

Rotational Raman coherence spectroscopy: Determining accurate structures of non-polar molecules

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Femtosecond time-resolved rotational Raman four-wave mixing (fs-RR-FWM) is a background-free rotational coherence spectroscopic technique. Broadband Raman scattering using nearly transform-limited fs pulses with a spectral bandwidth of 40-120 cm⁻¹ is employed to cover the range of $v''=0$ rotational Raman transitions without exciting vibrational Raman transitions to low-lying vibrational states [1].

By observing rotational recurrences during delay times up to several ns, the ground-state rotational and centrifugal constants can be obtained with an accuracy that only depends on the number of recurrences observed. Current typical relative accuracies are 10⁻⁶ to 10⁻⁷.

Unlike other RCS techniques, RR-FWM does not depend on the existence of bound excited electronic states. In contrast to microwave spectroscopy, the existence of a molecular dipole moment is not required. Useful RCS spectra can be obtained in gas cells (down to a few mbar pressure) or even in supersonic jet expansions.

Following an introduction to the fs-RR-FWM rotational coherence method and the experimental setup, current experiments on nonpolar cycloalkanes (cyclopentane, cyclohexane) and *n*-alkanes will be discussed.

[1] H. M. Frey, D. Kumpli, S. Lobsiger and S. Leutwyler, *High-Resolution Rotational Raman Coherence Spectroscopy with Femtosecond Pulses*, in *Handbook of High-Resolution Spectroscopy*, Vol. 2, Eds. M. Quack and F. Merkt (Wiley, 2011) pp. 1237-1265.