

Mapping the Evolution of the Coherent Vibrational Wavepacket of Molecules

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Synopsis evolution of the coherent vibrational wavepacket in photoexcited 2,4-difluorophenol and pyrimidine.

The energy flow of a coherent vibrational wavepacket, which is created by coherent excitation of the neighboring vibrational eigenstates, is manifested as quantum beat-modulated decays. The beats arise from quantum interferences among the superposition eigenstates.

The evolution of the coherent vibrational wavepacket in photoexcited 2,4-difluorophenol and its resulting energy flow are visualized by time-resolved ion yield (TR-IY) spectroscopy combined with photoelectron imaging. At the particular probe wavelengths, the exponential decay profiles of the parent ion are superimposed by the pronounced quantum beats. The observed beats correspond to the progression in the out-of-plane bent motion. The effective detection of the beats has strong dependence on the probing process, revealing the nonplanar structure of 2,4-difluorophenol on the lowest excited singlet electronic state (S1) but planar structure on the cationic ground state (D0), which are confirmed by the theoretical calculations. When the beats cannot be observed by the ion yield spectroscopy with a 400 nm probe, the time-energy map of the photoelectron intensity reveals a periodic change of the vibrational wavepacket between the planar and nonplanar geometry. The beating frequency determined by the photoelectron intensity is in good agreement with the parent ion yield.

The vibrational energy flow between 6a1...6b2 Fermi resonances in the S1 state of pyrimidine has been directly tracked by the femtosecond time-resolved mass spectroscopy coupled with photoelectron imaging. The temporal evolution of the coherent vibrational wavepacket prepared by a 315.3 nm laser pulse, with a broad bandwidth of 205 cm⁻¹, is directly visualized by the observed beats superimposed on the time-dependence of the parent ion yield and the specific photoelectron peak intensities. The oscillation frequencies (56 cm⁻¹) of the ion yield and the PKE peaks are in excellent accord with the energy separation between 6a1 and 6b2. Such an experiment, in which the PKE peaks corresponding to different vibrational modes

exhibits the reverse phase, suggests an efficient method of tracking the vibrational energy flow in excited states, such as IVR.

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