

FLUXIONAL MOLECULES

Trading places

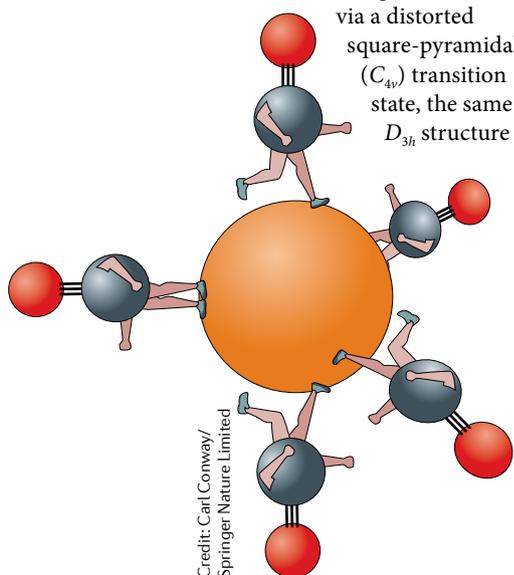


Fe(CO)₅ can now be used as a spectroscopic probe to characterize the nature of, and perhaps quantify, solvent–solute interactions



Pentacoordinate complexes can adopt a variety of structures that are often close in energy, such that the barriers associated with ligands trading places are small. This interconversion is degenerate for homoleptic species such as Fe(CO)₅, an archetypical fluxional molecule whose rapid solution-phase dynamics have long eluded spectroscopic quantification. Writing in *Organometallics*, an international team of Friedrich-Wilhelm Grevels, James Turner, Mike George, Michael Bühl and Peter Portius have now captured these dynamics by collecting infrared spectra and comparing them with simulations that account for coupled vibrations and complex line shapes.

Fe(CO)₅ is fluxional because its trigonal bipyramidal (*D*_{3h}) structure can undergo degenerate Berry pseudorotation, in which two apical ligands take up equatorial positions (and vice versa). This gives back, via a distorted square-pyramidal (*C*_{4v}) transition state, the same *D*_{3h} structure



and is called a pseudorotation because the net result is rotation about the stationary Fe–C_{equatorial} bond. Berry pseudorotation in Fe(CO)₅ is fast on the nuclear magnetic resonance timescale, with only one ¹³C signal being present even down to 103 K. Portius' team instead used infrared spectroscopy at 302–386 K — a temperature range over which Fe(CO)₅ remains intact and pseudorotation is accelerated enough to show effects on the infrared timescale. Moreover, these temperatures are amenable to using supercritical Xe as an infrared-transparent solvent that binds negligibly to both *D*_{3h} and *C*_{4v} structures so as not to change their relative energies. The spectrum collected at 302 K features bands at $\nu = 2,026 \text{ cm}^{-1}$ and $2,004 \text{ cm}^{-1}$, which are respectively assigned to asymmetric stretches of axial and equatorial CO ligands — the groups that effectively trade places in the pseudorotation. These bands do not coalesce over the temperature range, so pseudorotation cannot be faster than $\pi\Delta f/2^{1/2} \approx 1.5 \times 10^{12} \text{ s}^{-1}$ ($\Delta f = \Delta\nu$; where $c = 2.998 \times 10^{10} \text{ cm s}^{-1}$) and must be teased out from the temperature dependence of line broadening.

Simulating the spectra proved to be nontrivial and the team used Voigt functions (convolutions of Gaussian and Lorentzian distributions) to account for the many origins of line-broadening, including the uncertainty principle, Doppler effects from diffusion, as well as collisions. “We simulated the CO-stretching spectral region over the temperature range with an exchange matrix to account for

the pseudorotation mechanism, and input force-field parameters, linewidths, vibrational frequencies and pseudorotation rate constants,” says Portius. The rate constants that gave the best-fitting simulations (1.26×10^{11} – $3.15 \times 10^{11} \text{ s}^{-1}$) follow Arrhenius behaviour and afforded an activation barrier of $2.5 \text{ kcal mol}^{-1}$, a value in agreement with density functional theory predictions.

The dynamics of Fe(CO)₅ have vexed chemists but have independently been interrogated using 2D infrared spectroscopy, whereby a vibrational mode is populated with a fast pulse, and, following a delay, an absorption spectrum shows how energy is transferred to other modes. If one varies not only the excitation pulse wavelength but also the delay time, the changes in energy transfer observed with this new technique can unravel dynamics. In comparison, Portius' study shows how 1D infrared experiments, in combination with careful spectral simulations, afford a more accessible and generalizable approach to challenging problems. Further, by using a solvent that preferentially interacts with one geometry of Fe(CO)₅ (for example, by binding the *C*_{4v}-symmetric form to give a distorted octahedron), it becomes possible to learn about these interactions through the variable-temperature infrared approach. “Our much-improved understanding of the pseudorotation mechanism means that Fe(CO)₅ can now be used as a spectroscopic probe to characterize the nature of, and perhaps quantify, solvent–solute interactions in a range of media,” predicts Portius.

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ORIGINAL ARTICLE Portius, P. et al. Structure and dynamics of iron pentacarbonyl. *Organometallics* **38**, 4288–4297 (2019)