Intramolecular Processes and High-Resolution Cavity Ring-Down Spectroscopy of Supersonic Jet Expansions

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The general goal of our investigations is to understand primary molecular processes on different time scales with the help of high-resolution spectroscopy [1]. The density and complexity of such spectra of polyatomic molecules makes the assignment of transitions and the search for information pertaining to molecular dynamics beyond this assignment complex, requiring new developments in experimental techniques.
The coupling of the continuous wave (cw) - cavity ring-down (CRD) spectroscopy and the pulsed supersonic jet expansion techniques has the advantage of combining very high resolution, extreme sensitivity, and very low temperature for nearly isolated systems. This simplifies the spectrum and also reduces the Doppler width of rovibrational transitions, making it possible to precisely characterize their line shapes. The coupling of these two techniques as well as combining with FTIR spectroscopy was developed some years ago in our group for the investigation of combination and overtone bands in the near infrared region (reviewed in [2]).
Recent results on isolated molecules like methane [3], its isotopomers [4] and water [5], as well as results pertaining to hydrogen-bonded clusters of hydrogen fluoride [6] will illustrate how data of "stationary" spectroscopy, like the integrated absorption cross section, the linewidth or the patterns of rovibrational transitions can be used to investigate dynamics on time scales from femtoseconds to seconds. The molecular processes that will be discussed are intramolecular energy flow, and nuclear spin symmetry conservation and relaxation.

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