Optics and Spectroscopy, 2024, Vol. 132, No. 11

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EPR spectroscopy of CH_3 rotational states for the radicals trapped in solid CH_4 at liquid helium temperatures

© Y.A. Dmitriev

Ioffe Institute,
194021 St. Petersburg, Russia
e-mail: dmitriev.mares@mail.ioffe.ru

Received April 26, 2024
Revised August 01, 2024
Accepted October 30, 2024

Methyl radicals, CH_3, are vapor deposited in solid CH_4 on a substrate at $T_{dep} = 4.2$ K. EPR spectra of the radicals are taken in the temperature range $T_{rec} = 1.4-4.2$ K. The spectra processing, including intensity measurement of the forbidden electron-proton transitions and line shape analysis of the allowed transitions, reveals correlation of the orientational motions of the trapped radical and the nearest matrix molecules.

Keywords: electron paramagnetic resonance, matrix isolation, methyl radical, solid methane, molecular rotation.

DOI: 10.61011/EOS.2024.11.60302.6359-24

Methyl radical, CH_3, is a rotator with well expressed quantum properties even at moderate low temperatures. Due to low rotational constant, $B = 6.76$ K, for rotation around axis of third order, C_3, of free molecule the energy distance between lower rotational state is about 20 K. This results in the necessity to describe the methyl radical as quantum rotator even at temperatures much higher the temperatures of helium. It is considered that the angular moment of molecules is an ideal object for quantum control due to its inherent quantization, accurately described time evolution using known Hamiltonians with small set of rather definite parameters, and assurance of the transitions between rotational levels by external fields of various regions of electromagnetic spectrum [1]. The link of the rotational state with the vibrations of nuclei, with the orbital and spin moments of electrons, as well as the interaction of the molecule with the environment, if it is in the liquid or solid phase, complicates the structure of rotational levels. On other hand, listed circumstances present variety of levers or the quantum control [1]. The medium effect on the rotational dynamics of the molecular rotator arranged in it is studied using different approaches. So, models of the static crystal field and pseudo-rotating matrix cell were applied [2] to analyze spectra of EPR radicals CH_3, stabilized in solid Ar and Kr. For description of the rotator surrounded by quantum particles the model o quasiparticle, called angulon, was suggested [3] and is actively developed [4,5]. Describing the suggested model, the authors indicate that for detailed understanding of the quantum-mechanical behavior of the molecular impurity in the quantum matrix the required assumptions shall be based on the first principles, because of multiparticle task. In described model the angulon is polaron-like particle formed by the molecule — quantum rotator in „coat" of multiparticle excited states of matrix medium, able to have the angular moment. Although the model is positioned as applicable to the molecular rotators in liquid and solid quantum mediums, the only experiments, which are the model basis, are experiments on the molecular trapping into nanodrops of superfluid helium.

Note that the processes of molecules arrangement in the deposited thin films, and their orientation dynamics attracted during last years the special attention of researchers due to their exceptional importance during, for example, development of optoelectronic devices on organic materials, creation of new polymer materials. At the same time it is identified that understanding of these processes is far from satisfactory even based on the example of more simple inorganic molecules in solids.

To determine the features of orientation movement of the stabilized molecular radical in this paper the shape of spectra of EPR radical CH_3 — quantum rotator in solid CH_4 was analyzed for the first time. In presented study the methyl radicals, CH_3, stabilized in solid methane, CH_4, by deposition from gaseous phase on the substrate at helium temperatures. It is known that methane is the quantum solid due to large value of the de Boer quantum rotational parameter. The methyl radical in solid methane demonstrates properties unique for the stabilized methyl radical. So, rotational constant B is subjected to unprecedented decreasing as compared to shifts in other matrices. For comparison, shift relative to value for free molecule, $\Delta B/B_{free}$, is 53% for CH_3 in CD_4 [6], and only 18% for CD_3 in orto-D_2 [7] and 20% for CH_3 in Kr [2]. Besides, in solid methanes there is [6] not observed for methyl radicals in other matrices the molecule adaptation to matrix environment with change in its symmetry, namely with decrease from D_3 to C_3, indicating transition from geometry of flat free molecule to the pyramidal structure. In spite of that the energy advantage of the first structure as compared to the second structure is low for the free molecule, such transformation is not observed in other matrices. The present paper objective was detailed study of spectrum shape of EPR methyl radical in solid methane to determine features of low-temperature interaction of this

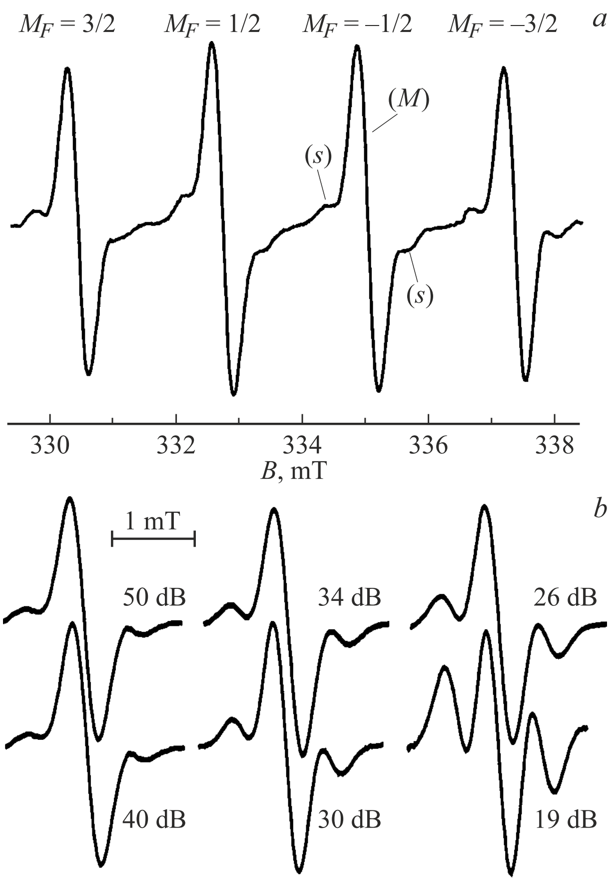

Figure 1. EPR spectrum of radical CH_3, stabilized in matrix of solid CH_4 deposed on the substrate at 4.2 K. (*a*) Experimental spectrum recorded at sample temperature 1.73 K and power decreasing of electromagnetic wave entering the microwave cavity, equal to 50 dB. Resonance frequency of the spectrometer $f_{res} = 9359.20$ MHz. Here s — forbidden transitions occurred as satellites of allowed transition, M. (*b*) High-field hyperfine component, $M_F = -3/2$, recorded at different attenuation levels of microwave power in resonator. Sample temperature is 1.41 K. For easy determination of shape transformation the amplitude lines of resonance curves at different power levels in the Figure are reduced to same value. In experiment they differ greatly.

quantum rotator with the matrix environment, formed by the quantum rotators.

Fig. 1, *a* presents EPR spectrum of radical CH_3, stabilized in matrix of solid CH_4 deposited on substrate at 4.2 K. The spectrum is unresolved superposition of quartet and doublet of hyperfine lines being the first derivatives of absorption lines. Symmetric nuclear spin states (the total nuclear spin is 3/2) give quartet of hyperfine components in EPR spectrum, while antisymmetric states (the total nuclear spin is 1/2) give the doublet. In Figure designation (M) corresponds to allowed transitions, and (s) — weak resonance satellite lines, associated with forbidden electron-nuclei transitions with simultaneous spin projection change of unpaired electron and spin projection of nucleus of neighboring matrix molecule. Relative intensity of satellites is determined as I_{sat}/I_0, where I_{sat} — satellite intensity, and I_0 — intensity of allowed line. Relative intensity of satellite ensures the possibility to obtain information [8] on number of nearest matrix molecules and distance to them: $I_{sat}/I_0 = (3g^2\beta_0^2 N_p/20H^2)\langle 1/R^3\rangle^2$. Here g — electron g-factor, β_0 — Bohr magneton, N_p — number of protons interacting with radical, H — external magnetic field, $\langle 1/R^3\rangle$ — averaged inverse cube of distance between unpaired electron and proton. Relative intensity significantly depends on the microwave power applied to the resonator, Fig. 1, *b*. Above formula is applicable provided that there is no lines saturation. In present experiment this condition

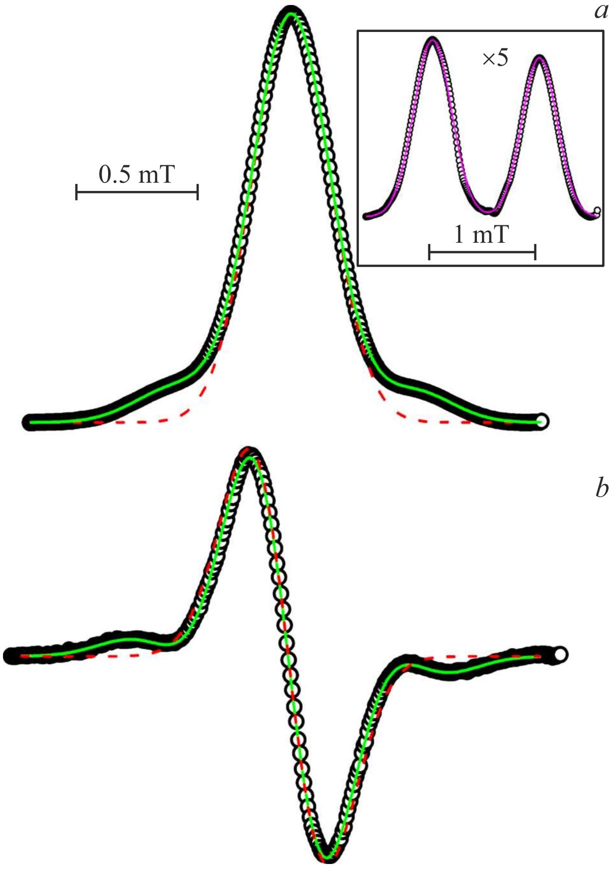

Figure 2. Modeling of high-field, $M_F = -3/2$, hyperfine component of EPR spectrum of radical CH_3. The spectrum was obtained at sample temperature $T_{rec} = 4.2$ K and and microwave power decreasing in resonator equal to 50 dB. (*a*) Modeling of absorption line. Here black circles — resonance curve, obtained by integration of the experimental spectrum; red dashed line — calculated Gaussian curve, modeling basic (allowed) line of EPR; green solid curve — modeling of experimental result by superposition of basic and satellite lines. The insert shows with five times magnification the difference curve of experimental (black circles) and calculated (red dashed line) resonances, presented the satellite spectrum. The modeling of this difference curve is shown by the purple line and is calculated as a superposition of two Gaussian resonance curves. (*b*) Modeling of the first derivative of absorption: black circles — experimental result, red dashed line — calculated Gaussian curve modeling the basic (allowed) EPR line, green solid curve — superposition of the basic and satellite lines.

is achieved upon decrease in power applied to resonator at level of 50 dB. Microwave power applied to attenuator is 15 mW. At the same time, EPR spectrum with a high signal-to-noise ratio was recorded, which made it possible to experimentally measure the relative intensity of the satellite for the first time. Integration of the experimental curve of hyperfine component $M_F = -3/2$ provided the resonance absorption line (Fig. 2, *a*). Allowed absorption line (black circles) was modeled by Gaussian-shaped curve (red dashed line in Figure). Spectrum of satellites was obtained as difference of experimental and calculated lines (insert in Fig. 2, *a*). Satellites were modeled by the superposition of two Gaussian lines (purple solid line). The absorption lines and its first derivative in Fig. 2, *a* and *b* indicate good matching of calculation (green solid line) and experiment. As a result, the relative intensity determined from the satellites of the high-field and low-field hyperfine lines of the *A*-symmetrical quartet in temperature range 1.4–4.2 K, was $(I_{sat}/I_0)_{\text{exp}} = 0.078(9)$. If we consider that molecules CH_4, neighboring with radical CH_3, are oriented in a random way, then for 12 neighbors located at distance 4.12 Å from radical, the calculation gives $(I_{sat}/I_0)_{\text{calc1}} = 0.046$. Experimental ratio of intensities in case of random orientation of matrix molecules corresponds to distance 3.77 Å between radical and neighboring randomly oriented matrix molecule CH_4. The methyl radical, CH_3, as per its geometric dimensions is similar to methane molecule, CH_4, so, we shall not expect relaxation of the lattice around similar substituent impurity with offset of matrix particles by 8.5% towards the stabilized radical. Really, in Kr matrix close by lattice parameter and energy of pair interactions of particles the contraction of the matrix environment around the substituent atom H, which is in fact a vacancy unlike to CH_3, is only 2.5% [9]. So, we conclude that the matrix molecules and stabilized methyl radical, making tunnel rotations at low temperatures, keep definite relative orientation as a result of these rotations correlation. Evaluations show that at definite orientations of methane molecules the relative intensity of satellites can significantly change. Such, for example, in the absence of lattice contraction and such arrangement of methane molecules when one of the hydrogen atoms of each neighboring molecule CH_4 is neigboring to radical, the relative intensity of satellites is 0.09.

Fig. 3 presents the modeling result of one of central hyperfine components, namely $M_F = 1/2$. The experimental results for the absorption line and its first derivative are presented by black circles in Fig. 3, *a* and *b*. Basic line is superposition of offset by 0.025 mT relative each other allowed transitions of *A*-symmetrical quartet and *E*-symmetrical doublet. Intensity of *A*-line shall be equal to the intensity of $M_F = -3/2$ component. But in this case the modeling by Gaussian lines ensures overestimated amplitude of allowed resonance (red dashed line in Fig. 3, *a*). Let's suppose that the allowed transition of *E*-symmetrical doublet, corresponding at low temperatures to the first excited $J = 1$ rotational state, is actually the superposition of Gaussian and Lorentz curves with relative contributions into intensity 0.59 and 0.41 respectively (blue dashed line in Fig. 3, *a*). Like to the component $M_F = -3/2$, satellites were modeled as per difference curve. The modeling result (green solid line) well represents the experiment (Fig. 3, *a* and *b*). Previously, we found that the spectrum of the same radical at the same temperatures in different matrices is described by curves of different shapes. So, spectrum of

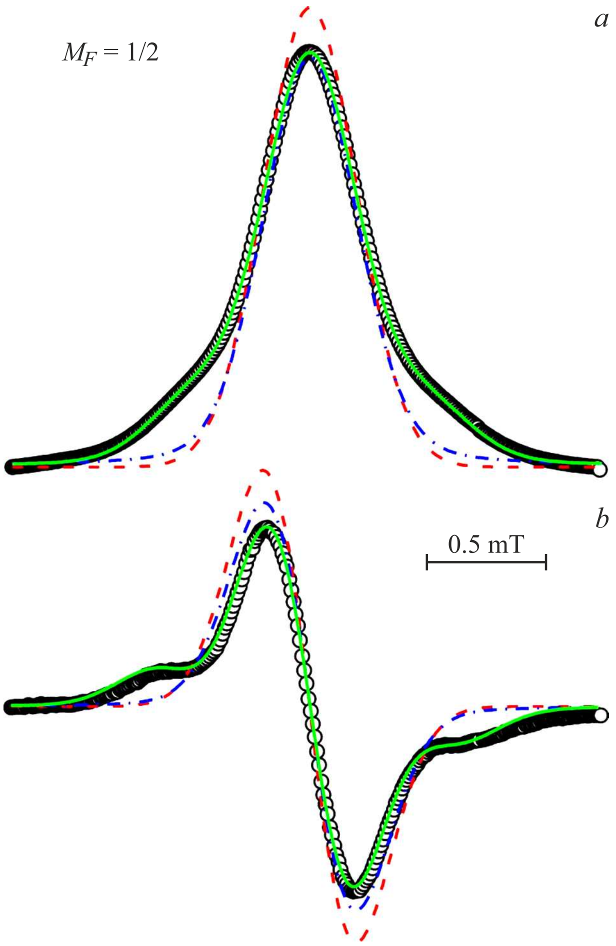

Figure 3. Modeling of hyperfine component $M_F = 1/2$ of EPR spectrum of radical CH_3. The temperature of the substrate during gaseous mixture deposition is $T_{dep} = 4.2$ K; spectrum is recorded at sample temperature $T_{rec} = 1.44$ K and decrease in the microwave power in the resonator, equal to 50 dB. (*a*) Modeling of absorption line: black circles — resonance curve obtained by integration of experimental spectrum, red dashed line — calculated curve modeling basic (allowed) line od EPR under supposition that both components of *E*-symmetrical doublet and *A*-symmetrical quartet have Gaussian shape, green solid curve is superposition of basic and satellite lines. Basic line is superposition of component of *A*-symmetrical quartet of Gaussian shape,and component of *E*-symmetrical doublet described by two components — Lorentz and Gaussian shape with relative contributions into intensity 0.59 and 0.41, respectively. The spectrum of the satellites is modeled by superposition of two Gaussian resonance curves. (*b*) Modeling of the first derivative of absorption. Designations for the experimental and calculated results correspond to above described for the absorption line.

HCO in solid CO was modeled by Lorentz lines, and in Ar — by Gaussian lines [10]. This depends, obviously, on nature of interaction between radical and matrix. It is reasonable to assume that matrix of linear molecules, such as CO, has a certain influence on the orientational motion of the formyl radical and, through this interaction — on the shape of EPR spectrum of HCO, which is characterized by significant anisotropy of both the UFS tensor and g-tensor. E-symmetrical doublet of spectrum CH_3 is characterized by higher anisotropy of parameters as compared to A-symmetrical quartet [11] and stronger interaction with matrix environment. These features result in occurrence and observation of the nonrotating radicals and lower microwave saturation E-symmetrical lines [11]. It is known [12] that in solid CH_4 quarter of molecule are orientationally disordered and are in the symmetry field O_h, and three-quarter of molecules are oriented and arranged in the matrix cells of symmetry D_{2d}. Presumably, inteaction of E-symmetrical radicals with two types of matrix molecules of methane determines the presence of homogeneous and heterogeneous broadening of doublet lines. Earlier the homogeneous broadening of the oscillation-rotation spectrum CH_3 in helium nanodrops was explained [13] under model of angulones by link of its angular moment with collective excitations of the matrix environment.

So, increased relative intensity of satellite lines as compared to the expected for the random orientation, like features of shape of allowed lines of hyperfine components, indicate the link of orientational movement of stabilized in solid CH_4 methyl radical and neighboring matrix molecules. Further progress in study of this phenomenon was achieved by EPR-study of samples in wide temperature range above helium temperatures.

Conflict of interest

The author declares that he has no conflict of interest.

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Translated by I.Mazurov