

## EXPERIMENTAL AND THEORETICAL ANALYSIS OF THE INTER- AND INTRA-MOLECULAR DYNAMICS OF FORMYL RADICAL TRAPPED IN SOLID CO

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A comparative experimental and theoretical EPR study of HCO and DCO radicals, stabilized in solid CO at the liquid helium temperatures, revealed the crucial role the radical inter- and intra-molecular motions play in the spin-Hamiltonian parameters and spectral line-shapes. The HCO and, especially, DCO spectra of the highest resolution made possible thorough comparison between the experimental results and theoretical EPR spectra obtained using a variety theoretical methods.

The effect from vibrational, rotational, and librational motion observed in the molecular states of formyl as a probe under low-temperature CO matrix isolation condition was obtained by motional averaging and revealed the clear proton isotope effect in the spectrum shape anisotropy using both classical and quantum approaches.

As the rovibrational/librational averaging of the EPR magnetic parameters of formyl is not incorporated in standard quantum chemistry calculations, a significantly smaller Fermi contact interaction is obtained for the lighter hydrogen nucleus in the HCO isotopomer compared to experimental values in solid CO matrix at cryogenic temperatures. However, no measurable effect of this kind was detected for the deuterated DCO formyl under identical considerations. This isotope effect is discernible by the disagreement of the theoretical gyromagnetic ratios of the H/D nuclei in the quantum mechanical computations of the Fermi contact interaction.