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Pseudo-rotation versus rotational diffusion in the ligand exchange 2D-IR spectra of iron pentacarbonyl

Wednesday, June 25, 2025 10:20 AM (20 minutes)

We re-visit the ligand exchange dynamics in $Fe(CO)_5$, a textbook example of fluxionality or Berry pseudo rotation, by high-resolution polarization-dependent 2D-IR spectroscopy. Coupling maps at short waiting times reveal detailed information about the anharmonic structure: a very small negative coupling between the IR-active CO stretch modes A2′′ and E′ and distinct diagonal and non-diagonal anharmonicities of the degenerate mode. Waiting-time dependent measurements in a series of alkanes of different chain lengths shows that Berry pseudo rotation takes place on a 10 ps timescale with very little dependence on solvent viscosity. In contrast, the anisotropy loss is much faster than pseudo rotation in short alkanes but longer in the most viscous ones. Both processes need to be considered to understand the redistribution of vibrational excitation during a pseudo-rotation step, and hence the actual exchange rate. We will discuss the implications for the determination of the rate of ligand exchange and the transition state geometry.

References

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