Interaction of formic acid with carbon monoxide and its effect on the tunneling driven conformational dynamics

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Quantum mechanical tunneling (QMT) is a fundamental phenomenon with implications for biochemistry, combustion chemistry, chemical catalysis, and interstellar chemistry.[1] QMT can affect the reactivity and selectivity of chemical reactions and tunneling control has emerged as a new reactivity paradigm in chemistry. [2] One of the main challenges regarding QMT is how the phenomenon can be exploited in chemical synthesis and other applications. One possible route for affecting the outcome of QMT driven reactions and conformational processes is through molecular interactions.

Complexes of formic acid (FA) with carbon monoxide (CO) were studied experimentally and computationally. Structures of the *trans*-FA···CO complex were deposited in cryogenic inert matrices and identified by infrared spectroscopy. Higher energy *cis*-FA···CO complexes were prepared by selective narrowband infrared light excitation of the *trans*-FA conformer in the *trans*-FA···CO complexes. [3,4] The structure, energetics, and vibrational spectra of the complexes were calculated at different levels of theory. The *cis*-FA···CO complex structures decay back to the *trans*-FA···CO structures via a tunneling driven conformational process. The effect of complexation on the tunneling lifetime of *cis*-FA is discussed and compared with the lifetime of *cis*-FA prepared in carbon monoxide matrices.

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