FEMTOSECOND ROTATIONAL RAMAN FOUR-WAVE MIXING SPECTROSCOPY

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Femtosecond time-resolved rotational Raman four-wave mixing (fs-RR-FWM) is a background-free rotational coherence spectroscopic (RCS) technique. Broadband rotational Raman scattering is achieved using fs pulses with a typical spectral bandwidth of 40-120 cm^{-1}, thereby covering the range of rotational Raman transitions without exciting low-lying vibrational Raman bands. This allows the direct determination of the ground state rotational and centrifugal constants. Unlike other RCS techniques, RR-FWM does not depend on the existence of bound excited electronic states, and in contrast to microwave and millimeter-wave spectroscopy it does not require the existence of a molecular dipole moment. Thus, fs-RR-FWM can be generally applied for the determination of the rotational constants of vibrational ground states and of low-lying vibrational states of nonpolar gas-phase molecules with a relative accuracy of $\sim 10^{-7}$.
After an introduction into the method and experimental setups (both gas-cell and supersonic jet), fs-RR-FWM rotational coherence measurements of cycloalkanes (cyclopropane, cyclopentane and cyclohexane) and n-alkanes will be discussed.