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# Gas phase structures of small alkanes by femtosecond rotational Raman coherence spectroscopy and ab initio calculations

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The gas phase rotational motion of the all trans alkanes butane to octane has been measured in real time using femtosecond (fs) time resolved rotational Raman rotational coherence spectroscopy (RR-RCS) at two temperatures T=160 and 295 K. Four-wave mixing transients are recorded over times up to 5 ns. The method probes the rotation of non-polar (and polar) gas phase molecules with fs time resolution. In addition to the dominant RCS signals of the lowest-energy all-trans form, for n-pentane to n-octane the rotational recurrences of several low energy gauche rotamers are also observed in the room temperature T=295 K gas-cell experiments, Due to large differences in structure, the contributions of the different gauche and trans rotamers to the RCS signal are clearly separated. At room temperature the low-energy thermally excited vibrational bending levels contribute up to 50% of the population for each given rotamer. Upon cooling the alkanes to 80 K in a supersonic jet, almost all the gauche rotamers and the thermally excited low frequency bending vibrations relax to the all trans v'=0 levels.
The supersonic jet measurements yield accurate B0 rotational constants. Combining these B0 with the results of all-electron coupled-cluster CCSD(T) calculations, the intermolecular distances can be predicted.

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