

## HYPERFINE MATRIX SHIFT AND EPR-LINESHAPE ANISOTROPY OF METHYL RADICALS IN SOLID NE, AR, KR AND P-H<sub>2</sub> MATRICES

YURIJ A. DMITRIEV<sup>a</sup>, *Ioffe Physical-Technical Institute, 26 Politekhnicheskaya str., 194021 St. Petersburg, Russia;* and NIKOLAS-PLOUTARCH BENETIS, *Department of Pollution Control, Technological Educational Institution, TEI, West Macedonia, Kozani 501 00, Greece.*

Earlier studies have shown that pure quantum mechanical effects of the “light” methyl radical at low temperature minimize the anisotropy of CW EPR spectra to a high resolution character while new experiments under different conditions display greater EPR anisotropy. In this work the effects of the solid H<sub>2</sub> quantum matrix and three other typical inert-gas solid matrices on the *hfi* (hyperfine interaction) constant of trapped methyl radicals, usually called matrix shifts, are studied in some detail. Experimental EPR data at liquid-He temperatures were used to explore the dependence of the broadening and the spectral anisotropy of the hosted methyl radicals. An attempt was made to correlate the experimental spectral anisotropy data to matrix-radical interaction. Models relating the anisotropy and the matrix shift of the hyperfine (*hf*) coupling constant to the van der-Waals (*vdW*) attraction and / or to the Pauli repulsion between the host-matrix molecules and the methyl radical showed that both must be involved to explain the matrix shift while the Pauli repulsion is the major source for the extra anisotropy. The present work defines a quantitative measure of the methyl spectrum anisotropy and assigns a significantly greater value to the Ne matrix than to the quantum p-H<sub>2</sub> matrix due to the enhanced motional freedom in the latter. On the contrary, depending on the closer radical-matrix approach the magnitude of the hf interaction of the methyl radical in the Ne matrix was greater compared to that of p-H<sub>2</sub>. Here, we also report new experimental results for EPR of CH<sub>3</sub> radicals in Ne, Ar and Kr matrices at temperatures above 4.2 K. Higher sample temperatures make possible EPR observation of higher CH<sub>3</sub> rotational states. Based on the experimental results, the hindrance of the radical rotation in  $J = 1$  state is discussed.

---

<sup>a</sup>Support by Russian Foundation for Basic Research under grant 08-02-90409-Ukr\_a is gratefully acknowledged