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Quantum rotor in solid gases: matrix effects on EPR

Our study(a) deals with the methyl radical – the simplest organic radical, which is often observed as a transient intermediate species in chemical reactions. Consequently, it has been widely studied both theoretically and experimentally through decades.

Key words: Quantum rotor matrix, radical chemical reaction

Ю. А. Дмитриев, В.Д. Мельников, К.Г. Стуров, М.А. Туманова
Квантовый ротор в плотных газах: матричные эффекты по ЭПР

Наше исследование имеет дело с метил радикалом – простым органическим радикалом, который часто наблюдается в переходном промежуточном виде в химических реакциях. Следовательно, он был широко изучен как теоретически, так и экспериментально в течение многих десятилетий.

Ключевые слова: квант, ротор, матрица, радикал, химическая реакция.

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Тығыз газдардағы квантты ротор: ЭПР бойынша матрицалық эффектілер

Біздің зерттеуде метил радикалдарымен қарапайым органикалық байланыспен қатысты, ол көп жағдайда химиялық реакциялардың екі өту аралығында байқалады. Демек, көптеген онжылдықтар аралығында ол кеңінен теориялық және эксперименттік тұрғыда зерттелінді.

Түйін сөздер: Квант, ротор, матрица, радикал, химиялық реакция.

Our study[a] deals with the methyl radical – the simplest organic radical, which is often observed as a transient intermediate species in chemical reactions. Consequently, it has been widely studied both theoretically and experimentally through decades. Theoretical studies of the spin density distribution showed that the radical possesses large anisotropy of the proton hyperfine coupling with three different principal values of the *hf* coupling tensor. However, in case of the free rotation, the components average out leaving an isotropic EPR spectrum. The trapped radical is another story: the methyl radical EPR spectrum lineshape depends on the radical surroundings which impose restriction on CH_3 rotation and contribute to the shifts of the EPR parameters. The residual anisotropy is a fingerprint of the interaction between the trapped radical the matrix surrounding which hinders the radical rotation. In the present report, we go through matrices of inert gases, solid para-H_2 and matrices of linear molecules to show how complex the rotation of the radical is, and how it is governed by matrix properties. The study relies on high-resolution EPR spectra of trapped CH_3 radicals.

Figure 1 evidences how closely the simulation based on the rotation model matches the experimental results. In our simulation, we started from the axially symmetrical *A* and *g*-tensor measured for CH_3 in N_2. Solid Ar and N_2 have near similar physical parameters: lattice structure, lattice constant, polarizability of the matrix particles. This similarity provides nearly equal EPR parameters, *A*- and *g*-tensors, for the trapped rigid CH_3 radical. The main exception between matrices is that the

solid N_2 is a matrix with orientation ordering and, thus, fixes the methyl radical three-fold axis at a certain direction. In that case, the radical is allowed to perform fast rotation about this axes (parallel rotation), while the reorientation about the in-plane axes (perpendicular rotation) is prohibited. As a result, the EPR spectrum takes a characteristic lineshape, Figure 2.
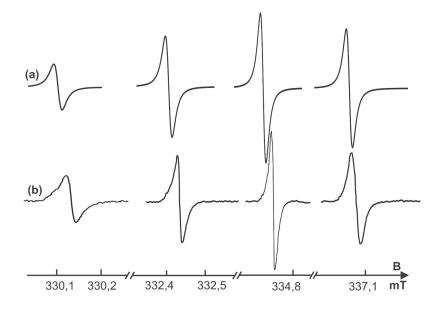

Figure 1. EPR spectrum of CH_3 in solid Ar. (a) an *EasySpin* simulation with parameters as follows: $A_\perp = -2.350\,\text{mT}$, $A_{//} = -2.252\,\text{mT}$, $g_\perp = 2.00262$, $g_{//} = 2.00225$, $\tau_\perp = 14\,\text{ns}$, $\tau_{//} = 1\,\text{ps}$. Here, $\tau_\perp$ and $\tau_{//}$ are correlation rimes for the perpendicular and parallel rotations, respectively (see the text for detail). (b) the experimental spectrum for CH_3 in solid Ar at 4.2 K.
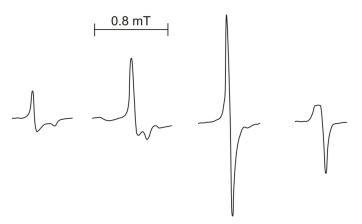

Figure 2 – Axially symmetrical EPR spectrum for CH_3 in solid CO obtained at 4.2 K. This spectrum is characteristic of CH_3 in matrices with orientation ordering, N_2, CO, N_2O, CO_2.

If a slow perpendicular rotation is allowed, the spectrum lineshape transforms into that one depicted in Figure 1.

Based on our finding, one may think of a new technique of studying the structural phase transition, orientational order-disorder, in solid gas films at a variety of conditions and on a variety of surfaces using the trapped CH_3 radical as a probe. This technique may provide insight into the structure dynamics at the microscopic level which is poorly

understood so far. In order to demonstrate potentials of the idea, we launch an investigation of N_2-Ar solid mixture based on tracking the EPR spectrum shape of the trapped CH_3 radicals. The first results clearly show the order-disorder transition depending on the Ar impurity content and sample temperature. We also suggest new insight into the structure peculiarities of the quench-condensed films of solid Kr which relies on the peculiar EPR shape of isolated CH_3.