

## ULTRAFAST COHERENT DISSOCIATION DYNAMICS IN NITROTOLUENE RADICAL CATIONS

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The ultrafast dynamics of polyatomic radical cations contribute to important processes including initiation of detonation in energetic molecules, radiation-induced DNA damage, and chemical reactions in the upper atmosphere and space. Probing these dynamics in the gas phase is challenging due to the rapid dissociation of many polyatomic radical cations following electron removal. This presentation will discuss how the pump-probe technique of femtosecond time-resolved mass spectrometry (FTRMS) can be a powerful tool for understanding time-resolved vibrational and dissociation dynamics of isolated radical cations and will highlight recent results in our laboratory on 2-, 3-, and 4-nitrotoluene (NT), which serve as model systems for nitroaromatic explosives such as TNT. Our experiments use strong-field, near-infrared (1200–1600 nm) pulses to induce adiabatic tunneling ionization, which prepares a large population of radical cations in the ground state that are amenable to subsequent optical excitation. The resulting electronically cold radical cation is typically prepared in a coherent superposition of highly excited vibrational states, i.e., as a nuclear “wave packet”. Excitation of the wave packet by the probe pulse at particular time delays accesses electronic excited states that lead to dissociation, thereby resulting in oscillations in the ion yields of the parent and fragment ions as a function of pump-probe delay. These coherent dynamics drive C–NO<sub>2</sub> bond dissociation in all three NT isomers, with each isomer exhibiting a distinct oscillation period depending on the coherently excited vibrational mode. The proximity of the NO<sub>2</sub> and CH<sub>3</sub> moieties in 2-NT also enable a hydrogen atom transfer reaction in the 2-NT cation that proceeds within  $\sim 20 - 60$  fs and preserves the initially prepared vibrational coherence, which demonstrates that coherent vibrational dynamics can continue following an intramolecular rearrangement reaction.