QUANTUM TUNNELING IN A DOUBLE-DECKER MOLECULAR CAROUSEL

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Metallocenes featuring two nearly parallel units that rotate in relation to one another around a metal center are often regarded as prototypes of molecular carousels.[1] Unsubstituted ferrocene is the simplest and the best-known archetype of molecular carousels among metallocenes. In ferrocene-based rotors, cyclopentadienyl rings can rotate around the Fe(II) metallic center into both staggered and eclipsed configurations, with an energy barrier that depends on the inserted substituents on the rings. For instance, the insertion of bulky groups, such as *tert*-butyl substituent, substantially increases the rotation barrier,[2] whereas the introduction of phenyl substituents leads to an unexpected concerted rotary motion.[3] Previous gas-phase investigations have shown that the intramolecular rotary motion in disubstituted ferrocene derivatives can be induced by protonation and deprotonation of carboxylate moieties, through which *trans* and *cis* conformations are selectively locked.[4]

In recent attempts to understand the intramolecular dynamics in metallocene molecular carousels using rotational spectroscopy, we observed spectral signatures of quantum tunneling emerging in a ferrocene-based rotary system in locked staggered and eclipsed conformations. In this contribution, we will present the results of our broadband microwave experiments, and discuss our strategy for analyzing the rotational spectra of a disubstituted ferrocene derivative using complementary quantum chemistry calculations.

References:

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