2019

Coherent vibrational and dissociation dynamics of polyatomic radical cations

Katharine M. Tibbetts

Follow this and additional works at: https://scholarscompass.vcu.edu/chem_pubs

Part of the Chemistry Commons
Coherent vibrational and dissociation dynamics of polyatomic radical cations

Katharine Moore Tibbetts

Abstract

The ultrafast dynamics of polyatomic radical cations contribute to important processes including energy transfer in photovoltaics, electron transfer in photocatalysis, 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 polyatomic radical cations following electron removal, which arises from excess electronic excitation of the molecule during the ionization process. This Concept article introduces the reader to how the pump-probe technique of Femtosecond Time-Resolved Mass Spectrometry (FTRMS) can overcome this challenge to capture coherent vibrational dynamics on the femtosecond timescale in polyatomic radical cations and enable the analysis of their dissociation pathways. Examples of FTRMS applied to three families of polyatomic radical cations are discussed.

1 Introduction

Polyatomic radical cations play a fundamental role in many physical, chemical, and biological processes. The reactions of aromatic radical cations and hydrogen atoms contribute to the formation of complex organic molecules observed in the interstellar medium.[1] The stability of electron donor radical cations in organic photovoltaics influences the rate of charge separation and transport, and thereby the device efficiency.[2] Radical cations formed upon oxidation by photoexcited Ru(bpy)$_2^{2+}$ act as intermediates in catalytic photoredox reactions for organic synthesis applications.[3] Decomposition mechanisms in energetic materials used as explosives and propellants can be initiated by radical cations and anions.[4] In biological systems, ionizing radiation generates radical cations in the DNA sugar-phosphate backbone and nucleobases, which can ultimately lead to DNA damage and diseases such as cancer.[5] The formation of radical cations in biological antioxidants such as carotenoids and flavonoids both mitigates these damaging radiation effects and contributes to light-harvesting efficiency in photosynthesis.[6]

In these examples, the reaction dynamics of radical cations occur on ultrafast timescales ranging from nanoseconds (ns, $10^{-9}$ s) to femtoseconds
Probing these ultrafast dynamics requires “pump-probe” techniques originally developed by the Zewail group in the 1980’s. In pump-probe measurements, two or more time-delayed ultrashort laser pulses sequentially interact with a molecule: First, the “pump” pulse excites the molecule, preparing an electronically excited or radical cation state. For a pump pulse sufficiently short in duration and broad in bandwidth, multiple vibrational states with accessible Franck-Condon factors are populated simultaneously, creating a coherent superposition, or vibrational “wave packet” in the upper state. Second, a time-delayed “probe” pulse interrogates the excited molecule at a series of delay times, thereby following the wave packet relaxation and reaction dynamics along their intrinsic timescales. A number of solution-phase pump-probe studies of electron-transfer dynamics involving charge-separated states in donor-acceptor molecules exhibit clear signals of coherent vibrational wave packet motion, and some aromatic molecules undergo the same photodissociation reactions following vibrational relaxation in both solution and as isolated systems. This Concept Article illustrates how pump-probe measurements with mass spectrometric detection, called Femtosecond Time-Resolved Mass Spectrometry (FTRMS), can elucidate coherent ultrafast vibrational dynamics and unimolecular dissociation pathways in isolated polyatomic radical cations, independent of solvent effects or other intermolecular interactions.

2 Background: Probing radical cation dynamics

2.1 Excitation scheme

The FTRMS excitation scheme to measure ultrafast radical cation dynamics in a generic molecule (Figure 1) is analogous to widely-used FTRMS schemes for probing dynamics on electronic excited states in neutral molecules. In the latter experiments, the pump pulse prepares a neutral excited state, whose dynamics are interrogated by an intense time-delayed probe pulse that ionizes the excited-state molecule. This technique enables determination of excited-state lifetimes through mass spectrometric detection of changing fragment ion distributions as the pump-probe delay is scanned. To measure radical cation dynamics, the roles of the pump and probe pulses are reversed: the pump pulse ionizes the molecule to prepare the ground-state radical cation and the time-delayed probe pulse interrogates the cation dynamics by populating an electronic excited state to induce dissociation.

The excitation scheme in Figure 1 proceeds as follows: From the ground $S_0$ potential energy surface (PES), the intense pump pulse removes an electron to populate the $D_0$ PES. As with excitation to a neutral excited state, the mismatch between the equilibrium $S_0$ and $D_0$ geometries can launch a vibrational wave packet along one or more coordinates corresponding to the strongest geometric displacements. As the nuclei relax to the equilibrium $D_0$
geometry, this wave packet propagates along the D\textsubscript{0} PES, oscillating back and forth in the potential well. As the wave packet propagates on D\textsubscript{0}, it can interact with the time-delayed probe pulse and be excited to an accessible electronic excited state D\textsubscript{n}. Because the excitation probability depends on dipole coupling and probe resonance with the D\textsubscript{0} \rightarrow D\textsubscript{n} transition, if these properties vary with the position along the coherently excited coordinate on the D\textsubscript{0} PES, then the excitation probability will oscillate in time as the wave packet moves back and forth on D\textsubscript{0}. Once excited to D\textsubscript{n}, the wave packet can return to the ground state upon radiationless relaxation through a conical intersection (CoIn) connecting D\textsubscript{n} and D\textsubscript{0}. CoIns, where two or more PESs intersect and become energetically degenerate, are ubiquitous features of both neutral and ionic excited state PESs that allow electronically excited molecules to relax by nonadiabatic, or non-Born-Oppenheimer, transitions.\[11\] Relaxation through a CoIn converts electronic energy into vibrational energy, which induces dissociation. As a result, excitation of the D\textsubscript{0} wave packet to a higher D\textsubscript{n} state may be inferred by the relative yields of the parent and fragment ions in the mass spectrum recorded at a series of pump-probe delays: if probe excitation occurs, an enhanced yield of one or more fragment ions is observed, while lack of excitation results in enhanced parent molecular ion yield. Coherent vibrational dynamics on the D\textsubscript{0} surface can therefore be tracked through oscillations in parent and fragment ion yields as a function of pump-probe delay time, with the oscillation frequency corresponding to that of the excited normal mode(s). It should be noted that the physical processes of photoexcitation and photoionization are quite distinct in that the outgoing electron can remove part of the electronic coherence on a sub-femtosecond timescale during the photoionization process.\[12\] However, this situation does not appear to affect the slower nuclear dynamics based on the widespread observation of vibrational wave packet dynamics in radical cations, as discussed below.

2.2 Preparation of ground-state polyatomic radical cations

The excitation scheme depicted in Figure\[1\] requires preparation of radical cations in the ground electronic state (D\textsubscript{0}). Achieving this requirement is challenging with excitation wavelengths readily available from femtosecond laser sources. Ionization with intense 800 nm pulses from Ti:Sapphire lasers typically induces extensive fragmentation due to nonselective population of multiple cationic excited states via nonadiabatic multiphoton absorption.\[13\] Wavelength conversion into the XUV or X-ray region through high harmonic generation \[14\] or free-electron lasers \[15\] yields photon energies greatly exceeding the typical ionization potentials of polyatomic molecules in the range of \(\sim 9 - 11\) eV, which also leads to nonselective cationic excited state population. Over the last 20 years, a number of studies have found that fragmentation can be significantly reduced for intense pulses in the near-
infrared region of ∼1200 – 1600 nm. Suppressed fragmentation at these wavelengths is attributed to the increased contribution of an adiabatic ionization process that limits energy transfer to the molecule itself during ionization. In atoms, the transition from nonadiabatic to adiabatic ionization is determined by the Keldysh adiabaticity parameter $\gamma$, given by the ratio of the laser frequency $\omega_0$ to the characteristic electron tunneling frequency $\omega_t$:

$$\gamma = \frac{\omega_0}{\omega_t} = \omega_0 \frac{\sqrt{2\Delta m_e}}{eE},$$

where $\Delta$ is the ionization potential, $m_e$ is the electron mass, $e$ is the electron charge, and $E$ is the laser electric field strength. When $\gamma > 1$, the laser frequency $\omega_0$ is too high to permit electron tunneling through the electrostatic potential barrier before the electric field switches sign. This situation induces nonadiabatic absorption of many photons during ionization, where the excess absorbed energy results in nonselective population of electronic excited states in the ion ($D_n$, $n > 0$, Figure 2(a)). In contrast, the probability for electron tunneling increases when $\gamma < 1$, resulting in a greater contribution of adiabatic ionization and predominant population of the ground state ionic state ($D_0$, Figure 2(b)).

The Keldysh framework oversimplifies the ionization mechanism of polyatomic molecules by neglecting multielectron interactions. Excited ionic states can be populated by direct excitation when the photon energy exceeds the energy gap between the ground and excited ionic states and by sequential excitation over multiple optical cycles when the photon energy is lower. When the energy gap between $D_0$ and an ionic excited state is resonant with the photon energy, significant parent ion depletion can occur. Nevertheless, significantly higher parent ion yields are consistently observed in polyatomic molecules at long excitation wavelengths. As an illustration, Figure 3 shows the mass spectra of 4-nitrotoluene (4-NT) (a) and dimethyl methylphosphonate (b) recorded with 800 nm (blue) and 1500 nm (red) excitation at a peak intensity of $\sim 7 \times 10^{13}$ W cm$^{-2}$. In both molecules, the parent molecular ion (marked with a *) is the most dominant peak with 1500 nm excitation where $\gamma \sim 0.6$, while smaller fragments dominate at 800 nm excitation where $\gamma \sim 1.1$. Although the same fragments in each molecule are formed at both excitation wavelengths, the increase in parent ion yield by at least a factor of two with 1500 nm excitation indicates enhanced $D_0$ population. This large $D_0$ population increases ion yield oscillation amplitudes at least fivefold for near-infrared wavelengths as compared to 800 nm excitation, as will be illustrated below.

### 2.3 Experimental implementation

A schematic FTRMS pump-probe setup for measuring radical cation dynamics is shown in Figure 4. Concepts underlying the technique are described
here, and details on constructing FTRMS setups are reported elsewhere.\textsuperscript{26, 27} To create a pump-probe pulse pair, the initial laser pulse is first split into two replicates with a beam splitter (BS). The pump pulse is taken from the output of an optical parametric amplifier (OPA) that produces tunable 1200 – 2500 nm pulses through nonlinear frequency conversion. The probe pulse is taken from a portion of the laser output split either before (shown) or after the OPA. Splitting prior to the OPA results in 800 nm probe pulses,\textsuperscript{26} while splitting after the OPA and frequency-doubling produces tunable probe wavelengths in the region of 600 – 800 nm.\textsuperscript{27} Because the pump and probe beams both travel at the speed of light along their respective paths, the time-delay between them can be controlled by specifying the distance that each beam travels. Here, the pump path length is fixed and the probe path length is scanned by varying the position of the translation stage, such that the probe can be made to travel a shorter distance and arrive before the pump or made to travel a longer distance and arrive after the pump (as shown). The pump and probe pulses are recombined with a dichroic mirror (DC) and focused into the extraction region of the time-of-flight mass spectrometer (TOF-MS), where they interact with the gas-phase target molecule. Mass spectra are recorded at each pump-probe delay to obtain time-resolved parent and fragment ion signals. While TOF-MS detection is used here, techniques such as velocity map imaging of photoelectrons and photoions,\textsuperscript{28} photoelectron-photoion coincidence measurements,\textsuperscript{25} and transient XUV absorption spectroscopy\textsuperscript{29} could provide additional insight into the initial ionic state populations and subsequent dissociation dynamics.

3 Illustrations

Over the past decade, multiple studies have reported on coherent vibrational dynamics in radical cations of diatomics \textsuperscript{30} and small polyatomics such as CO\textsubscript{2}.\textsuperscript{31} In these small molecules, coherent oscillations in ion yields with vibrational and rotational wave packet revivals at delay times up to 30 ps are typically observed. In contrast, the presence of multiple coupled normal modes leads to fast dephasing of initially prepared vibrational wave packets in polyatomic radical cations within at most several picoseconds of the initial ionization event. Nevertheless, coherent ion yield oscillations have been observed in many classes of polyatomic radical cations including halomethanes,\textsuperscript{32, 33} 1,3-dibromopropane,\textsuperscript{34} azobenzene,\textsuperscript{35} alkyl aryl ketones,\textsuperscript{21, 36, 37} nitrotoluenes,\textsuperscript{27, 38} and methylphosphonates.\textsuperscript{22, 39} While in most cases, the ion yield oscillations are attributed to dynamics on D\textsubscript{0}, dynamics on excited ionic states have also been reported.\textsuperscript{33, 37} The following discussion presents illustrative examples from this author’s work on three classes of polyatomic molecules, focusing on the coherent vibrational
dynamics detectable with the available 800 nm or 650 nm probe pulses. It should be noted that these molecules may have additional coherently excited vibrations that would only be detected with probe wavelengths that couple to higher-lying excited states. Nevertheless, the observed large-amplitude oscillations in parent and fragment ion yields demonstrate that probing coherent vibrational dynamics by excitation to ionic excited states can drive specific dissociation pathways at selected pump-probe delays when the coupling between ground and excited ionic states is strongest. The additional slow decay dynamics present in some molecules are not discussed in detail here because their origins and interpretation are as yet unclear and still under investigation.

3.1 Acetophenone

Acetophenone is a building block of aromatic ketones, which are widely used in sunscreens due to their efficient UV spectral absorption. Acetophenone and its substituted derivatives pose a challenge to measuring radical cation dynamics due to an ionic resonance between the D$_0$ and D$_2$ states at 0.9 eV. This resonance results in significant depletion of the parent molecular ion and selective enhancement of the benzoyl ion yield when the pump wavelength is 1370 nm as compared to 1270 nm or 1500 nm (Figure 5(a)). As a result of the ionic resonance, the time-dependent yields of the parent molecular ion, benzoyl ion, and phenyl ion strongly depend on the pump wavelength (Figure 5(b)). With a 1270 nm pump, the benzoyl ion exhibits antiphase oscillations with respect to the parent ion. The large oscillation amplitude with the 1270 nm pump is consistent with enhanced population of the cation D$_0$ state due to adiabatic ionization. In contrast, a 790 nm pump produces a small parent ion yield (Figure 5(a)) and oscillation amplitudes a factor of 6 smaller than for 1270 nm excitation (Figure 5(b)), reflecting nonselective initial excited state population.

The ion yield oscillations arise from the coherent torsional motion of the acetyl group with respect to the benzene ring initiated by relaxation to a non-planar geometry following ionization (Figure 5(c)). Calculations of the ionic PESs along the phenyl-acetyl dihedral angle at the EOM-IP-CCSD/6-311+G(d) level (Figure 5(d)) indicate the excitation mechanism that forms benzoyl ion. Beginning from the S$_0$ geometry with 0° dihedral angle, the wave packet requires 325 fs to propagate along the D$_0$ surface to the 90° angle where dipole coupling between D$_0$ and D$_2$ is strongest. Therefore, the most efficient transfer to the D$_2$ state occurs when the probe is delayed by 325 fs. The D$_2$ wavepacket can relax back to the ground state through the CoIn at 180°, inducing CH$_3$ loss. While the excitation scheme in Figure 5(d) effectively describes the parent and benzoyl ion dynamics for the 1270 pump (dashed vertical lines in Figure 5(b)), the dotted vertical lines in Figure 5(b) show that the benzoyl ion oscillations are phase-shifted.
with respect to the parent when the pump wavelength is 790 nm or 1370 nm. These oscillations are attributed to a wave packet initially prepared on the D1 and/or D2 states upon resonant one-photon absorption from D0 at 1370 nm or nonadiabatic multiphoton ionization at 790 nm. Subsequent pump-probe experiments and calculations of the higher-lying ionic excited PESs indicate that a two-photon excitation from D1 and/or D2 to the manifold of close-lying D3 – D6 states results in the production of the phenyl ion and other smaller dissociation products.[37]

3.2 Nitrotoluenes

The dissociation reactions of the mononitrotoluene isomers 2-, 3-, and 4-nitrotoluene (2-, 3-, and 4-NT) model dissociation in the military explosive 2,4,6-trinitrotoluene (TNT). The three NT isomers undergo common dissociation pathways including NO2 loss, which is the primary initiator of detonation in TNT.[41] This reaction results in the formation of C7H7+ in NT radical cations, which is observed in the mass spectra of NTs taken with 1500 nm pump pulses (Figure 6(a)-(c)). The dynamics of the parent C7H7NO2+ and C7H7+ ions (Figure 6(d)-(f)) obtained with 1500 nm pump and 800 nm probe pulses display antiphase oscillations at distinct frequencies in each isomer, as seen in the fast Fourier transform (FFT) of each signal (insets).[38] The 85−90 cm−1 (∼380−460 fs period) oscillations in 4-NT (Figure 6(d)) and 2-NT (Figure 6(f)) are similar to the slow oscillations in acetophenone, suggesting that they arise from a similar torsional vibration. In contrast, the oscillations in 3-NT are nearly twice as fast, indicating coherent excitation of a distinct vibrational mode.

Density functional theory (DFT) calculations at the B3LYP/Def2-TZVPP level of the D0 PES in 4-NT and 3-NT along the C-NO2 dihedral angle (Figure 7(a)) confirm that the torsional mode can be excited upon ionization of 4-NT, but not 3-NT.[38] The PES of 4-NT radical cation exhibits a double-well structure similar to that of acetophenone radical cation (c.f., Figure 5(d)), where ionization takes place at the 0° maximum of the PES. As a result, ionization drives relaxation along the dihedral coordinate, exciting the torsional mode that was calculated at 46 cm−1 (Figure 7(b)). The PES for 3-NT radical cation exhibits a completely different structure with a large barrier to rotation, consistent with the lack of torsional excitation. Based on the calculated geometry changes between the 3-NT neutral and cation, the oscillations were assigned to the bending mode calculated at 202 cm−1 (Figure 7(c)).

Additional coherent vibrational dynamics become visible in 2-NT when the probe wavelength is shifted from 800 nm to 650 nm, resonant with a transition predicted by time-dependent DFT (TDDFT).[27] The transient parent and fragment ions signals exhibit oscillations in the first ∼1000 fs after ionization, followed by slow decay dynamics visible over the 8000 fs
measurement window (Figure 8(a)). Because the relaxation processes contributing to these slow dynamics are not yet known, this discussion focuses on the oscillatory components left after subtracting the slow dynamics (Figure 8(b)). The \( \text{C}_{7}\text{H}_{6}\text{NO}^+ \) ion yield oscillates at a distinctly faster frequency than the parent ion, as seen in the respective frequencies of 114 cm\(^{-1}\) and 91 cm\(^{-1}\) retrieved by FFT (Figure 8(c)). The \( \text{C}_{6}\text{H}_{6}\text{N}^+ \) and \( \text{C}_{5}\text{H}_{5}^+ \) fragments exhibit antiphase oscillations with respect to the parent \( \text{C}_{7}\text{H}_{7}\text{NO}_2^+ \), while the \( \text{C}_{7}\text{H}_{7}^+ \) and \( \text{C}_{5}\text{H}_{5}^+ \) oscillate with a frequency in between the parent and \( \text{C}_{7}\text{H}_{6}\text{NO}^+ \) ions.

The distinct oscillation frequencies of \( \text{C}_{7}\text{H}_{7}\text{NO}_2^+ \) and \( \text{C}_{7}\text{H}_{6}\text{NO}^+ \) are attributed to the coherent excitation of two structures of 2-NT cation.\(^{[27]}\) The \( \text{C}_{7}\text{H}_{7}\text{NO}_2^+ \) oscillations arise from the coherent torsional motion of the parent 2-NT ion structure with a computed frequency of 48 cm\(^{-1}\) (Figure 8(d)), similar to 4-NT. The faster oscillations of the \( \text{C}_{7}\text{H}_{6}\text{NO}^+ \) transient are attributed to the coherent torsional motion of the \( \text{aci} \)-nitro tautomer of 2-NT cation. This structure forms via “H-atom attack” of a methyl hydrogen to a nitro oxygen and has been a known reaction of 2-NT cation for decades.\(^{[42]}\) DFT calculations at the \( \omega\text{B97XD}/\text{CBSB7} \) level with ADMP molecular dynamics trajectories indicate a transition state barrier of 0.76 eV above the vertical IP of 2-NT and an expected reaction of \( \sim 20 - 60 \) fs after ionization.\(^{[27]}\) The \( \text{aci} \)-nitro tautomer spontaneously loses OH to form \( \text{C}_{7}\text{H}_{6}\text{NO}^+ \),\(^{[42]}\) consistent with our computations showing that \( \text{C}_{7}\text{H}_{6}\text{NO}^+ + \text{OH} \) lies 0.59 eV below the initial transition state energy.\(^{[27]}\) Based on these results, the \( \text{C}_{7}\text{H}_{6}\text{NO}^+ \) ion constitutes the mass spectral signature of the 2-NT cation \( \text{aci} \)-nitro tautomer. The three computed structures of the \( \text{aci} \)-nitro tautomer all have faster calculated torsional frequencies ranging from 61 – 87 cm\(^{-1}\) as compared to the parent 2-NT ion (Figure 8(e)), consistent with the faster observed oscillations of the associated \( \text{C}_{7}\text{H}_{6}\text{NO}^+ \) product. The coherent torsional motion in the \( \text{aci} \)-nitro tautomer indicates the preservation of initially prepared vibrational coherence after an intramolecular rearrangement reaction, which had not been previously observed in radical cations.

3.3 Organic phosphonates

The organic phosphonates dimethyl methylphosphonate (DMMP), diethyl methylphosphonate (DEMP), and diisopropyl methylphosphonate (DIMP) model both the DNA sugar-phosphate backbone and organophosphorus nerve agents such as sarin and VX. Understanding the dynamics of these organophosphorus radical cations can provide insight into initial mechanisms of radiation-induced DNA damage because one-electron oxidation of the phosphate group induces the formation of sugar radical species that can lead to single- and double-strand DNA breaks.\(^{[43]}\) The molecule DMMP provides an excellent illustration of the improved dynamics visible with FTRMS experi-
ments when using near-infrared excitation (Figure 9(a)).[22] 800 nm excitation (blue) results in noisy and barely resolvable oscillations in the time-dependent DMMP\(^+\) parent ion yield, consistent with the low parent ion signal (c.f., Figure 3). In contrast, 1200 nm (green) and 1500 nm (red) excitation produce well-resolved 45 fs oscillations (dashed lines) enhanced by a factor of 5 relative to 800 nm excitation and visible over at least 12 cycles.[22] Similar dynamics consisting of fast oscillations overlaid on slow decays are visible in DEMP and DIMP (Figure 9(b)).[39] Because these slow exponential decay components (indicated by the dark solid least-squares fit lines in the figure) have not yet been explained, the oscillatory components of the ion signals remaining after subtraction of the slow dynamics (inset labeled “residual”) are the focus of the present discussion. Analysis of these oscillatory ion signals enables the identification of the normal modes that are coherently excited upon ionization.[39]

For DMMP, DEMP, and DIMP, Figure 10 shows the oscillatory dynamics of the parent and fragment ions (left), their FFT (middle), and assigned vibrational modes (right) based on DFT calculations at the B3LYP/6-311+G* level. In DMMP (top), each fragment ion oscillates almost perfectly antiphase with the parent, indicating that excitation from a specific wave packet position on the D\(_0\) PES can induce multiple dissociation pathways. FFT of these signals produces a peak at 732 cm\(^{-1}\) and a shoulder at 610 - 650 cm\(^{-1}\), assigned to the P–C stretch and symmetric O–P–O bend, respectively. In DIMP (bottom), both the parent DIMP\(^+\) and PO\(_3\)C\(_4\)H\(_{12}\)\(^+\) oscillate in-phase with each other and antiphase to the smaller fragments, indicating that dissociation to PO\(_3\)C\(_4\)H\(_{12}\)\(^+\) occurs on D\(_0\) and the smaller fragments are formed following excitation to one or more excited states when the wave packet is at a specific position on the D\(_0\) PES. As with DMMP, FFT analysis produces two peaks that can be assigned to the P–C stretch and symmetric O–P–O bend. In contrast, DEMP (middle) exhibits almost no oscillatory dynamics after 100 fs except for a revival in the parent ion yield at \(~\)220 fs. This situation may arise from the lack of a well-defined phase relationship between the parent and fragment ions in the first 100 fs, which would suggest that excitation from D\(_0\) is not dependent on the wave packet position. FFT of the parent ion signal possibly shows a single peak visible above the noise that could be assigned to the O–P–O bend. Comparing the dynamics of the three molecules shows that the same vibrational modes are coherently excited, while each molecule exhibits distinct oscillation frequencies that can enable discrimination between fragments produced from similar molecules.[39]
4 Conclusions and Outlook

Understanding the ultrafast dynamics and dissociation mechanisms of isolated radical cations not only gives insight into their reactions in low-density environments, but also provides a baseline view of their intrinsic reactions for comparison to condensed-phase processes such as radiation-induced DNA damage and photocatalytic reactions. The technique of FTRMS with near-infrared excitation limits fragmentation of polyatomic radical cations during the ionization process, which enables unprecedented resolution of coherent nuclear dynamics on the femtosecond timescale. Combined with high-level quantum chemical calculations of cationic PESs and vibrational frequencies, FTRMS can furnish detailed pictures of coherent vibrational and dissociation dynamics in complex radical cations, as illustrated for the examples of acetophenone, nitrotoluenes, and organic phosphonates in this Concept Article. Outstanding questions regarding dissociation mechanisms in radical cations still remain, including whether other vibrations may be coherently excited, which ionic excited states are accessed to form different dissociation products, and which relaxation processes drive the slow decay dynamics observed in many molecules. Answering these questions will likely require both detailed calculations of excited ionic PESs and complementary experimental techniques in addition to FTRMS. For instance, angle-resolved imaging of photoions and photoelectrons (e.g., velocity map imaging) could provide additional information about the electronic states contributing to both the ionization and dissociation dynamics. Finally, the rapid development of commercial high-power femtosecond laser sources capable of pumping multiple OPAs could provide fully tunable probe wavelengths that enable selective coherent excitation to distinct target ionic excited states from the D_0 PES. Such tailored excitation schemes may enable coherent control over cationic dissociation pathways, thereby making the longstanding dream of “bond selective chemistry” [7] a reality.

Acknowledgements

This work was supported by the US Army Research Office through Contract W911NF-18-1-0051.

References


Figures

Figure 1: Pump-probe excitation scheme to measure radical cation dynamics.

Figure 2: Illustration of nonadiabatic (a) and adiabatic (b) ionization mechanisms.
Figure 3: Mass spectra of (a) 4-nitrotoluene and (b) dimethyl methylphosphonate taken with 800 nm excitation (blue) and 1500 nm excitation (red). The * denotes the parent molecular ion.

Figure 4: Schematic illustration of FTRMS experimental setup.
Figure 5: (a) Mass spectra and (b) time-dependent ion yields of acetophenone measured with different pump wavelengths. (c) Geometries of acetophenone at $S_0$ and $D_0$ minima with coherently excited torsional mode. (d) Computed ionic PESs with probe excitation pathway. Adapted with permission from Ref. [21]. Copyright 2014 American Chemical Society.
Figure 6: Mass spectra of (a) 4-NT, (b) 3-NT, (c) 2-NT taken with 1500 nm pump pulses. Time-dependent yields of parent molecular ion (red) and c7h7 (blue) for (d) 4-NT, (e) 3-NT, and (f) 2-NT. Adapted with permission from Ref. 38. Copyright 2018 AIP Publishing.

Figure 7: (a) D0 PESs along the C−NO2 dihedral angle for 4-NT (blue) and 3-NT (red). Coherently excited C−NO2 torsional mode in 4-NT (b) and in-plane bending of NO2 and CH3 moieties in 3-NT (c). Adapted with permission from Ref. 38. Copyright 2018 AIP Publishing.
Figure 8: (a) Time-dependent parent and fragment ion signals from 2-NT. Oscillatory components (b) and FFT (c). Dashed and dotted lines correspond to features from C\textsubscript{7}H\textsubscript{7}NO\textsubscript{2}\textsuperscript{+} and C\textsubscript{7}H\textsubscript{6}NO\textsuperscript{+}, respectively. Torsional motion of (d) 2-NT cation and (e) 2-NT aci-nitro tautomer. Adapted with permission from Ref. [27]. Copyright 2019 American Chemical Society.

Figure 9: (a) DMMP\textsuperscript{+} signals taken with pump wavelengths of 800 nm (blue), 1200 nm (green), and 1500 nm (red). Adapted from Ref. [22] with permission from the PCCP Owner Societies. (b) Ion signals of DMMP\textsuperscript{+} (red), DEMP\textsuperscript{+} (magenta), and DIMP\textsuperscript{+} (violet). The thick solid lines denote fits to a sum of three exponential decays. Adapted with permission from Ref. [39].
Figure 10: Oscillatory ion signals (left), their FFTs (middle), and coherently excited modes (right) of DMMP, DEMP, and DIMP. Adapted with permission from Ref. [39].