ROTATION AND MATRIX EFFECTS ON THE EPR SPECTRA OF METHYL RADICALS TRAPPED IN GAS SOLIDS

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A study is presented on EPR spectra of methyl radicals, CH_3, matrix-isolated in gas solids at liquid helium temperatures. It was shown very recently [b] that the peculiar features of the trapped methyl rotor are attributed to the quantum effects of inertial rotary motion and its coupling to the nuclear-spin of the radical. Here, we report an investigation of the spectrum saturation behaviour and present a qualitative consideration of the spectrum anisotropy found earlier. However the broadening is by far smaller than in the expected powder of a fully anisotropic radical with rhombic hf-interaction and g-tensor anisotropy in the solid state. It is present as an asymmetric lineshape of the basic lowest rotational level EPR quartet with cross-relaxation due to the combination of the above mentioned hf interaction with the anisotropic Zeeman one. Splitting of the relatively sharp lines is also observed due to these interactions as well as due to the superimposition of the spectra of the CH_3 radical in other possible sites and/ or defects of the solid Kr-matrix, as well as from the first nontrivial rotational level. This is actually the only indication of the matrix interaction with the methyl radical which seems otherwise to perform almost free $3D$ rotation in the voids of the more or less "inert" matrix. Of course the basic reason for this behaviour is partially due to the insufficient transfer of thermal energy from the "lattice" to the radical motional degrees of freedom at these low temperatures of the experiments, between 1.5 and 5 K. We give prove that the anisotropy is governed, for the most part, by the repulsion interaction between the CH_3 radical and a matrix particle, while a matrix shift of the methyl hyperfine coupling constant is linked to both the repulsion and the attraction interactions.

[a] Support by Russian Foundation for Basic Research under grant 08-02-90409-Ukr_a is gratefully acknowledged

[b] Nikolas P. Benetis and Yurij Dmitriev *J. Phys.: Condens. Matter* **21**(10), 103201 March 2009.