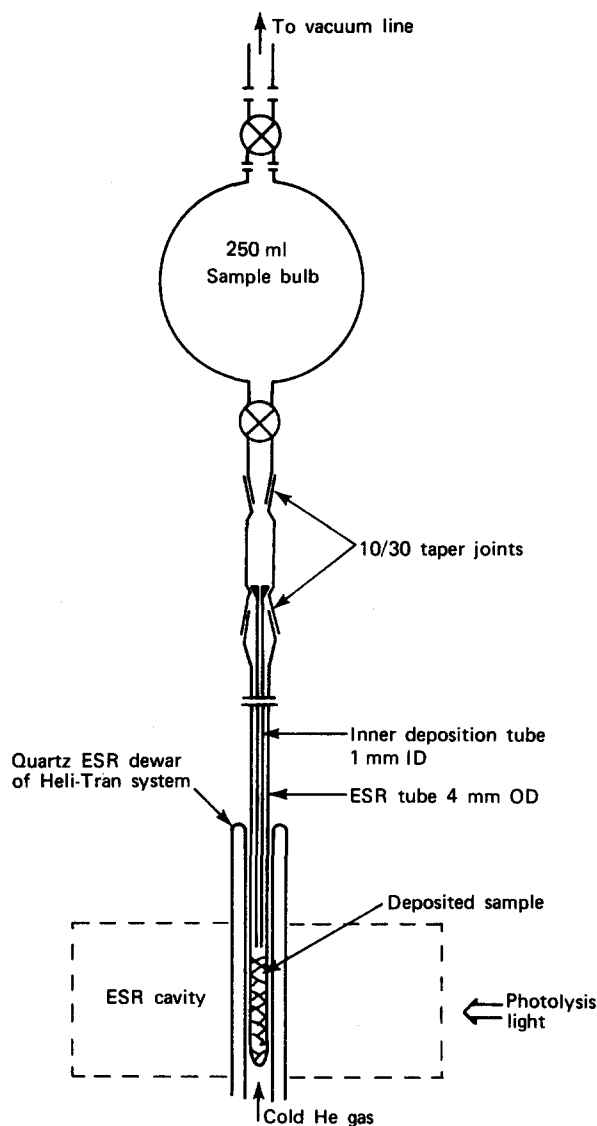
FIG. 1. Simple apparatus for matrix depositions using a helium flow-through ESR cryostat.

relaxation mechanisms involving magnetic interactions between the radicals and the methane protons as well as to various rotation related processes in the rotating radicals, is useful because the combination of the large population difference between electron spin energy levels at low temperatures and the ability to use high microwave power yields very intense ESR spectra.

1. HCO

Ultraviolet (UV) photolysis of an HI/CO:C^{17}O/CH$_4$ = 0.1/1/98.9 matrix (CO:C^{17}O = 0.62:0.38) with a 200 W high pressure Hg arc lamp for 5 min at 10 K yielded an intense H atom ESR spectrum and weak HCO and CH$_3$. The H atom spectrum exhibited an interesting superhyperfine structure, which we discuss later. On warming the matrix to 20 K the H atom spectrum almost completely disappeared and the intense isotropic HCO spectrum shown in Fig. 2 grew in, indicating that a substantial fraction of the H atoms reacted with CO to form HCO. This spectrum remained isotropic on recooling to 8 K, the lowest temperature obtainable with our apparatus, although there was some line broadening indicating a slowing of the radical reorientation rate.

The isotropic magnetic constants of HCO in CH$_4$ are: g = 2.0010, A_H = 135.4, A_C = 133.9, and A_O = −15.1 G. The signs of A_H and A_C have been determined previously[3,4] and A_O is taken to be negative because of the negative sign of the ^{17}O nuclear magnetic moment combined with the assumption of a positive spin density in the oxygen s orbitals analogous to the results obtained for the nitrogen hyperfine splittings in the isoelectronic HCN$^-$ radical.[5] These values are close to those measured for HCO in a CO matrix (g = 2.0093, A_H = 137.1, A_C = 134.8 G)[3,4] indicating there are at most only small differences in the radical–matrix interactions between the CH$_4$ and CO matrices despite the marked differences in rotational freedom of the radical in the two matrices.
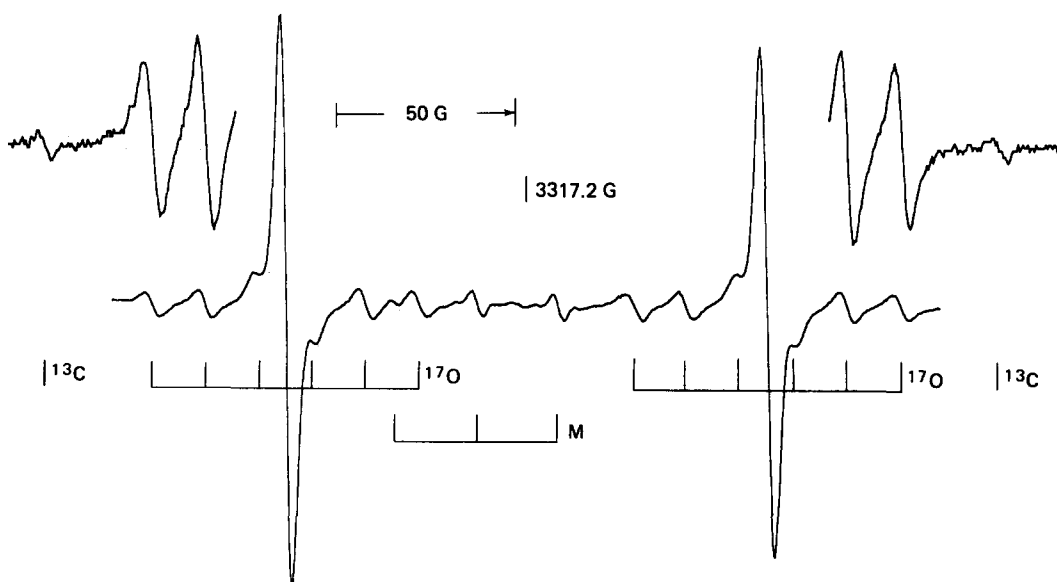

FIG. 2. Isotropic ESR spectrum of HCO/HC^{17}O in methane at 20 K. ^{17}O denotes the ^{17}O hyperfine sextet splittings of the HCO proton doublet. ^{13}C denotes the natural abundance ^{13}C hyperfine splittings of HCO, shown in the amplified expanded inserts at the high and low field ends of the spectrum. M is part of the methyl quartet. The microwave frequency is 9294.43 MHz.
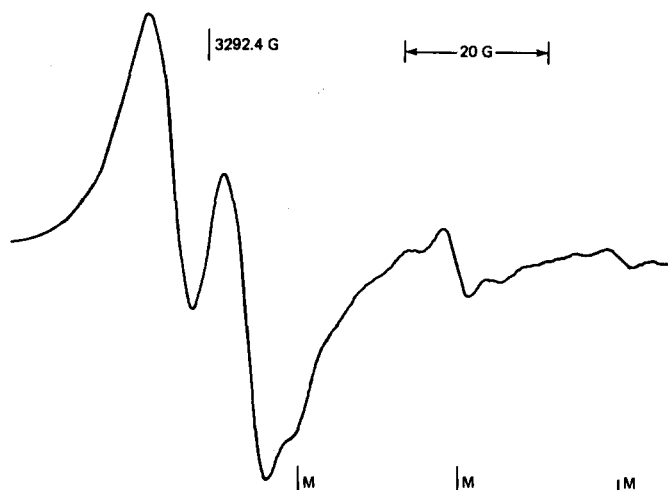
FIG. 3. Isotropic ESR spectrum of HO$_2$ in methane at 14 K. M denotes methyl radical lines. The microwave frequency is 9293.63 MHz.

The observed isotropic oxygen hyperfine splitting in HCO agrees well with values calculated by various unrestricted Hartree–Fock (UHF) and configuration interaction (CI) calculations but disagrees with the restricted Hartree–Fock (RHF) values,[6] which reiterates the well known fact that RHF calculations of spin density distributions in radicals are unreliable. If we assume that the ratio of the anisotropic to isotropic hyperfine constants for ^{17}O in HCO ($B_{\parallel,O}/A_O$) is the same as for nitrogen in the isoelectronic HCN$^-$ radical where experiment[5] gives $B_{\parallel,N}/A_N = 2$ then $B_{\parallel,O} = -30$ G which is in good agreement with the calculated value.[6]

It should be possible to measure $B_{\parallel,O}$ for HCO/HC^{17}O in a CO or other matrix where the radical does not rotate, especially with knowledge of the isotropic oxygen splitting to aid in analyzing the anisotropic powder pattern. This experiment will be undertaken as soon as our cryogenic apparatus is modified to enable us to reclaim the expensive C^{17}O sample after use.

2. HO$_2$

The ESR spectrum of HO$_2$, shown in Fig. 3, was produced by photolyzing an HI/O$_2$/CH$_4$ = 0.1/1/98.9 matrix for 10 min at 10 K, warming to 20 K to allow the H atoms from the HI photolysis to diffuse and react with O$_2$, and finally recooling to 14 K. Warming to higher temperatures between 30 and 40 K will remove more of the methyl radicals formed by reaction of methane with the "hot" H atoms from the HI photolysis (H + CH$_4$ → H$_2$ + CH$_3$) without significantly reducing the HO$_2$ concentration. On cooling below 14 K this spectrum becomes less well resolved and at the lowest temperature obtainable with our apparatus (8 K) is beginning to have the anisotropic powder pattern shape of HO$_2$ in argon,[7] but much less well resolved. Warming to 20 K and above causes the well resolved isotropic HO$_2$ spectrum observed at 14 K to deteriorate to a broad poorly resolved spectrum. Furthermore, all these temperature effects can be recycled repeatedly indicating they are not due to annealing of the matrix. The departure from an isotropic spectrum on cooling is reasonable, but we presently have no explanation

of the interesting warming effect, although possible causes are a change in radical–matrix interactions associated with the thermal anomaly in methane around 20 K,[8] or an increased rotational rate of HO$_2$ leading to line broadening due to increased spin-rotational coupling.

It is noteworthy that in methane the reaction of diffusing H atoms with O$_2$ to form HO$_2$ is very efficient. Comparison of the original integrated intensities of the H atom and HO$_2$ radical after photolysis at 10 K with the integrated intensities after warming to 20 K and recooling indicated that nearly all the H atoms were lost and half of them formed HO$_2$ radicals. The reaction of H and CO appeared to be similarly efficient from the strong observed HCO ESR signal, but was not actually measured.

The isotropic magnetic constants of HO$_2$ in methane are: $g = 2.0167$ and $A_H = -10.2$ G where the negative sign is from previous work on HO$_2$ in argon[7] where the corresponding constants from the anisotropic spectrum are: $g = 2.0160$ and $A_H = -10.2$. Again there is good agreement between the values obtained in methane and argon indicating only small matrix perturbations despite the differences in rotational freedom of the radical in the two matrices.

3. NO$_2$

The ESR spectrum of 0.01% of NO$_2$ in methane at 20 K is shown in Fig. 4. It was found that attempts to incorporate higher concentrations of NO$_2$ into the matrix led to no spectra being observed prior to photolysis, which result is probably due to complete dimerization of the NO$_2$ during condensation of the matrix. Photolysis of the higher NO$_2$ concentration matrices produced a strong NO$_2$ ESR signal, probably as the result of photodissociation of the N$_2$O$_4$ dimer, but this spectrum was quite different from the spectrum shown in Fig. 4 and probably is due to NO$_2$ in a nitrogen oxide matrix or a mixed methane–nitrogen oxide matrix, but not NO$_2$ in methane. When first formed by condensing the NO$_2$/CH$_4$ = 1/10000 matrix at 10 K the NO$_2$ spectrum was anisotropic and very similar to the spectrum of NO$_2$ in argon at 4 K.[9] On warming to 20 K the spectrum changed to the isotropic spectrum in Fig. 4.

The isotropic magnetic constants of NO$_2$ in CH$_4$ are: $g = 2.0001$ and $A_N = 54.0$ G which again are very close
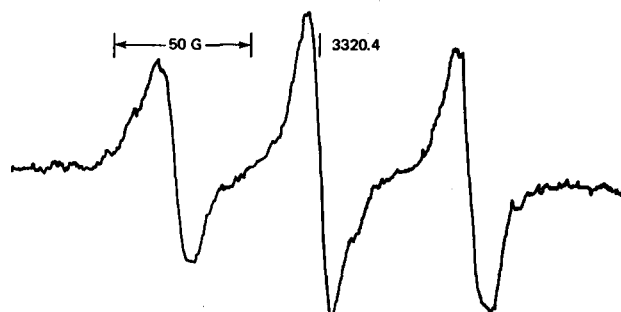

FIG. 4. Isotropic ESR spectrum of NO$_2$ in methane at 20 K. The microwave frequency is 9297.4 MHz.

to the values obtained from the anisotropic spectrum in argon (g = 1.9995 and A_N = 52.1 G).[9]

B. Matrix sites of H and CH₃

1. H atom

The ESR spectrum of H atoms in methane at 10 K has a superhyperfine structure as shown for the low field line in Fig. 5(a). The high field line has a similar structure. Examination of this spectrum and comparison with simulated spectra, such as the one shown in Fig. 5(b) for nine lines and a splitting of 2.0 G, indicate a superhyperfine interaction with eight protons. This is believed to be the correct assignment, even though the fit between the observed and computed spectrum is only fair in the wings where the computed spectrum falls off considerably faster than the observed spectrum, for two reasons: first, the agreement was considerably worse for other reasonable choices of the number of superhyperfine nuclei and, second, as we next discuss, the isotropic model used to simulate the spectra is only an approximation because the splittings in the observed spectrum are actually dominated by anisotropic rather than isotropic hyperfine interactions.

Attempts to interpret this structure as an isotropic spectrum encounter the following difficulties. The sites in the face-centered cubic methane lattice[8] where an H atom may be trapped are a substitutional site with 12 nearest neighbors, and two interstitial sites with octahedral and tetrahedral symmetry, and six and four nearest neighbors, respectively.[10] None of these sites immediately accounts for superhyperfine interactions with eight H atoms as

implied by the nine line superhyperfine structure in Fig. 5, and only the tetrahedral site offers any way out of the difficulty, namely, postulating nonrotating CH₄ molecules with superhyperfine interactions with those two H atoms of each CH₄ which point inward toward the H atom. The tetrahedral site is far too cramped to accommodate an H atom, however, since the H···CH₄ distance in such a site is 2.54 Å, which is substantially less than the sum of the H and CH₄ van der Waals radii (taken as 1.2 Å for H[11] and 2.06 Å for CH₄, which is half the nearest neighbor distance in the methane crystal[8]). Furthermore, and this is the clue to what we believe is the correct model for the superhyperfine interaction, the anisotropic hyperfine interaction from the electron-nuclear dipole-dipole interaction in such a cramped site is considerably larger than the observed 2 G splitting.

If the superhyperfine splittings in Fig. 5 are due to anisotropic rather than isotropic hyperfine interactions then the splitting can be accounted for by the following model: The H atom is trapped in the octahedral interstitial site with six adjacent CH₄ molecules which are reorienting fast enough that all the CH₄ hydrogens are magnetically equivalent. The ansiotropic hyperfine interactions yield an orientation dependent spectrum, which for the randomly oriented ensemble of methane crystallites is a so-called powder ESR spectrum.[1] As is typical of powder spectra, the sharp line features correspond to those crystallites which are oriented so the magnetic field is along a principal magnetic axis, i.e., a principal axis of the tensor representing the combined anisotropic hyperfine interactions of the various nuclei. In this cubically symmetric system the three principal axes are equivalent and involve hyperfine interactions of magnitude $a + b_\parallel$ with the eight H atoms of those two CH₄ molecules whose line of centers is parallel to the external field and hyperfine interactions of magnitude $a - \frac{1}{2}b_\parallel$ with the 16 hydrogens of the other adjacent CH₄ molecules, where a and $b_\parallel$ are the isotropic and anisotropic superhyperfine interaction constants. If $a + b_\parallel$ = 2 G $\gg a - \frac{1}{2}b_\parallel$ then only the eight 2 G splittings will be resolved and the spectrum will contain the observed nine lines.

The anisotropic superhyperfine interaction constant is readily calculated as the dipolar interaction of a methane proton with the hydrogen 1s electron. The result, when averaged over all orientations of the CH₄ molecule in the undistorted octahedral site [R(H···CH₄) = 2.94 Å] is $b_\parallel$ = 2.2 G which is close to the observed splitting if a is negligible, while the perpendicular splitting of 1.1 G will be too small to be resolved. It is unlikely, however, that the isotropic splitting will be exactly zero, although it is expected to be small since there is very little overlap of the hydrogen and methane orbitals at the H···CH₄ separation in this interstitial site. Furthermore, the anisotropic perpendicular splitting of 1.1 G, although unresolved, would contribute considerably more broadening of the individual lines than is observed. It is likely, therefore, that there is a slight outward expansion of the six CH₄ neighbors of the trapped H atom since the undistorted H···CH₄ distance of 2.94 Å is somewhat less than the sum of the H and CH₄ van der Waals radii,
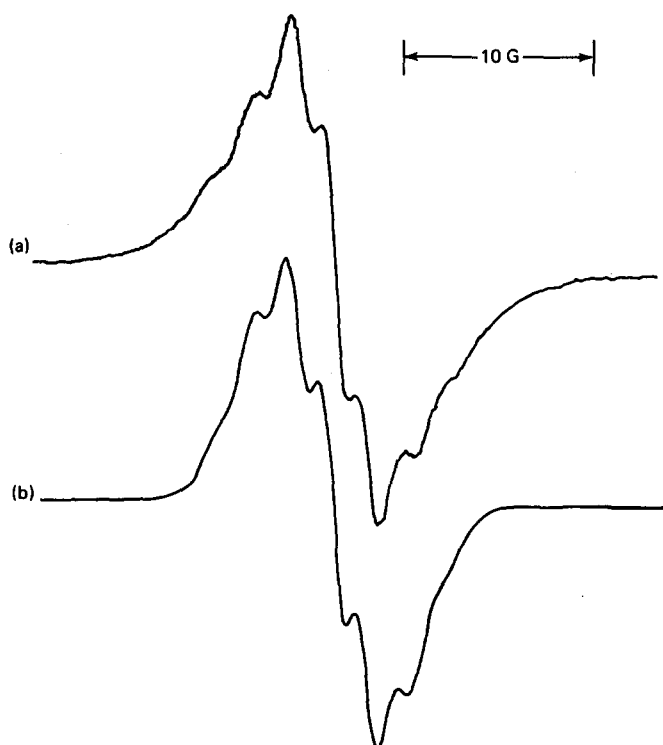

FIG. 5. Low field ESR line of the H atom in methane at 10 K (a) observed line, (b) Computed line.

which expansion gives a somewhat more realistic model. For an 11% expansion to the sum of the H and CH_4 Van der Waals radii $[R(H \cdots CH_4) = 3.26 \text{ Å}]$ the calculated $b_{\parallel}$ is 1.6 G which, with $a = 0.4$ G gives the observed splitting of 2 G while the splitting in the perpendicular direction is 0.4 G and is much too small to be resolved.

The H atom magnetic constants in CH_4 are $g = 2.0020$ and $A_H = 507.1$ G (1420.0 MHz). The g value is typical of those found for H atoms in low molecular weight matrices[10] while the hyperfine splitting constant is very close to the free atom value (1420.405 MHz).[12] This value is probably due to a balance between the negative van der Waals and positive exchange shifts of the hyperfine splitting,[13] and is consistent with our picture of the atom trapped in a slightly cramped interstitial site where the repulsive exchange forces are comparable to the attractive van der Waals interactions.

2. CH_3 radical

As noted previously, and as is weakly observable in both the HCO and HO_2 spectra in Figs. 2 and 3, photolysis of HI in CH_4 yields a moderately strong methyl radical spectrum, which probably results from the abstraction reaction between CH_4 and energetic H atoms just after their formation by photolysis of HI, i.e., $CH_4 + H$ (nonthermal) $\rightarrow CH_3 + H_2$. There is no evidence of an increase in the CH_3 ESR intensity on standing or on warming the matrix which allows the H atoms to diffuse and react with such species as CO and O_2. Thus, as noted previously, the tunnelling abstraction reaction between thermalized H atoms and higher alkanes, such as C_2H_6,[1,14,15] does not occur for CH_4 probably because the CH bond is somewhat stronger in the latter molecule.

As is apparent from the trace of CH_3 in the HO_2 spectrum in Fig. 3 and in the ESR spectrum of CH_3 alone in Fig. 6, each line of the methyl quartet is flanked by two satellite lines separated from the main line by approximately 5 G. It is well known that these are "forbidden" transitions in which the electron spin transition is accompanied by the flip of a proton on an adjacent molecule, here CH_4 molecules. These forbidden transitions are promoted by the anisotropic electron-nuclear dipolar interaction between the electron magnetic moment and the proton moments, which Trammel, Zeldes, and Livingston have shown yields the following expression for the satellite to main line intensity ratio[16]:

$$I_s/I_0 = (3g^2\beta_0^2 N_p/20H^2)\langle 1/R^3 \rangle^2, \qquad (1)$$

where g is the electron g factor, β_0 is the Bohr magneton, N_p is the number of protons interacting with the radical, H is the external magnetic field, and $\langle 1/R^3 \rangle$ is the average of the inverse cube of the separation between the unpaired electron and the proton. If the CH_4 molecules next to the CH_3 radical are reorienting fast enough to make the CH_4 protons equivalent, without which assumption the number of interacting protons is reduced to a point where the observed I_s/I_0 requires a dipolar interaction large enough to yield resolved superhyperfine interactions as in the H atom spectrum, then at the $CH_3 \cdots CH_4$ separations,
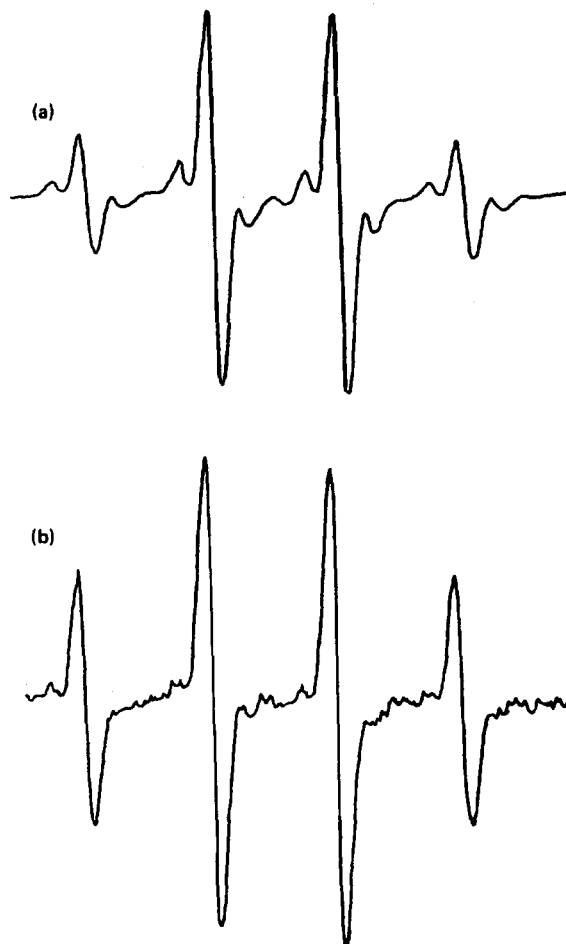

FIG. 6. ESR spectrum of the methyl radical in methane at 10 K (a) High microwave power, (b) Low microwave power.

$R(CH_3 \cdots CH_4)$, corresponding to CH_3 in either the substitutional site or the octahedrally symmetric interstitial site, one has approximately: $\langle 1/R^3 \rangle = 1/R^3(CH_3 \cdots CH_4)$.

The satellite to main line intensity ratio is microwave power dependent, as is shown in Fig. 6, because the allowed transitions saturate more readily than the forbidden ones, so the true intensity is obtained only at infinitely low power. In the present case this point appears to be reached in the low power spectrum in Fig. 6(b), which corresponds to a microwave power of approximately 0.01 mW. The intensity ratio can be only roughly estimated from this spectrum, where the signal to noise is low, but an average for the four satellites of the two stronger inner lines of the quartet yields approximately 0.05. Using this value for I_s/I_0 in Eq. (1) with $H = 3320$ G gives $R = 4.1$ Å for CH_3 in the substitutional site where $N_p = 48$, which value agrees well with the crystallographic nearest neighbor distance of 4.12 Å. On the other hand assuming the CH_3 radical is in the octahedrally symmetric interstitial site where $N_p = 24$ gives $R = 3.6$ Å, which agrees less well with the crystallographic distance of 2.92 Å.

It is thus likely that the CH_3 molecule is located in a substitutional site in the CH_4 matrix, which is very reasonable considering that the van der Waals radii of CH_3 and CH_4 should be very similar, and that formation of CH_3 by an H atom abstracting another H atom from

CH_4 is likely to leave the resulting CH_3 radical in the site occupied by the CH_4 molecule.

The present indications that H atoms and CH_3 radicals are trapped in the octahedrally symmetric interstitial site and substitutional site, respectively, of the methane host is interesting in connection with the observation of a triplet state H atom–methyl radical complex in γ-irradiated methane.[17] The observed triplet zero-field splitting indicates the separation of the pair is 6.76 Å, which compares well with the separation of an interstitial H atom and a CH_3 radical in a next nearest neighbor substitutional site, which distance is 6.52 Å.

In summary, methane appears to be an interesting matrix for isolating small free radicals, particularly if there is a need to obtain their isotropic ESR spectra. It also may find application in investigation of the interactions of small radicals with the simple methane molecule, and the interactions and reactions of small molecules and radicals with H atoms.

ACKNOWLEDGMENT

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