NEW JET-COOLED VIBRATIONAL SPECTROSCOPIC BENCHMARK DATA OF THE CYCLIC DIMER AND TRIMER OF FORMIC ACID

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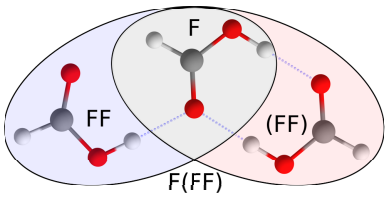

Using well-established FTIR and Raman jet spectroscopic set-ups, the gas phase vibrational database of the cyclic formic acid dimer, (FF), has been reviewed and updated for the slow fingerprint vibrations [below 1500 cm^{-1}] of the main and its three symmetrically deuterated isotopologues.[a] Experimental benchmarks validate the popular second-order vibrational perturbation theory approach in combination with high-level [hybrid] force fields which is shown to provide accurate predictions for moderate excitations of the intermolecular van der Waals[b] and intramolecular fingerprint vibrations[a] of (FF). The new and extended benchmark-quality database of (FF) is particularly useful to guide recent efforts[c] to accurately model the 24-dimensional vibrational dynamics of this prototypical model system in a 'bottom-up' approach. As a byproduct, the number of assigned vibrational fundamentals [and selected overtone bands] of the vacuum-isolated formic acid trimer, F(FF), has been drastically increased.[a] Since the polar dimer, FF, is a fragment of the trimer, the experimentally validated theoretical description of F(FF) promises to provide reliable spectral predictions for future gas phase spectroscopic searches of FF.

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[a] A. Nejad, K. A. E. Meyer, F. Kollipost, Z. Xue, M. A. Suhm , *J. Chem. Phys.* **2021**, *155*, 224301 and A. Nejad, PhD thesis, submitted (2022).

[b] A. Nejad, M. A. Suhm , *J. Indian Inst. Sci.* **2020**, *100*, 5.

[c] C. Qu, J. M. Bowman, *Phys. Chem. Chem. Phys.* **2019**, *21*, 3397 and A. M. Santa Daría, G. Avila, E. Mátyus, *Phys. Chem. Chem. Phys.* **2021**, *23*, 6526.