Charge accommodation dynamics of cluster and molecular anions produced by photo-initiated intracluster charge transfer

by

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Abstract

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Time-resolved photoelectron imaging spectroscopy is used to examine the dynamics of charge accommodation by solvent species and biomolecules upon photo-initiated intracluster charge transfer. Excitation of a charge transfer state of an iodide-complexed molecule or cluster with a UV pulse and subsequent interrogation by photodetachment with a lower energy probe enables detection of changes in photoelectron signals over hundreds of femtoseconds. Velocity map imaging detection permits simultaneous collection of electron kinetic energy (eKE) and photoelectron angular distributions that provide insight into the strength and structure of the association between the cluster or molecule and the excess electron.

Application of this methodology to iodide-containing clusters of small polar molecules such as water, methanol, and ethanol elucidates the stability and extent of intramolecular forces within a given cluster. In complexes of iodide with small solvent clusters ($\leq 10$ molecules), iodide is situated somewhat outside of the solvent network. Interaction of iodide-water clusters with a UV pulse to produce iodine and a free electron results in the partial solvation of the excess charge through hydrogen bonding interactions over hundreds of picoseconds before electron autodetachment. In contrast, methanol and ethanol cluster networks can only support the excess charge for tens of ps. Notably, stable bare water cluster anions have previously been measured with as few as two molecules, while upwards of seventy methanol molecules are necessary to stabilize an excess electron. Drawing an analogy between electron autodetachment and statistical unimolecular decay, an excited iodide-water cluster with a given number of water molecules might be expected to decay most rapidly given its significantly smaller density of states. The observation of the opposite pattern, as well as the similarity between iodide-methanol and -ethanol cluster anion lifetimes, suggests that energetics, rather than molecular structure, play a larger role in stabilizing an excess charge to autodetachment. Applying a thermionic emission model confirms this result.

The dynamics of charge accommodation are also examined for small biomolecules.
Radiative damage to DNA caused by low energy electrons is thought to originate in the attachment of an electron to a nucleobase unit of a nucleotide in the DNA double helix. Previous experiments have examined binding motifs and fragmentation patterns of transient negative ions (TNIs) of nucleobases using Rydberg electron transfer from excited noble gas atoms or collision of the nucleobase with a beam of electrons of defined energy. Here, nascent TNIs of the nucleobase uracil are created by intracluster charge transfer from a complexed iodide ion and their decay examined with time-resolved photoelectron imaging. Anions created with several hundred meV of excess energy appear as valence anions and are observed to decay biexponentially with time constants of hundreds of fs and tens of ps by iodine atom loss and autodetachment. Repetition of these experiments with uracil molecules methylated at the N1, N3, or C5 positions results in a dramatic reduction of the longer time constant. The addition of the methyl group may hasten the intramolecular vibrational energy redistribution process preceding autodetachment.

Photoelectron spectroscopy of isolated nucleobase anions has measured only the dipole-bound state (DBS) of the anion consisting of an electron weakly associated with the molecular dipole moment and very delocalized over the molecular structure. Though the valence anion has not been directly measured, the DBS has been posited to serve as a ‘doorway’ to the valence-bound state (VBS). Such a mechanism has also been proposed for nitromethane. In contrast, acetonitrile should only support a DB anion state. Examination of nascent acetonitrile and nitromethane anions excited near the vertical detachment energies of their corresponding iodide-molecule complexes indeed produces the DB acetonitrile anion, which then decays biexponentially with time constants of few and hundreds of ps by iodine atom loss and autodetachment. The nitromethane DB anion decays rapidly over hundreds of fs to form the valence anion, which decays biexponentially with time constants similar to those measured for the acetonitrile DB anion. This study marks the first direct observation of a transition from a dipole-bound anion to a valence anion and will inform future studies of iodide-nucleobase complexes.
I dedicate this dissertation to my family.
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Chapter 1. Introduction

1.1. Overview

The study of interactions of low energy electrons with molecular species provides crucial insight into solvation processes, chemical reactions, and radiative damage of biological molecules. The mechanisms by which small molecules or systems of molecules accommodate an excess charge are also of fundamental interest and represent an excellent target for pump-probe spectroscopy techniques in the gas phase.

The work described herein encompasses my efforts in the Neumark Group to understand the dynamics of charge accommodation by solvent species and small biomolecules and their analogues through the application of time-resolved photoelectron imaging (TRPEI). Chapter 1 introduces the motivation for this work and its basic principles, while Chapter 2 reviews relevant experimental techniques and instrumentation in more detail. Subsequent chapters describe the exploitation of charge-transfer-to-solvent phenomena to study excited state lifetimes of water and small alcohol clusters (Chapter 3) and investigations of the decay dynamics of transient negative ions of DNA and RNA nucleobases (Chapters 4 and 6) and small polar molecules (Chapter 5).

1.2. Small molecular networks

Gas phase spectroscopy of isolated target molecules of known size and chemical composition enables characterization of molecular properties and electronic structure in the absence of environmental effects. While studies of isolated species provide insight into the molecules themselves, an understanding of the properties governing their bulk behavior is often also desirable. Spectroscopy of homogeneous clusters of molecules has emerged as a powerful means to measure the onset of bulk-like properties as cluster sizes increase from monomers to larger networks toward the bulk. In particular, cluster anion species including an excess electron have been used to explore solvation and electronic relaxation mechanisms. Cluster anions are well suited for study in the gas phase due to their finite size and charge. Time-of-flight mass spectrometry has been widely implemented to isolate clusters with a desired number of molecules, and ion optics can be used to steer clusters toward interrogation regions. Though target ion concentrations are generally low due to experimental difficulties associated with ion generation, the field remains a rich one with enough experimental advantages to outweigh disadvantages. Small cluster systems are also readily treated theoretically.

Water cluster anions, \((\text{H}_2\text{O})_n^-\), represent the best example of such work, having been characterized from \(n = 2 - 500\) by several laboratory groups under a variety of experimental conditions. These cluster studies have permitted the elucidation of several electron binding motifs and suggested strong stabilization of the excess electron by bulk hydration. This solvated electron has long held interest to physical and biological research communities due to its potential involvement in DNA strand cleavage. Relaxation mechanisms of the excited
solvated electron have also been extensively studied in bulk and cluster environments.\textsuperscript{30, 32-43}

In complement to studies of homogeneous cluster systems, investigations of heterogeneous cluster anions can be used to illuminate ionic interactions and solvation processes.\textsuperscript{8} Halide solvent clusters of the form $\text{X}^-\cdot(S)_n$ have been extensively probed with a variety of spectroscopies.\textsuperscript{13, 44-48} The difference in electron affinities of the halide and solvent species permits examination of charge-solvent interactions and the building up of cooperative and asymmetric solvation networks.\textsuperscript{8} In iodide-water clusters, $\Gamma^-\cdot(\text{H}_2\text{O})_n$, for example, quantum chemical calculations demonstrate that water molecules build up a hydrogen bond network to which the iodide remains largely exterior for small ($< 20$) $n$.\textsuperscript{49} Iodide-methanol clusters, $\Gamma^-\cdot(\text{CH}_3\text{OH})_n$, construct similar networks with fewer hydrogen bonds,\textsuperscript{50-53} while tetrahydrofuran molecules form a distinct solvation shell around iodide.\textsuperscript{54}

Excitation of partially solvated halide species provides a model for charge-transfer-to-solvent (CTTS) phenomena observed in liquids. The iodide ion has an electron affinity of 3.06 eV and does not possess an electronically excited state in the gas phase. However, iodide solvation with even a single chromophore can produce solvent-stabilized excited states that can exist above the detachment continuum.\textsuperscript{55} Absorption spectra for bulk solvated iodide display two peaks separated by the spin-orbit splitting of neutral iodine below 300 nm,\textsuperscript{55} indicating that the excited states involve the transfer of the excess charge from iodide to the solvent network.\textsuperscript{56-59} These so-called CTTS states are red-shifted in clusters relative to bulk solution and have been measured for a variety of solute and solvent species.\textsuperscript{13, 44-47, 59}

In a bulk solvent containing iodide, excitation to a CTTS state produces neutral iodine and an adjacent electron that becomes embedded in the solvent network on an ultrafast timescale.\textsuperscript{59} Accessing the CTTS state thus provides a means of generating solvated electrons for subsequent study. Small solvent clusters doped with iodide do not have sufficient molecules to completely solvate a halide ion or excess electron in the same manner,\textsuperscript{44-49, 54} so their excited states are sometimes referred to as CTTS precursor states. Measurement of the dynamics of these excited states suggests the ability of a system to accommodate an excess charge and reflects the stability of a solvated electron in a corresponding homogeneous system. Returning to the example of small polar solvent molecules, CTTS states of iodide-water clusters survive for hundreds of picoseconds before decaying by electron autodetachment,\textsuperscript{60-62} while those belonging to iodide-methanol clusters display significantly shorter lifetimes due to the inability of small methanol clusters to stably solvate an electron.\textsuperscript{61, 63, 64} $\Gamma^-\cdot(\text{CH}_3\text{OH})_n$ clusters also demonstrate significant changes in structure as the hydrogen bond network adjusts to reorient $\text{O}—\text{H}$ bonds from the iodide ion to the excess electron.\textsuperscript{63}

1.3. Dipole-bound anions

Iodide-containing clusters of solvent molecules of varying identities have been demonstrated to stabilize CTTS states via charge-dipole interactions between the partially solvated electron and adjacent solvent molecules.\textsuperscript{15} Analogous excited states for iodide-solvent binary complexes tend to exist only for highly polar solvents that can stabilize the electron independently. For example, 4 or more xenon atoms are required to support a CTTS state\textsuperscript{47, 65} though 2 water molecules (net $\mu = 3.2$ D)\textsuperscript{46} or a single acetonitrile ($\mu = 2.9$ D) molecule are
capable of stabilizing such states.\textsuperscript{66} The ability of solvent monomers to stabilize CTTS states is highly correlated with their ability to support dipole-bound anion states.\textsuperscript{46,67}

For neutral molecules, no attractive Coulomb (1/r) potentials exist between the species and an excess electron. Thus, the ability of a polar, neutral species to bind an electron arises from the strength of the longest-range potential, the charge-dipole potential\textsuperscript{19,68,69}

\[ V_\mu = -\frac{\mu e}{r^2} \cos \theta \]  

(1.1)

In Equation 1.1, \( \theta \) represents the angle between the position vector, \( \mathbf{r} \), and the dipole vector. Early theoretical treatments of electron-dipole interactions calculated that any species with a dipole moment exceeding 1.63 D should be able to bind an electron, however models accounting for electronic-rotational couplings indicate that 2.5 D describes more accurately the critical dipole moment required for the formation of a stable dipole-bound anion.\textsuperscript{19} Electron binding energies (eBEs) of such species do not scale linearly with \( \mu \), as the electronic character and complexity of inner-shell electrons and dispersion interactions also play a role,\textsuperscript{19,70} though eBEs do generally increase with increasing \( \mu \).\textsuperscript{67} For example, the eBE of the acetonitrile dipole-bound anion has been measured to be 11 meV,\textsuperscript{71,72} while that for the nucleobase uracil (\( \mu \approx 5 \text{ D} \))\textsuperscript{73,74} is closer to 90 meV.\textsuperscript{75,76}

Dipole-bound anions have been measured upon excitation of corresponding iodide-solvent complexes\textsuperscript{66,77,78} as well as upon interactions with highly excited Rydberg atoms or high energy alkali atoms.\textsuperscript{79,80} Like the solvated electron, the excess electron bound to a rotating molecular dipole occupies a large orbital with s-like character.\textsuperscript{68} Though some species form ground-state dipole bound anions,\textsuperscript{67,75,79,81,82} dipole-bound anions have also been observed as excited states of conventional valence anions\textsuperscript{83-85} and have for some systems been described as ‘doorways’ to more stable valence anions.\textsuperscript{86,87}

### 1.4. Transient negative ions

The photoinitiated ejection of an electron from the valence of iodide and subsequent electron capture by an associated solvent molecule or cluster is analogous to electron scattering in the absence of iodide:

\[ I^- \cdot S_n \xrightarrow{h\nu} [I \cdots (S)_n]^{*+} \quad \text{(photoinitiated charge transfer)} \]

\[ e^- + S_n \rightarrow S_n^{*-} \quad \text{(electron scattering)} \]  

(1.2)

When charge transfer is initiated by an ultrafast pulse, a range of frequencies interact with the initial state to produce a vibrationally excited CTTS state, \([I \cdots (S)_n]^{*+}\). As a result, the CTTS state will likely decay via autodetachment or other means on a rapid timescale. Such a state can therefore be considered a transient negative ion (TNI). TNIs represent a broad class of short-lived anion species that typically decay via electron autodetachment or dissociation over picosecond or faster timescales.\textsuperscript{88} Such species have been widely studied using dissociative electron attachment (DEA) techniques in which a beam of electrons of known energy is impinged upon a molecular beam of neutral molecules to produce the TNI \( S_n^{*-} \). The TNI
generally fragments to produce a variety of more stable negative ions whose yields can be qualitatively or sometimes quantitatively compared.

Transient anion species are not only of fundamental interest but have also been widely implicated in DNA damage by electrons with energies below the ionization potentials of DNA components. Theoretical studies suggest that low energy electrons (LEEs) initially attach to \( \pi^* \) orbitals of a nucleobase, which eventually results in cleavage between the C—O \( \sigma \) bond between the sugar and phosphate components of the nucleotide. Understanding the nature of the electron-nucleobase interaction is thus crucial to characterizing the mechanisms of LEE-induced damage to biological molecules.

The formation and decay of transient biomolecule anions have been widely examined with DEA. In the case of nucleobases, B, hydrogen atom loss to produce the \([B - H]^-\) complex is the most dominant fragmentation channel by several orders of magnitude. Examination of ion yield spectra reveals resonances important to fragmentation. In particular, vibrational Feshbach resonances arising from interactions between the excited dipole-bound state and the unoccupied \( N_1 - H \) \( \sigma^* \) orbital are thought to govern hydrogen atom loss at low (< 1 eV) electron energies. However, these investigations provide little insight into the timescales associated with TNI decay nor the quality of electron binding between the molecule and electron.

In contrast, photoelectron spectroscopy (PES) studies enable examination of electron binding strengths and motifs via measurement of the kinetic energy and angular distributions of photodetached electrons. The photoelectron spectrum of the bare uracil anion generated in a supersonic expansion of argon gas shows a single, narrow peak at low eBE that is characteristic of a dipole-bound anion, for example, though complexation with a water molecule yields a broader peak characteristic of a valence anion. Because the time between ion generation and laser interaction is on the order of microseconds, ion interrogation with a single photon of light can only illuminate the energetics of relatively long-lived anion species. Interrogation of molecular species with two photons separated by variable time delays permits study of the evolution of metastable species from their formation to their decay. For a halide-molecule complex, the first photon can be used to excite the complex to the CTTS state. The excess electron can then be photodetached from the excited state by the second photon. By varying the time at which the second photon interacts with the ion species, the energetics and decay dynamics of the excited state can be directly probed. The time-resolved photoelectron spectroscopy (TRPES) scheme for such systems is summarized by Equation 1.3:

\[
I^- \cdot B \xrightarrow{hv_1} [I \cdots B]^+ \xrightarrow{\Delta t, hv_2} [?] + e^-
\]

TRPES measures the decay of the TNI via a range of potential pathways, permitting study of extremely short-lived anion species and providing insight into autodetachment and anion transformation mechanisms in addition to fragmentation. The application of this method to iodide-solvent and iodide-biomolecule complexes will be described in Chapters 4 – 6, while the principles of photoelectron spectroscopy will be explored in greater detail below.

1.5. Time-resolved photoelectron spectroscopy
As discussed above, anion photoelectron spectroscopy is a powerful experimental tool capable of revealing the electron binding patterns and vibrational excitation of targets using readily accessible laser wavelengths. Interaction of a species with a photon of energy \( h\nu \) induces the photodetachment of an electron with kinetic energy \( (eKE) \) equivalent to the difference in energy between the exciting photon and the binding energy of the species:

\[
eKE = h\nu - eBE
\] (1.4)

According to the Born-Oppenheimer approximation, this detachment process should occur without any changes to the structure of the anion species due to rapidity of electron motion relative to nuclear motion. Conservation of energy dictates that the interacting photon must exceed the energy by which the electron is bound in order for photodetachment to occur.

The spectrum measuring this transition should reflect the photodetachment cross section of the initial species, a quantity readily calculated from the transition rate, \( \Gamma_{f\leftarrow i} \), between initial state \( i \) and final state \( f \) using Fermi’s Golden Rule:

\[
\Gamma_{f\leftarrow i} = \frac{2\pi}{\hbar} |\langle f | V | i \rangle|^2 \rho_f(E)
\] (1.5)

In the above expression, \( V \) is the potential coupling the initial and final states and \( \rho_f(E) \) is the density of final states at energy \( E \). The potential should describe the interaction of all of the charges in the system with the photodetaching laser pulse. Because laser wavelengths used in anion photoelectron spectroscopy are significantly larger than molecular species of interest, the electric dipole approximation can be applied. Thus, the potential term should be proportional to the dipole operator, and the coupling matrix element can be cast as the transition dipole moment. In order for photodetachment to occur, the matrix element must be non-zero.

The transition dipole matrix element can be written as

\[
\langle f | \vec{\mu} | i \rangle = \langle \phi_f | \langle \chi_f | \vec{\mu} | \chi_i \rangle | \phi_i \rangle
\] (1.6)

where the initial and final wavefunctions have been separated into nuclear (\( \chi \)) and electronic (\( \phi \)) components as permitted by the Born-Oppenheimer approximation. Separating the dipole operator into nuclear and electronic components and regrouping terms, the matrix element is given by

\[
\langle f | \vec{\mu} | i \rangle = \langle \phi_f | \vec{\mu}_\ell | \phi_i \rangle \langle \chi_f | \chi_i \rangle + \langle \phi_f | \phi_i \rangle \langle \chi_f | \vec{\mu}_n | \chi_i \rangle
\] (1.7)

The initial and final electronic states of the excess electron should be orthogonal, so the second term in Equation 1.7 should vanish. Therefore, in order to obtain a non-zero coupling element, the overlap of the initial and final nuclear wavefunctions must be non-zero. The
The overlap term is referred to as the Franck-Condon factor and defines the vibrational selection rules for photodetachment. Accordingly, the shape and structure of the photoelectron spectra reflect the similarity between the geometries of the anion and neutral species. For example, in dipole-bound anion states, molecular structure is minimally perturbed by an electron bound in a diffuse orbital, so photoelectron spectra display sharp, narrow peaks. In contrast, photoelectron spectra of conventional anions typically display broader features due to the structural changes that may be incurred by binding an electron in a valence orbital. Thus, photoelectron spectra produced with a single photon can provide valuable insight into energetics and electron binding patterns of molecular anions.

When carried out in an ultrafast, time-resolved fashion, photoelectron spectroscopy can be used to investigate the dynamics of anion excited states and their corresponding neutral species. Absorption of an initial, ‘pump’ laser pulse creates a non-stationary excited anion state. Subsequent interrogation with a ‘probe’ pulse permits elucidation of the evolution of the non-stationary state via photodetachment of the excess electron. Both laser interaction events should be vertical transitions as depicted in Figure 1.1. In the diagram, the non-stationary state created upon absorption of the pump pulse evolves on the excited anion surface. If the probe pulse photodetaches the electron at the instant of excitation with the pump pulse, the measured spectrum will reflect the character of the anion excited state prior to any evolution. If, however, the probe pulse interacts after a time delay $\Delta t$, the evolution of the anion state will be projected onto the neutral state, potentially revealing a change in character or population. In the figure,
sample photoelectron spectra are displayed to the right of the potential energy curves. The relative peak intensities associated with different vibrational levels of the neutral surface reflect the magnitude of the respective Franck-Condon factors.\textsuperscript{103}

Although electron motion takes place on attosecond timescales, nuclear motion occurs on femtosecond timescales. Thus, in order to measure evolution on the anion excited state, it is necessary to utilize ultrafast laser pulses. Such pulses, though short in duration, have broad (> 10 meV) spectral profiles that can blur the vibrational states of the neutral species. Photoelectron spectra measured with femtosecond lasers will instead include broad features, the peaks of which correspond to the maximum Franck-Condon overlap between the initial and final species and are described as the vertical detachment energies (VDEs) of the initial states.

The time-evolving signal recorded with a time-resolved photoelectron spectrometer should be proportional to both the cross section for the absorption of the pump pulse by the initial anion state and the cross section for photodetachment of the intermediate species by the probe pulse. The signal can thus be described by

\[
S_f (\Delta t) \propto \left| \phi_f \cdot \chi_f \right| e_{\text{probe}} \cdot \hat{\mu} \left| \Psi^*(\Delta t) \right| \right|^2 \tag{1.8}
\]

in which \( e_{\text{probe}} \) describes the probing laser field and \( \Psi^*(\Delta t) \) is the non-stationary state evolving on the excited anion surface given by

\[
\left| \Psi^*(\Delta t) \right| \propto \sum_n e^{-iE_n\Delta t/\hbar} \left| \phi_n^* \cdot \chi_n^* \left\langle \phi_n^* \cdot \chi_n^* \left| \left( e_{\text{pump}} \cdot \hat{\mu} \left| \phi_i \cdot \chi_i \right| \right)\right. \right. \tag{1.9}
\]

In Equation 1.9, the second term relates to the cross section for absorption of the pump pulse by the initial state to access available states \( n \) with corresponding energies \( E_n \), while the first term describes the temporal evolution of the resultant wave packet.\textsuperscript{105, 106}

1.6. Photoelectron angular distributions

Though information about the orbital occupied by an excess electron can sometimes be inferred from electron kinetic energy distributions, photoelectron angular distributions (PADs) can provide considerably more detailed and accurate information. Such information is readily obtained from charge imaging detection techniques, which are frequently integrated with TRPES to perform time-resolved photoelectron imaging experiments.\textsuperscript{103} Upon photodetachment, ejected electrons scatter from their parent molecule in three dimensions. Measurement of the kinetic energies and ejection angles of the entire distribution of electrons with a 3D detector is not feasible. Instead, however, through manipulation of the electric fields steering the electrons toward the detector and control of the laser polarization the three-dimensional distribution can be imaged on a 2D position sensitive detector. The details of the experimental scheme and 3D image reconstruction methods will be presented in Chapter 2.

The most general description of a PAD is given by\textsuperscript{107}
\[
I(\theta, \phi) \propto \sum_{L=0}^{L_{\text{max}}} \sum_{M=-L}^{L} \beta_{LM} Y_{LM}(\theta, \phi)
\]  \hspace{1cm} (1.10)

wherein the intensity of ejected photoelectrons is proportional to the products of spherical harmonics \(Y_{LM}\) and anisotropy parameters \(\beta_{LM}\) that depend on the electron kinetic energy and the geometry, electronic structure, and orientation of the anion under study.\(^{108}\) Equation 1.10 derives from the partial wave representation of the photoelectron wavefunction such that \(\beta_{LM}\) parameters include information about the contributions of each partial wave \(Y_{lm}(\theta, \phi)\) and their interferences with each other partial wave.\(^{104, 108}\) This representation constrains the total orbital angular momentum \(L\) and the lab frame projection quantum number \(M\) to \(|l - l'| \leq L \leq |l + l'|\) and \(M = m + m'\) where the prime denotes quantum numbers for the final state and the unprimed numbers describe the initial state.\(^{108}\)

Symmetry and angular momentum restrictions imposed by molecular properties and experimental design limit the allowed values of \(L\) and \(M\). For an unpolarized target anion, \(L\) must take on an even value due to reflection symmetry and \(L_{\text{max}}\) equals \(2n\), where \(n\) gives the number of photons interacting with the target.\(^{108, 109}\) The imaging device implemented in our TRPEI experiment and described in the following chapter forces electrons to travel within cylindrically symmetric electric fields,\(^{110}\) thus eliminating any dependence on the azimuthal angle \(\phi\) and restricting \(M\) to a value of zero. For atomic species, for which \(l\) is a good quantum number, the photoelectron produced with a single photon of light can be represented with only two partial waves described by \(l \pm 1\). Molecular systems, however, are often significantly more complicated, defying assignment of particular \(l\) values and presenting opportunities for electron scattering within the molecular system that result in loss of angular information.\(^{108}\)

For the TRPEI experiment, for which the \(z\)-axis can be chosen to be parallel to both laser polarization vectors, Equation 1.10 can be rewritten as\(^{104, 111}\)

\[
I(\theta) = \frac{\sigma}{4\pi} \left[1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta)\right]
\]  \hspace{1cm} (1.11)

where \(\sigma\) is the photodetachment cross section, \(P_i\) are Legendre polynomials, and the angle \(\theta\) indicates the angle of photoelectron emission relative to the \(z\)-axis. For a PAD displaying greatest intensity parallel to the laser polarization axis (\(\cos^2 \theta\) distribution), \(\beta_2\) equals +2, while for a perpendicular distribution (\(\sin^2 \theta\) distribution) \(\beta_2\) equals -1. Isotropic distributions correspond to \(\beta_2\) values of zero. \(\beta_4\) does not contribute to single-photon detachment processes but can take on a wide range of values in two-photon detachment processes.

Though electrons ejected from atomic systems can in principle be readily characterized, partial wave interferences must be accounted for in systems as apparently simple as iodide. The PAD measured for single-photon detachment of iodide displays two rings with peak intensities at \(\theta = \pi/2\) and \(3\pi/2\) that are fit with a \(\beta_2\) value of -0.6. The excess electron of the iodide anion occupies a \(p\) orbital, so the photoelectron wavefunction is a superposition of \(s\) and \(d\) partial waves. However, accurately modeling the PAD for this system requires careful consideration of radial distributions and phase shifts in addition to angular contributions.\(^{112}\) Given the intricacy of this analysis, modeling larger systems such as iodide-molecule binary complexes or clusters to
analyze partial wave interferences is unrealistic. Thus, angular information available from photoelectron imaging of molecular systems is limited to suggestions of perpendicular, parallel, and isotropic photodetachment. Complementary evolution of associated anisotropy parameters and features in time-resolved electron kinetic energy distributions may also assist in the interpretation of anion electronic structure and geometry.

1.7. Summary of systems studied

1.7.1. Iodide-solvent clusters

Chapter 3 describes measurements of lifetimes of CTTS excited states over a range of UV excitation energies for \( \Gamma \cdot (H_2O)_n \), \( \Gamma \cdot (CH_3OH)_n \), and \( \Gamma \cdot (CH_3CH_2OH)_n \) \((4 \leq n \leq 10)\) clusters. Iodide solvation by solvent clusters of varying identity and size has been widely investigated by photoelectron spectroscopy and other methods. Stabilization of the iodide species, indicated by the difference between the VDE of the solvated species and the electron affinity of bare iodide, increases upon successive addition of solvent molecules. Highly polar species such as water and small-chain alcohols establish hydrogen bonding networks adjacent to iodide. While water molecules participate in multiple hydrogen bonds and can thus build simultaneously strong solvent-solvent and solvent-solute associations, alcohol species have half as many O—H groups and are thus limited in their ability to both stabilize iodide and form strong solvation networks.

Bulk water, methanol, and ethanol stably bind electrons in small solvent cavities. Anionic cluster analogues for the water and methanol systems have been shown to bind electrons both at cluster surfaces and at positions partially embedded within the solvent network. However, though \((H_2O)_n^-\) clusters with \(n\) as small as 2 support long-lived anion states, approximately 70 methanol molecules are required to establish a stable (lifetime ~ μs) anion species, and ethanol cluster anions have not been observed despite significant efforts in our laboratory.

Early investigations of the CTTS dynamics of iodide-water clusters revealed that clusters consisting of four water molecules can stabilize excited states for several picoseconds upon excitation with 263 nm light. Complementary studies of iodide-methanol clusters revealed associated CTTS states to be significantly less stable and suggested that the methanol network must undergo significant rearrangement to accommodate the excess electron upon charge transfer from iodide. We attempted to reconcile these observations in regards to the differing energetics and structures of water and small alcohol species. Time constants describing the decay of CTTS states of \( \Gamma \cdot (H_2O)_n \), \( \Gamma \cdot (CH_3OH)_n \), and \( \Gamma \cdot (CH_3CH_2OH)_n \) \((4 \leq n \leq 10)\) clusters were measured after excitation with a range of pump energies. Excited state lifetimes were generally found to increase with size and decrease with excitation energy due to the enhancement of solute stabilization with solvent network size and the increase in accessible neutral states with energy, respectively. Lifetimes of similarly sized methanol- and ethanol-containing clusters were nearly identical and were significantly shorter than those for water. From a statistical perspective, autodetachment rates (inverse lifetimes) for \( \Gamma \cdot (H_2O)_n \) CTTS states should be much faster than those for \( \Gamma \cdot (CH_3OH)_n \) or \( \Gamma \cdot (CH_3CH_2OH)_n \) due to the significantly smaller density of states for water-containing clusters. Thus, the opposite trend observed must result from
differences in solvent cluster energetics. Because small bare methanol and ethanol clusters do not stably bind electrons, the iodine-associated solvent network cannot accommodate the electron upon its ejection from the iodide valence and the electron rapidly autodetaches. Water-containing clusters, however, can stabilize the excess electron within their hydrogen bonding network, effectively delaying autodetachment. Results from the application of Klots’ model for thermionic emission\textsuperscript{117} lend support for the inference that electron autodetachment rates reflect energetic considerations more heavily than molecular details.

1.7.2. Time-resolved radiation chemistry of nucleobases

Chapters 4 and 6 summarize efforts to characterize interactions of nucleobases with low energy electrons using TRPEI of iodide-nucleobase binary complexes.\textsuperscript{118} Damage to biological molecules induced by LEEs has captivated the interests of researchers across a range of disciplines. Due to the complexity of nucleic acids, it is convenient to isolate small DNA and RNA components such as nucleobases for study. Attempts to characterize nucleobase anions theoretically are made difficult due to the molecules’ propensities for dipole binding, which necessitates the use of very diffuse basis sets,\textsuperscript{119} though theoretical estimates of electron affinities of dipole-bound (DB) nucleobase anions are consistent with the \textasciitilde 100 meV values measured with photoelectron spectroscopy.\textsuperscript{75,76} Stable valence-bound (VB) anions of the nucleobases uracil (U) and thymine (T) have not been directly measured, though signatures of coupling between the DB and VB anions of uracil have been observed following Rydberg electron transfer from excited Xe atoms.\textsuperscript{120,121} Complexation of uracil with a single Xe atom or water molecule stabilizes the VB species;\textsuperscript{102} extrapolation of \([\text{U}·(\text{H}_2\text{O})_n]^-\) cluster electron affinities estimated 150 meV for the electron affinity of the VB anion.\textsuperscript{76}

Given the similarity of the electronic structures of xenon and iodine, it is reasonable to expect that complexation of uracil with a single iodine atom might also stabilize the valence anion. However, the significantly higher electron affinity of iodine requires that an electron associate with the atomic species rather than uracil. In Chapter 4,\textsuperscript{118} uracil is revealed to stabilize iodide by over 1 eV, significantly more than any other single solvent molecule yet studied in our laboratory. TRPEI experiments on the iodide-uracil complex endeavoring to gain further insight into the nature of the electron-nucleobase interaction are also described.

Single-photon photoelectron spectra were recorded over a range of photodetachment energies. A near-zero eKE (NZeKE) feature corresponding to autodetachment was recorded at energies spanning 4 – 5 eV, however overlap between NZeKE and direct photodetachment features near 4 eV obscures the true range over which autodetachment occurs. The presence of the autodetachment feature signifies the access of a metastable excited state by the excitation pulse. For the iodide-uracil system, this excited state is the transient negative ion of uracil perturbed by a neutral iodine atom. The transient species created upon excitation with 4.69 – 4.90 eV photons observed in the time-resolved photoelectron spectra appears quite broad, indicating that the TNI has valence character. The TNI was observed to decay biexponentially via autodetachment and iodine atom loss with timescales in the 100s of fs and 10s of ps ranges. Due to the low probe energy (1.6 eV), fragmentation of the excited complex to form more stable species (for example, dehydrogenated uracil radical anion [EA=3.5 eV]\textsuperscript{122}) could not be directly observed. Interestingly, the dynamics of the NZeKE feature did not directly mirror those of the
transient as observed in iodide-solvent cluster studies\(^{62-64, 123}\) but rather showed significant enhancement several picoseconds after the pump-probe overlap.

Subsequent investigation of the iodide-thymine binary complex revealed notable differences between uracil and thymine (5-methyluracil) anion decay dynamics.\(^{124}\) Though both iodide-uracil and –thymine clusters stabilize iodide similarly between the N1 and C6 associated hydrogen atoms,\(^{118, 124}\) the thymine TNI displayed biexponential decay with significantly smaller time constants and its NZeKE feature did not show any evidence of post-overlap enhancement. Given the importance of the hydrogen atom loss channel in DEA studies, the systems were reexamined with higher energy probes to determine what effect, if any, H loss might have on the decay dynamics of the uracil and thymine TNIs. Uracil analogs methylated at the N1 and N3 positions, from which hydrogen atoms are expected to derive, were also studied. These efforts are described in Chapter 6. Though preliminary studies of uracil and methylated uracil TNIs with higher energy probes have proved inconclusive, TNIs of uracils methylated at the N1, N3, and C5 positions excited near 4.7 eV and probed at 1.6 eV have all been observed to decay similarly. This result suggests that the mere presence of the methyl group is sufficient to drastically increase the rate of decay of the metastable anion, most likely via enhancement of intramolecular vibrational energy redistribution (IVR)\(^{125-127}\) that leads directly to electron autodetachment.

### 1.7.3. Dipole-bound transient anions

Chapter 5 describes the application of TRPEI to the transient negative ions of iodide-acetonitrile and iodide-nitromethane complexes produced upon intracluster charge transfer from iodide with excitation pulses close in energy to the VDEs of the respective complexes.\(^{128}\) Dipole-bound anions of small polar solvent molecules have been observed in a variety of experimental settings. In a series of studies of iodide-complexed single solvent molecules\(^{66, 77, 78, 129}\), including acetonitrile (\(\text{CH}_3\text{CN}\)) and nitromethane (\(\text{CH}_3\text{NO}_2\)), the Johnson group demonstrated the formation of DB species upon excitation of the initial complex just below its VDE. The electron binding character of the mass-isolated photofragments was confirmed via subsequent photo- or field-induced detachment.

While for acetonitrile the dipole-bound anion represents the ground state anion\(^{79, 81}\) due to the absence of a low-lying valence orbital,\(^{130, 131}\) nitromethane can support both DB and VB anions. The nitromethane VB anion houses the excess electron in the \(\pi^*\) orbital associated with the nitro group, which is significantly distorted away from the plane containing the C—N bond compared to neutral nitromethane.\(^{132}\) Photoelectron spectra\(^{86, 133}\) of the species reflect this geometric difference in the large progressions in nitro-associated vibrational modes and indicate an electron affinity of 172 meV for the VB species.\(^{133}\) Rydberg electron transfer from laser excited atoms to nitromethane readily produce the weakly bound (EA ~ 8 meV)\(^{86, 133}\) nitromethane DB state, however the yields of the DB state measured for collisions with Rydberg atoms with different principal quantum numbers imply coupling with the valence anion.\(^{86, 134}\) The DB anion is also difficult to measure with photoelectron spectroscopy,\(^{86, 133, 135}\) suggesting that the species is unstable to autodetachment. Transformation of the DB species into the VB species has also been widely speculated.\(^{86, 136}\)
In our TRPEI studies of $\Gamma \cdot \text{CH}_3\text{CN}$, the acetonitrile excited state corresponds to a feature in the photoelectron spectra characteristic of a DB species. The acetonitrile TNI decays biexponentially via iodine atom loss and autodetachment; fragmentation and other decay channels should not be accessible due to the low excitation energies utilized.

In contrast, excitation of $\Gamma \cdot \text{CH}_3\text{NO}_2$ near its VDE leads to the formation of a DB state that rapidly decays over several hundred fs to form the VB anion, representing the first direct observation of a DB to VB anion transformation. The VB species also exhibits biexponential decay attributable to autodetachment and translation of the iodine atom away from the nascent anion, however dissociation via radical-anion reactions to yield $\text{NO}_2^-$ or $\Gamma^-$ fragments is also feasible. The rapid DB to VB anion transformation produces a highly vibrationally excited VB state and the process is likely mediated by IVR from methyl-associated modes to nitro-associated modes. These observations may have important implications for systems such as uracil, for which a DB to VB anion transformation has also been proposed.

1.8. References


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Chapter 2. Experimental apparatus

2.1. Overview

The first version of the time-resolved photoelectron imaging apparatus in the Neumark group was designed by Martin Zanni and Benjamin Greenblatt to study photodissociation, chemical reactions, and related processes. The dissertations of Zanni\textsuperscript{1} and Greenblatt\textsuperscript{2} present detailed drawings and schematics of the instrument and associated electronic components. The later implementation of charged particle imaging detection is described in the dissertations of Alison Davis\textsuperscript{3} and Arthur Bragg,\textsuperscript{4} while changes to the ion generation methods and laser system have been discussed by Graham Griffin\textsuperscript{5} and Ryan Young.\textsuperscript{6}

This chapter will present a brief overview of the experimental apparatus, with particular attention to anion generation and velocity map imaging. Some details of the femtosecond laser system will also be presented.

2.2. Generation of cluster anion species

In recent decades, molecular beams have emerged as powerful tools with which to examine gas phase molecular properties and reaction dynamics. Creation of molecular beams requires establishing a large pressure differential between two chambers separated by a small orifice, the access to which can remain open continuously or be pulsed. Upon exiting the pre-expansion chamber into the low pressure region, the substance undergoes adiabatic expansion to create a supersonic beam, so called because the beam velocity exceeds the local speed of sound within the expansion. The central, isentropic portion of the expanded beam can be collimated with skimmers en route to the interrogation region.\textsuperscript{7,8}

Efficient generation of cluster species is readily achieved in supersonic expansions of a noble gas seeded with the material(s) of interest. Upon expansion, molecular and atomic species undergo extensive collisions, some of which result in cluster formation. Cluster growth by successive monomer addition can result in very large clusters, though cluster size distributions depend heavily on source conditions and material properties. Evaporative cooling occurs when the internal energy of the cluster exceeds the binding energy of monomers to the cluster seed.\textsuperscript{9,10} The combination of evaporative and collisional cooling yield cluster beams with temperatures in the range of 150 K.

All of the experiments described herein involve the study of iodide-containing solvent complexes and clusters. For generation of iodide-solvent species, several atmospheres of argon or neon gas are first flowed over a reservoir containing the solvent of interest. The gas pressure and solvent temperature are varied empirically; due to their high vapor pressures, acetonitrile and nitromethane were chilled to 0°C with an ice bath, while effective ethanol clustering was only achieved by warming the reservoir and gas manifold with heating tape. The seeded gas mixture then flows over a reservoir of methyl iodide, which has been found to be much more effective at
producing iodide-doped clusters than iodine gas. The mixture passes through an Even-Lavie pulsed solenoid valve\textsuperscript{11} and is expanded into the source chamber, the pressure of which is approximately $1 \times 10^{-5}$ Torr during operation. The pulsed valve reduces the gas load of the experiment, enabling operation at high (100 – 500 Hz) repetition rates with manageable pumping requirements.

The employment of an ionizer after the supersonic expansion enables the formation of iodide-containing cluster anions. A ring electrode ionizer consisting of a thoriated tungsten filament and supplied with approximately 4 A of current pulses 10s of μs after the valve, producing high energy (100s of eV) electrons that scatter off the expanding beam to produce lower energy secondary electrons. Interaction with these species induces dissociation of methyl iodide and subsequent attachment of solvent moieties to iodide or, in the case of larger clusters, attachment of iodide to solvent clusters.\textsuperscript{12}

The iodide-solvent cluster studies described in Chapter 3 were carried out using the project’s original Even-Lavie valve with a 250 μm nozzle pulsing at 100 Hz and remaining open for 10 μs. A new, high temperature, high repetition rate valve with a 150 μm nozzle was acquired for subsequent experiments. Though nominally operable at 1 kHz, the valve operates more stably at 500 Hz and accepts a large gas load of several hundred psi. Prior to the expansion region, gas passes through a small cartridge wherein a chemical can be placed and resistively heated up to 250 °C. Iodide-nucleobase complexes can be produced with heating in the range of 160 °C, though significantly better ion production is observed at 205 °C with approximately 50 psig of argon or neon backing gas. Biomolecule materials begin to decompose at higher temperatures, and materials stored in the cartridge often display signs of deterioration after only a few days of operation. The quality of the high pressure tube assembly that comprises the valve’s solenoid also degrades rapidly upon exposure to nucleobase species, developing a bluish patina. Frequent sonication in methanol improves the condition, while occasional cleaning with 5% acetic acid solution or treatment with a slight abrasive such as toothpaste are also useful. However, when viewed under a microscope, the solenoid component shows significant surface damage after such treatments. Valve operation worsens correspondingly, necessitating regular replacement of the high pressure tube assembly for continued study of biomolecule species.

2.3. Cluster anion manipulation and mass selection

A diagram of the TRPEI instrument is depicted in Figure 2.1. Following ion production, the coldest portion of the beam passes through a skimmer into a second, lower pressure region containing a three-plate Wiley-McLaren time-of-flight (TOF) mass spectrometer\textsuperscript{13} consisting of three, gridless square plates, the first two of which are pulsed at -2000 V and ~ -1500 V and the last of which is grounded. The time-of-flight mass spectrometer perpendicularly extracts the negatively charged ions and separates them in time according to their mass, while the remaining neutral species are removed by pumps. The pressures of the source region and this “0D” differential pumping region are regulated with two ~4000 l/s diffusion pumps (DPs; Varian VHS-10) backed by two mechanical forepumps. Diffusion pumps operate by heating high viscosity pump oil to generate a jet of hot fluid that is directed toward the cooled walls of the pump and condensed. These pumps have an unfortunate tendency to eject pump oil into the attached vacuum chambers, which can accumulate on charged plates and electrical connectors.
and affect the stability of the ion beam. Despite this inconvenience, the diffusion pumps operate rapidly and inexpensively compared to other pumps and require infrequent maintenance. Future incorporation of optical components into the source chamber may necessitate the construction of a barrier between the pump openings and anion source or replacement of the pumps with a cleaner alternative (i.e., turbomolecular pumps).

The extracted negative ions exit the “0D” chamber through a 3 mm orifice and pass into the “1D” differential pumping chamber where they immediately interact with a pair of deflector plates designed to control the flight path of the ion packet. These deflectors are held at voltages less than ±40 V and steer the ions through an Einzel lens, which consists of three, gridless circular plates held at ground, ~ -300 V, and ground and focuses the beam radially without changing its net speed. A pneumatic gate valve separates the “1D” and subsequent higher vacuum (~3 x 10^{-9} Torr) “2D” region, evacuated by a diffusion pump (Varian VHS-6, 1600 l/s) and a turbomolecular pump (TMP; Varian V-301 Navigator, 250 l/s), respectively. A second set of deflectors in the “2D” region enable further control of the ion beam into the detection region.

The second Einzel lens is mounted to a plate that divides the “2D” and detector regions with a small aperture. The detector region is evacuated with a second turbomolecular pump (Varian V-250, 250 l/s) to ~2 x 10^{-8} Torr and contains the imaging electrodes, photoelectron detector, and a retractable ion detector consisting of a small microchannel plate (MCP) pair behind a grid. The impact of ions on the MCPs generates a cascade of electrons whose current can be detected using an oscilloscope to collect mass spectra. The mass spectra can be tuned by adjusting voltages applied to steering electrodes, accelerating or decelerating the ion beam, and changing the timings, gas pressure, and other parameters associated with the ion source. In order to interrogate a certain ion packet with the pump and probe laser pulses, it is desirable to isolate this species. Mass selection is achieved using a re-referencing tube that pulses from -4 kV to 0 V
to permit entry by the ion packet of interest and then pulses back to -4 kV within 500 ns to both reject subsequent ions and accelerate the isolated ions in the detection region. Further details of the re-referencing tube assembly are presented in the following section.

2.4. Velocity map imaging detection

Charged particle imaging detection provides a means of extracting information about three dimensional processes using two dimensional detection. The interaction of photoelectrons with a cylindrically symmetric inhomogeneous electric field results in the mapping of photoelectrons with the same velocity vectors to the same points on the position sensitive detector. This scheme, aptly named velocity map imaging (VMI), enables the simultaneous collection of angular and radial information via reconstruction of the spherical distribution of photoelectrons produced upon laser interrogation. In its collinear implementation, it also enables nearly 100% collection of photoelectrons with an incredibly simple design.

The VMI device, presented in Figure 2.2, consists of three electrodes, named the repeller (R), extractor (E), and ground (G) plates, with gridless apertures. For imaging of negative particles, the voltages increase from negative to ground as the particles move through the assembly. The precise voltages employed control the spatial spread of the photoelectrons on the detector, with faster electrons striking the detector further from the center, and are thus highly dependent on the apparatus geometry, while the ratio of the voltages of the extractor and repeller plates, E/R, controls the focusing of the image and is generally held at 0.70. Given the experimental geometry and the general range of energies studied using the anion TRPEI instrument, R is usually pulsed at -4 kV while E is held at -2.8 kV, which enables imaging of electrons with as much as 5 eV of kinetic energy on a chevron-stacked 70 mm MCP pair located at the opposite end of the detection region.

The original VMI stack in our TRPEI instrument was constructed around 2001. The VMI assembly is supported by four Macor rods mounted onto a plate that attaches to a welded collar at the entrance of the detection region. Aluminum spacers support the first, grounded plate, featuring a 0.8” diameter opening covered with a fine, 30 lines per inch electroform mesh. Along with a second plate with a 0.2” diameter gridded aperture offset by 2 mm by Vespel spacers, this component slows the ion packet prior to entry into the re-referencing tube for mass isolation. The second plate directly contacts the tube, which also serves as the VMI repeller electrode. The plates at either end of the 3” long, 1” diameter tube are 3” in diameter, like all other plates in the assembly. The front end of the tube directly contacts a plate with a 5 mm open aperture and is separated by 1.5 cm Vespel spacers from the extractor and ground plates, which feature 0.8” diameter gridless apertures. During operation, the ion beam interacts with the laser pulse between the extractor and repeller components, as indicated in the figure. The VMI assembly is surrounded by a mu-metal tube 4" in diameter and 12” long to shield photoelectrons from magnetic fields such as the ~0.6 Gauss field of Earth. A second, larger mu-metal tube (6” in diameter, 14” long) overlaps the end of the smaller tube and shields photoelectrons during their flight toward the electron detector. The larger tube includes a 1.5” x 3” cutout on one side to accommodate the retractable ion detector.

The electron cascade induced by the impingement of photoelectrons on the dual MCP
detector produces an image on a phosphor screen that is captured by a charge coupled device (CCD) camera pulsed at 30 Hz and interpreted by a LabVIEW data acquisition program. Details of the initial program’s operation are presented in the dissertation of Ryan Young, while updates will be described by Sarah King. The phosphor screen is held at +4 kV and the back MCP at +1600 V, while the front MCP is pulsed from ground to +700 V after the arrival of the photoelectrons to slow residual ions. Due to the fragile nature of the CTTS excited states accessed in these experiments, a significant number of slow electrons strike the detector near its center. Over time, the quality of the MCPs and phosphor screen can degrade and develop inhomogeneity in their centers and other areas as a result. Four-way image symmetrization is applied in the image reconstruction process to reduce this effect and enhance signal levels. Image reconstruction is performed using the Basis Set Expansion (BASEX) or Polar Onion Peeling (POP) methods. BASEX involves projecting the image onto a set of prescribed analytical basis functions and extracting expansion coefficients and proves less sensitive to noise than other methods except along the symmetry axis, while POP employs radial distribution functions in polar coordinates and reconstructs the image from its boundary to its center. POP introduces center point noise to images, impairing its usefulness for systems producing an abundance of low energy electrons, however it provides excellent angular information at larger radii. Both BASEX and POP are computationally inexpensive and can function almost in real time, permitting users to examine photoelectron images as they are collected. A more detailed review of reconstruction methods and our data analysis suite will be discussed in the dissertation of Sarah King.

Though the design of the VMI device is very simple, properly implementing such a
device can prove extremely difficult. Due to the positioning of the small mu-metal tube around the VMI electrode stack, the wires connecting the extractor and repeller plates to their voltage supplies at the bottom of the chamber must wrap around the edge of the tube and extend, in the case of the extractor supply, several inches inside it. This requirement necessitates extreme care in the positioning of the electrical wires. The original implementation used unshielded thick copper wire attached to the extractor plate via a ceramaseal connector, while the repeller wire was similarly thick but was covered with small ceramic beads. While these wires were adequate to carry high voltages, the lack of insulation eventually resulted in arcing between the plates and the mu-metal tubing when the wires made incidental contact in the spring of 2012. These components were subsequently replaced with Kapton insulated wires rated to ±10 kV DC and ±3 kV AC (Accu-Glass Products, Inc.) for safer operation. Unfortunately, however, though replacement and careful manipulation of the wire eliminated the arcing problem, images recorded with the reassembled VMI stack were off-centered and asymmetrically distorted. The images recorded were similar to those reported by Vrakking and co-workers\textsuperscript{17} at low voltages.
appearing as circles stretched at θ=135 and 315° (Figure 2.3).

Several steps were taken to investigate this issue. To ensure adequate electrical isolation of the VMI components, the experiment was attempted without the small mu-metal tube. Though ions still impinged upon the center of the electron detector, the photoelectron image was drastically shifted from the center though the ions remained roughly centered, demonstrating the importance of the magnetic shielding to ensuring free electron flight. Initial inspection of the VMI stack revealed that the assembly was somewhat loosely held in place on the mounting plate. In order to better stabilize the assembly, the seats for the Macor rods on the mounting plate were re-machined. While the VMI components appeared well aligned with one another and firmly attached, the centering of both ions and electrons appeared changed with this correction. Using a scope borrowed from the crossed molecular beam experiment, the alignment of the VMI stack, 2D/detector region aperture, and 1D/2D region aperture was examined. The attachment points of the mounting plates for the VMI assembly and the second Einzel lens were widened to permit more careful alignment. During this process, it was noted that the 0D/1D aperture was not well aligned with the subsequent components. The defectors in the 1D region should compensate for this misalignment somewhat, however the aperture should at some point be adjusted to promote better ion transmission throughout the instrument. The effects of the gridded electrodes in the VMI assembly on ion transmission were also examined by replacing the mesh on the first plate of the repeller component with a finer, woven, Ni 200 mesh (Unique Wire Weaving Co., 50 x 50 wires per inch, 0.002” wire diameter). This substitution resulted in decreased ion transmission and the visualization of mesh lines on the electron detector and so the fine mesh was replaced with the original mesh.

In the initial examination of the VMI assembly following the emergence of the arcing issue, it was noted that the mu-metal tubing had developed blue speckles. Though the origin of this patterning is unclear, we speculated that it may have arisen from partial magnetization of the magnetic shielding. The materials were thus re-annealed to reset their shielding properties; indeed, the blue coloration disappeared during the treatment. It was also speculated that the VMI electrodes may have become magnetized, perhaps as a result of the arcing between the electrodes and shielding components. To test this hypothesis, the VMI stack was rotated 90°. The distortion observed in the resultant images was also rotated, indicating that the asymmetry originated at least in part in the plates themselves. The ground and extractor plates as well as the first and last repeller plates were replaced with new stainless steel plates. With these new components, the asymmetry was reduced as to be almost unnoticeable for photoelectrons with moderate kinetic energies (< 3 eV within the -2.8/-4 kV extractor/repeller E/R scheme). The very slight asymmetry remaining results in a slight broadening of peak widths in electron kinetic energy spectra. In the velocity map imaging scheme, momentum vectors map directly onto the detector so electron kinetic energy scales as \( \bar{p} \propto \bar{r} \propto E^{1/2} \). Thus, the energy resolution of the detector is given by \( \Delta E \propto r\Delta r \propto E^{1/2} \) such that faster electrons correspond to broader peaks in electron kinetic energy distributions. The broadening effect caused by any residual magnetization or alignment issues with the VMI assembly thus manifests itself more strongly for electrons with larger eKEs. However, the use of ultrafast lasers inherently broadens peaks due to the ultrafast lasers’ broad spectral widths such that very narrow peak widths should not be expected at any eKE. The energy resolution of the instrument thus usually measured in the range of 50 meV and indeed \( \Delta E/E \) was measured at approximately 7% with the repaired VMI.
assembly.

2.5. Femtosecond laser system

In order to examine the ultrafast dynamics of charge transfer and accommodation processes, mass isolated cluster anions are interacted with ultrashort laser pulses. Ultrashort pulses originate in the KM Labs Griffin Oscillator pumped by a Coherent Verdi V-5 Nd:YVO₄ pump laser. The pump laser provides 4.2 W of 532 nm light to a cavity containing a Ti:sapphire crystal, enabling through the Kerr lens effect¹⁸ the formation of pulses centered around 790 nm that are less than 30 fs in duration. The Verdi laser power supply contains optical diodes that provide light to the laser head where green light is produced. Though such systems are generally quite robust, the Verdi head required replacement after slightly less than 10,000 hours of use (December 2012).

The femtosecond pulses generated in the oscillator are created with low power. A chirped-pulse, multi-pass amplification scheme is used in a KM Labs Dragon Amplifier to enhance the power of the ultrafast pulses for use in the TRPEI experiment. This scheme involves first stretching the pulse to approximately 150 ps duration, spreading the frequencies in time using a single grating stretcher, followed by selection of a single pulse from a pulse train with a Pockels cell, which rotates the polarization of light upon application of an electric field. The pulse rate of the Pockels cell controls the repetition rate of the experiment: while the pulses created in the oscillator are separated by only 12 ns, after interaction with the Pockels cell the majority of pulses will be eliminated and the time between two pulses increased to approximately 1 ms. Upon exiting the Pockels cell, the beam passes through a cryogenically cooled and laser-pumped Ti:sapphire crystal 13 times before proceeding to a two grating device for pulse compression. Amplification is achieved in the cooled crystal through interaction of the seed beam with about 15 W of 532 nm light produced by a second pump laser.

The iodide-solvent cluster experiments described in Chapter 3 were carried out with the laser system pulsed at 600 Hz using a Photonics Industries DM-30 Nd:YLF pump laser. While this laser outputted a very nice transverse mode, the output power was unreliable. A Lee Laser LDP-200MQG Nd:YAG laser replaced this system in the fall of 2011. Though comparatively easy to maintain, the Lee Laser produces a poor mode and preferentially operates at significantly higher repetition rates than those achievable with the DM-30. Thus, experiments carried out after its installation have utilized a 1 kHz repetition rate.

Variance of the laser system’s repetition rate is enabled by the cryogenic cooling of the Ti:sapphire crystal in the amplifier. Cooling also increases the efficiency of conversion of pump power to 790 nm light by reducing thermal lensing effects.¹⁹, ²⁰ The crystal is surrounded by indium foil and housed between two copper pieces in contact with a cooling head. Contact between the two components was initially maintained with high vacuum grease which, over several years, wicked down between the copper pieces and eventually obscured the face of the crystal. The crystal was removed from its mounting for cleaning and the grease replaced with a layer of indium foil in late 2011. At this time, the indium foil surrounding the crystal was replaced with a high vacuum compatible solder material. However, the crystal position was unsteady in this mount, and the system was ultimately remounted in the spring of 2012.
Following amplification, the chirped pulse is re-compressed to approximately 30 fs. A single-shot autocorrelator (Coherent) can be used to characterize the pulse duration. The 790 nm (1.57 eV) laser output, commonly referred to as the “fundamental”, is widely applicable in our TRPEI experiments, in which photodetachment of weakly bound excited states requires low photon energies (< 1 eV). To access CTTS excited states of iodide-containing cluster systems, pump energies must exceed the electron affinity of iodide (3.06 eV). Ultraviolet laser pulses are accessible through two mechanisms: sum frequency generation using nonlinear optical crystals or optical parametric amplification. In the first scheme, the fundamental (ω₁) pulse can be frequency doubled in a thin (< 500 μm) beta barium borate (BBO) crystal to produce 3.14 eV light (ω₂ = 2 ω₁). Spatially and temporally overlapping the fundamental and frequency doubled pulses in a second BBO crystal enables frequency tripling (ω₃ = ω₁ + ω₂). Though mixing in nonlinear crystals can yield short pulses with sufficient intensities for spectroscopy, the frequencies generated are limited to the laser harmonics.

Optical parametric amplification provides an alternative means to generate ultraviolet pulses in a tunable fashion. This tunability permits mapping of trends across excitation energies and access to a wider range of cluster anion excited states. The TOPAS-C optical parametric amplifier (Light Conversion) produces a white-light continuum in a sapphire plate from a small portion of the pump beam. The frequencies of the continuum are spread in time by a zinc selenide crystal such that a defined frequency can be overlapped with the pump beam in a nonlinear crystal to produce a third frequency by difference frequency generation. The frequency selected from the white light continuum is commonly referred to as the signal, while the difference between the seed and signal frequencies is referred to as the idler. Conservation of energy requires that production of the idler frequency is accompanied by amplification of the signal according to ω₄ = ω₃ + ω₅. Overlapping the newly created frequencies with the major fraction of the pump pulse amplifies both the signal and idler pulses. The TOPAS-C generates light nearly continuously from 1140 to 2600 nm; frequency doubling of the signal or idler pulses or sum frequency generation with the fundamental using external nonlinear crystals and beam splitters can produce light down to approximately 230 nm (5.4 eV).

Pulses emergent from the TOPAS-C are elongated relative to the seed pulse. The pulse duration of the experiment is measured with a cross correlation outside the instrument according to

$$\sigma_{\text{cross-correlation}} = \left(\sigma_{\text{pump}}^2 + \sigma_{\text{probe}}^2\right)^{1/2}$$  \hspace{1cm} (2.1)

where σ describes the width of the Gaussian pulse. The fundamental probe pulse typically passes through fewer than three thin transmissive optics that would stretch the pulse in time according to group delay dispersion; thus, the full width at half maximum of the cross correlated pulses reflects the pulse duration of the pump pulse. This value is generally in the range of 150 fs. If the compressor in the KMLabs Dragon Amplifier is tuned to chirp the fundamental, pulses of 100 fs can be measured, however frequency spread in the pump pulse is undesirable. In the future, both frequency distributions and pulse durations will be examined using a frequency-resolved optical gating (FROG) tool for more complete pulse characterization. A fiber compression tool may also be implemented to shorten the ultraviolet pulses produced by the
optical parametric amplifier.

2.6. References

Chapter 3. Effects of excitation energy on the autodetachment lifetime of small iodide-doped ROH clusters (R=H–, CH3–, CH3CH2–)

3.1. Abstract

The effect of excitation energy on the lifetimes of the charge-transfer-to-solvent (CTTS) states of small (4 ≤ n ≤ 10) iodide-doped water and alcohol clusters was explored using femtosecond time-resolved photoelectron imaging. Excitation of the CTTS state at wavelengths ranging from 272 – 238 nm leads to the formation of the I···(ROH)\textsubscript{n}\textsuperscript{−} (R = H–, CH3–, and CH3CH2–) species, which can be thought of as a vibrationally excited bare solvent cluster anion perturbed by an iodine atom. Autodetachment lifetimes for alcohol-containing clusters range from 1 – 71 ps, while water clusters survive for hundreds of ps in this size range. Autodetachment lifetimes were observed to decrease significantly with increasing excitation energy for a particular number and type of solvent molecules. The application of Klots’ model for thermionic emission from clusters to I\textsuperscript{−}·(H\textsubscript{2}O)\textsubscript{5} and I\textsuperscript{−}·(CH\textsubscript{3}OH)\textsubscript{7} qualitatively reproduces experimental trends and reveals a high sensitivity to energy parameterization while remaining relatively insensitive to the number of vibrational modes. Experimental and computational results therefore suggest that the rate of electron emission is primarily determined by the energetics of the cluster system rather than by details of molecular structure.


3.2. Introduction

Charge stabilization by bulk and local solvent environments has been a major focus of study in recent years in part due to the interest surrounding solvated electron phenomena in chemical, physical, and biological research communities.\textsuperscript{1,2} While electron solvation is generally considered a “bulk” phenomenon, gas phase cluster studies of excess electrons bound to a known number of solvent molecules have provided significant insights into electron binding motifs and the fundamental processes associated with the formation and accommodation of a solvated charge.\textsuperscript{3–5} These studies have been complemented by experiments on halide-solvent...
clusters in which the excess electron on the halide is ejected onto the solvent network via excitation of the cluster analog of the charge-transfer-to-solvent (CTTS) band in the ultraviolet producing, after some dynamics, a solvated electron and providing a direct comparison to the analogous process in bulk solvents. Cluster dynamics studies performed to date have focused on femtosecond time-resolved experiments on an iodide anion bound to water, methanol, and other solvating species. These studies show a strong dependence of the electron solvation dynamics on the size and composition of the cluster, and that the CTTS excited state in iodide-water and iodide-methanol clusters decays by autodetachment to a neutral cluster and a free electron. In this paper, we focus on this decay mechanism in more detail and investigate the autodetachment dynamics subsequent to CTTS excitation over a range of excitation energies in $\Gamma^-(\text{H}_2\text{O})_n$, $\Gamma^-(\text{CH}_3\text{OH})_n$, and $\Gamma^-(\text{CH}_3\text{CH}_2\text{OH})_n$ clusters. We also examine whether the autodetachment rates and associated electron kinetic energy distributions can be accurately described by statistical models.

Previous work on charge-transfer-to-solvent dynamics in iodide-doped water and methanol clusters revealed notable differences between the electron solvation processes in the two species. Time-resolved photoelectron spectra for iodide-water clusters suggested that upon excitation of the CTTS band the excess electron was first promoted to a diffuse state near the iodine atom before solvent rearrangement leading to stabilization over a few picoseconds. After tens of ps, the vertical detachment energy (VDE), a measure of electron binding strength, was observed to decrease slightly as the iodine atom departed the cluster. The lifetime of the CTTS state ranged from approximately 0.6 – 3000 ps for $n = 3 – 10$ with excitation at 4.65 eV (267 nm). The decay of this state was mirrored by the recovery of a second spectral feature near zero electron kinetic energy attributed to electron autodetachment. This feature was also present in single-photon UV spectra, suggesting that it is the ultimate decay mechanism for the CTTS state.

Photoelectron spectra of iodide-doped methanol clusters also revealed autodetachment and pump-probe features with near-identical time constants, but the iodide-methanol CTTS state lifetimes were much shorter, ranging from 0.8 – 86 ps for $n = 4 – 11$ with excitation at 4.71 eV (263 nm). This difference was attributed to the instability of bare methanol cluster anions in this size range with respect to electron loss. As in water, the ejected electron in the methanol-containing clusters is thought to first occupy a diffuse state near the iodine atom before solvent rearrangement leads to an initial stabilization. This stabilization is short lived, however, as both the VDE and the width of the CTTS spectral feature were observed to evolve dramatically before the decay of the CTTS state by autodetachment. These dynamics were suggested to result from a concerted rotation of one or more methanol molecules to enhance the cluster’s hydrogen bonding network. Ethanol has the same hydrogen bonding capability as methanol but more vibrational modes, raising the question of how the CTTS dynamics of $\Gamma^-(\text{ethanol})_n$ and $\Gamma^-(\text{methanol})_n$ clusters would compare.

Studies of charge-transfer-to-solvent dynamics in iodide-doped water and methanol clusters have previously involved the use of a single excitation energy to promote the charge transfer onto the solvent network. CTTS bands blue-shift to the deep UV (219 – 230 nm for ethanol, methanol, and water) with increasing cluster size as $n$ increases. The resonance of the CTTS transition is therefore size-dependent. While the studies of Verlet et al. and Kammrath
et al. of $\Gamma^-(\text{H}_2\text{O})_n$ clusters$^{8,9}$ and that by Ehrler et al. of $\Gamma^-(\text{CH}_3\text{CN})_n$ clusters$^{13}$ utilized different photon energies to access the CTTS band in different size ranges, no study yet presented has investigated the effect of pumping different regions of the CTTS band for a cluster of a particular size.

In order to better understand dynamics in iodide-solvent clusters following CTTS excitation, we have investigated for the first time the effects of excitation energy on autodetachment lifetimes for small ($4 \leq n \leq 10$) iodide-doped ethanol, methanol, and water clusters as a function of solvent type and cluster size. We have also applied Klots’ microcanonical formalism for thermionic emission to model observed trends.$^{19}$ Autodetachment lifetimes were determined to increase with cluster size and decrease with excitation energy. Lifetimes for methanol- and ethanol-containing clusters were nearly identical for the same excitation energy and number of molecules and were significantly smaller than those observed for iodide-doped water clusters. We find that the Klots model effectively recovers these differences from approximate vibrational frequencies and appropriate energy parameterization, and that it reproduces the form of the low kinetic energy photoelectron signal resulting from autodetachment. The high sensitivity of modeling results to energetics and the low sensitivity of experimental results to the number of vibrational modes implies that the energetics of the various cluster systems are more important in determining their excited state lifetimes than the precise structural identities of the molecules therein.

3.3. Experimental

Details of the femtosecond time-resolved photoelectron imaging experiment have been described elsewhere.$^{20,21}$ Argon gas at 5 – 20 psig was flowed over reservoirs of ROH ($R = \text{H}^-, \text{CH}_3^-, \text{CH}_3\text{CH}_2^-$) and methyl iodide and expanded through an Even-Lavie valve pulsed at 100 Hz.$^{22}$ The solvent reservoir and gas line were heated slightly for effective $\Gamma^-(\text{ethanol})_n$ production. The pulsed beam was then passed through a ring-shaped ionizer to generate cluster anions via secondary electron attachment before their perpendicular extraction with a Wiley-McLaren time-of-flight mass spectrometer.$^{23}$ Clusters of the desired mass were isolated with a pulsed electrostatic switch before entering the interaction region where they were intercepted by femtosecond pump and probe laser pulses. The resulting photoelectrons were then collinearly accelerated via velocity map imaging$^{24}$ to a pair of chevron-mounted microchannel plates coupled to a phosphor screen. Images from the phosphor screen were captured with a charge-coupled device camera and reconstructed using the basis-set expansion method (BASEX)$^{25}$ following four-way symmetrization to address detector inhomogeneities. The reconstructed images provided both electron kinetic energy and photoelectron angular distributions (PADs). Anisotropy parameters, $\beta_i$, describing the detached electron’s angular momentum were obtained by fitting PADs to an even series of Legendre polynomials;$^{26,27}$

$$I(\theta) = \frac{\sigma_{\text{total}}}{4\pi} \left[ 1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta) \right]$$

(3.1)

where $I$ represents intensity, $\theta$ the angle between the laser polarization and the ejected electron, and $\sigma_{\text{total}}$ the total photodetachment cross section. One-photon detachment is described with a single anisotropy parameter, $\beta_2$, while two-photon detachment requires an additional parameter.
Figure 3.1. Time-resolved photoelectron spectrum for $\Gamma^-(\text{CH}_3\text{CH}_2\text{OH})_8$ with excitation energy = 4.85 eV (256 nm). Electron kinetic energy (eKE) increases from right to left, while pump-probe delay increases from front to back. The intensity of the peak near zero eKE, “A”, is scaled by 0.1 for ease of viewing. The inset in the upper left corner shows the normalized integrated intensities of “A” (autodetachment, AD) and “B” (resonant pump-probe signal, [1+1’]). The inset at right shows the evolution of these features with pump-probe delay in processed images. The vertical arrow indicates the laser polarization while the gradient indicates the feature’s intensity.

Femtosecond pump and probe laser pulses were generated with a Ti:sapphire oscillator and multi-pass amplifier (KM Laboratories Griffin Oscillator and Dragon Amplifier). The resulting 790 nm pulses were approximately 35 fs in duration and ~2 mJ/pulse at a 600 Hz repetition rate. Most of this light was used to generate a UV pump pulse either with a third-harmonic generator to produce 263 nm light (~ 20 μJ/pulse) or by second harmonic generation of the sum frequency of the fundamental and the high or low frequency output of an optical parametric amplifier (Light Conversion TOPAS-C) to produce 238 – 272 nm (~ 10 μJ/pulse) tunable UV light. The remainder of the fundamental was used as the probe pulse (~ 150 μJ/pulse). Cross-correlation measurements taken at the entrance to the vacuum chamber reveal pulse widths ranging from 80 – 200 fs.
Figure 3.2. Normalized integrated intensities for “B” of iodide-doped clusters of seven molecules of ethanol (upper panel), methanol (middle panel), and water (bottom panel) with excitation energies of 263 (red), 253 (black) and 246 nm (blue). Lines between points are fits described in the Analysis section.

3.4. Results

Time-resolved photoelectron imaging was used to investigate the effects of changing excitation energy on CTTS dynamics in iodide-doped ethanol, methanol, and water clusters of four to ten molecules. Figure 3.1 displays reconstructed images, normalized integrated intensities, and photoelectron spectra for I−-(ethanol)$_8$, which are typical for the size range studied here. Electron kinetic energy is shown increasing from right to left with pump-probe delay increasing from front to back. Two features are evident in the spectra and images: a peak with near zero electron kinetic energy (scaled by 0.1 in the figure for clarity) labeled Feature A
Table 3.1. Lifetimes (ps) of iodide-doped solvent clusters at various excitation energies.

<table>
<thead>
<tr>
<th></th>
<th>$\Gamma\cdot(CH_3OH)_n$</th>
<th>$\Gamma\cdot(CH_3CH_2OH)_n$</th>
<th></th>
<th>$\Gamma\cdot(H_2O)_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>263 nm $^a$</td>
<td>255 nm</td>
<td>245 nm</td>
<td>238 nm</td>
</tr>
<tr>
<td>4</td>
<td>0.8 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.1 ± 0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.4 ± 0.5</td>
<td>6.6 ± 0.6</td>
<td>5.9 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>19.6 ± 0.5</td>
<td>12.4 ± 0.5</td>
<td>10.9 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>32.6 ± 0.4</td>
<td>20.4 ± 1.4</td>
<td>16.3 ± 1.1</td>
<td>13.0 ± 1.7</td>
</tr>
<tr>
<td>9</td>
<td>49.7 ± 0.8</td>
<td>41.2 ± 2.1</td>
<td>31.6 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>70.9 ± 2.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Young et al. 2011.$^{10}$

$^b$Kammrath et al. 2005.$^5$ See text for details on fitting.

and a peak near 1.5 eV denoted Feature B that emerges at positive pump-probe delays. At 263 nm, Feature A dominates the spectra for the smallest cluster size and decreases in relative intensity as $n$ increases and the charge-transfer-to-solvent band blue shifts. Similar trends are observed with higher excitation energies. The images in the inset reveal that Feature A is isotropic, while the intensity of Feature B is maximized parallel to the laser polarization.

For all cluster sizes and excitation energies, the integrated intensities of Features A and B demonstrate complementary time dependence (Figure 3.1). The population of Feature A is relatively constant for negative and very positive pump-probe delays. When the pump-probe delay is near zero, the intensity of Feature A decreases sharply as Feature B appears. The two features return to their initial values in an exponential fashion.

The spectral features and trends described for $\Gamma\cdot$(ethanol)$_n$ clusters are similar to those observed for $\Gamma\cdot$(water)$_n$ and $\Gamma\cdot$(methanol)$_n$ clusters and were observed here for all solvent identities, cluster sizes, and excitation energies sampled.$^9, 10$ The evolution of the peak center and width of the CTTS spectral feature with pump-probe delay is also similar for iodide-doped ethanol and methanol clusters. Based on the similarities between these results and previous work, Feature A is attributed to vibrational autodetachment of the pump-excited cluster anion, while Feature B is assigned to resonant pump-probe detachment via the CTTS state. The two decay channel model implied by these assignments explains the similar time-dependence of the two features: the excited CTTS state must either undergo autodetachment or experience
Figure 3.3. Top panel: Lifetimes of $\Gamma^-(\text{CH}_3\text{OH})_n$ (circles) and $\Gamma^-(\text{CH}_2\text{CH}_2\text{OH})_n$ clusters (triangles). Bottom panel: Lifetimes of $\Gamma^-(\text{H}_2\text{O})_n$ (squares) clusters. Lifetimes presented are measured with excitation energies of 272 (orange), 263 (red), 253 (black), 246 (blue) and 238 (purple) nm. Wavelengths used are known to within ±2 nm. Lifetimes for $\Gamma^-(\text{CH}_3\text{OH})_n$ at 263 nm are taken from Young et al.,\textsuperscript{10} and lifetimes for $\Gamma^-(\text{H}_2\text{O})_n$ at 263 nm are taken from spectra measured by Kammrath et al.,\textsuperscript{9} as described in the text.

photodetachment by the probe pulse.\textsuperscript{9,10,13}

Figure 3.2 displays the normalized integrated intensities of the CTTS feature excited at various pump energies for iodide-doped ethanol, methanol, and water clusters containing seven solvent molecules. The CTTS excited states of ethanol- and methanol-containing clusters reveal similar time-dependent behavior while that for water-containing clusters appears much longer lived. The lifetimes of the excited state feature appear to decrease as the excitation energy
increases for all solvents. These trends are observed for all cluster sizes, \( n \).

3.5. Analysis

The complementary time dependence exhibited by the autodetachment and CTTS features for each cluster solvent, size, and excitation energy studied can be analyzed after extraction of integrated intensities at each pump-probe delay. Population dynamics are modeled with single or bi-exponential decay; for \( t \geq t_0 \), where \( t_0 \) is the zero of pump-probe delay, the multiexponential function is convoluted with a Gaussian function to account for experimental response. A delta function centered at \( t_0 \) accounts for coherence artifacts during the period of cross-correlation of the pump and probe pulses while an offset, \( I_0 \), addresses background:

\[
I = I_0 + a_0 \delta(t-t_0) + \sum_i a_i \exp \left[ -\frac{(t-t_0)}{\tau_{X_i}} \right], \quad t \geq t_0,
\]

In Equation 3.2, \( \sigma \) represents the temporal width of the Gaussian function and \( X \) is either A or B (CTTS). In general, the smallest clusters (i.e., \( n = 4, 5 \)) exhibit single exponential decay from \( t_0 \) (\( i = 1 \)) while larger clusters (\( n > 5 \)) achieve their maxima after \( t_0 \) before beginning to decay (\( i = 2 \)). The rise time \( \tau_{B1} \) for clusters following a biexponential pattern is approximately 1 ps for all materials studied. Time constants for Features A and B are generally within error bars of each other, with those for Feature A often larger due to the inherent difficulty in measuring small changes over a large background. Thus, lifetimes presented in Table 3.1 and graphically summarized in Figure 3.3 are time constants \( \tau_{B1} \) for processes described by single exponential decay and \( \tau_{B2} \) for biexponential decay processes. These lifetimes increase with cluster size and decrease with excitation energy for each system. Varying the source backing pressure between 5 and 20 psig did not noticeably affect lifetime measurements.

It should be noted that lifetimes presented for I\(^-\)·(water)\(_n\) at 263 nm were obtained using the fit function described here with data taken previously in our research group. The values reported by Kammrath et al.\(^9\) were measured by first fitting the signal at each pump-probe delay to a Gaussian function and then applying a multieponential fit to the calculated peak centers, neglecting values less than the maximum. The refitted lifetimes fall approximately within error bars of those previously reported for \( n = 4 \text{-} 7 \); for \( n = 8 \), the lifetime differs more significantly as the decay is now treated with the convolution of a Gaussian and a multieponential function where biexponential character captures a late rise to a maximum followed by decay rather than a complex decay from a maximum intensity.

3.6. Discussion

The results in Table 3.1 and Figure 3.3 show that for all solvent molecules and cluster sizes studied here, the excited state lifetime at fixed wavelength increases with cluster size, but for a fixed cluster size, decreases with increasing excitation energy. For all clusters, the longest and shortest lifetimes differ by about a factor of two over the range of wavelengths used here (272 – 238 nm). The other notable trend is that at a given excitation wavelength, the lifetimes...
for $\Gamma^{-}\cdot(H_{2}O)_{n}$ clusters are considerably longer than for comparably-sized $\Gamma^{-}\cdot(CH_{3}OH)_{n}$ and $\Gamma^{-}\cdot(CH_{2}CH_{2}OH)_{n}$ clusters, while clusters with the same number of CH$_{3}$OH and CH$_{2}CH_{2}$OH solvent molecules have essentially the same excited state lifetimes. For example, the lifetimes of $\Gamma^{-}\cdot$ (methanol)$_{8}$ and $\Gamma^{-}\cdot$ (ethanol)$_{8}$ at 263 nm excitation are 33 ps and 36 ps, respectively, but that for $\Gamma^{-}\cdot$ (water)$_{8}$ is 595 ps.

As discussed in previous work, the excited states in these halide-clusters are accessed by the cluster analog of CTTS transitions.$^{6, 10}$ The complementary dynamics of Features A and B in the time-resolved photoelectron images show that these states decay by autodetachment. Hence, the overall autodetachment mechanism is

$$I^{-}(ROH)_{n} \xrightarrow{h\nu_{pump}} I\cdots(ROH)_{n} \xrightarrow{\tau_{a}} I\cdots(ROH)_{n} + e^{-} \quad (3.3)$$

Given the large number of vibrational modes in these clusters and the very low energies of the electrons ejected by autodetachment, it is reasonable to see if these results can be understood within the framework of cluster thermionic emission. This is a statistical decay process that can be treated assuming either a canonical or microcanonical ensemble of clusters.$^{28}$ The microcanonical model developed by Klots$^{19}$ has previously been successfully applied to neutral and negatively charged clusters$^{29, 30}$ and thus provides a useful framework within which we
would like to explain the qualitative and quantitative trends seen here for halide-solvent clusters.

In this model, the rate of electron emission $k(E)$ is given by

$$
k(E) = \frac{W(E, E_b)}{h \rho(E)} \tag{3.4}
$$

where $h$ is Planck’s constant, $E$ is the total energy, $E_b$ is the adiabatic binding energy, $W(E, E_b)$ is the total number of neutral states, and $\rho(E)$ is the density of anion states. The totality of neutral states and density of anion states should both increase dramatically with increasing energy. Each of these quantities should also be strongly dependent on the number of vibrational modes in the species of interest as they express the partitioning of energy among states with energy $\leq (E - E_b)$ for $W(E, E_b)$ and between $(E$ and $E + dE)$ for $\rho(E)$.

Equation 3.4 is similar to the RRKM expression for unimolecular dissociation, but the numerator in Equation 3.4 refers to the total number of available product states as opposed to the total number of states at the unimolecular transition state. The expressions are essentially equivalent in the limit of a transition state at infinite fragment separation, with the caveat that the number of nuclear degrees of freedom considered in the numerator and denominator of Equation 3.4 is the same. Hence, some of the trends seen here are readily understood based on well known results from RRKM theory. In particular, the increasing autodetachment rate with excitation energy and the decreasing rate with cluster size are characteristic of statistical decay models.
On the other hand, the dependence of the autodetachment rate on solvent is less intuitive. For a given cluster size, one might have expected the autodetachment rate to be considerably faster for I⁻·(H₂O)ₙ than for the corresponding I⁻·(CH₃OH)ₙ or I⁻·(CH₃CH₂OH)ₙ cluster since the density of states at a particular excitation energy (i.e., the denominator is Equation 3.4) is much smaller for iodide-water clusters. Instead, we find considerably slower autodetachment for water and about the same rate for methanol and ethanol clusters.

We therefore must carefully consider the energetics involved in Equation 3.4 and determine how these differ for water- and methanol-/ethanol-containing clusters. With respect to Equation 3.3, E is the excess energy of the I···(ROH)ₙ⁻ intermediate created by the pump pulse and E_b is the adiabatic detachment energy (ADE) of this intermediate relative to the I···(ROH)ₙ + e⁻ products, as indicated in Figure 3.4. The binding energy of the iodine atom to the intermediate is estimated to be ~ 50 meV for water-containing clusters,¹⁹, ³², ³³ and if that is neglected, then E_b is the adiabatic electron binding energy of the (ROH)ₙ⁻ cluster.³⁴ Given that small water cluster anions are readily seen in mass spectrometry³, ³⁵ but methanol cluster anions are not observed until n ~ 70,¹⁵ it is reasonable to assume that E_b is positive for water cluster anions but negative or only slightly positive for methanol (and presumably ethanol) cluster anions. This effect is the most likely origin for the slower autodetachment rates in water as it will significantly reduce the number of accessible product states (i.e., W(E, E_b) in Equation 3.4) for iodide-water clusters compared to the other solvent species.

To explore these effects more quantitatively, we need to explicitly evaluate the quantities in Equation 3.4. For microcanonical thermionic emission,¹⁹ the numerator is related to the kinetic energy distribution of the ejected electrons, p(ε), by

\[ W(E, E_b) = \int_0^{E-E_b} p(\varepsilon) d\varepsilon \quad (3.5) \]

The electron energy distribution is obtained from

\[ p(\varepsilon) = \rho_v(E-E_b-\varepsilon)(L_{\text{max}}+1)^2 \quad (3.6) \]

where

\[ L_{\text{max}} = \frac{b}{\lambda} \quad (3.7) \]

in which \( \rho_v(x) \) is the density of neutral states, \( \lambda \) is the de Broglie wavelength of the electron and neutral species, and \( b \) is the classical hard-sphere collision radius. \( W(E, E_b) \) is then given by

\[ W(E, E_b) = \int_0^{E-E_b} \rho_v(x) \left[ 1 + 2 \left( \frac{\mu b^2 (E-E_b-x)}{\hbar^2} \right) / \hbar^2 \right]^{1/2} + \left( \frac{2\mu b^2 (E-E_b-x)}{\hbar^2} \right) \right] dx \quad (3.8) \]

where \( \mu \) is the reduced mass (effectively the mass of the electron). An electron spin degeneracy factor of 2 should also be included. The expressions given above assume that the rotational energy level spacing is much smaller than the excess energy imparted to the system and that the transmission coefficient, \( T(\lambda, L) \), or “sticking probability”, is 1 for \( L \leq L_{\text{max}} \) and 0 for \( L > L_{\text{max}} \).
Figure 3.5. Simulated and experimental photoelectron spectra for $\text{I}^-(\text{CH}_3\text{OH})_7$ excited at 4.87 eV (upper panel) and 5.06 eV (lower panel).

Let us consider $\text{I}^-(\text{H}_2\text{O})_5$ and $\text{I}^-(\text{MeOH})_7$ as specific examples. Figure 3.4 shows that the excess energy $E$ is given by

$$E = h\nu - \text{ADE}(\text{I}^-(\text{ROH})_n) + E_b \quad (3.9)$$

where $\text{ADE}(\text{I}^-(\text{ROH})_n)$ is the adiabatic detachment energy of the initial cluster anion. For $\text{I}^-(\text{H}_2\text{O})_5$, this was obtained either by extrapolating the adiabatic detachment energies described by Serxner et al. or by selecting the onset of the spectral feature in the photoelectron spectrum.
of Markovich et al., yielding 4.22 eV and 4.43 eV, respectively. Since the binding energy of the neutral iodine atom is quite weak and probably similar in both the intermediate anion and final neutral state, we took $E_b$ to be the ADE of $(\text{H}_2\text{O})_5^-$, and estimated it as 0.22 eV from the onset of the photoelectron spectrum of this cluster. We note that the extraction of adiabatic rather than vertical detachment energies from unstructured photoelectron spectra is subject to considerable uncertainty, but our goal here is only to come up with reasonable initial estimates for use in Equation 3.4.

Iodide-methanol energetics can be similarly described. The difference in energy between the $\Gamma$·(CH$_3$OH)$_n$ and I···(CH$_3$OH)$_n$ states was taken as the ADE estimated from unpublished single-photon photoelectron spectra measured at 240 nm in our laboratory, giving 4.60 eV for $\Gamma$·(CH$_3$OH)$_7$. Again neglecting the weak binding of the iodine atom, ADEs of the bare methanol cluster anions could be used to estimate $E_b$, however no such values exist in this size range. Instead, a selection of values ranging from slightly positive to slightly negative energies was utilized to test the effect of $E_b$ on the autodetachment rate.

The evaluation of Equation 3.4 also requires vibrational frequencies for determination of the total number and density of states. For consistency, frequencies calculated for neutral (H$_2$O)$_5$ and (CH$_3$OH)$_7$ clusters were used for both the intermediate (ROH)$_n^-$ and final (ROH)$_n$ species, under the assumption that the highly averaged quantities in Eq. 4 are relatively insensitive to the presence of an excess electron. As it is unclear if the iodine atom leaves the cluster before autodetachment occurs, particularly for $\Gamma$·(CH$_3$OH)$_n$ clusters, vibrational frequencies associated with the iodine atom were not included. The geometries for various (H$_2$O)$_5^-$ isomers calculated with density functional theory by Herbert and Head-Gordon were used as starting points for calculation of the corresponding neutral geometries. Neutral geometries were optimized with the B3LYP density functional and the 6-31(1+, 3+)G* basis set using the Q-Chem electronic structure programming suite. Frequencies were calculated using MP2/6-311(2+, 3+)G**. This method and basis set combination was previously used for geometry optimization for benchmark VDE calculations for clusters in our size range of interest. A cyclic methanol cluster geometry was generated based on the lowest energy structure proposed by Buck et al. and was optimized with B3LYP/6-31(1+, 3+)G*; frequencies were also calculated with this method and basis set. Vibrational densities of states were obtained from the Beyer-Swinehart direct counting algorithm, which calculates all possible combinations of energy partitioning among vibrational modes of a system of harmonic oscillators. The value of $b$ needed for calculation of the electron emission rate was estimated from optimized structures.

Autodetachment rates and lifetimes were calculated over a range of values for ADE($\Gamma$·(ROH)$_n$) and $E_b$ to test the model’s sensitivity to these parameters. The full set of results is presented in the Supplementary Information. Since calculated lifetimes for $\Gamma$·(H$_2$O)$_5$ were found to be relatively insensitive to cluster geometry, the results displayed are those for a representative structure. Table 3.2 lists the energetics that lie within about an order of magnitude of the experimental results for all excitation wavelengths. For $\Gamma$·(H$_2$O)$_5$, using 4.30 eV for the initial cluster anion ADE and either 0.30 eV or 0.22 eV for $E_b$ gave acceptable agreement with experiment. These numbers are close to the initial estimates obtained from previous experimental work as described above. For $\Gamma$·(CH$_3$OH)$_7$, acceptable agreement was found for values of 4.60 eV and 0.04 eV for ADE($\Gamma$·(ROH)$_n$) and $E_b$, respectively. The parameters
displayed in Table 3.2 were biased toward giving slightly faster rather than slower autodetachment compared to experiment as the calculations neglected effects due to anharmonicity of the vibrational modes that would be expected to increase the density of states and thus slow autodetachment.\textsuperscript{30}

The results in Table 3.2 and the SI show that, as expected, Equation 3.4 always yields lifetimes that decrease with increasing excitation energy, however in general calculated lifetimes changed more steeply with excitation energy than did measured lifetimes. Though changing either ADE value notably changes autodetachment lifetimes, we found that increasing $E_b$ has a much greater effect than increasing ADE($\Gamma^\cdot$(ROH)$_n$) by the same amount, i.e. that the energy difference between the neutral and excited anion states is more important than the energy difference between the neutral and initial states. This trend is consistent with the greater stability of water cluster anions compared to small-chain alcohol cluster anions leading to lower electron emission rates for water-containing clusters. Interestingly, we found that even slightly negative values of $E_b$ gave autodetachment lifetimes that were orders of magnitude larger than the experimental values. Whether this means that weakly-bound bare methanol cluster anions in this size-range can exist remains open to investigation; as of yet, none have been seen in mass spectra of clusters from our ion source.\textsuperscript{15}

We can also calculate the electron kinetic energy distribution from autodetachment, $p(\varepsilon)$, using Equation 3.6. Examining Equation 3.6, it is apparent that the choices of $E - E_b$ and $L_{max}$ are the only parameters used to model the autodetachment spectral feature. As expressed in Eq. 9, the value of $E - E_b$ is equivalent to the difference between the excitation energy and the ADE of the initial state, so changing either value should simply shift the simulated curve for a constant $L_{max}$, altering the curvature of the normalized distribution in the energy range of interest. Calculations were performed assuming exclusively $s$-wave electron emission ($L_{max} = 0$). The assumption of $s$-wave emission is consistent with the isotropic ($\beta_2 \sim 0$) photoelectron angular distribution of the autodetachment feature (Figure 3.1); note that $s$-wave detachment does not involve a centrifugal barrier\textsuperscript{45} and thus is expected to dominate for the low energy electrons associated with autodetachment in these experiments.

Simulated and measured spectra for $\Gamma^\cdot$(CH$_3$OH)$_7$ excited with two different photon energies are shown in Figure 3.5. The simulated traces follow the shape of the autodetachment spectra reasonably well, though in both examples the curvature appears too shallow for eKE values near zero. This discrepancy may in part result from the neglect of anharmonicity in density of states calculations, which, while simplifying, should result in the increasingly significant underestimation of the neutral and, most prominently, anion density of states with increasing excess energy.\textsuperscript{30}

The analysis outlined herein demonstrates that the microcanonical thermionic emission model put forth by Klots can reproduce the trends in our autodetachment rates for $\Gamma^\cdot$(ROH)$_n$ clusters involving two different solvents as well as the electron kinetic energy distribution from autodetachment. This agreement is obtained using reasonable energetics for the quantities in Figure 3.4. It thus appears that our conceptual view of the autodetachment process as outlined in Equation 3.3 is qualitatively correct, as is the idea that small variations in energetics have a significant effect on the autodetachment rate, thus explaining the slower autodetachment from
\( \Gamma \cdot (H_2O)_n \) clusters relative to comparably-sized \( \Gamma \cdot (CH_3OH)_n \) and \( \Gamma \cdot (CH_3CH_2OH)_n \) clusters. On the other hand, more sophisticated treatments including anharmonicity are needed to improve agreement between calculated and measured autodetachment rates. The neglect of anharmonicity may be particularly important in the clusters containing methanol and ethanol because the resulting increase in the density of states will have to be compensated to some extent by reducing \( E_b \), possibly yielding a negative value that would be more consistent with the non-observation of bare cluster anions in this size regime.

3.7. Summary

Femtosecond time-resolved photoelectron imaging has been used to study the charge-transfer-to-solvent process of iodide-doped water and alcohol clusters as a function of excitation energy. \( \Gamma \cdot (\text{ethanol})_n \ (4 \leq n \leq 10) \) clusters were also studied for the first time. The autodetachment decay channel was observed to deplete the CTTS excited state within 1 – 71 ps for iodide-doped methanol and ethanol clusters with 263 nm excitation while water-containing clusters were significantly more stable with respect to autodetachment due to the enhanced stability of bare water cluster anions compared to alcohol cluster anions. The similarity between iodide-methanol and iodide-ethanol cluster lifetimes with the same number of molecules alluded to an insensitivity to the quantity of vibrational modes in the system and provided further support for the idea that energetics are the driving factors for electron emission rates. The CTTS state for all systems studied was decreasingly stable to autodetachment as the excitation energy was increased from 4.57 to 5.06 eV as expected for a statistical process. Autodetachment lifetimes for \( \Gamma \cdot (H_2O)_5 \) and \( \Gamma \cdot (CH_3OH)_7 \) were modeled according to Klots’ expressions for thermionic emission from clusters and the results found to qualitatively reproduce the trend of decreasing lifetime with increasing energy as well as the large discrepancy in length between the two solvents’ lifetimes with reasonable energy parameterization. The quantitative difference between calculated and experimentally observed lifetimes likely results in part from the neglect of anharmonicity in density of states calculations and also from uncertainties in the energetics used to describe the system.
### 3.8. Supporting Information

Table 3.3. Autodetachment rates and lifetimes calculated using Klots’ microcanonical rate expression at three excitation energies for the iodide-water pentamer.

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<th>Initial State</th>
<th>Excited State ($E_0$)</th>
<th>Pump (eV)</th>
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### 3.9. Acknowledgements

This work was supported by the National Science Foundation (NSF) under Grant CHE-0649647. M.A.Y. acknowledges funding from a National Defense Science and Engineering Graduate (NDSEG) Fellowship through the Air Force Office of Scientific Research (AFOSR), 32 CFR 168a. S.B.K. is grateful for funding through an NSF Graduate Research Fellowship.

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Chapter 4. Decay mechanisms of transient negative ions of nucleobases measured with time-resolved photoelectron imaging

4.1. Abstract

Time-resolved photoelectron imaging has been utilized to probe the energetics and dynamics of the transient negative ion of the nucleobase uracil. This species is created through charge transfer from an iodide anion within a binary iodide-uracil complex using a UV pump pulse; the ensuing dynamics are followed by photodetachment with a near-IR probe pulse. The photoelectron spectra show two time-dependent features, one from probe-induced photodetachment of the transient anion state and another from very low energy electron signal attributed to autodetachment. The transient anion is observed to decay biexponentially with time constants of 100s of fs and 10s of ps, depending on the excitation energy. These dynamics are interpreted in terms of autodetachment from the initially excited state and a second, longer-lived species relaxed by iodine loss. Hydrogen loss from the N1 position may also occur in parallel.


4.2. Text

The observation that low energy electrons can lead to DNA and RNA strand cleavage via temporary negative ion states\(^1\) has motivated numerous studies of nucleic acid constituents. Gas phase studies of DNA and RNA building blocks, including individual nucleobases, nucleosides, and nucleotides, have sought to provide insight into the mechanisms of this radiation damage.\(^2\) Transient anion states of nucleobases have been posited to play a major role in DNA mutagenesis, perhaps via a charge transfer process from an initially charged nucleobase moiety to a sugar-phosphate bond.\(^3\), \(^4\) In this Chapter, we explore the dynamics of transient anion states of uracil via time-resolved photoelectron imaging\(^5\) of an iodide-uracil binary complex.

The interaction of excess electrons with uracil and other nucleobases has been studied in the gas phase using low energy electron scattering,\(^6\), \(^7\) negative ion photoelectron spectroscopy,\(^8\)\(^-\)\(^10\) and Rydberg electron transfer.\(^11\) Total electron scattering cross section measurements show structure below 2 eV associated with unoccupied \(\pi^*\) orbitals of uracil,\(^6\) while dissociative electron attachment (DEA) studies have shown that hydrogen atom loss from the N1 position in the transient negative ion \(\text{U}^{*-}\) occurs at collision energies as low as 0.7 eV.\(^6\), \(^7\), \(^12\)-\(^14\)
The nature of the uracil anion has been directly probed in photoelectron spectroscopy (PES) and Rydberg electron transfer (RET) studies. PES experiments have measured the binding energy of the dipole-bound species as ~ 90 meV and estimated that valence anions of uracil bind excess electrons by 10s to 100s of meV. These species are clearly distinguishable in photoelectron spectra, as dipole-bound states consist of narrow features with low electron binding energies reflecting the similarity between the anion and neutral geometries, while valence-bound anions have characteristically broader features. Only dipole-bound anions of uracil have been observed using conventional ion generation methods, but the uracil anion can transform from a dipole-bound to a valence-bound state upon complexation with one xenon atom or water molecule.

Though DEA and single-photon PES experiments probe aspects of the uracil anion, neither provides a complete picture of its energetics and dynamics. Here we describe a novel approach to investigating the time-resolved dynamics of electron attachment to uracil based on photo-initiation of intracluster charge transfer in a binary halide-nucleobase complex, $I^- \cdot U$, to form a transient negative ion (TNI) of uracil, $I\cdots U^{*-}$:

$$I^- \cdot U \xrightarrow{hv_{\text{pump}}} I\cdots U^{*-} \xrightarrow{\text{?}}$$

(4.1)

Upon applying a femtosecond ultraviolet pump pulse at or above the threshold for direct detachment of the iodide-uracil complex, the excess electron is ejected with low kinetic energy and can interact with the uracil moiety to form a TNI, in analogy to DEA studies. A second time-delayed femtosecond pulse at 790 nm (1.57 eV) detaches the electron. The resulting electron kinetic energy (eKE) distribution is measured using photoelectron imaging, thereby probing the lifetime and decay dynamics of the TNI.

Iodide-uracil clusters were prepared by flowing argon gas over a methyl iodide reservoir into an Even-Lavie valve containing uracil heated to 205°C and operating at a pulse repetition rate of 500 Hz. Further details of the femtosecond time-resolved photoelectron spectrometer have been described elsewhere.

Figure 4.1 shows one-photon photoelectron spectra of the iodide-uracil binary complex recorded at excitation energies ranging from 4.21 eV to 5.31 eV and plotted as a function of electron binding energy (defined as $eBE = h\nu - eKE$). Two main features are apparent in the spectra: an energy invariant peak A centered at 4.11 eV, representing the vertical detachment energy (defined as $VDE = h\nu - eKE_{\text{max}}$) of $I^- \cdot U$, and a feature C appearing at approximately $eBE = h\nu$, corresponding to electron signal at nearly zero kinetic energy for all five excitation energies. The top panel also shows an additional direct detachment feature B arising from the $^2P_{1/2}$ spin orbit state of complexed iodine that is inaccessible at lower excitation energies. The VDE obtained from feature A indicates a solvent shift of 1.05 eV with respect to bare iodide. This shift is noticeably larger than that seen in binary complexes of iodide with THF (0.25 eV), water (0.45 eV), and aniline (0.53 eV).

Figure 4.2 displays time-resolved PE spectra plotted against eKE for the binary cluster
excited at 4.69 eV and probed at 1.57 eV. Features A and C at 0.6 eV and near zero kinetic energy, respectively, are apparent at every pump-probe delay, while a third, broad, low intensity feature D appears between 1.0 – 1.6 eV at zero pump-probe delay ($\Delta t = 0$) and survives for several picoseconds. Similar spectra are observed for excitation energies ranging from 4.32 – 5.02 eV, but owing to low signal-to-noise outside of a central range only results obtained for 4.69 – 4.90 eV pump energies will be discussed here.

The integrated intensities of features C and D are shown in Figure 4.3 to reveal complementary yet differing dynamics. At $\Delta t = 0$, the transient feature D appears and feature C is depleted. The transient feature then exhibits biexponential decay; Table 4.1 shows time constants derived from fitting its dynamics to a biexponential function convoluted with a
Figure 4.2. TRPE spectrum of the I⁻·U complex excited at 4.69 eV and probed at 1.57 eV. The inset shows the optimized iodide-uracil cluster geometry.

Gaussian function\(^{23}\) with a full width at half maximum of 150 fs. We find fast decay time constants of 300 – 600 fs and slow decay time constants of 10 – 50 ps. Time constants are observed to decrease with increasing excitation energy. The depletion and initial recovery of feature C mirror the early-time dynamics of feature D, however feature C overshoots its initial intensity within 1 – 2 ps and continues to rise for approximately 20 ps before decaying over 50 – 100 ps.

Geometry optimizations of the binary cluster were carried out using the Gaussian 09 software package\(^{24}\) at the MP2/aug-cc-pVDZ level with an aug-cc-pVQZ pp pseudopotential\(^{25}\) for iodide. The inset of Figure 4.2 shows the optimized structure, which has C\(_s\) symmetry with the iodide anion residing between the hydrogen bound to N1 and the neighboring vinyl hydrogen near the positive pole of the ~ 5 D permanent dipole moment of uracil\(^6\), \(^{26}\). Compared to the previously calculated equilibrium geometry of neutral uracil\(^{27}\) the N1–H and C5–C6 bonds of the iodide-complexed species are slightly elongated and the hydrogen atoms bound to N1 and C6
angle inward by several degrees. Subsequent energy optimizations at the CCSD level found a VDE of 4.13 eV, consistent with experimental results and previous DFT calculations.\textsuperscript{28}

Comparison between measured TRPE spectra for the \textit{I}−·\textit{U} cluster and those for iodide-containing solvent clusters\textsuperscript{19, 29-31} suggests that feature D arises from probe-induced photodetachment from the \(\text{I}··\text{U}^{*−}\) state created by the pump pulse, whereas the low eKE feature C represents vibrational autodetachment from this species, i.e.

\[
\begin{align*}
\text{I}−·\text{U} & \xrightarrow{hv_{\text{pump}}} \text{I}··\text{U}^{*−} \xrightarrow{hv_{\text{probe}}} \text{I}··\text{U} + \text{e}− \quad \text{(feat. D)} \\
& \xrightarrow{k_{\text{b}}} \text{I}··\text{U} + \text{e}− \quad \text{(feat. C)}
\end{align*}
\]

However, as discussed below, Equation 4.2 represents only a partial picture of the \(\text{I}··\text{U}^{*−}\) decay dynamics.

The cluster excited state \(\text{I}··\text{U}^{*−}\) is formed by transferring the excess electron from iodide to the uracil molecule to create an excited uracil anion perturbed by an iodine atom. The broadness of the corresponding transient feature D in the photoelectron spectrum is characteristic of a valence-bound state. Moreover, the VDE of feature D lies between 0 – 0.6 eV, close to the calculated VDE of 0.6 eV for the valence-bound state of the uracil anion formed by adding an electron to the low-lying, unoccupied \(\pi^*\) orbital of the uracil molecule.\textsuperscript{27} It thus appears that the TNI formed by charge transfer from the iodide anion is this valence-bound species rather than a dipole-bound state. The presence of the iodine atom may suppress initial formation of a dipole-bound state as it resides within the region of maximum electron density for the dipole-bound state of the bare anion.\textsuperscript{14}

Our experiment can be considered in terms of intracluster electron scattering: the electron produced by photodetachment from the iodine moiety will either be ejected into free space, resulting in the direct detachment features A and B, or undergo indirect scattering from the uracil molecule, forming the TNI from which the time-dependent features C and D derive. The effective electron collision energy \(E_c\) is then given by \(E_c = hv_{\text{pump}} - \text{VDE}\), where the VDE of the \(\text{I}−·\text{U}\) cluster is 4.11 eV as determined from feature A in Figure 4.1. Thus, \(E_c\) varies from 0.1-1.2 eV over the range of excitation energies considered and includes the energy range where electron scattering experiments and theoretical studies show attachment to the uracil \(\pi^*\) orbital.\textsuperscript{32, 33}

Direct absorption of the UV photon by the uracil moiety itself is possible as the excitation energies utilized fall on the low energy side of its \(\pi \rightarrow \pi^*\) absorption band.\textsuperscript{34, 35} This process would lead to a complex comprised of the iodide anion and the electronically excited uracil molecule. Photodetachment of such a species by the infrared probe photon would not be feasible. However, if charge transfer could occur within this complex from the iodide into the singly-occupied \(\pi\) orbital of the excited uracil, the same \(\text{I}··\text{U}^{*−}\) final state discussed above would result. This process would most likely lead to an observable delay in the buildup of feature D, which is inconsistent with the near instantaneous rise time observed for this signal. Moreover, the ten-fold enhancement of the absorption cross section for uracil between 4.5 and 5.3 eV would be reflected by a substantial increase in the autodetachment yield relative to the direct detachment yield in single-color PE spectra, but no such trend is observed. It thus appears
that the results presented here do not come about through this mechanism.

We next consider the possible decay pathways for the transient negative ion state. The complementary early-time dynamics of the transient and autodetachment features imply that the
I···U*− state created by the pump pulse decays at least in part via autodetachment, as shown in Equation 4.2. While the canonical tautomer of neutral uracil is planar,27 the π* valence-bound anion state has a non-planar, puckered structure,10, 27, 28 so electron attachment into the π* orbital will result in significant vibrational excitation in the anion state that will then be metastable with respect to autodetachment.

We observe the general trend that the decay rate of the TNI increases with excitation energy, which translates into increased vibrational energy in the TNI. This behavior is expected for a statistical process such as vibrational autodetachment,19 which has also been identified as the primary decay mechanism for other iodide-containing cluster systems.19, 29-31 However, the results for I−·U differ from these previous experiments because (i) the transient feature D exhibits biexponential rather than monoexponential decay, and (ii) the autodetachment feature C does not simply mirror the time-dependence of feature D. We therefore must consider other decay mechanisms for the TNI that could occur in addition to autodetachment.

The observation of biexponential decay for the transient feature implies that the TNI decays not only by autodetachment but also to another state with a longer lifetime. TRPE spectra do not display an accompanying shift in VDEs for the transient feature D, indicating that the second state has a VDE similar to that of the initial state. A plausible mechanism involves atomic iodine loss followed by autodetachment in addition to the dynamics in Equation 4.2:

\[
I^-\cdot U \xrightarrow{hv_{pump}} I\cdots U^\cdots \xrightarrow{k_1} I + U^\cdots \xrightarrow{hv_{probe}} I + U + e^- 
\]

In this case, \(\tau_1 = 1/(k_1+k_2)\) and \(\tau_2 = 1/k_3\). The binding energy of the neutral iodine atom to the initially prepared I···U*− state is expected to be on the order of 50 meV,29, 36 so iodine loss should be feasible due to the vibrational excitation of the initial TNI. The resulting anionic uracil fragment, U*−, would be a valence-bound state with a VDE similar to that of the initial TNI. Thus, probe-induced detachment would contribute to feature D, however the U*− state should autodetach more slowly than the initial state due to its reduced vibrational energy.

Another channel to consider is hydrogen atom loss from the N1 position of uracil to form the deprotonated uracil anion, (U − H)−.6, 7, 12-14, 37 Electron transmission spectroscopy and DEA studies have estimated the threshold energy for this channel to be at most 0.8 eV.6, 12 In our experiment, the analogous process could occur via

\[
I^-\cdot U \xrightarrow{hv_{pump}} I\cdots U^\cdots \xrightarrow{hv_{probe}} I\cdots (U - H)^- + H 
\]

The previously defined effective electron collision energy in our experiment, \(E_{ec}\), exceeds the threshold for DEA at excitation energies of 4.9 eV or lower. These values are close to the calculated threshold of 4.6 eV for hydrogen atom loss from I−·U.28 Thus, the H loss channel likely opens in the range of excitation energies used herein and so may occur in parallel with
autodetachment and iodine loss. Direct observation of this process is not possible, however, because the binding energy of the I···(U - H)^− species is expected to exceed 3 eV,38-41 a value well above the infrared probe energy.

Comparison between the transient and autodetachment signals in Figure 4.3 reveals that the “overshoot” and decay of the autodetachment feature C occur during the longer-time decay of feature D. Assuming that our assignment of this longer-time decay to autodetachment from vibrationally excited U^∗ is correct (Equation 4.3), the time-dependence of feature C may indicate that the probe laser enhances autodetachment signal from this species in addition to detaching it directly. Such a process could occur if the probe laser were resonant with an electronic transition in the U^∗ fragment; a similar mechanism has been invoked to explain probe-enhanced autoionization in time-resolved experiments on He droplets.42 Further consideration is needed to confirm this interpretation of the feature C dynamics.

The experiments described herein represent the first direct measurements of the lifetime of the transient negative ion of uracil. The insight gained into the temporary uracil anion state in this TRPE spectroscopy study demonstrates the strong link between TRPES and DEA experiments and establishes time-resolved photoelectron spectroscopy as a powerful method for probing the energetics and dynamics of electron attachment to nucleobases. Thus, we have shown that time-resolved radiation chemistry can be used to examine transient negative ions of nucleic acid building blocks in the gas phase from their formation to their decay via fragmentation or relaxation.

4.3. Acknowledgements

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4.4. References

Chapter 5. Decay dynamics of nascent acetonitrile and nitromethane dipole-bound anions produced by intracluster charge transfer

5.1. Abstract

Decay dynamics of nascent dipole bound states of acetonitrile and nitromethane are examined using time-resolved photoelectron imaging of iodide-acetonitrile (I⁻·CH₃CN) and iodide-nitromethane (I⁻·CH₃NO₂) complexes. Dipole-bound anions are created by UV-initiated electron transfer to the molecule of interest from the associated iodide ion at energies just below the vertical detachment energy of the halide-molecule complex. The acetonitrile anion is observed to decay biexponentially with time constants in the range of 4 ps and 900 ps. In contrast, the dipole bound state of nitromethane decays rapidly over 400 fs to form the valence bound anion. The nitromethane valence anion species then decays biexponentially with time constants of 2 ps and 1200 ps. The biexponential decay dynamics in acetonitrile are interpreted as iodine atom loss and autodetachment from the excited dipole-bound anion, followed by slower autodetachment of the relaxed metastable ion, while the dynamics of the nitromethane system suggest that a dipole-bound anion to valence anion transition proceeds via intramolecular vibrational energy redistribution to nitro-group modes in the vicinity of the iodine atom.

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5.2. Introduction

In recent decades, much theoretical and experimental work has focused on the study of dipole-bound anions. Fermi and Teller predicted that fixed dipoles with dipole moments \( \mu \) greater than 1.6 Debye should bind electrons via dipolar \((-1/r^2)\) interactions,\(^1\)\(^-\)\(^2\) while Crawford and Garrett later determined that rotating molecules in the gas phase with dipole moments greater than 2 D should stably bind electrons in diffuse orbitals with low electron affinities (10s of meV).\(^3\)\(^-\)\(^7\) Polar species such as acetonitrile (CH₃CN),\(^8\),\(^9\) the water dimer,\(^10\) the nucleobases uracil and thymine,\(^11\) and small ketones and aldehydes\(^12\) have been observed to form ground-state dipole-bound anions. Dipole-bound states (DBSs) have also been detected as excited electronic states or vibrational Feshbach resonances of conventional valence anions in cyanomethide\(^13\) and other species.\(^14\),\(^15\) In nitromethane (CH₃NO₂), the DBS of the anion has been described as a ‘doorway’ to a more stable valence-bound state (VBS), with the DBS to VBS transition occurring on a timescale competitive with electron autodetachment.\(^16\)-\(^18\) In this study, we carry out time-resolved photoelectron imaging on I⁻·CH₃CN and I⁻·CH₃NO₂ binary complexes to directly observe the formation and lifetimes of the dipole-bound anions of acetonitrile and nitromethane as well as the DBS to VBS transition in CH₃NO₂⁻.
The dipole-bound ground state of CH$_3$CN$^-$ was one of the first such species to be examined. The diffuse orbital bearing the excess electron is supported at the electropositive methyl end of acetonitrile by a large dipole moment ($\mu = 3.92$ D) and minimally distorts the geometry of the molecule from that of the neutral. Acetonitrile anion formation via Rydberg electron transfer (RET) collisions with Xe atoms in highly excited Rydberg states occurs most efficiently for atoms with principal quantum numbers near $n = 13$, while field detachment of these species estimated an electron binding energy (eBE) of approximately 11 meV, characteristic of diffuse dipole-bound states. In experiments by Johnson and co-workers, CH$_3$CN$^-$ was produced by photo-induced intracomplex charge transfer in I$^- \cdot$CH$_3$CN near 3.54 eV, the peak of the photoelectron spectrum (the vertical detachment energy, VDE) of the complex. This species was identified as a dipole-bound state via its photoelectron spectrum, which displayed a single narrow peak with an eBE of about 10 meV. The lifetimes of weakly excited dipole-bound anions of acetonitrile generated by RET have been observed to exceed microseconds with electron autodetachment or black-body induced photodetachment identified as the primary decay mechanisms for the metastable species. No acetonitrile valence anion is expected to exist as the lowest unoccupied molecular orbital occurs nearly 3 eV above the neutral ground state.

Formation of the nitromethane anion, CH$_3$NO$_2^-$, has been observed upon RET from rare gas and alkali atoms to CH$_3$NO$_2$ and in collisions of CH$_3$NO$_2$ with high energy alkali atoms. The anion has been investigated by PES and its vibrational spectrum has been measured via autodetachment spectroscopy. Nitromethane has a dipole moment of 3.46 D, which is sufficient to support a dipole-bound anion. However, RET experiments show that the range of Rydberg states over which electron transfer to CH$_3$NO$_2$ occurs is considerably broader than that observed when a pure DBS state is formed (i.e. in CH$_3$CN), implying coupling between the nitromethane anion DBS and the more strongly bound VBS. Indeed, the negative ion photoelectron spectrum of nitromethane anions produced in a supersonic expansion of seeded argon gas reported in the same paper was quite broad, with extensive, partially resolved vibrational structure and a VDE of ~1 eV. Such a spectrum is characteristic of a valence anion with a geometry differing from that of the neutral species, as opposed to the dominance of the vibrational origin typically seen at very low eBE in the photoelectron spectrum of a dipole-bound anion.

The photoelectron spectrum of CH$_3$NO$_2^-$ measured by Weber and co-workers shows features attributable to both the DB and VB anions with adiabatic detachment energies of 8 meV and 172 meV, respectively, placing the VBS 164 meV below the DBS. The absence of the DBS signature in other PE spectra and the suppression of the DBS in RET to CH$_3$NO$_2$ complexed to a single Ar atom suggest that the dipole-bound anion of nitromethane is a fragile species formed only under restricted conditions, consistent with the picture of a low-energy curve crossing with the VBS. The experimental evidence suggestive of a DBS to VBS transition for the nitromethane anion is in accordance with electronic structure calculations that show the VBS to be more stable than the DBS.

The I$^- \cdot$CH$_3$NO$_2$ complex studied here has previously been investigated by photofragment action spectroscopy and photoelectron imaging. The action spectroscopy experiments, in
which anionic and neutral fragments were detected as functions of excitation energy, yielded an electronic absorption spectrum of the complex peaking just below 3.60 eV, the VDE of the initial complex. The electronic band was attributed to a dipole-bound excited state of the complex, which was observed to decay to CH$_3$NO$_2^-$ as well as I$^-$ and NO$_2^-$. The CH$_3$NO$_2^-$ photofragment was characterized by electric field stripping experiments which, by comparison with similar experiments on anions formed via RET,$^{16}$ suggested that the photofragment anion exhibited some DBS character. The authors attributed vibrational resonances measured in the action spectra of the other photofragments to nitro-associated modes relevant to the valence anion, providing further evidence for mixing of the DBS and VBS states.

In this work, we examine the nature and decay dynamics of acetonitrile and nitromethane anions produced upon photoexcitation of binary iodide-molecule complexes using time-resolved photoelectron spectroscopy (TRPES). These experiments represent a continuation of efforts in which TRPES is used to study electron-induced cluster dynamics induced by photodetachment of a complexed iodide anion.$^{41, 42}$ In analogy to our earlier work with iodide-nucleobase complexes$^{43, 44}$ and the work of others,$^{25, 39}$ transient negative ions (TNIs) of the form [I···M]$^-$ are generated via photo-initiated charge transfer from iodide to the associated molecule by a femtosecond UV pulse $h\nu_1$ with energy near the VDE of the complex:

$$\Gamma^- \cdot CH_3CN \xrightarrow{h\nu_1} [I \cdots CH_3CN]^- \xrightarrow{\Delta t} ?$$

$$\Gamma^- \cdot CH_3NO_2 \xrightarrow{h\nu_1} [I \cdots CH_3NO_2]^- \xrightarrow{\Delta t} ?$$

(5.1)

The dynamics of the TNIs are monitored by photodetachment with a femtosecond near-IR probe pulse $h\nu_2$ by recording electron kinetic energy (eKE) and photoelectron angular distributions (PADs) of the resultant electrons using photoelectron imaging. The acetonitrile anion is formed in and remains a DBS, decaying via autodetachment and iodine atom loss over hundreds of picoseconds, while the nitromethane anion is initially formed in a DBS but decays within hundreds of femtoseconds to form the VBS. The resulting vibrationally excited VBS exhibits biexponential decay with time constants of 2 ps and 1200 ps that is attributed to decay via autodetachment and iodine atom loss. This study provides further insight into the decay mechanisms of biologically relevant systems such as pyrimidine nucleobase anions that also exist as both dipole- and valence-bound states.$^{11, 45, 46}$

5.3. Experimental Methods

The I$^- \cdot$CH$_3$CN and I$^- \cdot$CH$_3$NO$_2$ complexes were studied using femtosecond time-resolved photoelectron imaging. Detailed descriptions of the imaging apparatus and laser system have been presented elsewhere.$^{47-49}$ Binary complexes were created by flowing 50 psig of neon gas over a supply of iodomethane and a reservoir of the liquid of interest chilled with ice water. The gaseous mixture was subsequently expanded through an Even-Lavie valve$^{50}$ pulsed at 500 Hz and crossed with a ring electrode ionizer to create halide-molecule cluster anions. The anionic clusters were then perpendicularly extracted with a Wiley-McLaren time-of-flight mass spectrometer$^{51}$ and steered with ion optics toward a mass gate for isolation of the relevant species.
Figure 5.1. Optimized structures for the a) I$^-\cdot$CH$_3$CN and b) I$^-\cdot$CH$_3$NO$_2$ complexes. Calculations were performed at the MP2/aug-cc-pVDZ level using the aug-cc-pVDZ pseudopotential for iodide. Relevant parameters are listed in Table 5.1.

Table 5.1. Relevant structural parameters for the I$^-\cdot$CH$_3$CN and I$^-\cdot$CH$_3$NO$_2$ complexes and the respective bare neutral and valence anion species. Bond distances are presented in Angstroms, angles in degrees, and dipole moments in Debye. The value $\alpha$ is the angle between the C—H bond and the C—C bond axis in CH$_3$CN, while $\theta_{\text{tilt}}$ is the angle between the plane containing the nitro group and the C—N bond axis of CH$_3$NO$_2$.

<table>
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<tr>
<th></th>
<th>CH$_3$CN$^a$</th>
<th>CH$_3$CN$^-$$^a$</th>
<th>I$^-\cdot$CH$_3$CN</th>
<th>CH$_3$NO$_2$$^b$</th>
<th>CH$_3$NO$_2^-$$^b$</th>
<th>I$^-\cdot$CH$_3$NO$_2$</th>
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<td>R(C—N)</td>
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<td>1.097</td>
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<td>R(C—H)</td>
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<td>1.098</td>
<td>1.082</td>
<td>1.088</td>
<td>1.093</td>
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<tr>
<td>R(C—I)</td>
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<td>3.609</td>
<td>R(N—O)</td>
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<td>1.314</td>
<td>1.242</td>
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<td>$\alpha$</td>
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<td>109.9</td>
<td>111.2</td>
<td>R(C—I)</td>
<td>3.511</td>
<td></td>
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<tr>
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<td></td>
<td></td>
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</tr>
<tr>
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<td></td>
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<td></td>
<td></td>
<td>107.92</td>
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<td></td>
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<td></td>
<td>1.53</td>
<td>33.73</td>
</tr>
</tbody>
</table>

$^a$Reference 21.
$^b$Reference 20.

The ultraviolet pump pulse was generated from a 1 kHz, 1.6 mJ near-IR pulse (KM Labs Griffin Oscillator and Dragon Amplifier) by frequency doubling the second harmonic signal of an optical parametric amplifier (Light Conversion TOPAS-C). Pump photon energies were selected based on the relative photoabsorption cross sections reported by Johnson and co-workers.$^{25,39}$ Most data were taken at two excitation energies for each system: one resonant with the maximum absorption (3.53 eV and 3.60 eV for the acetonitrile and nitromethane systems, respectively) and one slightly off-resonant (3.47 eV and 3.53 eV, respectively). The fundamental at 1.56 eV was used as the probe. Cross correlations measured outside the chamber
Figure 5.2. Representative POP-reconstructed Cartesian photoelectron images for a) \( \Gamma^-\cdot\text{CH}_3\text{CN} \) excited at 3.47 eV and b) \( \Gamma^-\cdot\text{CH}_3\text{NO}_2 \) excited at 3.60 eV. Both systems are probed at 1.56 eV. As images are four-way symmetrized for analysis, only a single quadrant is displayed. The laser polarization is indicated to be vertical. The grey spot in the center of each image represents near-zero kinetic energy electrons, which are several orders of magnitude more intense than transient photoelectron signals.

yielded values below 150 fs.

Photoelectrons were directed toward a chevron-stacked pair of microchannel plates coupled to a phosphor screen using a 3-plate velocity map imaging ion optical assembly. 2D photoelectron distributions were imaged using a charge-coupled device camera; from these images, 3D photoelectron kinetic energy (eKE) distributions and photoelectron angular distributions (PADs) were reconstructed using the basis-set expansion (BASEX)\(^{52}\) and polar onion peeling (POP)\(^{53}\) methods. The BASEX method produces more reliable eKE distributions near zero eKE (corresponding to the image center) than POP, for which center-point noise obscures photoelectron signal in this energy region. However, PADs obtained from BASEX reconstruction suffer from more noise away from the image center than those obtained with POP. Thus, eKE distributions were examined with BASEX, while PADs were examined with POP.

Anisotropy parameters, \( \beta_i \), were extracted by fitting the photoelectron angular distributions according to\(^{54}\)

\[
I(\theta) = \frac{\sigma_{\text{total}}}{4\pi} \left[ 1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta) \right]
\]

(5.2)
in which $\sigma_{\text{total}}$ represents the total photodetachment cross section, $\theta$ is the angle between the laser polarization and the ejected electron, and $P_i$ is a Legendre polynomial. $\beta_2$ is constrained to values between -1 and 2, corresponding to perpendicular and parallel detachment processes, respectively. Single-photon processes should show no dependence on $\beta_4$.

5.4. Theoretical Methods

Geometry optimizations of the binary anion complexes were performed using the Gaussian 09\textsuperscript{55} computational suite at the MP2/aug-cc-pVDZ level with an aug-cc-pVDZ pseudopotential\textsuperscript{56} for iodide. Optimized structures of the I$^-\cdot$CH$_3$CN and I$^-\cdot$CH$_3$NO$_2$ complexes are presented in Figure 5.1, while relevant bond distances and other parameters are summarized in Table 5.1. Previously calculated\textsuperscript{20, 21} parameters for the acetonitrile DB anion, the nitromethane VB anion, and both bare neutral species are also included. The linear alignment of the iodide with the methyl end of the acetonitrile molecule is consistent with previously calculated structures.\textsuperscript{37-39} The iodide is situated 3.61 Å from the methyl carbon atom and minimally perturbs the structure of the molecule.\textsuperscript{21} In the nitromethane system, the iodide sits slightly closer and non-collinearly to the molecular axis and interacts more strongly with the methyl group, noticeably reorienting two of the hydrogen atoms. The plane containing the nitro group is also slightly tilted relative to this axis in both I$^-\cdot$CH$_3$NO$_2$ and neutral CH$_3$NO$_2$, and is significantly distorted in the nitromethane valence anion.\textsuperscript{37} VDEs for I$^-\cdot$CH$_3$CN and I$^-\cdot$CH$_3$NO$_2$ were calculated to be 3.55 and 3.62 eV, in good agreement with experimental values.\textsuperscript{25, 39}

5.5. Results

5.5.1. Iodide-acetonitrile

Time-resolved photoelectron images for I$^-\cdot$CH$_3$CN were recorded at excitation energies ranging from 3.43 eV to 3.59 eV. Representative POP-reconstructed Cartesian images measured at three pump-probe delays using a pump photon energy of 3.47 eV are displayed in Figure 5.2a. At negative pump-probe delays, where the 1.56 eV probe pulse arrives prior to the UV pump pulse, the only signal observed is an intense, isotropic feature A at the image center, corresponding to near-zero electron kinetic energy. At $\Delta t = 0$, two additional features B and C appear. Both features display anisotropy, showing greater intensity at approximately $\theta = \pi/4$. At $\Delta t = 267$ fs, feature B is no longer apparent, and the photoelectron angular distribution of feature C is most intense at $\theta = 0$, suggestive of parallel detachment.

Figure 5.3a shows a contour plot of eKE distributions for the iodide-acetonitrile complex over a range of pump-probe delays. Feature A is several orders of magnitude more intense than the other features and shows no notable intensity variation with pump-probe delay, so it is largely excluded for clarity. The weak feature at 1.1 eV shows minimal time variation and is assigned as three-probe-photon detachment of I$^-\cdot$CH$_3$CN. Feature B rapidly appears and disappears around $\Delta t = 0$. Its eKE of $\sim$0.6 eV corresponds to an electron binding energy, eBE, of 0.96 eV (eBE = $h\nu$ – eKE). Feature C emerges at $\Delta t = 0$ and undergoes a large decrease in intensity as well as a small change in eKE over 1 ps, eventually settling at 1.54 eV and persisting for hundreds of ps. Both features B and C are relatively narrow, displaying widths limited by the
Figure 5.3. Time-resolved photoelectron (TRPE) spectra at short pump-probe delays for a) $\Gamma \cdot \text{CH}_3\text{CN}$ excited at 3.55 eV and b) $\Gamma \cdot \text{CH}_3\text{NO}_2$ excited at 3.60 eV. Panel c) shows photoelectron spectra at selected delays for $\Gamma \cdot \text{CH}_3\text{NO}_2$. Both systems were probed at 1.56 eV.
Figure 5.4. Integrated intensities of the transient features observed in $\Gamma^{-}\cdot$CH$_3$CN TRPE spectra pumped with 3.47 eV and probed at 1.56 eV. Panel a) shows the early decay dynamics of features $C_1$ (gray squares) and $C_2$ (black circles) and the cross-correlation limited feature B (blue triangles), while panel b) shows the long-time decay of feature C. Fits are displayed as solid lines.
Figure 5. Comparison of integrated intensities of the transient feature C illustrating the variance in the relative intensities of features $C_1$ (gray background) and $C_2$ (white background) observed in $\Gamma\cdot\text{CH}_3\text{CN}$ TRPE spectra measured with a range of pump energies and probed at 1.56 eV.

Figure 5.4a displays the integrated intensities of the transient features B and C at short pump-probe delays. Feature B peaks at $\Delta t = 0$ and then disappears, while feature C is markedly different near and away from $\Delta t = 0$, mimicking feature B around $\Delta t = 0$ and then decreasing in intensity to a slowly decaying signal. Accordingly, feature C is best described as consisting of two components, $C_1$ and $C_2$, at early ($\Delta t < 120$ fs) and later delays, respectively, as delineated in Figure 5.4a. The intensity of feature $C_2$ decays to approximately half of its initial intensity by 1 ns, the longest pump-probe delay sampled (Figure 5.4b). Figure 5.5 shows that the relative integrated intensities of features $C_1$ and $C_2$ vary significantly with excitation energy, with the highest value $C_2/C_1$ seen at 3.53 eV (green triangles), closest to the peak in the electronic absorption spectrum. As shown in Figure 5.6, over the range of pump energies used here, the central eKE observed for feature $C_2$ remains static, while that for $C_1$ shifts to higher eKE as the pump energy is increased.

The anisotropy parameters associated with feature C for $\Gamma\cdot\text{CH}_3\text{CN}$ excited at 3.47 eV are shown in Figure 5.7a, superimposed upon the integrated intensity of the feature. At $\Delta t = 0$, where feature $C_1$ dominates, $\beta_2$ is approximately 0.3 while $\beta_4$ is -0.6. These values increase to asymptotic values near 0.9 and 0, respectively, for feature $C_2$. Anisotropy parameters do not exhibit any notable changes with excitation energy.

energy resolution of the femtosecond photoelectron spectrometer ($\sim 50$ meV).
Figure 5.6. Comparison of electron kinetic energies (eKEs) of features C₁ (red dotted lines) and C₂ (blue lines) of \( \Gamma \cdot \text{CH}_3\text{CN} \) measured with several different excitation energies. The gray dashed line denotes 1.54 eV, the peak eKE value for C₂ with all excitation energies.

5.5.2. Iodide-nitromethane

Representative photoelectron images for \( \Gamma \cdot \text{CH}_3\text{NO}_2 \) excited at 3.60 eV are displayed in Figure 5.2b. As observed for \( \Gamma \cdot \text{CH}_3\text{CN} \), at negative delays, the images are dominated by a central isotropic feature (D). The additional weak feature at larger eKE is barely apparent at later times and is attributable to three-photon detachment of \( \Gamma \cdot \text{CH}_3\text{NO}_2 \) by the probe pulse. The
Figure 5.7. Anisotropy parameters associated with the a) transient feature C observed in I⁻·CH₃CN TRPE spectra excited at 3.47 eV and the transient features b) E and c) F observed in I⁻·CH₃NO₂ TRPE spectra excited at 3.60 eV. Both systems were probed at 1.56 eV. Representative $\beta_2$ (red squares) and $\beta_4$ values (blue triangles) are shown against the integrated intensities (black circles) of the features.
image at $\Delta t = 0$ includes a well-defined anisotropic feature E similar to feature C observed for the $\Gamma' \cdot \text{CH}_3\text{CN}$ system. In addition to this feature, a low intensity, weakly anisotropic feature F spans eKEs between features D and E. In the last image, at $\Delta t = 3267$ fs, feature E has disappeared and the intensity of feature F has significantly increased.

Figure 5.3b displays eKE distributions for $\Gamma' \cdot \text{CH}_3\text{NO}_2$ over a range of pump-probe delays. Like feature A observed for $\Gamma' \cdot \text{CH}_3\text{CN}$, the largely excluded feature D at low eKE dominates the time-resolved photoelectron spectra and varies minimally with pump-probe delay. The narrow feature E at 1.54 eV shows no variation in eKE with excitation energy and decays rapidly after $\Delta t = 0$. The decay of feature E precedes the rise of the more intense feature F, an uneven and broad feature that spans the energy range 0.3 – 1.5 eV. The intensity of feature F achieves a maximum after approximately 1 ps and then decreases slowly over hundreds of ps. Photoelectron spectra at selected short pump-probe delays are presented in Figure 5.3c. The spectra emphasize the apparent intensity exchange between features E and F and their distinct spectral signatures. Some overlap between features E and F occurs in the range of 1.4 eV.

The integrated intensities of features E and F are presented in Figure 5.8. Feature E exhibits fast decay over hundreds of fs while feature F displays a near-complementary rise, peaking at about 1 ps before decaying biexponentially (see Section V) over hundreds of ps. Time-dependent anisotropy parameters $\beta_2$ and $\beta_4$ are superimposed on the integrated intensities of features E and F in Figures 5.7b and 5.7c. $\beta_2$ for both features shows minimal variation with pump-probe delay and maintains a value near 0.6. Some variation in $\beta_4$ is apparent near $\Delta t = 0$ for both features, with the value increasing from slightly negative values to approximately 0 within 200 fs.

5.6. Analysis

The time evolution of the transient features observed can be described by a convolution of a Gaussian laser response function

$$L(t) = \frac{1}{\sigma_{cc}\sqrt{2\pi}} \exp\left(-\frac{t^2}{2\sigma_{cc}^2}\right)$$

and a molecular response function

$$M(t) = I_0 \quad t < 0$$

$$I_0 + \sum_i A_i \exp\left(-\frac{t}{\tau_i}\right) \quad t \geq 0$$

in which $I_0$ is the signal background, $A_i$ are coefficients, $\tau_i$ are time constants, and the full width at half-maximum of the Gaussian function represents the cross correlation $\sigma_{cc}$ of the pump and probe pulses. The integrated intensity of feature E in $\Gamma' \cdot \text{CH}_3\text{NO}_2$ can be fit by a single exponential function, while features C for $\Gamma' \cdot \text{CH}_3\text{CN}$ and F for $\Gamma' \cdot \text{CH}_3\text{NO}_2$ require two exponential functions to describe their decay. Feature F requires an additional exponential function to capture its belated rise. To reduce the influence of the spectral overlap between
Figure 5.8. Integrated intensities of the transient features E and F observed in \( \Gamma^{-} - \text{CH}_3\text{NO}_2 \) TRPE spectra pumped with 3.60 eV and probed at 1.56 eV. Panel a) shows the initial decay of feature E (black circles) and the concomitant rise of feature F (red squares) near the zero of pump-probe delay, while panel b) shows the long-time decay of the two features. Fits are displayed as solid lines.
Table 5.2. Timescales describing integrated intensities of features C, E, and F for the $\Gamma \cdot \text{CH}_3\text{CN}$ and $\Gamma \cdot \text{CH}_3\text{NO}_2$ complexes.

<table>
<thead>
<tr>
<th>$h\nu_1$ (eV)</th>
<th>Feature</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma \cdot \text{CH}_3\text{CN}$ complex</td>
<td>3.47</td>
<td>C</td>
<td>3.4 ± 1.8</td>
<td>840 ± 140</td>
</tr>
<tr>
<td>3.53</td>
<td>C</td>
<td>5.9 ± 1.8</td>
<td>920 ± 90</td>
<td></td>
</tr>
<tr>
<td>$\Gamma \cdot \text{CH}_3\text{NO}_2$ complex</td>
<td>3.55</td>
<td>E</td>
<td>0.63 ± 0.11</td>
<td></td>
</tr>
<tr>
<td>3.60</td>
<td>E</td>
<td>2.3 ± 0.2</td>
<td>1100 ± 200</td>
<td>0.37 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>2.4 ± 0.4</td>
<td>1300 ± 200</td>
<td>0.42 ± 0.05</td>
</tr>
</tbody>
</table>

features E and F, only the high energy side of feature E was examined in the fitting.

Table 5.2 summarizes the parameters used in the fittings at two excitation energies for each system. Fitted parameters were extracted from concatenate fitting of multiple data sets and do not exhibit any notable trends with excitation energy. For feature C of the $\Gamma \cdot \text{CH}_3\text{CN}$ system, average $\tau_1$ and $\tau_2$ values are 4.7 ps and 880 ps. Feature E of $\Gamma \cdot \text{CH}_3\text{NO}_2$ decays with time constants in the range of 500 fs while decay time constants for feature F are near 2 and 1200 ps. The rise of feature F is described by $\tau_{3F}$ as approximately 400 fs.

5.7. Discussion

UV excitation of an iodide-molecule complex in the range of the VDE of the complex according to Equation 5.1 can be considered an electron scattering process wherein photodetachment of an electron from iodide can either produce a free electron and a neutral iodine-molecule complex or a transient negative ion of the form $[\text{I}\cdots \text{M}]^-$. The nature and decay of such TNIs has been explored experimentally using photoelectron and action spectroscopies for small solvent molecules and with TRPES for the nucleobases uracil and thymine. For acetonitrile and nitromethane, characterization of anionic photofragments suggests that the TNI represents the result of intracluster charge transfer from the iodide to the adjacent electropositive methyl groups of the associated molecules. In the following sections, we consider the charge-transfer processes for these systems from a time-resolved perspective and explore the dynamics of their resultant TNIs in detail.

5.7.1. Dynamics of the iodide-acetonitrile complex

In the time-resolved photoelectron spectra of the photoexcited $\Gamma \cdot \text{CH}_3\text{CN}$ complex, feature A occurs at low eKE and displays minimal temporal evolution. Because the excitation energies used are close in value to the VDE of the initial complex, direct single-photon detachment of $\Gamma \cdot \text{CH}_3\text{CN}$ should contribute to this low energy signal via production of the $\text{I}^2\text{P}_{3/2}\cdot \text{CH}_3\text{CN}$ neutral complex and a slow free electron. Electron autodetachment from the metastable TNI or other species can also produce low energy electron signal. Thus, the processes contributing to feature A can be summarized by the following equation:
In contrast to feature A, features B and C, exhibit notable dependence on excitation energy and pump-probe delay. As shown in Figures 5.3a and 5.4, these features appear as Gaussian peaks with widths reflective of the cross-correlation of the pump and probe pulses, indicating that both pulses contribute to the respective photoelectron signals. Feature C, becomes more intense relative to feature C, near the fringes of the photoabsorption spectrum of the DBS (Figure 5.5), appearing most dominant at energies furthest from the VDE of the initial complex, 3.54 eV. Moreover, as shown in Figure 5.6, the eKE of feature C tracks the pump photon energy, in contrast to feature C which remains fixed. These observations suggest that feature C is only weakly associated with the absorption resonance, if at all. The position and intensity of feature B in the time-resolved photoelectron spectra reflects the same trends as feature C, as it always occurs at about 0.9 eV higher electron binding energy than feature C. This energy difference corresponds to the spin-orbit splitting of iodine, suggesting that features B and C arise from photodetachment of a species with the electronic character of iodide as opposed to an excited charge-transfer complex. Thus, features B and C are assigned to two photon, two-color photodetachment (2CPD) of the initial I−·CH₃CN complex, a channel unavailable outside of the overlap of the two pulses. Indeed, the central eKE of feature C is consistent with that expected for 2CPD of the complex to yield iodine (²P₃/₂)-acetonitrile, while feature B is consistent with the formation of iodine (²P₁/₂)-acetonitrile:

\[
I^-\cdot CH_3CN \xleftarrow{hv_{pump}} \xrightarrow{hv_{probe}} I(²P_{3/2})\cdot CH_3CN + e^-(eKE \approx 1.54 \text{ eV}; \text{ feature C})
\]

\[
I(²P_{1/2})\cdot CH_3CN + e^-(eKE \approx 0.60 \text{ eV}; \text{ feature B})
\]

The anisotropy parameters for feature C are consistent with the assignment of the cross-correlation limited features to 2CPD (Figure 5.7a). The near-zero value of \(\beta_2\) measured at \(\Delta t = 0\) differs from the value of approximately -0.6 expected for single-photon detachment of both bare iodide and the iodide-acetonitrile complex. However, the non-zero value of \(\beta_4\) at \(\Delta t = 0\) and the corresponding photoelectron angular distribution displayed in Figure 5.2a indicate a multiphoton process.

The transient negative ion [I···CH₃CN]− created upon photoexcitation of I−·CH₃CN represents the result of intracluster charge transfer from iodide to the acetonitrile molecule. In previous studies, this state was described as a dipole-bound acetonitrile anion perturbed by an iodine atom. The dipole-bound anion of bare acetonitrile has an electron binding energy smaller than 20 meV and produces a sharply peaked photoelectron signal. Iodine is expected to minimally perturb the acetonitrile DBS, and the binding energy of neutral iodine to molecules and cluster anions has been estimated as approximately 50 meV. Thus, the narrow and weakly bound (VDE = 20 meV) feature C can reasonably be assigned to direct photodetachment of the dipole-bound acetonitrile anion by the probe pulse. The asymptotic anisotropy values depicted in Figure 5.7a also support this assignment, as the \(\beta_2\) value of unity matches previously reported values, while the \(\beta_4\) value of zero is consistent with single-photon photodetachment. \(\beta_2\) values near unity are expected for dipole-bound electrons, which are generally well-described by hybrid s-p orbitals with predominantly s character.
As discussed above, the intensity of feature C2 decays biexponentially with time constants of few and hundreds of ps. Because the dipole-bound state is so weakly bound, autodetachment of low energy electrons according to Equation 5.4 should be facile if the TNI is formed with any vibrational excitation. The biexponential behavior observed is characteristic of a sequential process, however, indicating that other processes must also be considered. The TNI created upon charge transfer from iodide to acetonitrile should consist of an iodine atom complexed to the methyl end of a weakly excited dipole-bound acetonitrile anion, and can be described as I···CH3CN*−. Only a small amount of energy should be available to the DBS because the excitation energy is close to the VDE of the initial complex. Thus, dissociation of the C—C bond to produce cyanide and a methyl radical or of a C—H bond to form a proton or hydrogen atom and a singly or doubly charged allene-like H2C2N anion should not occur.72, 73

The most viable decay pathway is thus iodine atom loss to yield the bare CH3CN*− DBS. With some excess energy carried away in translation by the departing iodine atom, the remaining CH3CN*− species should be further stabilized with respect to autodetachment and its rate of autodetachment should decrease.

Iodine loss has previously been invoked to explain biexponential decay of the transient negative ions of iodine-complexed uracil and thymine,43, 44 and it has been hypothesized to occur for Π·(CH3CN)n complexes with n ≥ 1. For example, in a TRPES study of n = 5 – 10 clusters, a 50 meV drop in the cluster anion species’ VDE was interpreted as the loss of iodine to yield the bare cluster anions.74 Johnson and co-workers,25 noted the exclusive production of CH3CN− upon excitation of the Π·CH3CN binary complex near its VDE, suggesting that iodine is ineffective at electron recapture. Theoretical studies59, 75 have also cited iodine loss as a process accompanying or subsequent to cluster rearrangements; a recent ab initio study by Mak et al.,59 indicated that a translation of iodine by several Å away from the acetonitrile moiety dominates the early dynamics of the photoexcited n = 1 cluster and reduces the VDE of the anion by less than 10 meV, a change difficult to observe in our experiment. Similarly, Takayanagi75 used high level calculations to show that iodine translation away from the asymmetric, linear n = 2 cluster occurs with minimal change in VDE over hundreds of femtoseconds. The decay dynamics proposed for photo-excited Π·CH3CN are summarized in Equation 5.7:

\[
I \cdots CH_3CN^* \rightarrow \begin{array}{c}
k_1 \rightarrow I \cdots CH_3CN + e^- (eKE \approx 0 \text{ eV}) \\
k_2 \rightarrow I + CH_3CN^* \rightarrow k_3 \rightarrow I + CH_3CN + e^- (eKE \approx 0 \text{ eV})
\end{array}
\] (5.7)

Within this scheme, the time constants can be related to rate constants according to

\[
\tau_1 = \frac{1}{k_1 + k_2} \quad \tau_2 = \frac{1}{k_3} \quad (5.8)
\]

The autodetachment rate for the unperturbed DBS is given by \(k_3 \sim 1 \times 10^9/s\). The autodetachment rate \(k_1\) of the I···CH3CN*− state is difficult to disentangle from the rate of iodine loss. However, given that \(k_1 + k_2 \sim 2 \times 10^{11}/s > k_3\), we would expect that \(k_1 << k_2\) unless loss of iodine reduces the autodetachment rate by two orders of magnitude, which seems unlikely.
5.7.2. Dynamics of the iodide-nitromethane complex

The time-resolved photoelectron spectra for I⁻·CH₃NO₂ differ significantly from those for I⁻·CH₃CN (Figure 5.3). While spectra for both systems include an intense low energy feature and a feature with eKE comparable to the energy of the probe pulse, feature C observed for I⁻·CH₃CN persists for hundreds of ps while feature E appears to rapidly decay to the much broader feature F in I⁻·CH₃NO₂ spectra. As discussed below, this divergence is attributable to a DBS to VBS transition in the nitromethane system that is not accessible for acetonitrile.

The time-resolved photoelectron spectra of the I⁻·CH₃NO₂ complex are dominated by a low eKE, near-time-invariant feature D. Direct detachment of the initial complex by the exciting pulse and autodetachment from the weakly bound transient negative ion state should both contribute to this photoelectron signal according to Equation 5.5. In contrast to the I⁻·CH₃CN system, two photon, two-color photodetachment of I⁻·CH₃NO₂ at the overlap of the pump and probe pulses is only weakly observed.

Intracluster charge transfer from the iodide to the nitromethane moiety initiated with a UV pulse close in energy to the VDE of the initial complex has previously been observed to produce a nitromethane anion with dipole-bound character, as inferred from the comparison of field-stripping measurements with previous work on known dipole-bound states. The eBE of the nitromethane DBS was measured to be approximately 10 meV in RET and PES experiments; interaction between the nitromethane anion and a neutral iodine atom may somewhat increase the VDE of the TNI complex. The narrow feature E with its VDE of approximately 20 meV is consistent with this description and is therefore identified as the DBS of nitromethane. The positive value of the associated β₂ anisotropy parameter supports the assignment of this feature as described in the previous section.

The overall structure and spectral extent (0.3 – 1.5 eV eKE) of feature F are characteristic of a valence-bound anion for which large deviations between neutral and anion geometries produce broad Franck-Condon envelopes. In previous single-photon photoelectron spectroscopy measurements, the valence anion of nitromethane was generated in supersonic expansions of argon gas and its VDE and onset estimated to occur at 0.9 eV and 172 meV, respectively. Associated β₂ values were measured in the range of 0.5 – 1.25 consistent with detachment from the a’ highest occupied molecular orbital of nitromethane. The energetic and anisotropy parameters observed for feature F match those previously reported and therefore support the assignment of F as the VBS of nitromethane. Here, no vibrational structure is observed, reflecting our energy resolution and the expectation that the valence anions have non-negligible vibrational excitation, leading to a spectrally congested spectrum.

The rapid decay of the DBS and coincident rise of the VBS implies that transformation to the VBS is the primary decay mechanism of the dipole-bound anion. The time constants τ₁E and τ₃F describing the decay of feature E and the rise of feature F, respectively, are roughly equivalent in value; the slightly larger values of τ₁E most likely result from residual contamination of feature E by feature F. As discussed for the acetonitrile anion, autodetachment and iodine atom loss could possibly also contribute to the initial decay of the iodine-stabilized DB anion of nitromethane. However, given that the decay of feature E is best captured with a
Figure 5.9. Schematic of the potential energy surfaces involved in the transition from the dipole-bound state (blue curve) to the valence-bound state (bold red curve, lower right) of CH$_3$NO$_2^-$. The potential energy surface for neutral CH$_3$NO$_2$ is shown in gray.

The transformation from the DBS to the VBS will now be considered in greater detail. The rate of the transformation is given by the rise $\tau_{3F}$ of feature F as approximately 400 fs. To our knowledge, this represents the first measurement of the rate of transfer between two such states. The transition had previously been predicted to occur on a sub-microsecond timescale based upon a calculated coupling element between the two states of 30 meV.\textsuperscript{17} The transformation from the DBS to the VBS will now be considered in greater detail. The rate of the transformation is given by the rise $\tau_{3F}$ of feature F as approximately 400 fs. To our knowledge, this represents the first measurement of the rate of transfer between two such states. The transition had previously been predicted to occur on a sub-microsecond timescale based upon a calculated coupling element between the two states of 30 meV.\textsuperscript{17}

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\begin{equation}
I \cdots CH_3NO_2^* \xrightarrow{k} I \cdots CH_3NO_2^{+} 
\end{equation}

where $I \cdots CH_3NO_2^{+}$ represents the iodine-associated valence anion described by feature F.

Figure 5.9 shows schematic diabatic potential energy curves for the relevant states.\textsuperscript{76} The grey curve is neutral CH$_3$NO$_2$, the blue curve is the anion DBS, which is slightly lower in energy relative to the neutral with a very similar geometry, and the red curve is the anion VBS, lying lower in energy than the DBS and exhibiting considerably more pyrimidalization at the NO$_2$ group (see Table 5.1). The transition from the DBS to the VBS must thus involve activation of the vibrational modes associated with the nitro group that dominate the photoelectron spectra of the VBS.\textsuperscript{16, 34}
Figure 5.9 emphasizes the presumed role of the DBS as a Feshbach resonance and, consequently, a ‘doorway’ into the valence anion state.\textsuperscript{16, 17, 37, 39} The transition from the DBS should proceed upon vibrational energy redistribution\textsuperscript{35, 76} into nitro group modes over a small barrier to produce a highly vibrationally excited valence anion. The height of this barrier has not been calculated, but RET studies measuring mixed dipole-valence character nitromethane anions suggest that it should be small.\textsuperscript{16, 23, 35} The limited previous observations of the DBS of nitromethane outside of RET experiments\textsuperscript{34, 39} confirm the fragile nature of DBS emphasized by this scheme, as does the rapid DBS-VBS transition seen in the work presented here.

The highly vibrationally excited valence anion created upon this curve-crossing motion should be susceptible to decay via autodetachment and other mechanisms. The integrated intensity of the anion VBS exhibits clear biexponential behavior described by 2 ps and 1200 ps time constants. Notably, the spectral profile of feature F does not appear to change with $\Delta t$. As discussed above, the nature and rapidity of the DBS to VBS transformation suggests that the iodine remains associated with the nitromethane moiety during the transition. Hence, the same explanation proposed for the biexponential decay in $\Gamma^-\cdot$CH$_3$CN (Equation 5.7) may well hold here.

Dissociation of the complex by loss of the nitrite ion or regeneration of the halide should also be considered. In action spectroscopy studies of bromide- and iodide-nitromethane complexes excited near their VDEs, Johnson and co-workers\textsuperscript{39} noted the formation of both such species, invoking a radical-anion reaction to explain their formation with such small available energies.\textsuperscript{8, 77-80} However, neither NO$_2^-$ nor I$^-$ can be detached at the probe photon energy used here,\textsuperscript{81} so the separate contribution of these channels to the decay of feature F cannot be assessed.

The dynamics describing the decay of the valence anion species are presented in Equation 5.10:

\[
I \cdots CH_3NO_2^+ \xrightarrow{k_2} I \cdots CH_3NO_2 + e^- (eKE \approx 0 \text{ eV}) \\
\quad \xrightarrow{k_3} I + CH_3NO_2^+ \xrightarrow{k_4} I + CH_3NO_2 + e^- (eKE \approx 0 \text{ eV}) \\
\quad \xrightarrow{k_5} CH_3I + NO_2^- \\
\quad \xrightarrow{k_6} CH_3NO_2 + I^-
\]

(5.10)

in which CH$_3$NO$_2^+$ represents the relaxed valence anion and for which time constants are represented by

\[
\tau_{1F} = \frac{1}{k_2 + k_3 + k_5 + k_6}, \quad \tau_{2F} = \frac{1}{k_4} 
\]

(5.11)

The autodetachment rate for the relaxed valence anion, $\tau_{2F}$, is approximately 1 x 10$^9$/s, similar to that measured for the decay of the bare CH$_3$CN dipole-bound anion.
5.7.3. Comparison to iodide-nucleobase complexes

The experiments performed here were motivated by our earlier TRPES studies of iodide-uracil (I⁻·U) and iodide-thymine (I⁻·T) complexes. In those experiments, the complexes were excited approximately 0.7 eV above their respective VDEs, with the goal of producing nucleobase transient negative ions and elucidating their decay dynamics. For both complexes, a single, broad transient feature resembling the valence anion was observed. TNIs for both species decayed biexponentially, with the rates of uracil anion decay being considerably slower than those describing the thymine anion. These dynamics were interpreted as autodetachment of the iodine-complexed and bare anions, respectively, using similar arguments as those proposed here for I⁻·CH₃CN and I⁻·CH₃NO₂ complexes.

Nucleobases are known to support dipole bound anion states and very close-lying valence bound states. However, in contrast to the work presented here, our early experiments on I⁻·U and I⁻·T showed no evidence for DBS formation even as a short-lived transient species. Moreover, the biexponential decays measured for I⁻·CH₃CN and I⁻·CH₃NO₂ are noticeably slower than for the nucleobase complexes. These differences may simply reflect the higher pump photon energies relative to the VDE in the experiments on iodide-nucleobase complexes or something more fundamental to the relaxation of the various TNIs.

Excitation of iodide-nucleobase complexes closer to their VDEs may yield iodine-stabilized dipole-bound anions in analogy to the acetonitrile and nitromethane systems. If so, an intermediate excitation energy may exist at which both the DBS and the VBS could be observed. Such an observation could provide considerable insight into the interaction of nucleobases with low energy electrons and may assist in the understanding of radiation-induced damage to larger biological systems.

5.8. Conclusion

The decay dynamics of the acetonitrile and nitromethane dipole-bound anions created by UV-initiated charge transfer within the corresponding iodide-molecule complexes have been investigated using time-resolved photoelectron imaging. The ground-state acetonitrile anion exists as a dipole-bound species, and the formation of a valence anion is not anticipated below 3 eV. The acetonitrile DBS generated upon electron transfer from iodide decays biexponentially with timescales of 4 ps and 900 ps, corresponding to translation of the iodine atom away from the molecule and electron autodetachment from the bare DBS. For the nitromethane system, both dipole-bound and valence anions are observed. The fast (400 fs) rise of the valence species and biexponential decay over 2 ps and 1200 ps timescales are suggestive of a DBS to VBS transition mediated by vibrational energy redistribution from methyl- to nitro-associated vibrational modes. The highly vibrationally excited VBS subsequently decays via autodetachment, iodine atom loss, and other dissociation mechanisms. These measurements mark the first direct observation of the transformation of a dipole-bound anion to a valence anion and may provide insight into the interactions between similar states in more complex systems such as uracil and thymine nucleobases.
5.9. Acknowledgements

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5.10. References

Chapter 6. Time-resolved radiation chemistry of methyl-substituted uracil

6.1. Abstract

The energetics and dynamics of the transient negative ions (TNIs) of methylated uracil molecules are examined using time-resolved photoelectron imaging. Methyluracil anions are generated by photo-initiated intracluster charge transfer from an associated iodide ion to the molecule of interest and their decay dynamics probed by photodetachment with a near-IR pulse. TNIs of uracils methylated at the N1 and N3 positions are observed to decay biexponentially on timescales similar to those recorded for 5-methyluracil (thymine) and significantly faster than those measured for uracil with no methyl substitutions. These dynamics were previously attributed to iodine translation away from the nucleobase anion and electron autodetachment, a mechanism considered further in this work. The near-zero electron kinetic energy feature observed in time-resolved photoelectron spectra for methylated uracil anions also displays dynamics more akin to those for the thymine anion, lacking the pronounced intensity overshoot seen in uracil anion spectra. That the decay dynamics of all methylated uracil TNIs studied are so similar imply that the difference in timescales between methylated and non-methylated uracil anions results from the enhancement of the rate of intramolecular vibrational energy redistribution afforded by the addition of the methyl rotor.

Unpublished work

6.2. Introduction

The observation that electrons with energies below the ionization energies of DNA and RNA components can induce DNA strand cleavage has prompted intense interest in the mechanisms of such radiation damage in the chemical and biological research communities.\(^1\)\(^-\)\(^4\) The complexity of large biological systems obscures the details of their interactions with such low energy electrons. Thus, significant theoretical and experimental efforts have focused on individual components of nucleic acids such as nucleotides and nucleobases. Strand cleavage events have been proposed to occur via severance of the C—O bond connecting the phosphate and sugar groups of a nucleotide following electron attachment to the $\pi^*$ network of the nucleobase.\(^5\)\(^-\)\(^7\) Understanding the nature of the transient negative ion (TNI) created upon electron-nucleobase interaction and the subsequent decay of the TNI are therefore crucial to producing an accurate description of DNA damage induced by low energy electrons. In this work, we build upon our previous studies of uracil and 5-methyluracil (thymine) TNIs\(^8\),\(^9\) to explore the effect of methylation on TNI decay mechanisms using time-resolved photoelectron imaging.
Nucleobase anions have been extensively studied using photoelectron spectroscopy (PES), Rydberg electron transfer (RET), and dissociative electron attachment (DEA). The bare nucleobases uracil and thymine have large (> 4 Debye) dipole moments that support the formation of dipole-bound (DB) anions consisting of diffuse electron clouds largely exterior to the supporting molecule. DB anions display characteristic sharp, low energy peaks in their photoelectron spectra reflecting very similar geometries to the neutral species produced by photodetachment.

The electron affinities (EAs) of the uracil (U) and thymine (5mU) DB anions estimated from PE spectra are approximately 90 and 70 meV, respectively, and N-site methylation is expected to lower the EAs of uracil. PES experiments have demonstrated that complexation with a polar species such as a xenon atom or single water molecule stabilizes the valence anion of U, but isolated pyrimidine nucleobase valence anions have not been directly measured. Extrapolation of the EAs of U complexed with varying numbers of water molecules suggests that the electron affinities of the DB and valence anion species of U should be similar in magnitude.

RET studies have demonstrated the formation of the U¯ valence anion upon evaporation of complexed argon atoms and found an EA slightly higher than that measured for the DB state. However, theoretical estimates of the valence anion EA vary drastically, ranging from negative to small positive values. The PE spectra of valence anions generally display extended vibrational progressions, the structure of which reflects the displacement between the neutral and anion potential energy surfaces. These spectra are often characterized by vertical detachment energies (VDEs), the energy difference between the anion and the neutral in the anion geometry. The VDEs of the U¯ and 5mU¯ valence anions, expected to be most stable in puckered ring geometries, have been calculated to be in the range of 600 meV.

In contrast to PES studies, in which kinetic energies of photodetached electrons (eKEs) are used to infer anion properties, dissociative electron attachment (DEA) experiments expose the species of interest to a beam of electrons of known energy to generate TNIs and measure the yields of resultant ion fragments. For nucleobases, the yield of dehydrogenated nucleobase anions is significantly greater than that of all other fragments. Methylation and deuteration of U and 5mU species at the N1 position significantly decreases the ion yield produced by scattering electrons with energies below 1 eV. The TNI of 3-methyluracil (3mU) formed upon interactions with low energy electrons is not observed to demethylate, however.

Recent experiments performed in our laboratory united ideas of electron scattering and photoelectron spectroscopy to provide an integrated picture of the energetics and dynamics of nucleobase TNIs via time-resolved photoelectron (TRPE) spectroscopy of iodide-nucleobase complexes. TNIs were generated by photo-initiated charge transfer from the iodide anion to the nucleobase with an ultrafast UV pulse and the resulting dynamics were monitored by photodetachment with a near-IR probe pulse. The TRPE spectra featured TNIs with valence character, the biexponential decay of which was attributed to autodetachment and iodine atom loss. The time constants describing the decay of the uracil TNI, I···U*¯, were 100s of femtoseconds and 10s of picoseconds, but the fast decay constant of the thymine TNI, I···5mU*¯, was approximately half that for I···U*¯ while the slow decay constant was an order of magnitude smaller. These differences were posited to result from the small differences in the available energy of the TNIs, which have previously been demonstrated to dramatically affect autodetachment rates. The dominant near-zero electron kinetic energy (NZeKE) peak in the
spectra of both species also displayed drastically different behavior, mirroring the rise and subsequent decay of the transient species in the 5mU case while for U significantly overshooting the initial intensity of the feature to achieve a post-depletion maximum after 10s of ps.

One question raised by these results was whether autodetachment of the TNI was its primary decay channel, or if cleavage of the N1-H bond was also occurring. In the current work, we seek to examine the role of methylation on the decay dynamics of iodide-complexed uracil molecules methylated at the N1 or N3 positions. N-methylated uracil systems display dynamics comparable to 5-methyluracil complexes, suggesting that autodetachment rather than hydrogen atom loss is the most significant driver of nucleobase TNI decay and implicating the methyl group as the primary cause of decay rate difference between methylated and non-methylated uracil transient negative ions.

6.3. Experimental methods

The time-resolved photoelectron imaging spectrometer has been described in detail previously. Briefly, iodide-(methyl)uracil clusters were generated in a supersonic expansion of 50 psig argon gas seeded with the nucleobase heated to between 160°C – 180°C by a solenoid valve pulsed at 500 Hz. Cluster anions were formed via attachment of electrons produced by a ring electrode ionizer and were perpendicularly extracted with a Wiley-McLaren time-of-flight mass spectrometer. The species of interest was isolated using a pulsed mass gate prior to interaction with pump and probe laser pulses and analysis with a velocity map imaging spectrometer. The BASEX reconstruction algorithm was used to extract photoelectron kinetic energy distributions from the resultant images. Photoelectron angular distributions (PADs) were derived using the polar onion peeling algorithm. For our scheme, in which electrons detached with \( m \) photons of linearly polarized light are measured in a detector with cylindrical symmetry, PADs can be fit by

\[
I(\theta, \varepsilon) \propto \frac{\sigma}{4\pi} \left[ 1 + \sum_{i=1}^{m} \beta_{2i}(\varepsilon) P_{2i}(\cos \theta) \right] 
\]

(6.1)

where \( \theta \) is the angle between the laser polarization and the photoelectron wave vector, \( \sigma \) represents the total photodetachment cross section, \( \beta_{2i} \) is an anisotropy parameter describing the departing electron’s angular momentum, and \( P_{2i} \) is the \( m \)th order Legendre Polynomial. \( \beta_2 \) can range from -1 and 2, the former value representing electron ejection perpendicular to the laser polarization and the latter parallel detachment.

A Ti:sapphire laser system (KM Laboratories Griffin Oscillator and Dragon Amplifier) produced a 1 kHz pulse train of 35 fs pulses centered around 1.57 eV. This fundamental served as the probe pulse. The UV pump (4.35 eV – 5.28 eV) was generated by routing a portion of the beam into an optical parametric amplifier (Light Conversion TOPAS-C) and frequency doubling the sum frequency idler or signal output. The measured cross correlation between the pump and probe pulses at the chamber entrance was less than 150 fs.
Figure 6.1. Optimized structures of binary complexes a) $\Gamma^-\cdot U$, b) $\Gamma^-\cdot 1mU$, c) $\Gamma^-\cdot 3mU$, and d) $\Gamma^-\cdot 5mU$ calculated at the MP2/aug-cc-pVDZ level using the aug-cc-pVDZ pseudopotential for iodide. Atom color coding is as follows: blue=N, gray=C, red=O, purple=I, white=H. Relevant molecular parameters are summarized in Tables 6.1 and 6.2.

6.4. Results

6.4.1. Electronic structure calculations

Geometry optimizations of the initial iodide-nucleobase species were performed at the MP2 level using the aug-cc-pVDZ basis set and the aug-cc-pVDZ-pp pseudopotential\textsuperscript{43} for iodide using the Gaussian 2009\textsuperscript{44} computational suite. Optimized structures are displayed in Figure 6.1 and associated relevant parameters are summarized in Tables 6.1 and 6.2.\textsuperscript{8,9} Dipole moments $\mu$ calculated for the bare neutral species are also included. For each complex, the iodide ion resides near the positive end of the ~5 Debye dipole moment between the hydrogen atom bound to C6 and the moiety bound to N1 of the planar nucleobase. Bond distances and angles of the nucleobases are slightly perturbed by the presence of the iodide ion: notably, the
Table 6.1. Relevant bond distances (Angstroms) and energetics of iodide-(methyl)uracil structures optimized at the MP2/aug-cc-pVDZ level using the aug-cc-pVDZ pseudopotential for iodide. Dipole moments $\mu$ (Debye) are calculated for the bare neutral nucleobase species.

<table>
<thead>
<tr>
<th>Species</th>
<th>N1–H</th>
<th>H(N1)–I</th>
<th>H(C6)–I</th>
<th>C5–C6</th>
<th>H(C6)–C6</th>
<th>VDE (eV)</th>
<th>$\mu$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uracil$^b$</td>
<td>1.039</td>
<td>2.506</td>
<td>3.035</td>
<td>1.370</td>
<td>1.094</td>
<td>4.13</td>
<td>5.1</td>
</tr>
<tr>
<td>1-methyluracil</td>
<td>1.471</td>
<td>3.912</td>
<td>2.677</td>
<td>1.370</td>
<td>1.100</td>
<td>3.98</td>
<td>5.4</td>
</tr>
<tr>
<td>3-methyluracil</td>
<td>1.038</td>
<td>2.510</td>
<td>3.045</td>
<td>1.368</td>
<td>1.094</td>
<td>4.08</td>
<td>4.9</td>
</tr>
<tr>
<td>5-methyluracil$^b$</td>
<td>1.037</td>
<td>2.527</td>
<td>3.001</td>
<td>1.371</td>
<td>1.095</td>
<td>4.09</td>
<td>5.8</td>
</tr>
</tbody>
</table>

$^a$For 1-methyluracil, H(N1) is CH$_3$(N1).
$^b$These structures have previously been described in references 8 and 9.

Table 6.2. Relevant bond angles of iodide-(methyl)uracil structures optimized at the MP2/aug-cc-pVDZ level using the aug-cc-pVDZ pseudopotential for iodide.

<table>
<thead>
<tr>
<th>Species</th>
<th>H(N1)H(C6)$^a$</th>
<th>N1H(N1)$^a$</th>
<th>C6H(C6)I</th>
<th>H(C6)H(C6N1)</th>
<th>H(N1)N1C6$^a$</th>
<th>H(N1)N1C2$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uracil$^b$</td>
<td>46.8</td>
<td>145.0</td>
<td>119.4</td>
<td>112.9</td>
<td>116.0</td>
<td>120.9</td>
</tr>
<tr>
<td>1-methyluracil</td>
<td>41.5</td>
<td>96.4</td>
<td>166.7</td>
<td>114.7</td>
<td>120.7</td>
<td>117.4</td>
</tr>
<tr>
<td>3-methyluracil</td>
<td>46.8</td>
<td>144.8</td>
<td>118.9</td>
<td>113.3</td>
<td>116.2</td>
<td>120.4</td>
</tr>
<tr>
<td>5-methyluracil$^b$</td>
<td>47.0</td>
<td>143.8</td>
<td>120.7</td>
<td>112.7</td>
<td>115.8</td>
<td>120.9</td>
</tr>
</tbody>
</table>

$^a$For 1-methyluracil, H(N1) is CH$_3$(N1).
$^b$These structures have previously been described in references 8 and 9.

C5–C6 and N1–H bonds are slightly elongated and H(N1) and H(C6) are rotated toward the iodide anion. In the case of the 1-methyluracil (1mU) complex, iodide is located further from the nucleobase and closer to H(C6) than in other systems. Energy optimizations carried out using CCSD yielded VDEs of 3.98 eV and 4.08 eV for 1mU and 3mU systems, respectively. VDEs previously calculated for U$^8$ and 5mU$^9$ clusters using this method and basis set were in excellent agreement with measured values.

6.4.2. Single-photon photoelectron spectra

Figures 6.2a and 6.2b show the single-photon photoelectron spectra for I$^-\cdot$1mU and I$^-\cdot$3mU, respectively, taken over a range of excitation energies. Spectra are plotted against electron binding energy (eBE), defined as the difference between the excitation energy and the measured electron kinetic energy (eBE = h$\nu$ – eKE). Photoelectron spectra for each species include a dominant, energy invariant peak centered near 4 eV, feature A, that represents direct detachment to the neutral I($^3P_{3/2}$)-nucleobase complex. The VDEs, obtained from the eBE at the peak of feature A, are measured to be 3.87 eV and 4.04 eV for 1mU and 3mU systems, respectively. Notably, the 1mU molecule is more weakly associated with iodide than the other systems, shifting the binding energy of bare iodide by only 0.81 eV compared to 0.98, 0.99, and 1.05 eV for 3mU, 5mU$^9$, and U$^8$, respectively. Due to these differences, for the purposes of comparison between methyluracil species, spectral features will be considered in terms of the effective electron collision energy, $E_c$, defined as the difference between the excitation energy and the VDE of the system under examination ($E_c = h\nu - \text{VDE}$).

Direct detachment to the higher energy spin-orbit level of iodine appears 0.94 eV above feature A in the single-photon photoelectron spectra and is denoted feature B. A third peak,
Figure 6.2. Single-photon photoelectron spectra of a) \(\Gamma \cdot 1mU\) and b) \(\Gamma \cdot 3mU\) binary complexes at various excitation energies. Features A, B, and C represent direct detachment of the binary complex to the corresponding methyluracil-iodine \((^3P_{3/2})\) and -iodine \((^3P_{1/2})\) spin-orbit states and autodetachment of the transient negative ion species, respectively.

feature C, occurs at \(eBE \approx h\nu\) near zero eKE and is attributable to electron autodetachment from the TNI. Overlap between features B and C for \(\Gamma \cdot 1mU\) obscures the excitation energy at which feature C achieves its maximum value relative to feature B; for the \(\Gamma \cdot 3mU\) complex, this maximum occurs with excitation near 4.77 eV. As was seen in the U and 5mU complexes,\(^8\),\(^9\) feature C occurs over a wide range of excitation energies for both species, from approximately 4.4 eV to at least 5.3 eV, the highest energies accessed in this study.

6.4.3. Time-resolved photoelectron spectra

The temporal evolution of the photoelectron spectra for a representative methyluracil cluster system, \(\Gamma \cdot 3mU\), excited at 4.75 eV and probed at 1.56 eV is depicted in Figure 6.3. Time-resolved photoelectron spectra are plotted against eKE, with pump-probe delay increasing from back to front. The intensities of features A and C appear to remain constant in time, but examination of the integrated intensity of feature C reveals low amplitude modulation beginning at the zero of pump-probe delay, \(\Delta t = 0\). The intensity depletes nearly instantaneously before recovering over several picoseconds. The drop in intensity of feature C is complemented by the appearance of the broad feature D below 1.6 eV which is ascribed to direct detachment of the \(I \cdot \cdot (m)U^*\) TNI by the probe pulse. Because the low eKE side of the feature appears to overlap
Figure 6.3. Time-resolved photoelectron spectrum of the $\Gamma^{-}\cdot3mU$ complex excited at 4.75 eV and probed at 1.56 eV. Features A, C, and D represent direct detachment of the binary complex and autodetachment and photodetachment of the transient negative ion species, respectively.

with feature A, only the region between 1.0 – 1.6 eV was considered in our analysis. The low intensity feature D is barely distinguishable above background noise and survives for only a few picoseconds before disappearing.

TRPE spectra measured for $\Gamma^{-}\cdot1mU$ and $\Gamma^{-}\cdot3mU$ appear similar for the excitation energies examined (for $\Gamma^{-}\cdot1mU$, 4.51 eV and 4.59 eV, corresponding to $E_c$ values of 0.64 eV and 0.72 eV; for $\Gamma^{-}\cdot3mU$, 4.64 eV and 4.74 eV, corresponding to $E_c$ values of 0.60 eV and 0.70 eV). These spectra are consistent with those previously recorded for $\Gamma^{-}\cdot5mU$ with similar $E_c$ values.9

Figure 6.4 compares the integrated intensities of features C and D for iodide-(methyl)uracil complexes. For each chromophore, the intensity of feature D increases sharply at $\Delta t = 0$ and, as shown in Section 6.5, subsequently decays biexponentially. Though the fits for the decay of the 3mU and 5mU TNIs match one another well, decaying within a few picoseconds, the decay of the 1mU system appears slightly slower, and that for $\Gamma^{-}\cdotU$ complexes is significantly slower. The dynamics of feature C for the methylated uracil systems appear to mirror those of feature D, displaying a rapid depletion prior to a fast recovery. While the integrated intensity of feature C for $\Gamma^{-}\cdotU$ dramatically overshoots its initial value for approximately 20 ps before decaying back to it,8 feature C for neither $\Gamma^{-}\cdot1mU$ nor $\Gamma^{-}\cdot3mU$ showed strong evidence of overshoot, in agreement with previous studies of $\Gamma^{-}\cdot5mU$.9 It should be noted, however, that the quality of the integrated intensities of feature C suffers somewhat due to the challenge of measuring small changes over a large background.
Figure 6.4. a) Integrated intensities of feature D shown with concatenate fits for iodide-(methyl)uracil species excited with sufficient pump energy to give 0.6 eV collision energy. b) Integrated intensities for feature C.

6.4.4. Photoelectron angular distributions

Anisotropy parameters $\beta_2$ associated with feature A in the single-photon photoelectron spectra measure between -$0.7$ – -$0.3$, while $\beta_2$ values for feature C in both single-photon and time-resolved photoelectron spectra are approximately zero. Because the algorithm used to derive anisotropy parameters works from high to low eKE, producing center point noise that obscures the true anisotropy near zero eKE, only $\beta_2$ values for the higher eKE portion of feature C were examined. Neither $\beta_2$ nor $\beta_4$ values demonstrate notable time dependence for feature C.

In the eKE range corresponding to feature D, $\beta_2$ values increased from approximately -$0.5$ to nearly $0$ at $\Delta t = 0$ before decaying to their initial values following the same dynamics as
Figure 6.5. Short (a) and long (b) time constants for the decay of feature D plotted against collision energy for iodide-(methyl)uracil complexes.

the transient feature D. Because of the very low intensity of feature D, it is likely that anisotropies in this region are affected by the overlapping laser noise background. Thus, the time evolution of \( \beta_2 \) for feature D should be discounted as a residual intensity effect and the precise values of \( \beta_2 \) disregarded.

6.5. Analysis

The temporal evolution of the integrated intensities of feature D for the respective iodide-(methyl)uracil complexes were fit by the convolution of a Gaussian laser response function and a molecular response function of the form
Table 6.3. Energetics (eV) and time constants for the decay of feature D for various iodide-(methyl)uracil species. Values are derived from concatenate fitting of several datasets and presented with their standard errors. The fraction of the signal resulting from fast decay, \( F_1 \), as well as the area under the fitted curve, are also included. Note: Values previously reported for \( \Gamma^- \cdot U \) and \( \Gamma^- \cdot 5mU \) in references 8 and 9 were variance weighted means of several datasets rather than concatenate fits.

<table>
<thead>
<tr>
<th>Species</th>
<th>( hV_{\text{pump}} )</th>
<th>VDE</th>
<th>( E_c )</th>
<th>( \tau_1 ) (fs)</th>
<th>( \tau_1 ) error</th>
<th>( \tau_2 ) (ps)</th>
<th>( \tau_2 ) error</th>
<th>( F_1 )</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>4.69</td>
<td>0.58</td>
<td>620</td>
<td>60</td>
<td>20</td>
<td>0.85</td>
<td>248</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>4.79</td>
<td>4.11</td>
<td>680</td>
<td>90</td>
<td>31</td>
<td>0.84</td>
<td>146</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.90</td>
<td>0.79</td>
<td>300</td>
<td>40</td>
<td>11</td>
<td>0.87</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1mU</td>
<td>4.51</td>
<td>3.87</td>
<td>640</td>
<td>90</td>
<td>3.2</td>
<td>0.8</td>
<td>0.37</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.59</td>
<td>0.72</td>
<td>460</td>
<td>50</td>
<td>5.6</td>
<td>1.4</td>
<td>0.69</td>
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<tr>
<td>3mU</td>
<td>4.64</td>
<td>4.04</td>
<td>60</td>
<td>50</td>
<td>9.0</td>
<td>2.0</td>
<td>0.53</td>
<td>23</td>
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<tr>
<td></td>
<td>4.74</td>
<td>0.7</td>
<td>170</td>
<td>70</td>
<td>1.2</td>
<td>0.3</td>
<td>0.60</td>
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<tr>
<td>5mU</td>
<td>4.60</td>
<td>0.55</td>
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<td>60</td>
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<td>1.2</td>
<td>0.83</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>4.69</td>
<td>4.05</td>
<td>640</td>
<td>70</td>
<td>1.5</td>
<td>0.5</td>
<td>0.68</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.79</td>
<td>0.74</td>
<td>160</td>
<td>50</td>
<td>0.92</td>
<td>0.19</td>
<td>0.61</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>

\[
M(t) = I_0 \quad t < 0 \\
I_0 + \sum_{i=1}^2 A_i \exp \left( -\frac{t}{\tau_i} \right) \quad t \geq 0
\]  

(6.2)

in which \( I_0 \) represents the initial intensity, \( \tau_i \) are time constants, and \( A_i \) are coefficients. The fitted values presented in Table 6.3 and summarized in Figure 6.5 represent multiple datasets fitted together. Though the short time constants \( \tau_i \) are of similar magnitude for all systems examined, fitting to hundreds of fs, the long time constants \( \tau_2 \) are an order of magnitude longer for \( \Gamma^- \cdot U \) than for \( \Gamma^- \cdot mU \) species, yielding values between 11 ps – 60 ps for \( \Gamma^- \cdot U \) and 0.9 ps – 6 ps for \( \Gamma^- \cdot mU \) complexes. Both time constants were slightly longer for \( \Gamma^- \cdot 1mU \) than for other methyluracil species. Time constants previously recorded for \( \Gamma^- \cdot U \) and \( \Gamma^- \cdot 5mU \) decreased with increasing excitation energy,\(^8,9\) although this trend is not replicated for \( \Gamma^- \cdot 1mU \) and \( \Gamma^- \cdot 3mU \), the time constants measured at different \( E_c \) values are within the calculated standard error of one another. The fraction of the signal resulting from fast decay, \( F_1 \), was slightly higher for \( \Gamma^- \cdot U \) than for other systems.

6.6. Discussion

6.6.1. Single-photon photoelectron spectra

In analogy to previous work on \( \Gamma^- \cdot U \) and \( \Gamma^- \cdot 5mU,^8,9 \) features A and B observed in single-photon photoelectron spectra for \( \Gamma^- \cdot 1mU \) and \( \Gamma^- \cdot 3mU \) represent direct photodetachment of the initial iodide-nucleobase complex by the UV pump pulse to form the corresponding \( I(2P_{3/2}) \cdot (\text{methyl})\text{uracil} \) and \( I(2P_{1/2}) \cdot (\text{methyl})\text{uracil} \) complexes, respectively. The negative \( \beta_2 \) values associated with feature A are typical of iodide-containing binary clusters.\(^45\) The VDEs of the 3mU- and 5mU-containing complexes are close in value to that of the \( \Gamma^- \cdot U \) complex,
however the VDE of $I\cdot 1mU$ is somewhat lower. This difference likely reflects the weaker interaction between the iodide and the methyl group in the $I\cdot 1mU$ complex compared to the hydrogen bonding interaction between the iodide and H(N1) in the other species.

In addition to photodetaching the initial species, the UV pulse can also excite the iodide-nucleobase complex to the charge-transfer state $I\cdots 1mU^*-$ or $I\cdots 3mU^*$. The energy available to these species is approximately equivalent to the effective collision energy, $E_c$, so the nucleobase anion species should be highly vibrationally excited and metastable with respect to electron autodetachment, as indicated by the high intensity of the isotropic feature C observed in the single-photon photoelectron spectra. These processes are summarized by Equation 3:

\[
\begin{align*}
I^- \cdot (m)U & \xrightleftharpoons[h_{\text{uv}}]{\text{pump}} \ I(2P_{3/2}) \cdot (m)U + e^- (\text{feature A}) \\
I(2P_{1/2}) \cdot (m)U & + e^- (\text{feature B}) \\
I \cdots (m)U^* & \xrightleftharpoons[k]{\text{autodet}} \ I \cdots (m)U + e^{-} (eKE \approx 0 \text{ eV}; \text{ feature C}) 
\end{align*}
\]

(6.3)

6.6.2. Time-resolved photoelectron spectra

The dynamics of features C and D for the $I\cdot mU$ complexes mirror one another, and the time constants for the decay of feature D can be used to describe the recovery of feature C as was previously demonstrated for the $I\cdot 5mU$ complex. The low eKE feature displays a very different pattern for $I\cdot U$, however, as indicated in Figure 4. The lack of overshoot observed for the methyluracil systems, for which the transient anion decays much more rapidly, suggests that the TNI must be involved. The overshoot feature may result from a probe-enhanced autodetachment process or detachment of a species with approximately 1.6 eV, although the existence of such a species in these studies is unlikely. The overshoot could be examined in greater detail by employing probe pulses of varying energies.

Feature D in the time-resolved photoelectron spectra corresponds to direct photodetachment of the transient excited state by the probe pulse. The broad, unstructured shape and large energetic extent of the feature are characteristic of a valence anion and do not appear to evolve in time. Similar spectra were observed for $I\cdot U$ and $I\cdot 5mU$. Though the low eKE side of the feature overlaps with feature A, the highest intensity of feature D appears to occur in the range of 1 eV eKE, consistent with calculations of the VDE of the valence anion.

Previous photoelectron spectroscopy studies of uracil and methyluracil anions have exclusively measured the dipole-bound anion in the absence of a complexing species, though a xenon atom or water molecule was observed to stabilize the valence anion of uracil. Because iodine and xenon are similarly polarizable, iodine may also stabilize nucleobase valence anions.

The formation of the isolated uracil valence anion has been posited to occur indirectly from the corresponding DB state. A barrier of several hundred meV is thought to exist between these states, an amount easily overcome at the excitation energies used here. Although this transformation mechanism appears to be operative for uracil and 5-methyluracil at low excitation energies ($h\nu_1 \sim \text{VDE}[I\cdot (m)U]$) and has also been directly observed for the iodide-nitromethane complex, the absence of the dipole-bound state for all (methyl)uracils studied at the higher excitation energies used here at even very short pump-probe delays suggests
that the valence anion is directly formed upon charge-transfer from the iodide to the nucleobase moiety.

6.6.2.1. Biexponential decay of the TNI

The TNIs for both I−·1mU and I−·3mU exhibit biexponential decay with two time constants similar to those recorded for I−·5mU. The biexponential decay dynamics are indicative of a sequential decay process. The initial TNI, I···(m)U*−, should be metastable with respect to electron autodetachment and so some fraction of its population should decay directly to form the corresponding neutral species and a slow free electron. In accordance with the measured decay dynamics, the I···(m)U*− state can also decay to a second state, X−, which can also autodetach. This scheme is summarized in Equation 6.4:

\[ I^− \cdot (m)U \xrightarrow{hv_{pump}} I \cdots (m)U \xrightarrow{k_1} I \cdots (m)U + e^−(eKE \approx 0 \text{ eV}) \]
\[ \xrightarrow{k_2} X^- \xrightarrow{k_3} X + e^- (eKE \approx 0 \text{ eV}) \]

for which fitted time constants correspond to

\[ \tau_1 = \frac{1}{k_1 + k_2}, \quad \tau_2 = \frac{1}{k_3} \]  

(6.5)

As shown in Equation 6.5, the two time constants measured describe three processes. While the rate of autodetachment from the second state, \( k_3 \), is directly available from the fitting, the relative magnitudes of \( k_1 \) and \( k_2 \) are not immediately obvious. However, this relationship is readily derived. As described in Appendix 1, the transient signal should have the form

\[ S(t) = I_0 + \frac{A_1}{2} \exp \left( \frac{\sigma_{CC}^2}{2 \tau_1^2} \frac{t}{\tau_1} \right) \left[ 1 + \text{erf} \left( \frac{t}{\sigma_{CC} \sqrt{2}} - \frac{\sigma_{CC}}{\tau_1 \sqrt{2}} \right) \right] \]
\[ + \frac{A_2}{2} \exp \left( \frac{\sigma_{CC}^2}{2 \tau_2^2} \frac{t}{\tau_2} \right) \left[ 1 + \text{erf} \left( \frac{t}{\sigma_{CC} \sqrt{2}} - \frac{\sigma_{CC}}{\tau_2 \sqrt{2}} \right) \right] \]

(6.6)

where \( I_0 \) is the background intensity, \( \sigma_{CC} \) is the cross correlation of the pump and probe pulses, \( A_i \) are coefficients, and \( \tau_i \) are the time constants given in Equation 6.5. Denoting the I···(m)U*− state B and the X− state C, the time dependent concentrations of B and C are given by

\[ [B](t) = [B]_0 e^{-(k_1 + k_2)t} \]
\[ [C](t) = \frac{[B]_0 k_2}{(k_3 - k_1 - k_2)} \left[ e^{-(k_1 + k_2)t} - e^{-k_3t} \right] \]

(6.7)

As photodetachment of both states are expected to yield signal in the same eKE region of the time-resolved photoelectron spectrum, the measured signal should be
\[ [\text{Trans}] (t) = \beta [B](t) + \kappa [C](t) = \left[ \beta [B]_0 + \frac{\kappa k_2 [B]_0}{(k_3 - k_1 - k_2)} \right] e^{-(k_1 + k_2)t} - \left[ \frac{\kappa k_2 [B]_0}{(k_3 - k_1 - k_2)} \right] e^{-k_3 t} \]  

(6.8)

in which \( \beta \) and \( \kappa \) reflect photodetachment cross sections and experimental parameters. For simplicity, the values \( \beta \) and \( \kappa \) are taken to be approximately equal. The coefficients \( A_i \) in Equation 6.6 can be directly extracted from the exponential coefficients in Equation 6.8. Following the logic of Zewail and co-workers, these coefficients can be used to derive expressions for the rate constants \( k_1, k_2, \) and \( k_3 \) by defining the fraction of the signal from the fast decay as \( F_1 = A_1 / (A_1 + A_2) \). Rearranging and substituting time constants, expressions for the rate constants are obtained:

\[ k_1 = F_1 \left( \frac{1}{\tau_1} - \frac{1}{\tau_2} \right) + \frac{1}{\tau_2} \]

\[ k_2 = (1 - F_1) \left( \frac{1}{\tau_1} - \frac{1}{\tau_2} \right) \]  

(6.9)

\[ k_3 = \frac{1}{\tau_2} \]

Calculated values are summarized in Table 6.4. According to the results of the model, the autodetachment rate \( k_1 \) from the I···(m)U*¯ state exceeds the rate \( k_2 \) of accessing the second state by approximately one order of magnitude for the uracil TNI and slightly less so for methyluracil species. Notably, the rate of electron autodetachment from the initial TNI is also faster than that from the second state by two orders of magnitude for uracil and one order of magnitude for methyluracils.

The biexponential decay dynamics for the I···U*¯ and I···5mU*¯ states were previously interpreted as iodine atom loss and autodetachment from the initial TNI and subsequent autodetachment from the bare (m)U*¯ state:

\[ I^- \cdot (m)U \xrightarrow{h\nu_{\text{exp}}} I \cdots (m)U^- \xrightarrow{k_2} I \cdots (m)U + e^- (eKE \approx 0 \text{ eV}) \]

\[ \xrightarrow{k_3} I + (m)U^*^- \xrightarrow{k_3} I + (m)U + e^- (eKE \approx 0 \text{ eV}) \]  

(6.10)

Because the spectral profile of the transient species is not observed to evolve in time, the second state must have an electron binding energy comparable to that of the initial TNI and so should not represent a ring-opened or otherwise fragmented nucleobase anion. The mechanism proposed in Equation 6.10 satisfies this requirement, as the binding energy between the iodine atom and the molecular moiety should be on the order of 10s of meV.

Due to the lack of bath molecules, the iodine atom loss channel would provide a facile vibrational cooling mechanism for the system. Autodetachment from the initial TNI, I···(m)U*¯, should occur more rapidly than that from the relaxed (m)U*¯ state \( (k_1 > k_2) \) because the energetic cost of iodine loss should reduce the vibrational excitation of the TNI. However,
Table 6.4. Estimated rate constants for the decay of iodide-(methyl)uracil TNIs.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\nu_{pump}$</th>
<th>VDE</th>
<th>$E_c$</th>
<th>$k_1$ (x10^10/s)</th>
<th>$k_2$ (x10^10/s)</th>
<th>$k_3$ (x10^10/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>4.69</td>
<td>0.58</td>
<td>140</td>
<td>24</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.79</td>
<td>0.68</td>
<td>200</td>
<td>38</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.90</td>
<td>0.79</td>
<td>290</td>
<td>42</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>1mU</td>
<td>4.51</td>
<td>3.87</td>
<td>0.64</td>
<td>130</td>
<td>160</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>4.59</td>
<td>0.72</td>
<td>160</td>
<td>62</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>3mU</td>
<td>4.64</td>
<td>4.04</td>
<td>0.6</td>
<td>710</td>
<td>540</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>4.74</td>
<td>0.7</td>
<td>390</td>
<td>200</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>5mU</td>
<td>4.69</td>
<td>4.05</td>
<td>0.64</td>
<td>290</td>
<td>110</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>4.79</td>
<td>0.74</td>
<td>420</td>
<td>200</td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>

given the low iodine-TNI binding energy and the only minor perturbation in nucleobase structure induced by the presence of the iodine atom, the departure of the iodine atom should not dramatically alter the autodetachment rate. The two order of magnitude difference in autodetachment rates for the iodine associated and bare TNIs for uracil are inconsistent with this expectation. In addition, iodine atom loss from species sharing the same iodine binding motif (I···U*¯, I···3mU*¯, and I···5mU*¯) and excited with the same values of $E_c$, should occur at similar rates but instead occurs more rapidly for methylated uracil species. A second model may thus also merit consideration.

Rather than an iodine-absented state, the second state accessed by $k_2$ may instead correspond to a vibrationally relaxed state I···(m)U†:

$$I^- \cdot (m)U \xrightarrow{\nu_{pump}} I \cdots (m)U^* \xrightarrow{k_1} I \cdots (m)U + e^- (eKE \approx 0 \text{ eV})$$

$$\xrightarrow{k_2} I \cdots (m)U^+ \xrightarrow{k_3} I \cdots (m)U + e^- (eKE \approx 0 \text{ eV})$$

(6.11)

The rate $k_2$ would therefore describe the rate of intramolecular vibrational energy redistribution (IVR) throughout the nucleobase vibrational modes following the localization of the excess charge over the C5—C6 double bond induced by the charge-transfer process. The nascent TNI should be highly vibrationally excited at the collision energies $E_c$ used here, so IVR may be rapid. Autodetachment from the initial and relaxed TNIs would likely occur via different mechanisms, as autodetachment from the I···(m)U*− state with rate constant $k_1$ is faster than IVR and so should not require a complete redistribution of vibrational energy to occur. In contrast, autodetachment from the relaxed I···(m)U†− state occurs significantly more slowly due to the stabilization afforded the TNI by the IVR process. These ideas are explored in detail below.

In the context of the second model, complete IVR throughout the I···(m)U*− state to yield I···(m)U†− occurs approximately an order of magnitude slower in I···U*− than in its methylated counterparts. IVR rates are very sensitive to isotopic substitution, skeletal torsion, and the presence of unhindered methyl rotors. The latter effect has been extensively examined
by Parmenter and co-workers, who recorded a change in IVR rates of nearly two orders of magnitude in para-fluorotoluene relative to 1,4-difluorobenzene. They attributed the acceleration of IVR to coupling between the low frequency internal rotation of the methyl group and ring vibrational modes leading to a large enhancement in the density of states. Thus, coupling between the methyl rotor and low frequency motions of the pyrimidine ring could account for the increased IVR rate of methyluracil TNIs relative to the uracil TNI. This would be striking given that coupling through a nitrogen atom or carbon atom in very different parts of the ring would produce the same effect. The effect could be further explored by examining TNI autodetachment rates for iodide-complexed isopropyl- or dimethyl-uracil species.

IVR acceleration by methyl rotors has also been observed in vibrational predissociation (VP) studies of weakly bound van der Waals clusters. Such studies typically involve the excitation of a high energy vibrational mode of a molecular target and the subsequent monitoring of parent or dissociation products through fluorescence or photoionization techniques. VP of a weakly associated species such as a noble gas atom from the molecular target is thought to proceed via redistribution of vibrational energy into the low frequency coupling modes between the two species. Levy and co-workers recorded an increase in VP rates of at least one order of magnitude for methylated derivatives of tetrazine complexed to argon atoms. The Zewail group observed drastic changes in VP rates from cresol-benzene complexes compared to phenol-benzene complexes: methylation of phenol at the para position led to the emergence of biexponential behavior that the authors attributed to predissociation from an initial state and an IVR relaxed second state or predissociation from the initial state and from the remote methyl bath modes, in analogy to the model suggested herein. Comparison between vibrational predissociation studies and the autodetachment dynamics of I···(m)U* species raises the question of the role of iodine in the model presented in Equation 6.11. The deposition of energy within the coupling modes between the iodine atom and the nucleobase should precede the possible departure of the iodine atom and should occur during the course of IVR. Thus, it is possible that the iodine atom departs from the nucleobase anion as or after vibrational energy is redistributed throughout the system. The contribution of this process to the overall dynamics, whether through the model presented in Equation 6.10 or in Equation 6.11, cannot be directly evaluated, however.

According to the scheme presented in Equation 6.11, although IVR is rapid, the rate of autodetachment from the initial TNI exceeds that of IVR ($k_1 > k_2$). Because IVR is a statistical process, autodetachment from the I···(m)U* state must then be non-statistical such that electron detachment proceeds upon concentration of vibrational energy within a relevant vibrational mode or combination of modes prior to the complete IVR throughout the system. The rate $k_1$ thus depends on both the amount of energy available to the system as well as the rapidity of distributing the energy to the relevant modes and may or may not demonstrate dependence on the number of vibrational modes, in agreement with the similar rates estimated for uracil and methylated uracil complexes.

Prior to the photoinitiation of charge transfer from iodide, the neutral uracil ring is planar. Upon charge transfer, the highly vibrationally excited nucleobase anion should distort to a puckered ring structure along the N3···C6 axis. Specifically, the ring folding process involves out of plane motion along this axis and at the C5 position, elongation of the C5—C6 bond and
pyramidalization of C6 have also been found to be relevant to the relaxation dynamics of neutral (methyl)uracils.\textsuperscript{25, 63, 64} Non-statistical electron ejection is likely to occur upon the activation of these modes. Interestingly, relaxation dynamics of photoexcited neutral 5mU have been observed to be slower than those for U, with the difference attributed to kinematic effects resulting from methyl substitution at the C5 position.\textsuperscript{63, 65} That the non-statistical autodetachment rate $k_I$ is similar in value for I···U* and I···mU* species may be indicative of competition between steric and energetic effects.

In comparison to the autodetachment measured from the initial TNI, autodetachment from the IVR relaxed state I···(m)U* occurs much less rapidly and displays a greater sensitivity to methylation. The fraction of the signal deriving from the fast decay processes, $F_1$, is somewhat larger for the uracil-containing complex, indicating that the initial decay processes are more dominant for I···U* than for the other systems. If the entire population of the I···(m)U* excited states eventually autodetach with rates $k_I$ or $k_3$ according to Equation 6.5, then the larger $F_1$ value reflects the rapidity of the IVR process compared to the initial autodetachment and can be taken to mean that decay from the initial TNI dominates the relaxation dynamics. Subsequent autodetachment from the relaxed state account for less than 20% of the overall decay in the case of uracil and somewhat more for methyluracil species, suggesting that the nascent excited methyluracil anions may be more stable to autodetachment, perhaps due to dispersion of excess vibrational energy into the methyl group.

Autodetachment from the IVR relaxed I···(m)U* state should be statistical. If iodine atom loss does not proceed upon IVR, the total energy of the initial and relaxed TNIs remains unchanged. In this instance, the difference in autodetachment rates observed at similar excitation values $E_c$ for a given system owes to the stabilizing effect afforded by the redistribution of vibrational energy. The smaller value of $k_3$ measured for uracil compared to methyluracil species is contrary to the expected statistical behavior. Considering autodetachment in analogy to a unimolecular dissociation process,\textsuperscript{34} species with larger numbers of modes should autodetach more slowly than similar smaller species. Autodetachment rates for water, methanol, and ethanol cluster anions (ROH)$_n^-$ (4 ≤ $n$ ≤ 10) studied in our laboratory were not observed to follow this pattern however, a result attributed to the greater importance of energetics than molecular structure for those systems. A similar effect may be operative here: it is possible that methylated uracil TNIs cannot stabilize the excess charge as effectively as can the uracil TNI, leading to faster autodetachment from the relaxed state. Exploring this effect within the context of a nucleoside or nucleotide species would be of great interest.

If iodine atom loss occurs during or as a result of the IVR process, the total energy of the TNI should be reduced as described earlier in the section. The slower rate of autodetachment $k_3$ measured for the uracil TNI may also owe to energetic differences between the uracil and methyluracil species in this case. Thus, while the model proposed in Equation 6.11 for the relaxation dynamics of the nucleobase TNIs appears more viable than that depicting $k_2$ as corresponding directly to iodine atom loss, the role of iodine in the decay dynamics merits further consideration.
6.6.2.2. Hydrogen atom dissociation

In addition to iodine atom loss and autodetachment, fragmentation of the excited (methyl)uracil moieties merits consideration. Impingement of beams of low energy electrons (> 0.7 eV) on isolated nucleobases results in high yields of nucleobase anions from which a hydrogen atom has been excised from the N1 position.\textsuperscript{14-16, 26-29, 66} Though the probe pulse utilized here is not energetic enough to detect these species (EA[(U–H)\textsuperscript{−}] = 3.48 eV),\textsuperscript{67} the contribution of hydrogen atom loss to the overall dynamics can be indirectly evaluated via comparisons between the I\textsuperscript{−}·1mU complex, for which the fragmentation channel is not accessible, and I\textsuperscript{−}·3mU and I\textsuperscript{−}·5mU systems. The initial decay rate measured for the excited I\textsuperscript{−}·1mU complex is similar enough to that for other iodide-methyluracil complexes to suggest that hydrogen atom loss should occur substantially more slowly than IVR such as to not be competitive with the rate $k_2$. Were iodine to depart the TNI and reduce its vibrational energy, hydrogen atom loss from the bare mU\textsuperscript{−} species would likely be energetically inaccessible; the dehydrogenation rate should therefore be captured by only the initial exponential decay. In principle, comparison between the transient signal (feature D) and the depletion of NZeKE signal (feature C) for I⋯3mU\textsuperscript{*−} and I⋯5mU\textsuperscript{*−} relative to I⋯1mU\textsuperscript{*−} could be used to infer the fraction of the transient population that does not autodetach but rather undergoes hydrogen atom dissociation. Unfortunately, this contribution to the overall decay dynamics cannot be easily estimated due to the relatively small changes in signal level in the NZeKE that render its integrated intensities quite noisy. A minimal contribution would be consistent with calculations that predict that the C—O $\sigma$ bond of the nucleotide, rather than the N1—C $\sigma$ bond linking the nucleobase and sugar components, cleaves as a result of the interaction of low energy electrons with nucleobase species.\textsuperscript{5, 7} The contribution could be estimated by repetition of these experiments with a higher energy probe capable of photodetaching the (U–H)\textsuperscript{−} and (mU–H)\textsuperscript{−} fragments.

6.7. Conclusion

The relaxation dynamics of 1-methyluracil and 3-methyluracil transient negative ions have been examined with time-resolved photoelectron imaging. These biexponential dynamics are consistent with those measured for 5-methyluracil and demonstrate significantly faster decay than does the uracil TNI. A two state model involving autodetachment from the nascent and IVR relaxed TNI is proposed, and the acceleration of IVR rates for the methyluracil species compared to uracil species attributed to coupling between the internal rotation of the methyl group and the vibrational modes of the uracil ring. Comparisons between decay constants and coefficients for the methyluracil complexes do not readily indicate the contribution of hydrogen atom loss from the N1 position to the overall dynamics.

6.8. Acknowledgements

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6.9. References

Appendix 1. Modeling biexponential decay kinetics

A.1. Decay dynamics

Time-resolved photoelectron spectroscopy involves the excitation of an initial state to form an excited state that is interrogated by a probe pulse. Photodetachment of the excited species yields a transient signal, the population dynamics of which reflect the lifetime and decay mechanisms of the excited state. In the case of iodide-nucleobase clusters ( Chapters 4 and 6 ) , the transient anion state created upon excitation with a UV pump pulse decays biexponentially. In order to understand the dynamics of this decay, it is useful to examine a kinetic model for this system and relate it to a fitting function.

The biexponential decay behavior of the iodide-nucleobase system can be described with the simple two-state model shown below:

\[
\begin{align*}
I^- \cdot NB & \xrightarrow{hv_{pump}} I \cdots NB^*^- \xrightarrow{hv_{probe}} I \cdots NB + e^- \text{ (transient)} \\
& \xrightarrow{k_1} I \cdots NB + e^- \text{ (NZeKE)} \\
& \xrightarrow{k_2} I + NB^*^- \xrightarrow{hv_{probe}} I + NB + e^- \text{ (transient)} \\
& \xrightarrow{k_3} I + NB + e^- \text{ (NZeKE)}
\end{align*}
\]  

(A.1)

The pump pulse excites the initial $I^- \cdot NB$ state to the $I\cdots NB^*^-$ charge transfer state. The transient negative ion can then decay via autodetachment to produce a near-zero eKE (NZeKE) signal according to $k_1$ or it may decay to a lower energy state via iodine loss according to $k_2$. In this model, the NB*^- state may only decay via autodetachment according to $k_3$. The time constants describing decay from the $I\cdots NB^*^-$ and NB*^- states are then given by

\[
\tau_1 = \frac{1}{k_1 + k_2} \quad \quad \tau_2 = \frac{1}{k_3}
\]  

(A.2)

Both the $I\cdots NB^*^-$ and NB*^- states are interrogated by the probe to produce the transient signal. Assuming that the $I^- \cdots NB$ and autodetached states are created instantaneously, the population dynamics of the $I\cdots NB^*^-$ and NB*^- states can be described by

\[
\begin{align*}
\frac{d}{dt} [A] &= -(k_1 + k_2) [A] \\
\frac{d}{dt} [B] &= k_2 [A] - k_3 [B]
\end{align*}
\]  

(A.3)
where A represents I···NB*¯ and B represents NB*¯. Integration of the $\frac{d}{dt}[A]$ expression yields

$$[A](t) = [A]_0 e^{-(k_1+k_2)t} \quad (A.4)$$

Substitution of this expression into the $\frac{d}{dt}[B]$ expression and subsequent integration gives

$$[B](t) = \frac{[A]_0 k_2}{(k_3-k_1-k_2)} \left[ e^{-(k_1+k_2)t} - e^{-k_2t} \right] \quad (A.5)$$

With these expressions in hand, an expression for the NZeKE feature, abbreviated NZ, can be derived from

$$\frac{d}{dt}[NZ] = k_1[A] + k_3[B] \quad (A.6)$$

by substitution of the expressions for [A] and [B] and integration. The integration constant can be determined by considering that at $t=0$, the probe should detach a fraction of the initial amount of A proportional to its photodetachment cross section to produce transient signal, reducing the amount of A available for autodetachment:

$$[\text{Trans}](t = 0) = \alpha[A]_0$$

Initial condition:

$$[NZ](t = 0) = [A]_0 - \alpha[A]_0 \quad (A.7)$$

$$[NZ](t) = \frac{[A]_0}{(k_3-k_1-k_2)} \left[ k_2e^{-k_2t} - \frac{k_1(k_3-k_1-k_2)+k_2k_3}{(k_1+k_2)} e^{-(k_1+k_2)t} \right] + [A]_0 (2-\alpha) \quad (A.8)$$

The transient signal should be proportional to the concentrations of A and B multiplied by constants $\alpha$ and $\beta$ that reflect photodetachment cross sections, laser-ion interaction volumes, etc.:

$$[\text{Trans}](t) = \alpha[A](t) + \beta[B](t) = \left[ \alpha[A]_0 + \frac{\beta k_2[A]_0}{(k_3-k_1-k_2)} \right] e^{-(k_1+k_2)t} - \left[ \frac{\beta k_2[A]_0}{(k_3-k_1-k_2)} \right] e^{-k_2t} \quad (A.9)$$

A.2. Fitting transient decay

Assuming vertical excitation of the initial I¯·NB state to form the transient negative ion I···NB*¯, the transient photoelectron signal’s biexponential decay behavior can be fit with a function representing a convolution of an instrumental response function and a molecular response function. The instrumental response function is a laser response function that describes the cross correlation between Gaussian pump and probe laser pulses with non-negligible widths. The cross correlation itself is a convolution of two Gaussian functions which yields the cross
correlation width

\[ \sigma_{cc} = \frac{FWHM_{cc}}{2\sqrt{2\ln 2}} \]
where \( FWHM_{cc} = (FWHM_{pump}^2 + FWHM_{cobe}^2)^{1/2} \) \hspace{1cm} (A.10)

The laser response function, \( L(t) \), therefore has the form

\[ L(t) = \frac{1}{\sigma_{cc} \sqrt{2\pi}} \exp \left( \frac{-t^2}{2\sigma_{cc}^2} \right) \] \hspace{1cm} (A.11)

The molecular response function, \( M(t) \), can be described by

\[ M(t) = \begin{cases} I_0 & t < 0 \\ I_0 + A_1 \exp \left( \frac{-t}{\tau_1} \right) + A_2 \exp \left( \frac{-t}{\tau_2} \right) & t \geq 0 \end{cases} \] \hspace{1cm} (A.12)

\( M(t) \) can therefore be represented as the sum of a baseline value \( I_0 \) and a Heaviside step function multiplying the sum of two exponential functions with scaling factors \( A_i \) and time constants \( \tau_i \):

\[ M(t) = I_0 + \left( A_1 \exp \left( \frac{-t}{\tau_1} \right) + A_2 \exp \left( \frac{-t}{\tau_2} \right) \right) h(0) \] \hspace{1cm} (A.13)

The convolution of the laser and molecular response functions is described by the general form

\[ S(t) = \int_{-\infty}^{\infty} M(z) L(x-z) dz \] \hspace{1cm} (A.14)

Following the logic laid out by Pedersen and Zewail\(^1\) and in the dissertation of Graham Griffin,\(^2\) the form of the signal function \( S(t) \) can be derived as

\[ S(t) = I_0 + \frac{A_1}{2} \exp \left( \frac{\sigma_{cc}^2}{2\tau_1^2} - \frac{t}{\tau_1} \right) \left[ 1 + \text{erf} \left( \frac{t}{\sigma_{cc} \sqrt{2} - \tau_1 \sqrt{2}} \right) \right] \]
\[ + \frac{A_2}{2} \exp \left( \frac{\sigma_{cc}^2}{2\tau_2^2} - \frac{t}{\tau_2} \right) \left[ 1 + \text{erf} \left( \frac{t}{\sigma_{cc} \sqrt{2} - \tau_2 \sqrt{2}} \right) \right] \] \hspace{1cm} (A.15)

The time constants \( \tau_i \) are given in Equation A.2. The relationship between \( S(t) \) and the transient photoelectron signal is derived by relating the scaling factors \( A_i \) to the factors multiplying the corresponding exponentials. Thus, the second term in the \( S(t) \) expression corresponds to the \( e^{-(t_1+k_2 \tau)} \) term and the third term in \( S(t) \) to the \( e^{-k_2 \tau} \) term in the \( [\text{Trans}] (t) \) expression. Thus, the scaling constants can be written as


\[ A_1 = \gamma \left[ \alpha [A]_0 + \frac{\beta k_2 [A]_0}{(k_3 - k_1 - k_2)} \right] \]  \hspace{1cm} (A.16)

\[ A_2 = \gamma \left[ -\frac{\beta k_3 [A]_0}{(k_3 - k_1 - k_2)} \right] \]  \hspace{1cm} (A.17)

In the equations above, \( \gamma \) is a scaling factor that relates the measured intensity to the actual concentration.

In certain instances, non-resonant 2-photon (pump + probe) detachment of the initial species may be visible in photoelectron spectra. This process should only occur when the pump and probe pulses are precisely overlapped in time; thus, when considered in the fitting function this feature should be represented as a convolution of the laser response function and a delta function, yielding the laser response function. \( S(t) \) may then be written as

\[
S(t) = I_0 + \frac{A_1}{2} \exp \left( \frac{\sigma_{cc}^2 - t}{2\tau_1^2} \right) \left[ 1 + \text{erf} \left( \frac{t}{\sigma_{cc}\sqrt{2}} - \frac{\sigma_{cc}}{\tau_1\sqrt{2}} \right) \right] \\
+ \frac{A_2}{2} \exp \left( \frac{\sigma_{cc}^2 - t}{2\tau_2^2} \right) \left[ 1 + \text{erf} \left( \frac{t}{\sigma_{cc}\sqrt{2}} - \frac{\sigma_{cc}}{\tau_2\sqrt{2}} \right) \right] + \frac{A_3}{2} \exp \left( -\frac{t^2}{2\sigma_c^2} \right)
\]  \hspace{1cm} (A.18)

When the fitting function \( S(t) \) is applied to measured photoelectron signal, values for \( I_0, A_1, A_2, \tau_1, \tau_2, \) and \( \sigma_{cc} \) are obtained. The cross correlation width can be related to a physical cross correlation of the pump and probe laser pulses performed outside of the instrument chamber. The calculated value of \( \tau_2 \) yields the constant \( k_3 \) describing the rate of autodetachment from \( \text{NB}^* \), however the rate constants \( k_1 \) and \( k_2 \) cannot easily be extracted from the expression. As autodetachment is a statistical process, the rate of autodetachment is not expected to proceed more quickly than 0.001 fs\(^{-1}\), corresponding to a time constant of 1 ps. Separation between the iodine atom and the nucleobase moiety should decrease the amount of energy available to the excited species and thus slow the rate of autodetachment; thus, \( k_1 \) might be expected to be somewhat larger than \( k_2 \). Assuming that these rate constants are of the same order of magnitude, and that iodine loss occurs more rapidly than autodetachment, the time constant \( \tau_1 \) may be approximated as \( 1/k_2 \).

As an example, the iodide-uracil cluster excited at 4.69 eV with pulses with a cross correlated FWHM of 150 fs yields time constants \( \tau_1 \) and \( \tau_2 \) and of approximately 600 fs and 50 ps. Thus, the rate of autodetachment from \( \text{U}^* \) is \( 2 \times 10^{-3} \text{ fs}^{-1} \). If the rate of decay of I···U\(^*\) by autodetachment is assumed to be much slower than iodine loss, the rate of iodine loss can be approximated as \( 2 \times 10^{-3} \text{ fs}^{-1} \). The rate constant \( k_1 \) cannot readily be determined from the fitting parameters due to uncertainty of the values of \([A]_0, \alpha, \beta, \) and \( \gamma \). Using the values given above and assuming \( k_1 \approx k_3 \), modeling the function with Microsoft Excel yields a biexponential decay function that can be made to follow the dynamics the transient photoelectron signal. Under the conditions described, the fit performs best when \( \alpha > \beta \), that is when photodetachment from I···U\(^*\) by the probe occurs with higher probability than detachment from U\(^*\). The model
described has also been demonstrated to apply generally to other iodide-nucleobase systems.

A.3. References

## Appendix 2. Index of Acronyms Used

<table>
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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>2CPD</td>
<td>Two-photon two-color photodetachment</td>
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<td>ADE</td>
<td>Adiabatic detachment energy</td>
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<td>BASEX</td>
<td>Basis Set Expansion</td>
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<tr>
<td>BBO</td>
<td>Beta-barium borate</td>
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<td>CCD</td>
<td>Charge-coupled device</td>
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<td>CCSD</td>
<td>Coupled-cluster singles doubles</td>
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<td>CTTS</td>
<td>Charge-transfer-to-solvent</td>
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<td>DB</td>
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<td>DBS</td>
<td>Dipole-bound state</td>
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<td>Dissociative electron attachment</td>
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<td>DFT</td>
<td>Density functional theory</td>
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<td>Deoxyribonucleic acid</td>
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<td>Diffusion pump</td>
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<td>Low energy electrons</td>
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<td>Microchannel plates</td>
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<td>Møller-Plesset perturbation theory to second order</td>
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Appendix 3. Publications from Graduate Work


