

NONLINEAR TIME-DOMAIN CRYOGENIC ION VIBRATIONAL SPECTROSCOPY WITH ULTRAFAST INFRARED PULSES

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Nonlinear infrared spectroscopy in condensed phases offers valuable structural and dynamical information, but can be challenging to interpret due to factors like spectral congestion, solvent background, and low sensitivity. Cryogenic Ion Vibrational Spectroscopy (CIVS) overcomes some of these challenges by measuring infrared spectra of isolated ions quenched into their lowest-energy configurations. Spectra must be recorded indirectly using an action response, typically the photodissociation of weakly bound “tag” molecules like N₂. Traditionally, CIVS employs tunable single-color laser sources with few-cm⁻¹ bandwidth and ns pulse durations. The combination of ultrafast laser sources with the sensitivity of CIVS presents an exciting new platform to directly probe vibrational dynamics in complex molecular ion systems. Here, the instrumentation and methodology for time-resolved CIVS will be discussed, and preliminary nonlinear (pump-probe) spectra of N₂-tagged tris(acetonitrile)tricarbonyl rhenium(I) (Re(CO)₃(CH₃CN)₃⁺·N₂) will be presented. The pump-probe experiments capture the bleaching signals of the asymmetric and symmetric carbonyl stretching modes. Excited-state absorption features are not observed, consistent with the expected Feynman pathways and previous action-based nonlinear measurements. The intensities of the two carbonyl stretch transitions oscillate with pump-probe delay time with a period equal to the energy difference between the transitions, demonstrating coherent coupling between the modes. These studies show the potential of combining CIVS with ultrafast sources into a single platform. This technique is expected to be extended to two-dimensional nonlinear spectroscopy and other systems of chemical and biological interest.