

Low-temperature matrix effects on orientational motion of Methyl radical trapped in gas solids: Angular tunneling vs. libration



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ABSTRACT

EPR investigation of the lineshape of matrix-isolated methyl radical, CH₃, spectra recorded in solid N₂O and CO₂ was carried out. Reversible temperature-dependent line width anisotropy was observed in both matrices. This effect is a fingerprint of the extra-slow radical rotation about the in-plane C₂ axes. The rotation was found to be anisotropic and closely correlated to the orientational dynamics of the matrix molecules. It was suggested that a recently discovered “hopping precession” effect of matrix molecules in solid CO₂ is a common feature of matrices of the linear molecules CO, N₂O, and CO₂. A new low-temperature matrix effect, referred to as “libration trap”, was proposed which accounts for the changing CH₃ reorientational motion about the radical C₃-axis from rotation to libration. Temperature dependence of the intensity of the EPR satellites produced by these nonrotating—but librating methyls was presented. This allowed for a rough estimation of the rotation hindering potential due to correlation mismatch between the radical and the nearest matrix molecules' librations.

1. Introduction

EPR investigation of methyl radical trapped in low temperature matrices dates back to the late 1950s. The first experimental studies were performed by Jen et al. [1] and Smaller and Matheson [2] on CH₃ in solid methane, CH₄. The characteristic spectrum of the four hyperfine lines that they observed required a theoretical approach in order to be interpreted. The first step toward that goal was achieved by McConnell and Chesnut [3] who developed a theory for isotropic hyperfine interactions in π -electron radicals applicable to CH₃. McConnell was also the first to bring attention to rotation—nuclear spin coupling and its effect on the EPR line shape for CH₃ radical trapped at low temperatures [4]. The anisotropic EPR interactions in π -electron radicals were addressed theoretically for the first time by McConnell and Strathdee [5]. The authors criticized the unsatisfactory amount of experimental work on measurements of anisotropic proton hyperfine interactions in organic solids. This situation did not change until the observation of an anisotropically split hyperfine EPR of methyl radical isolated in solid CO matrix [6]. However, the anisotropy in methyl radical is partially averaged by the radical reorientation about the three-fold, C₃, and two-fold, C₂, axes. The residual anisotropy obtained from the EPR line shape is,

therefore, a very important feature providing information for the radical rotation dynamics.

A thorough review of the literature demonstrates very different treatments of methyl radical orientational motion in solids: from CH₃ which “may rotate in argon matrix” [7], according to infrared and ultraviolet data, to “no evidence for rotation of CH₃” found for the radical in para -H₂ [8]. A 3D, free quantum-rotor motional model was found consistent with high-resolution experimental EPR on methyl radical isotopomer combinations in solid Ar [9]. This approach was a generalization considering the interaction of the electronic subsystem with symmetric nuclear groups, including the effect of the nuclear statistics. The Pauli principle, in combination with D₃ point-group symmetry of methyl, resulted in an interesting exclusion of EPR transitions for both the proton and the deuteron methyl rotor. For example, the fully symmetric nuclear state of the ground rotational state applicable to the protons as fermions in CH₃ gave the well-known 1:1:1:1 quartet instead of the classical 1:3:3:1 intensity distribution. In addition, the only possible anti-symmetric ground nuclear spin-rotational state applied for the deuterons as bosons in CD₃ supported the experimentally obtained unexpected EPR singlet at liquid helium temperature, instead of the complicated, classical binomial multiplet [9]. The inconsistency of

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accepting symmetric proton and antisymmetric deuteron spin-rotation states with respect to exchange of identical Fermions and Bosons, respectively, is deceiving. It depends on the antisymmetry of the electronic degrees of freedom in methyl radical isotopomers, conforming to the correct overall symmetry [10] of the system.

High-resolution EPR spectroscopy of methyl and close inspection of the residual anisotropy turned out to be a powerful tool in resolving the above rotation's feasibility problem of methyl in different matrices [11–16]. New experimental findings on EPR of CH₃ radicals in solid CO matrix [17] revealed a complex rotational motion of the radical in the *E*-symmetry state at liquid helium temperatures including extra-slow anisotropic reorientation about the C₂ axes. However, the *A*-symmetry CH₃ radicals in CO performed isotropic C₂-rotation. Subsequently, the anisotropic rotation was also observed for the *A*-symmetry state of CH₃ in CO₂ solid [18].

The following achievements of the present study give new insight into the possible mechanisms of the rotation hindrance of methyl radical vs. correlated orientational motion of matrix molecules at low temperatures.

1. Experimental information is gathered on the rotation of the CO₂-stabilized CH₃ radical in the *E*-symmetry state, which is stronger coupled to the matrix surroundings compared to the *A*-state.
2. EPR study is carried out aimed at evaluating the CH₃ slow reorientation in solid nitrous oxide (N₂O) matrix. Its structure is analogous to the CO₂ matrix but with weaker interaction between matrix molecules and the isolated methyls.
3. Temperature dependence of the EPR signal intensity of the recently discovered non-rotating methyls [13,19] is obtained.

2. Experimental techniques

Both the set-up and the experimental technique used are described in detail elsewhere [20]. The solid N₂O and CO₂ were obtained by gas condensation on the thin-walled bottom of a quartz finger cooled down with liquid He vapor. The bottom was located at the center of the evacuated microwave cavity of the EPR spectrometer.

The substrate temperature during deposition was kept in the range of 16–25 K in the CH₃/N₂O experiments, and in the range of 31–39 K in the CH₃/CO₂ experiments. A gaseous CH₄:He mixture passing through a rf-discharge zone was delivered to the quartz finger bottom through a separate channel. Typically, the CH₄ admixture was 2.5–10% in the CH₃/N₂O experiments and 2–10% in the CH₃/CO₂ experiments. Based on the geometry of the deposition system and the known quantities of the gaseous flows, we estimated the whole CH₄ impurity content in the matrix to vary from 0.2 to 1% in the CH₃/N₂O experiments and from 0.17 to 1.3% in the CH₃/CO₂ experiments. Deposition time varied in different runs from 30 to 50 min in the CH₃/N₂O and CH₃/CO₂ experiments. The sample temperature was measured using Ge film on a GaAs resistance thermometer [21] supplied by the V. Lashkaryov Institute of Semiconductor Physics, and MicroSensor Company, Kiev (V. F. Mitin, MicroSensor available from <http://www.microsensor.com.ua>). The thermometer was attached to “Triton” temperature gauge (<http://terex.kiev.ua>). The spectra were simulated and analyzed using WINEPR SimFonia 1.25 software. The methyl radical EPR spectrum was simulated by superimposing a quartet and a doublet to mimic the unpaired electron interaction with the molecular F = 1/2 and 3/2 coupled nuclear spin representations.

3. Results and discussion

3.1. Extra-slow anisotropic tunneling reorientation of trapped methyl monitored by line width anisotropy

As opposed to the CO-matrix, the EPR line shape of CH₃ radical in solid CO₂ reveals line width anisotropy not only for the *E*-line doublet but also for the *A*-line quartet. This anisotropy turned out to be temperature

dependent (as is clearly seen from Fig. 1) showing the two central lines of the composite spectrum of Fig. 2 in Dmitriev et al. [18], where the temperature dependence of the two outer lines of the same CH₃ spectrum in solid CO₂ was investigated.

These outer lines are exclusively due to the *A*-quartet and demonstrate the drastic line width anisotropy variation of the *A*-line with sample temperature. The same effect for the shape of the *E*-line is also seen in Fig. 1.

The parallel and perpendicular components, ΔH_{\parallel} and ΔH_{\perp} , respectively, of assumed axial line width tensors for both the *A*- and *E*-states of the CH₃/CO₂ system are plotted vs. temperature in Fig. 2a and b, assuming inhomogeneously broadened EPR transitions.

Fig. 2a and b suggest a nearly monotonic decrease of the perpendicular line width component with increasing temperature. On the other hand, the parallel component is less sensitive to temperature variation but changes in a more complicated fashion, involving a shallow minimum. In particular, it decreases in the beginning smoothly with temperature and after the minimum a weak local maximum appears before a final stabilized section.

The temperature variation of the isotropic line width, defined as $\Delta H_{iso} = (\Delta H_{\parallel} + 2 \Delta H_{\perp})/3$ [22], is plotted in Fig. 3. The *E*-lines are somewhat broader than the *A*-lines, suggesting stronger coupling of the radical *E*-state to the matrix surroundings. However, this difference is not as prominent as in the case of solid CO [17]. One more observation verifying the relatively stronger matrix *E*-state interaction is revealed by the greater temperature, ca. 70 K, where the width for the *E*-state becomes approximately constant, compared to about 55 K for the *A*-state.

Close inspection of the EPR line shape of CH₃ in solid N₂O (see Fig. 4) reveals line width tensor anisotropy [23]. It presents the temperature

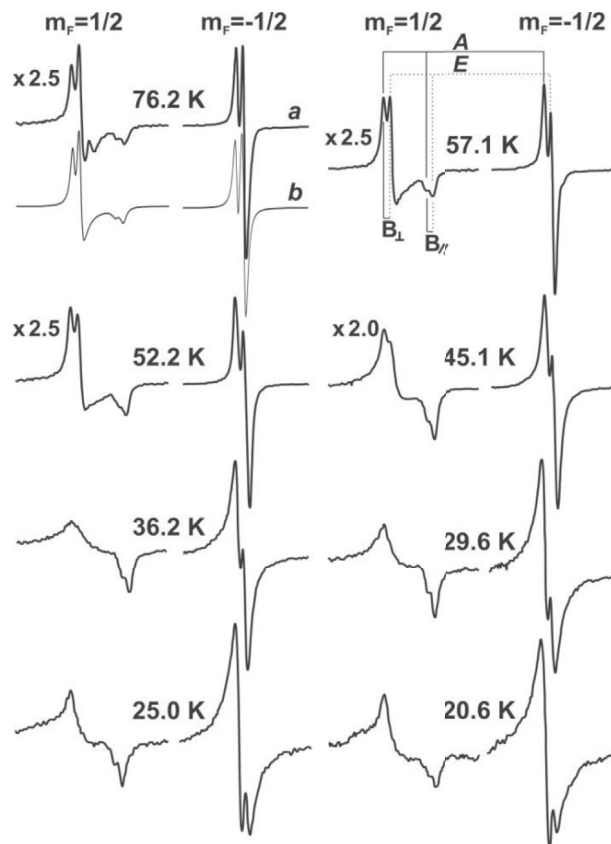


Fig. 1. Experimental EPR spectrum of CH₃ in solid CO₂ recorded at various sample temperatures. The figure shows the observed temperature dependence of the shape of the two central $m_F = \pm 1/2$ components which comprise a superposition of the *A*- and *E*-transitions. In the spectrum at 76.2 K, two sets of data are present: a—experimental curves and b—simulation.

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