Short notes

Peculiarities of EPR spectra of methyl radicals in quench-condensed krypton films

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Methyl radicals are trapped in the solid Kr film by simultaneous condensation of gaseous Kr and the products of the gas discharge in CH_4 doped Kr on the low temperature (4.2 K) substrate located at the center of the microwave cavity. The observed EPR spectrum is a superposition of broad-line and narrow-line series. At a low resonance microwave power, the latter one consists of four hyperfine components with nearly equal intensities, and shows small axial anisotropy of both g- and A-tensors. At a sufficiently large power, two central narrow lines split so that the narrow-line series takes an appearance recorded elsewhere for CH_3 in Ar at higher temperatures above 12 K. Simultaneously, the intensity of two central broad lines increases dramatically while the outer components become saturated. The possible explanation is discussed.

Methyl radical, CH_3, is among the simplest polyatomic molecules which attract attention of both experimentalists and theoreticians in attempting to verify theoretical approaches used to analyze characteristics of a molecule in various substances. For example, a theory predicts a fairly large anisotropy of the proton hyperfine tensor for the free CH_3 molecule. While the anisotropy was actually observed with CH_3 radicals in $CH_3COONa \cdot 3D_2O$ monocrystal [1], only symmetrical hyperfine lines were obtained in powder samples, which suggest practically isotropic interaction. This is closely related to the rotational motion of the CH_3 radical in such matrices as frozen gases which averages out the hyperfine components, A_{xx} and A_{yy}, yielding a spectrum of axial symmetry with the perpendicular component, $A_\perp = \frac{1}{2}(A_{xx} + A_{yy})$, and with the parallel component $A_\parallel = A_{zz}$. Since these components are nearly equal in value, the effective hyperfine tensor is nearly isotropic [2]. Indeed, based on the free radical parameters, these values are estimated as being $A_\perp = -60$ MHz, $A_\parallel = -61$ MHz [2]. Recently, the anisotropy of the EPR spectrum of CH_3 molecules was reported for CO, Kr [3,4], N_2 [3], Ar [4] and Ne [5] powder matrices. The most prominent effect was found in CO where $A_\perp = -23.4$ G,

$A_\parallel = -22.3$ G, $g_\perp = 2.0027$, $g_\parallel = 2.0022$, thus giving $\Delta A = |A_\perp| - |A_\parallel| = 1.1$ G > 0, $\Delta g = |g_\perp| - |g_\parallel| = 5 \cdot 10^{-4} > 0$. Interestingly, ΔA is negative for the free radical as seen from the above quantities and positive for CH_3 not only in CO but in $CH_3COONa \cdot 3D_2O$ monocrystal as well [1]: $A_\perp = -22.33$ G, $A_\parallel = -21.53$ G, $\Delta A = 0.8$ G. It is quite reasonable to attribute the difference in the ΔA signs for the free and trapped molecules to a different effect a matrix has on $A_\perp$ and $A_\parallel$ parameters. The nonzero Δg is, probably, a fingerprint of the nonplanar structure of the trapped methyl radical [6]. It has been shown earlier [4] that $\Delta A < 0$ for both Ar and Kr matrices while Δg is negative for Ar and positive for Kr. The whole set of experimental data was noncontradictory explained assuming fast rotation of the molecule around its C_3 axis in CO, Ar and Kr while the reorientation of this axis is suppressed in the matrix with orientation ordering, CO, and occurs through, possibly, tunneling motion in Ar and Kr. Very recently, high-resolution EPR measurements were carried out on CH_3 trapped in solid Ar [7]. With the linewidth of about 0.15 G, the authors were able to resolve a structure of the low field hyperfine component. The splitting of the line is owing to the hyperfine coupling and g-tensor anisotropy. In cases of the broader lines, the anisotropy reveals itself

in varying amplitudes of the hyperfine components: 1:1.6:2.5:1.6 for samples at 14 K [7]. This sequence is close to that obtained earlier for the CH_3 in Ar at 4.2 K: 1:1.9:3.4:2.1 [4]. As for the value of the anisotropy in rare gas solids, this was estimated to be $|\Delta A| \approx 0.16$ G, $|\Delta g| \approx 3 \cdot 10^{-5}$ in solid Kr [3]. For the Ar matrix, experimental and simulated spectra showing the anisotropy were presented elsewhere [4]. The corresponding parameters used in simulation and not indicated in Ref. 4 are as follows: $|\Delta A| \approx 0.21$ G, $|\Delta g| \approx 5 \cdot 10^{-5}$. These may be compared with the results of Ref. 7: $|\Delta A| \approx 0.1$ G, $|\Delta g| \approx 3 \cdot 10^{-5}$. The two estimates are, thus, in line with each other. One may suppose that somewhat smaller $|\Delta A|$ at 14 K compared to the result at 4.2 K is due to the anisotropy decreasing when the sample temperature rises up from 4.2 K to 14 K. Further study is needed to elucidate possible temperature dependence of the anisotropy. Comparing two atomic matrices, Kr and Ar, the anisotropy in Kr is no larger than in Ar, which fact is opposed to the statement in Ref. 7. This is also substantiated by the amplitude sequence in Kr at 4.2 K: 1:1.7:1.4:0.7 observed in the present set of experiments. The experimental procedure was described elsewhere [4]. Briefly, a sample is obtained on the low temperature substrate located at the center of the microwave cavity by simultaneous condensation of gaseous Kr and the products of the gas discharge in CH_4 doped Kr (approximately from 3% to 10% of CH_4 in the gas mixture). Taking into account geometry of the deposition system, the whole CH_4 impurity content in the solid is estimated to vary from 0.15% to 0.5%. We found no effect of the impurity concentration varying in the above range on the obtained results. Because Kr and CH_4 solids are soluble in each other in any concentration, no CH_4 microcrystals are expected to form within Kr solid which might otherwise trap CH_3 radicals, thus having an effect on the recorded EPR spectra. The amplitude sequence for Kr matrix is a mirror image of that observed in Ar. A reason for the finding was discussed earlier [4]. Interestingly, an extent of the anisotropy is found to be close not only in Ar and Kr matrices but in Ar and Ne also [5] despite the different values of the pair CH_3–Rg (where Rg denotes a rare gas atom) interaction. Based on the experimental data, the anisotropy seems to be more prominent in matrices with orientation ordering, e. g., CO, CO_2, N_2O, than in matrices without orientation ordering, Ar, Kr, Ne, H_2. The matrix structure, thus, mostly governs freedom of rotation of trapped CH_3 molecule.

The most striking result obtained in the present study is an observation of additional CH_3 lines, Fig. 1. Two sets of additional lines are found: four broad components with the peak-to-peak linewidth $\Delta H \approx 1.8$ G and two narrow ones with $\Delta H \approx 0.2$ G. At a low microwave power in the cavity the broad components are of nearly equal intensity.
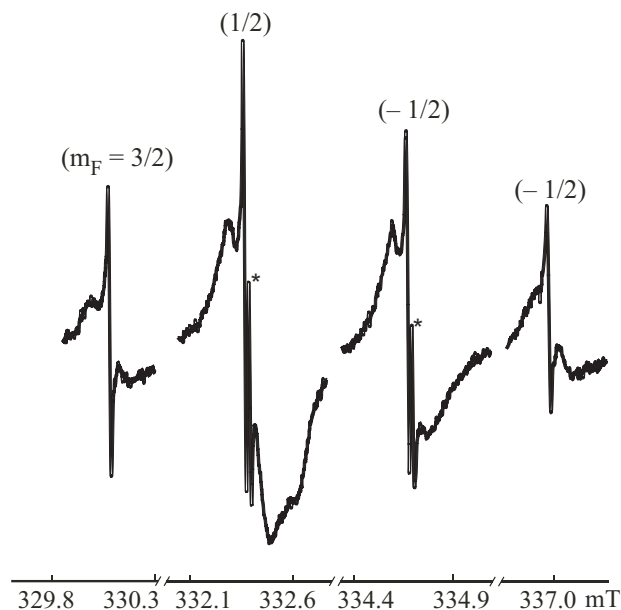

Fig. 1. The 4.2 K EPR spectrum of methyl radicals trapped in solid krypton. Resonance frequency f_{res} = 9344.22 MHz. The attenuation of the microwave power is 26 dB. Narrow lines of the doublet of *E*-symmetry are marked as stars. The projection m_F corresponds to the *z* component of the total nuclear spin.

The same holds for the spectrum of four narrow lines observed previously [3]. Normally, three equivalent protons would be expected to give a quartet with intensity ratio of 1:3:3:1. It was first pointed out by McConnel [8] that, at sufficiently low temperatures, the methyl radicals might show for lines of equal intensity. Three protons of the radical are considered to move in the matrix in a threefold potential well with finite barrier height. The lowest torsional rotational energy level is split into two: lower one of *A*-symmetry and upper, doubly degenerated one of *E*-symmetry. At low enough temperatures and a moderate barrier height the torsional splitting [9] becomes far in excess of kT so as to make only the lowest mixed spin-rotational *A*-state with four symmetric nondegenerate nuclear spin functions being populated. So the EPR spectrum is a 1:1:1:1 quartet. The rotation is considered as being a tunneling motion so as to occur even at liquid helium temperatures. As the sample temperature rises, the population increases of the doubly degenerated *E*-state that yields two components nearly coinciding with the two central *A*-lines. With the sufficiently broad lines, this temperature transformation of the spectrum results in the ratio of amplitudes of approximately 1:3:3:1. *A*- and *E*-lines have been firstly resolved in $CH_3COONa \cdot 3D_2O$ monocrystal [1]. Until recent years, such an effect has not been observed with CH_3 radicals matrix-isolated in powder samples. Reference 10 was the first work where high-resolution spectra of CH_3 in solid Ar showed well resolved *A*- and *E*-lines at temperatures above 12 K, the latter ones being high-field shifted compared to two central *A*-compo-

nents by about 0.24 G. The same result was obtained in Ref. 7 for CH_3 in Ar at temperatures above 14 K. *E*-lines show up at a sufficiently large microwave power in the cavity suggesting a shorter spin-lattice relaxation time as compared to *A*-lines [7]. With temperature decreasing, not only the intensity of *E*-lines decreases due to depopulation of $J = 1$ rotational state but the lines themselves sufficiently broaden [7,10]. These two trends contribute to a fast drop of the amplitude of *E*-lines as the temperature lowers. For example, *E*-states nearly not seen from the EPR spectrum at 14 K [7] are fairly high populated: $P_A/P_E \approx 0.5$ as may be calculated from the data presented in Ref. 7. Being so, one would not hope to see any signs of *E*-lines at the liquid helium temperatures. Amazingly, the results of the present study suggest that, in Kr matrix, *E*-lines clearly show up at 4.2 K. Indeed, two narrow additional lines in Fig. 1 are high-field shifted by 0.245(25) G compared to central *A*-lines, thus, occupying exactly the expected *E*-line positions. Moreover, Fig. 2 shows that additional lines saturate far more slowly than *A*-lines, which effect was registered for *E*-lines in Ar [7]. Based on the present observation, one may suppose that the spectrum of broad lines is, actually, a superposition of quartet and doublet series. The quartet *A*-line series is probably closely related to the broad EPR lines found for hydrogen atoms trapped in highly disordered regions in the lattice of quench-condensed Kr matrix [11]. Indeed, the EPR spectrum of H atoms recorded simultaneously contains
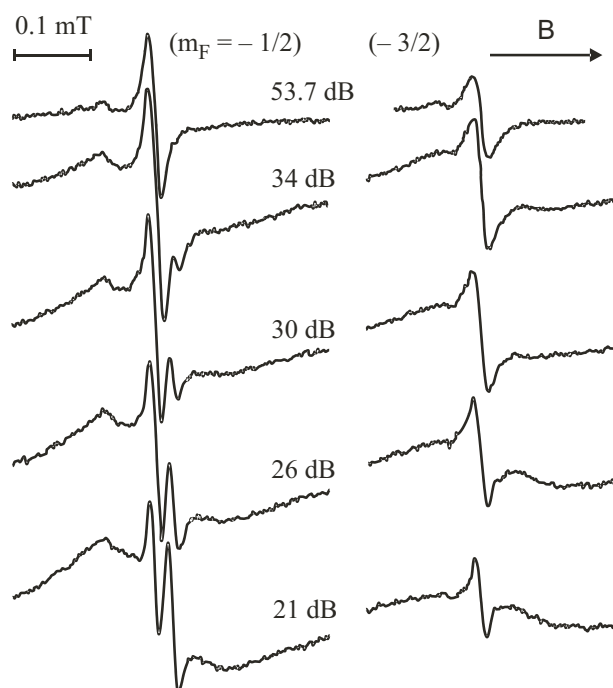

Fig. 2. Microwave power dependent EPR spectrum of CH_3 radicals in solid Kr. The numbers in figure show the power attenuation in the cavity. *E*-lines both broad and narrow become prominent as the power increases. The sample temperature is 4.2 K.

two broad hyperfine components. Taking the intensity of a line as being proportional to the product of the amplitude and the squared linewidth, we come to the conclusion that CH_3 radicals are preferably trapped in the disordered regions. The most intriguing question is why we observe *E*-lines at such a low temperature as 4.2 K and even down to 1.5 K. Based on the results for the narrow lines, the ratio of level populations, P_A/P_E, estimated for nonsaturated conditions from the present spectra obtained at high microwave power leads to an energy difference, ΔE, between $J = 0$ and $J = 1$ lying in the approximate range 22–25 K. In this case, the energy distance would be not only far above the corresponding value of 16.09 K for CH_3 in Ar [7] but the gas phase level separation, 20.6 K, as well. On the other hand, ΔE is expected to be smaller for CH_3 in matrices than in the gas phase. Moreover, it may be reasonably assumed that this energy separation in Kr is less than in Ar, because of the stronger CH_3–Kr pair interaction. One more discrepancy to be solved concerns the linewidth. It has been mentioned in the above discussion that *E*-lines rapidly broaden with temperature lowering, e. g., from 0.1 G at 25 K to 0.3 G at 12 K for CH3 in Ar [10]. The temperature dependence is nonlinear [7,10] so as the linewidth at 4.2 K would be far in excess of 1.4 G expected for the linear dependence. However, the corresponding widths obtained in the present study for narrow lines are close to 0.2 G. We suppose that the possible answer to the above question lies in the suggestion that the narrow line series originate from overlapping EPR spectra of CH_3 radicals trapped in two different matrix surroundings. One of these is the substitutional position with cubic symmetry in the non-distorted fcc Kr crystal lattice which gives no observable *E*-lines at liquid helium temperatures. Another one is a regular position in the lattice with axial symmetry which yields «*A*-lines» and «*E*-lines» at low temperatures possibly due to the small ΔE and an admixture of the high-energy states to the lowest rotational state. Probably, the host of this kind is the hcp crystallites which may form in the quench-condensed Kr [11]. The disordered regions giving rise to broad line series provide the CH_3 surroundings of low symmetry. Again, because of the low symmetry, «*E*-lines» emerge at sufficiently high microwave power. A change of the spectrum with varying the sample temperature below 4.2 K is now under study.

1. S. Kubota, M. Iwaizumi, Y. Ikegami, and K. Shimokoshi, *J. Chem. Phys*. **71**, 4771 (1979).
2. J.Y. Lee and M. T. Rogers, *J. Chem. Phys*. **65,** 580 (1976).
3. Yu.A. Dmitriev and R. A. Zhitnikov, *J. Low Temp. Phys*. **122**, 163 (2001).
4. Yu.A. Dmitriev, *Physica* **B352**, 383 (2004).
5. Yu.A. Dmitriev, *J. Low Temp. Phys.* **139**, 541 (2005).

6. E.A. Misochko, V.A. Benderskii, A.U. Goldschleger, A.V. Akimov, A.V. Benderskii, and C.A. Wight, *J. Chem. Phys*. **106**, 3146 (1997).

7. E. Popov, T. Kiljunen, H. Kunttu, and J. Eloranta, *J. Chem. Phys*. **126**, 134504 (2007).

8. H.M. McConnel, *J. Chem. Phys*. **29**, 1422 (1958).

9. J.H. Freed, *J. Chem. Phys*. **43**, 1710 (1965).

10. T. Yamada, K. Komaguchi, M. Shiotani, N.P. Benetis, and A.R. Sornes, *J. Phys. Chem*. **A103**, 4823 (1999).

11. Yu.A. Dmitriev, *Fiz. Nizk. Temp*. **33**, 661 (2007) [*Low Temp. Phys*. **33**, 493 (2007)].