QUARANTINED CC-STRETCHED FORMIC ACID: MOLECULAR WORK-OUT IN (SELF) ISOLATION

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Vibrational spectra of small molecules effectively probe the underlying potential energy hypersurface, which can be tested when combined with accurate anharmonic calculations.[a] Particularly suited for a performance test of quantum chemical gas phase calculations are spectra recorded in a supersonic expansion, as significant rotational cooling is achieved while the molecules or molecular clusters remain isolated in the gas phase. One of the smallest reference systems for such a benchmarking study is the formic acid monomer with its cis-$trans$-torsional isomerism.[b] Recently, new vibrational reference data on the stretching vibrations of all four H/D isotopologues of the higher-energy cis-conformer were provided via the combination of Raman jet spectroscopy with thermal excitation.[c] Another very interesting carboxylic acid for such a study is the smallest acetylenic acid, HCC-COOH, whose cis- and $trans$-rotamers will be discussed in this contribution. Of particular interest are two almost isoenergetic $trans$-fundamentals of different symmetry which are shown to be a particularly useful benchmarking target, but also the dimers of the CC-stretched formic acid prove to be an insightful reference system for benchmarking.[d]

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