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Nonadiabatic Dynamics Studied by Liquid-Jet Time-Resolved Photoelectron Spectroscopy

Published as part of the Accounts of Chemical Research special issue "Applications of Liquid Microjets in Chemistry".

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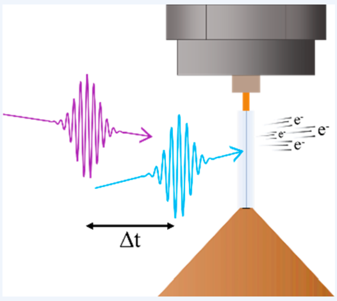
Cite This: https://doi.org/10.1021/acs.accounts.2c00609 Read Online



CONSPECTUS: The development of the liquid microjet technique by Faubel and co-workers has enabled the investigation of high vapor pressure liquids and solutions utilizing high-vacuum methods. One such method is photoelectron spectroscopy (PES), which allows one to probe the electronic properties of a sample through ionization in a state-specific manner. Liquid microjets consisting of pure solvents and solute−solvent systems have been studied with great success utilizing PES and, more recently, time-resolved PES (TRPES). Here, we discuss progress made over recent years in understanding the solvation and excited state dynamics of the solvated electron and nucleic acid constituents (NACs) using these methods, as well as the prospect for their future.

The solvated electron is of particular interest in liquid microjet experiments as it represents the simplest solute system. Despite this simplicity, there were still many unresolved questions about its binding energy and excited state relaxation dynamics that are ideal problems for liquid microjet PES. In the work discussed in this Account, accurate binding energies were measured for the solvated electron in multiple high vapor pressure solvents. The advantages of liquid jet PES were further highlighted in the femtosecond excited state relaxation studies on the solvated electron in water where a 75 ± 20 fs lifetime attributable to internal conversion from the excited p-state to a hot ground state was measured, supporting a nonadiabatic relaxation mechanism.

Nucleic acid constituents represent a class of important solutes with several unresolved questions that the liquid microjet PES method is uniquely suited to address. As TRPES is capable of tracking dynamics with state-specificity, it is ideal for instances where there are multiple excited states potentially involved in the dynamics. Time-resolved studies of NAC relaxation after excitation using ultraviolet light identified relaxation lifetimes from multiple excited states. The state-specific nature of the TRPES method allowed us to identify the lack of any signal attributable to the $^1n\pi^*$ state in thymine derived NACs. The femtosecond time resolution of the technique also aided in identifying differences between the excited state lifetimes of thymidine and thymidine monophosphate. These have been interpreted, aided by molecular dynamics simulations, as an influence of conformational differences leading to a longer excited state lifetime in thymidine monophosphate.

Finally, we discuss advances in tabletop light sources extending into the extreme ultraviolet and soft X-ray regimes that allow expansion of liquid jet TRPES to full valence band and potentially core level studies of solutes and pure liquids in liquid microjets. As most solutes have ground state binding energies in the range of 10 eV, observation of both excited state decay and ground state recovery using ultraviolet pump−ultraviolet probe TRPES has been intractable. With high-harmonic generation light sources, it will be possible to not only observe complete relaxation pathways for valence level dynamics but to also track dynamics with element specificity by probing core levels of the solute of interest.

KEY REFERENCES

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Received: September 8, 2022

https://doi.org/10.1021/acs.accounts.2c00609
Acc. Chem. Res. XXXX, XXX, XXX−XXX

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- Elkins, M. H.; Williams, H. L.; Shreve, A. T.; Neumark, D. M.Relaxation mechanism of the hydrated electron. *Science***2013**, *342*, 1496−1499.[4]*Measurement of the p → s relaxation of the hydrated electron using TRPES to differentiate between the internal conversion and solvent equilibration lifetimes, resolving previous ambiguities in the assignment of a relaxation mechanism.*

1. INTRODUCTION

The development of vacuum-compatible liquid water microjets, first reported in 1988,[5] has greatly expanded the range of chemical physics experiments that can be performed on water and other volatile solvents. Liquid jets enable one to apply very powerful tools based on photoelectron spectroscopy to properties and dynamics of volatile solvents and the solutes dissolved within. Photoelectron spectroscopy (PES) is a well-established technique in which a sample is ionized, and the resulting electron kinetic energy distribution is measured. It is typically used to determine electron binding energies and the electronic properties of gases and solids, but its application to liquids was restricted to those with exceedingly low vapor pressures[6] owing to the high vacuum requirements of a photoelectron spectrometer. By applying PES to liquid microjets in a vacuum, it has been possible to investigate the electronic properties of pure volatile liquids[7−10] and solutes.[11−13] One photon PES measurements of binding energies have been used to characterize the electronic structure of both pure liquids[10,14] and solutes,[15−17] elucidating shifts in the binding energy in both solutes and individual solvent molecules due to interactions with surrounding solvent. Experiments of this type represent an active frontier in modern physical chemistry; in addition to providing a novel probe of structure and energetics within liquids, they link gas phase studies of isolated molecules and clusters to chemical dynamics in the liquid phase.

A powerful variant of PES used in many areas of chemical dynamics is time-resolved photoelectron spectroscopy (TRPES). TRPES is a pump−probe technique that is capable of following the dynamical evolution of a excited state wavepacket.[18] The overall experimental scheme is as follows:

$$A \xrightarrow{h\nu_{\mathrm{pu}}} A^* \xrightarrow{\Delta t, h\nu_{\mathrm{pr}}} A^+ + e^- \qquad (1)$$

In Scheme 1, a femtosecond pump pulse ($h\nu_{\mathrm{pu}}$) photoexcites the system of interest (A), which then evolves in time (Δt) before being ionized to a resultant cationic state (A^+) by a femtosecond pulse ($h\nu_{\mathrm{pr}}$) that probes the evolution of the excited system (A^*). The pump-induced dynamics are encoded in the resulting photoelectron kinetic energy distribution, which is measured as a function of pump−probe delay. TRPES is particularly sensitive to nonadiabatic transitions, since the various electronic states that participate in the dynamics tend to have distinct electron binding energies. With pulses of sufficiently short duration and appropriate wavelengths, TRPES can be used to track the complete relaxation process of a given excited state from initial excitation through any intermediates that are populated en route to the ground state. TRPES has been shown to have significant advantages including high sensitivity stemming from exceptional intrinsic collection and detection efficiencies[19] and allowing the direct observation of the transient electronic states responsible for driving the ultrafast dynamics of interest.[12] For these reasons, TRPES has for many years been an excellent tool for the study of dynamics in both neutral and anionic gas phase molecules and clusters,[18,20] as well as the photophysics and photochemistry of metal and semiconductor surfaces.[21,22] With the advent of liquid jet technology, it is now possible to apply TRPES to investigate the dynamics of electronically excited solutes in bulk liquid,[1,4,23,24] thereby adding a powerful new tool that complements time-resolved techniques, such as transient absorption[25−27] and nonlinear spectroscopies,[28−30] that have been used to investigate liquids for many years.

While liquid jet TRPES (LJ-TRPES) carries with it advantages intrinsic to the PES technique, there are also limitations one must be cognizant of when interpreting these spectra. For example, experiments and simulations show that the inelastic mean free path of these photoelectrons ranges from 1 to 3 nm, depending on their kinetic energy.[31] Under these circumstances, one must consider whether photoelectrons are created at the liquid-vacuum interface or within the bulk liquid.[32] In addition, a TRPES experiment is only capable of observing dynamics involving electronic states in which the probe photon energy is sufficient to photoionize/photodetach from a given region of a potential surface.[18] As such, insufficient probe photon energies can lead to a TRPES experiment being blind to certain electronic states relevant to the complete relaxation dynamics of the system and can even artificially shorten the observed lifetimes of electronic states with binding energies that fall outside of the observable range during the relaxation process.[33] This limitation has been a major motivating factor behind extending the probe photon energy range of LJ-TRPES experiments into the XUV using high-harmonic generation.

Applications of TRPES using liquid jets (LJ-TRPES) considered here include the investigation of the solvated electron, a benchmark condensed phase solute, and exploration of the role that the solvent plays in the nonadiabatic relaxation dynamics of nucleic acid constituents (NACs). The ground and excited states of the solvated electron have been well studied in a variety of solvents using electron spin resonance, transient absorption, and PES in an effort to understand both its ground state structure and excited state relaxation dynamics.[34] However, extraction of the p → s internal conversion (IC) lifetime from transient absorption experiments is ambiguous,[35,36] while LJ-TRPES yields a clear IC lifetime that is critical in assessing the mechanism for electronic relaxation of the hydrated electron.[4] The work on NACs in motivated by experiments in the gas phase and in aqueous solution showing that excited state lifetimes after ultraviolet excitation are typically well under 1 ps.[37,38] As a result, relaxation to the ground state can occur more rapidly than excited state dissociation,[38] leading to high photostability of DNA and its constituents. Using a bottom-up approach, LJ-TRPES can in principle map out the complete set of electronic states that participate in this mechanism and thus complement previous experimental and theoretical work on NAC dynamics. To reach its full potential, however, the probe photon energy used in LJ-TRPES experiments must be extended to be able to ionize the intermediate and ground electronic states that play a role in the overall relaxation mechanism. This consideration motivates the last section of this Account in which the beamline used to generate femtosecond extreme ultraviolet (XUV) pulses is described.

2. EXPERIMENTAL APPARATUS

The liquid microjet apparatus used for carrying out the photoelectron spectroscopy studies discussed here has been modified since originally described[3,39] but at its core remains the same. The design of the liquid microjet is based on the design developed by Wilson[40] and similar to the type pioneered by Faubel.[41] In brief, the microjet is formed by forcing a solution through an approximately 10 mm long segment of fused silica capillary with an inner diameter ranging from 10 to 30 μm at pressures of 40 to 120 atm. These microjet diameters are necessary to collect photoelectrons while minimizing inelastic scattering in the surrounding vapor.[10]

The liquid microjet assembly, shown in Figure 1, is affixed to a three-axis piezoelectric actuator allowing it to be positioned 1 mm above the intersection of the detector and laser axes. After passing through the interaction region, the jet can be frozen in a cryogenically cold vessel at the bottom of the interaction region or captured in a heated copper catcher similar to those implemented by Hummert et al.[24] and Riley et al.[42] The catcher, which is attached to the same mounting apparatus as the jet, is kept approximately 1 cm below the jet and can be translated independent of the jet for alignment purposes. The jet passes through a 500 μm aperture in the catcher, which is kept at 75 °C, and flows into a bottle in an ice bath that is evacuated to a few Torr. Catching the liquid as opposed to freezing it has been shown to be advantageous as it mitigates the effects of electrokinetic charging on the photoelectron spectrum[42] in addition to lowering the measured chamber pressure by nearly an order of magnitude.

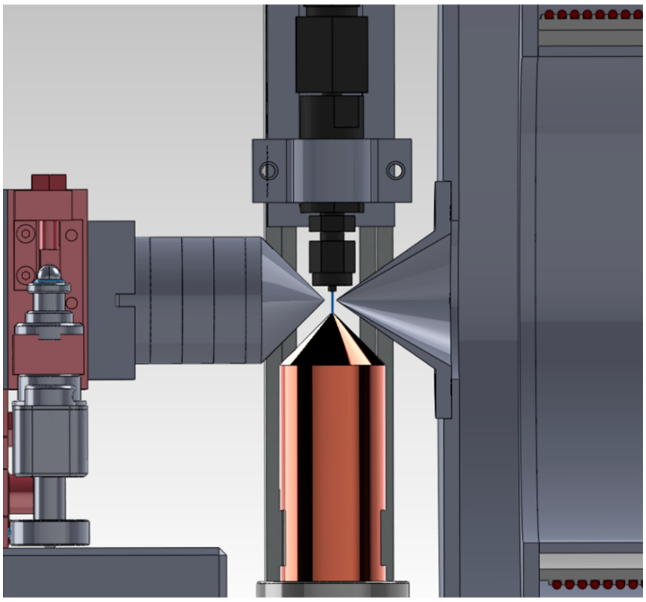

Figure 1. Schematic diagram of the interaction region where the femtosecond pump and probe pulses cross the liquid jet (from above) and subsequent photoelectrons are steered through a skimmer into the differentially pumped MB-TOF detector region (right) by a strong permanent magnet stack (left). Remaining sample is collected in the heated copper catcher (below).

Early work on liquid microjets in the Neumark group[39,43] utilized ultraviolet light generated by frequency quadrupling or quintupling the output of a nanosecond Nd:YAG laser which could then be used to excite and photoionize solutes of interest within the duration of a single ~35 ns duration laser pulse. More recent explicitly time-resolved iterations of the experiment[1−4,44] have utilized femtosecond pulses from a Ti:sapphire oscillator/amplifier, the output of which can then be frequency doubled, tripled, and quadrupled, or directed into an optical parametric amplifier to obtain ultraviolet pump and probe pulses with energies as high as 6.20 eV. To achieve even higher probe photon energies, we have built a beamline employing high-harmonic generation to selectively generate 21.7 eV photons (see section 3.3). The femtosecond pulses are delayed relative to one another and then cross the liquid microjet, emitting photoelectrons. The photoelectrons are collected and energy-analyzed using a magnetic bottle time-of-flight spectrometer and microchannel plate detector.[45]

3. RESULTS AND DISCUSSION

3.1. Ultrafast Dynamics of Solvated Electrons

The solvated electron was the first system to be extensively studied by LJ-TRPES experiments. This species is of fundamental interest in solution chemistry, as a reducing agent in organic chemistry, a product in the radiolysis of water, and in the attachment to and subsequent damage of DNA.[46] Its dynamics after photoexcitation have been investigated with an impressive array of experimental[34] and theoretical[47] methods. From the perspective of gas phase chemistry, water cluster anions $(H_2O)_n^-$ have been studied using one-photon[48] and time-resolved PES,[46] electronic spectroscopy,[49,50] and vibrational spectroscopy,[51,52] with one goal being to understand the relationship of these finite systems to the bulk hydrated electron. LJ-TRPES experiments offer a unique and explicit link between the cluster and aqueous phase environments of an excess electron in water. The primary focus of these experiments has been to determine the vertical detachment energy of the hydrated electron and to probe its relaxation dynamics after photoexcitation.

In solution, solvated electrons can be readily generated from a variety of simple solutes such as iodide or ferrocyanide upon UV excitation of charge-transfer-to-solvent (CTTS) transitions,[53] adding to the simplicity of these studies. Initial LJ-PES investigations by Siefermann et al.,[54] Tang et al.,[55] Lübcke et al.,[56] and Shreve et al.[39] yielded values ranging from 3.3 to 3.6 eV for the binding energy of the bulk solvated electron, in good agreement with the values extrapolated from measurements of internally solvated electrons in water cluster anion studies.[46,48] These initial LJ-PES measurements of the solvated electron binding energy remain in good agreement with recent

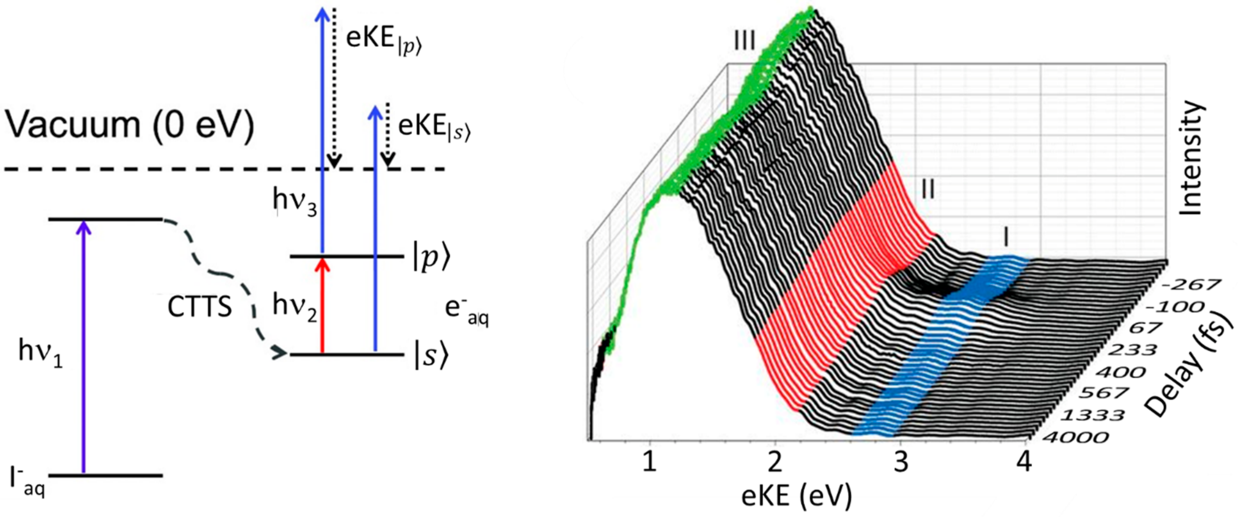

Figure 2. Left: Energy level diagram showing the states relevant to three pulse experiments in which solvated electrons are generated by CTTS excitation ($h\nu_1$) and the p-state relaxation dynamics are studied using an 800 nm pump ($h\nu_2$) and a 267 nm probe ($h\nu_3$). Right: LJ-TRPES spectra showing excited state relaxation of the solvated electron after 800 nm irradiation. Reprinted in part and adapted from ref 4. Copyright 2013 American Association for the Advancement of Science.

measurements yielding a value of 3.7 ± 0.1 eV that include corrections for factors such as energy-dependent scattering cross sections.[32] These corrections, while not applied to the work presented in this Account, are becoming increasingly important in LJ-PES studies for accurate determination of electron binding energies where increasingly wider ranges of probe energies can be applied to the same system. Recent investigations of the solvated electron with probe energies ranging from 3.6 to 13.6 eV have highlighted both the accuracy these corrections, retrieving the same 3.7 eV vertical binding energy from a data set with uncorrected vertical binding energies ranging from 3.3 to 4.5 eV.[32]

Further studies on solvated electrons have demonstrated the utility of LJ-TRPES to elucidate the time-resolved dynamics of these species. In aqueous solution, the solvated electron can be excited to a manifold of p-states through excitation in the near-infrared and has been shown through optical spectroscopy to relax back to the ground s-state with three time constants ranging from 50 fs to 1 ps.[36,57] The interpretation of these time constants in terms of the overall relaxation mechanism has been ambiguous. Two mechanisms have been invoked, the nonadiabatic and adiabatic mechanisms.[47] These can in principle be distinguished by measuring the time constant for p → s internal conversion, which is on the order of 50 fs in the nonadiabatic model and 400 fs in the adiabatic model. In size-selected water cluster anions, TRPES was used to measure this IC lifetime; the extrapolation of these lifetimes to the bulk limit yielded a value of ∼60 fs, strongly favoring the nonadiabatic model for relaxation.[46] However, given the uncertainty in how electrons bind to finite water clusters and how the electron binding motif affects the excited state lifetime,[58] it seemed prudent to carry out TRPES in bulk water.

Using LJ-TRPES, experiments have been carried out as shown schematically in Figure 2.[4] Solvated electrons are generated from CTTS excitation of iodide at 240 nm after which an 800 nm pump pulse excites solvated electrons to the p-state. Subsequent dynamics are tracked by a 267 nm probe pulse and can be assigned unambiguously based on their respective binding energies. These experiments have also been used to observe the initial thermalization and recombination of electrons initially generated by the CTTS excitation prior to excitation.[3] In Figure 2, signal at a binding energy of 2.2 ± 0.2 eV is assigned to the p-state and relaxes with a time constant of 75 ± 20 fs.[4] This excited state population transfers to a region nearly 1 eV higher in binding energy, assigned to hot ground state signal, which then thermalizes with $\tau = 410 \pm 40$ fs. This study solidifies the nonadiabatic mechanistic picture of solvated electron relaxation as it directly observes the p-state relaxation, resolving differing interpretations of transient absorption (TA) experiments. A subsequent investigation by Karashima et al.[59] using time- and angle-resolved photoemission from a liquid microjet showed that the first component of the relaxation process, with a lifetime of 60 fs, was associated with anisotropic photoemission while the second component and ground state corresponded to isotropic photoemission. The evolving angular distribution reflects the change in orbital symmetry going from the excited p-state manifold to the ground s-state, supporting the assignment of the fast component in the excited state relaxation mechanism to a nonadiabatic transition from the excited state to a hot ground state. These results motivated similar LJ-TRPES experiments carried out on the solvated electron in D_2O[44] and methanol,[3] with resulting measurements of the internal conversion lifetime and solvent isotope effect also consistent with a nonadiabatic mechanism.

3.2. Ultrafast Excited State Dynamics in NACs

Nucleic acid constituents have been studied widely[38] owing to their importance in biology as well as their complex photochemistry. NACs absorb light in the UV−C region with large absorption bands near 270 and 200 nm attributed to $\pi\pi^*$ transitions.[60] These wavelengths are typically destructive as the energy imparted on the molecule is on the order of typical bond dissociation energies.[37] Despite this, NACs have a remarkable photostability owing to ultrafast relaxation that efficiently funnels the excess electronic energy from the excited state into vibrational energy on the ground electronic surface, which can then be dissipated to the surrounding medium.[38,61] The underlying mechanism has been studied in solution using transient absorption and fluorescence upconversion (FU).[37,38,61] TRPES has been applied to this problem in both gas phase[33,62−64] and liquid jet[1,2,65−67] experiments using UV pump and probe pulses. As was the case for hydrated electrons, a comparison of TRPES experiments in the gas phase and aqueous solution offers a unique opportunity to carry out complementary experiments of the same system in two very different environments.

The relaxation dynamics of NACs rely heavily on the relative position of the various possible excited states that could be involved,[68] most notably the lowest energy $^1\pi\pi^*$, $^1n\pi^*$, and $^3\pi\pi^*$ states, shown schematically in Figure 3 for aqueous thymine. In the gas phase, excitation in the 270 nm band of isolated NACs populates the $^1\pi\pi^*$ state, which is energetically above both the $^1n\pi^*$ and $^3\pi\pi^*$ states, allowing for population of these states as the molecule undergoes relaxation. In aqueous solution, this $^1\pi\pi^*$ state is stabilized relative to the nearby $^1n\pi^*$ state, as illustrated in Figure 3, putting it at comparable if not lower energy.[65] The $^3\pi\pi^*$ state would also be stabilized in a comparable fashion. The relaxation pathways possible involving these states involve passage through a conical intersection (CI) from the $S_1(^1\pi\pi^*)$ state to the ground state, internal conversion to the $^1n\pi^*$ state, or intersystem crossing (ISC) to the $^3\pi\pi^*$ state shown in Figure 3.

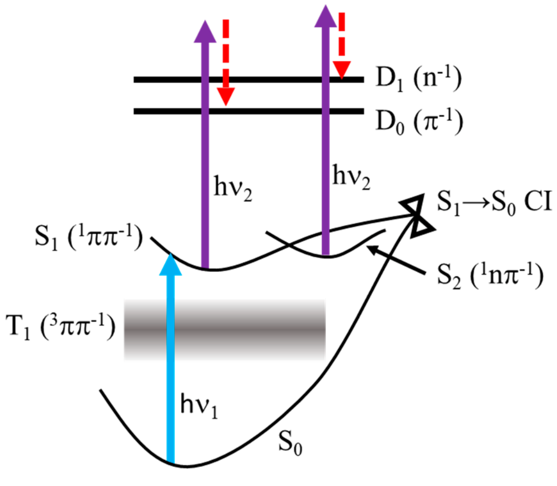

Figure 3. Schematic representation of the relevant electronic states involved of aqueous T, Thd, and TMP related to the relaxation dynamics after UV excitation.

In solution, TA experiments indicate notably different relaxation mechanisms for thymine and adenine derived NACs. In adenine, the relaxation was shown to involve only direct internal conversion through a CI from the S_1 excited state to the ground electronic state with no evidence of any contributions from intermediate excited states.[69] In thymine-derived NACs, TA experiments found a delay for ground state recovery that was attributed to intermediate excited states involved in the relaxation dynamics from the initially populated $^1\pi\pi^*$ state.[70,71] Early studies attributed this delay to a long-lived intermediate $^1n\pi^*$ state through which stepwise IC to the ground state occurred.[70] This assignment has been called into question by more recent TA studies, in which time-resolved UV/vis and IR spectroscopy experiments of thymine and TMP were performed.[71] In the gas phase, TRPES experiments were carried out to observe the relaxation dynamics of isolated nucleobases.[64,72,73] These studies show adenine and pyrimidine bases both have rapid transfer of population out of the initially populated $^1\pi\pi^*$ state within <100 fs to an intermediate

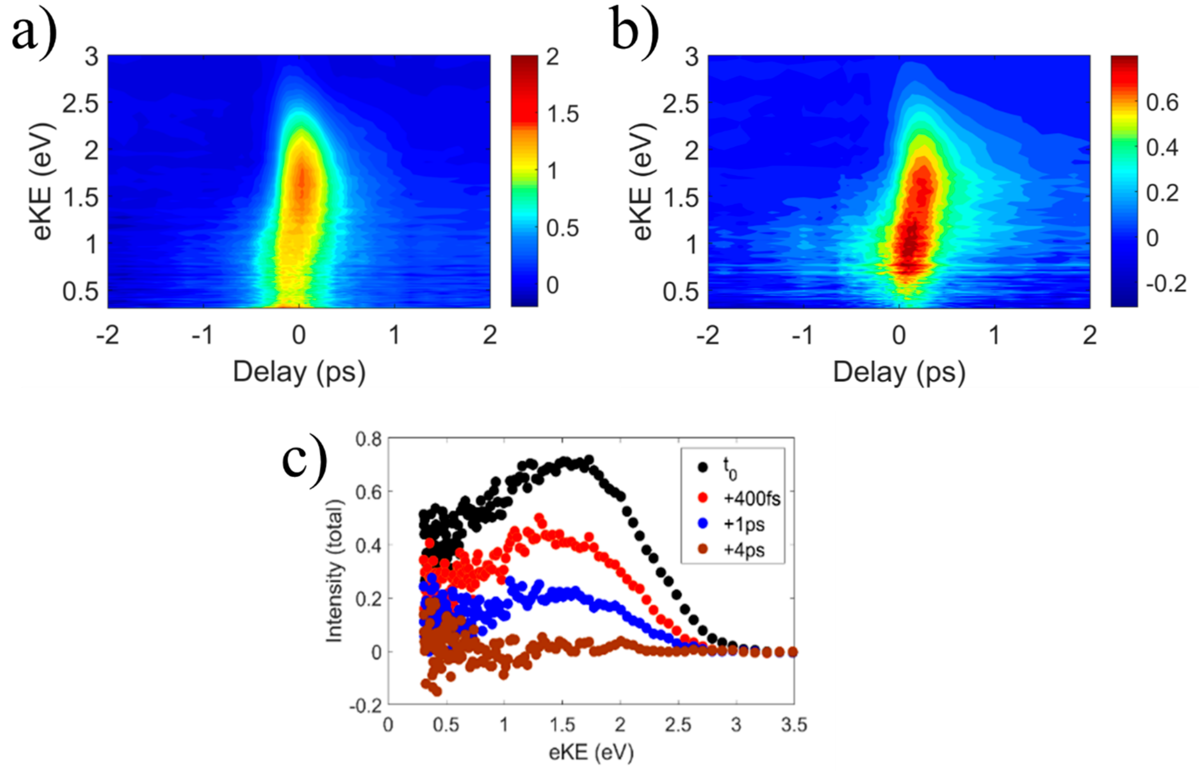

Figure 4. TRPE spectra of (a) thymine and (b) TMP showing 5.17 eV pump/6.20 eV probe data at positive delays. (c) Static spectra at given delays for thymine show no identifiable signal past 4 ps. Reproduced in part from ref 1. Copyright 2019 American Chemical Society.

electronic state.[64,72] Later work used a higher energy probe capable of capturing a more complete picture of the relaxation process, as earlier studies lacked sufficient probe energy to observe dynamics beyond ∼1 ps. That study showed that the $^3\pi\pi^*$ state was populated from the $^1n\pi^*$ state in isolated thymine with a rise time of approximately 3.5 ps.[73] These observations of rapid transfer of population to the $^1n\pi^*$ state in gas phase TRPES experiments and the possible involvement of excited states other the $^1\pi\pi^*$ state in solution serve as motivation to perform comparable TRPES experiments in aqueous solution.

Initial experiments using liquid microjet TRPES to study NACs were performed by Buchner et al, who observed femtosecond relaxation lifetimes of adenine, adenosine,[67] thymine, thymidine,[65] and guanosine[66] using a tunable UV (238 to 248 nm) and 267 nm pump−probe scheme. For adenosine and adenine, they presented the first direct observation of the evolution of excited NACs along a potential surface using femtosecond TRPES. This work not only determined the lifetimes of the solvated NACs, but also tracked the average kinetic energy of electrons from the excited state as a function of time to infer dynamics of the population on the excited state surface itself. These studies were then extended in our laboratory using a pump−probe scheme utilizing similar tunable UV pump pulses and 200 nm rather than 267 nm probe pulses.[1,2,65,67] This scheme extended the maximum probe energy by 1 eV in an effort to observe as much of the dynamics as possible, as relaxation along the excited state surface or population of a lower-lying intermediate state could increase the ionization energy of the evolving system beyond the lower probe photon energy. We applied this pump−probe scheme to adenosine (Ado), thymine (T), and thymidine (Thd) in addition to adenosine monophosphate (AMP) and thymidine monophosphate (TMP). Extending the LJ-TRPES studies to include the nucleotides AMP and TMP was important to further the bottom-up approach to understanding the dynamics in macromolecular DNA after radiation absorption. Key results are as follows.

3.2.1. Relaxation from the $S_1(^1\pi\pi^*)$ Excited State.

Figure 4 shows LJ-TRPES results for T and TMP at pump and probe energies of 4.74 and 6.20 eV, respectively. As discussed above, the relaxation dynamics from the $S_1(^1\pi\pi^*)$ state in aqueous T, Thd, and TMP have been hotly debated, with uncertainty surrounding the involvement of the lowest lying $^1n\pi^*$state in the relaxation from an initially prepared $^1\pi\pi^*$ state absorbing at ∼260 nm.[38] LJ-TRPES studies of T, Thd, and TMP find lifetimes for the $S_1 \rightarrow S_0$ relaxation in T and Thd at 4.74 eV pump energy to be 360 and 390 fs respectively, in excellent agreement with previous LJ-TRPES experiments and slightly shorter than but comparable to TA and FU experiments. The corresponding lifetime in TMP is considerably longer, 870 fs, as can be seen by comparing Figure 4a and 4b. Moreover, no excited state signal is observed beyond 4 ps, as shown in Figure 4c for T, even with the 6.2 eV probe energies employed. This observation adds further evidence that the $^1n\pi^*$ state has no significant involvement in the relaxation dynamics of aqueous T, Thd, and TMP. This state has been observed in the gas-phase with a lifetime of ∼10 ps and has a measured vertical ionization energy of 6.5 eV.[73] Given these values, one could expect signal from the $^1n\pi^*$ state to appear with ∼1 eV eKE given solvent stabilization of the resulting cationic state after photoionization. Lacking any persistent signal in this spectral region, the involvement of the $^1n\pi^*$ in the solution phase relaxation dynamics of thymine compounds is highly unlikely. Instead, it is possible the persistent signal seen in TA experiments is attributable to the $^3\pi\pi^*$ state, as predictions for the binding energy of this state lie anywhere from 0.6 eV above to 0.6 eV below the probe energy available in this experiment, which would at best yield electron kinetic energies near the lower detection limit of the detector used.

In LJ-TRPES experiments of aqueous Ado and AMP using the same TUV pump to excite to the $S_1(^1\pi\pi^*)$ state, monoexponential excited state lifetimes on the order of 220 to 250 fs were found,[2] in general agreement with previous work.[67] Photoelectron spectra showed no delay dependent energy shifting of the excited state population, emphasizing the rapid time scales on which these dynamics occur. In addition, the $S_1 \rightarrow S_0$ lifetime observed at the highest TUV pump energy of 4.97 eV was essentially identical with the lifetime observed when exciting at 4.69 eV, in contrast to previous work where the lifetime at 4.66 eV pump and 5.0 eV probe energies is approximately double the retrieved lifetime with those pump and probe energies switched.[2,67] The difference in probe energy here is key; the previous study used a 4.66 eV probe while this work used a 6.2 eV probe. The additional 1.54 eV probe energy allowed observation of the full excited state wavepacket and retrieval of an accurate lifetime not artificially shortened by excited state population relaxing to a portion of the excited state surface that could not be readily ionized at 4.66 eV.

3.2.2. Differences in Nucleotide Relaxation Lifetimes.

Our experiments on TMP show that the lifetime of the $S_1(^1\pi\pi^*)$ state is nearly double that of T and Thd. While this trend had been observed previously in TA and FU experiments, no explanation for the substantial increase in lifetime had been proposed. To this end, molecular dynamics simulations were performed, finding the dominant conformation of aqueous Thd to be the syn-conformer whereas the dominant TMP conformation was the anti-conformer, shown in **1a** and **2b** of Figure 5, respectively.[1] These conformational differences are important since the conical intersections responsible for the rapid relaxation to the ground state involve distortions of the pyrimidine ring. The effects of these ground

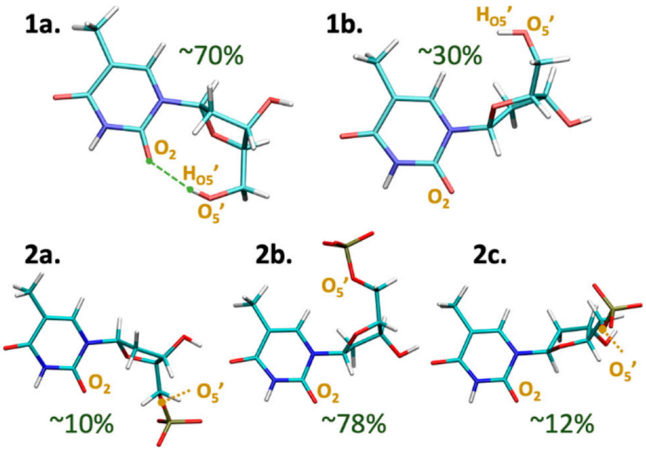

Figure 5. Main conformers of Thd (**1a** and **1b**) and TMP (**2a**, **2b**, and **2c**) determined by percentage occupation in a MM trajectory calculation. Reproduced from ref 1. Copyright 2019 American Chemical Society.

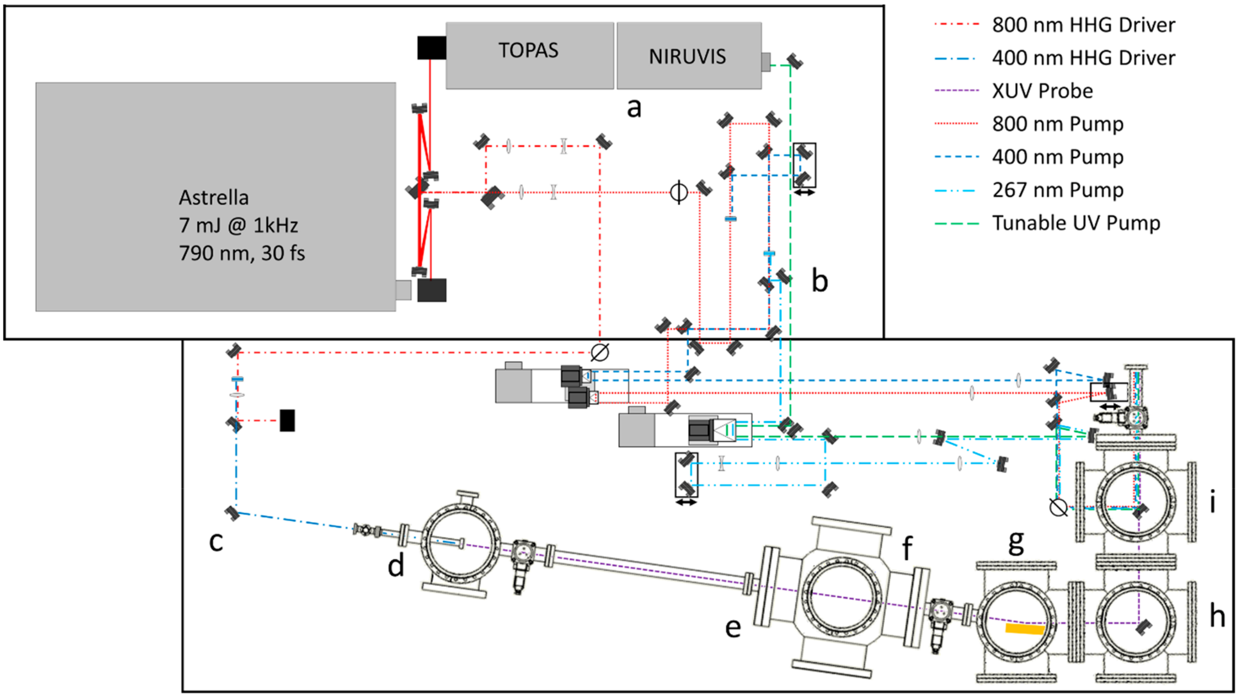

Figure 6. Optical layout used to generate pump and probe pulses in our XUV LJ-TRPES project. The layout consists of (a) an OPA, (b) a BBO-based third harmonic generation setup, and (c) a HHG beamline consisting of (d) a semi-infinite gas cell, (e) a 200 nm thick Al filter, (f) a beam analyzer for spectral characterization, (g) a toroidal mirror, (h) a multilayer mirror, and (i) an annular mirror.

state conformational differences on the dynamics of the photoexcited species are currently under theoretical investigation.

3.3. Future Prospects of Using Femtosecond XUV Probes

TRPES is capable, in principle, of tracking the complete relaxation pathway of a photoexcited system from the initially excited electronic state down to its ground state. The extent to which one can do this is determined by the probe photon energy and the type of system under study. In negative ion TRPES experiments, electron affinities are typically 5 eV or less. Hence, ground state negative ions can be photodetached by readily accessible UV femtosecond laser pulses generated by standard nonlinear optical methods. TRPES using femtosecond probe pulses at 7.9 eV produced by four-wave mixing has also recently been reported.[74] However, the ionization potentials of neutral molecules in the gas phase and in solution can be 10 eV or higher. Hence, the ability to generate femtosecond probe pulses in the extreme ultraviolet (XUV) region of the electromagnetic spectrum will significantly enhance the dynamical range of TRPES, as has been demonstrated in gas phase experiments using both table-top laser systems[75,76] and free electron lasers.[73,77,78]

Advances in optical physics have brought about the high-harmonic generation (HHG) technique, in which high energy harmonics of a driving laser field can be generated by focusing the intense laser field into a diffuse gaseous medium.[79] These harmonics can be generated on a tabletop setup such as that shown in Figure 6 utilizing the same types of lasers typically used in TRPES experiments, so HHG is well suited for overcoming the aforementioned probe energy limitations, as was first demonstrated by Leone and co-workers on gas phase Br_2.[75] HHG sources for PES require relatively narrowband femtosecond pulses with energy resolution of the order of 10s to 100s of meV so as to minimize the width of photoelectron energy distributions from a given electronic state.[80] To this effect, XUV beamlines employing HHG yielding discrete harmonics and either multilayer mirrors or time-compensating extreme ultraviolet (XUV) monochromators[24,81−83] have been built. These afford temporal durations of XUV pulses on the order of 10s of femtoseconds while bandwidth in the range of 200−500 meV is attainable. Various implementations of this approach have yielded femtosecond high-harmonic sources with isolated harmonics ranging from 7 eV[83] to 100 eV.[84]

LJ-TRPES using XUV probe pulses presents its own special challenges. Most notably, any time-resolved dynamics resulting from photoexcitation and photoionization of solute molecules competes with very strong signals from one-photon ionization of water, for which the vertical ionization energy is 11.33 eV.[85] Nonetheless, several such experiments have already been performed, ranging from fundamental processes in pure liquids to solute dynamics in systems such as the solvated electron,[12] organic chromophores,[24,86] and organometallic complexes.[87] These studies of increasingly complex molecules illustrate the trend toward larger systems that can be effectively studied by the LJ-TRPES method given the advances in light sources and detector technology.

An additional challenge in implementing XUV probe pulses is that of probe depth considerations, as these relate directly to whether electrons detected in these LJ-PES experiments carry information about the dynamics of solute molecules solvated in bulk solution or at the vacuum-water interface. Detailed simulations have been performed to determine the degree to which inelastic and elastic scattering impact probe depth. These simulations show that for a photoelectron emitted with 35 eV kinetic energy, near the minimum inelastic mean free path (IMFP) for electrons in liquid water,[31] approximately half of the ejected photoelectrons originate deeper than 3 water monolayers inside the liquid jets and could be considered bulk.[32] Given these results, it can be assumed most LJ-TRPES experiments can indeed probe bulk solute dynamics with minimal influence from signal originating from the vacuum-liquid interface, though choosing to probe solutions near the IMFP minimum would yield signals more heavily influenced by the interface and could be exploited to selectively study solutes at the interface. Using HHG to generate discrete harmonics in the XUV allows for studying dynamics at varying probe depths simply by selecting a different harmonic, allowing both the refinement of scattering corrections by improving measurements of energy-dependent scattering cross sections and, to some extent, preferential probing of bulk and interfacial dynamics.

The setup in our laboratory to carry out XUV TRPES on liquid jets is shown in Figure 6. Here, 400 nm light is used to generate harmonics in a semi-infinite gas cell.[88] Driving harmonics with 400 nm affords both a wide harmonic spacing of 6.2 eV and has the advantage of higher HHG conversion efficiencies, as the efficiency scales with driving laser wavelength as approximately λ^{-5}–λ^{-6}, though this also reduces the highest attainable photon energies.[89,90] Harmonic generation parameters in the semi-infinite gas cell, highlighted in Figure 6d, are optimized to maximize flux in the seventh harmonic of 400 nm (21.7 eV) and minimize contributions from higher energy harmonics. The seventh harmonic is isolated using a multilayer mirror developed by the Center for X-ray Optics at Lawrence Berkeley National Laboratory designed to suppress the fifth and ninth harmonics while efficiently reflecting the seventh harmonic at a 45° angle of incidence as shown in Figure 6h. This selection is done in conjunction with an oxidized aluminum foil that both blocks the driving laser light and suppresses the fifth harmonic at 15.5 eV. This design maximizes harmonic flux at the liquid jet by minimizing the optics necessary to select and refocus a single harmonic, with only 3 optics in the harmonic beamline prior to pump–probe recombination using an annular mirror shown in Figure 6i.

Initial experiments will focus on using probe pulses at 21.7 eV to perform valence ionization of photoexcited neutral and ionic solutes. In the near future, we plan to extend our photon energy range into the soft X-ray regimes in order to take advantage of the elemental specificity offered by core-level PES in liquids.[15]

4. CONCLUDING REMARKS

In this Account, the ultrafast dynamics of the solvated electron as well as thymine- and adenine-derived nucleic acid constituents as studied by liquid jet time-resolved photoelectron spectroscopy are summarized. These experiments, aimed at developing a greater understanding of the role solvent plays in relaxation dynamics, form the basis for insight into the initial dynamics relevant to DNA damage both indirectly by free electrons in solution and by direct absorption of ultraviolet light. The generation and relaxation of the solvated electron was investigated in H_2O, D_2O, and MeOH. In these studies, it was shown that an initially excited charge-transfer-to-solvent transition readily generates free electrons that persist for nanoseconds. When these electrons are photoexcited, p → s internal conversion occurs on a ~100 fs time scale in all three solvents. This time scale is consistent with the so-called nonadiabatic relaxation mechanism for solvated electrons. Additionally, experiments interrogating the relaxation dynamics of thymine- and adenine-derived NACs from the $S_1(^1\pi\pi^*)$ state allowed measurement and comparison of lifetimes associated with these states across the different NACs. The thymine- and adenine-derived NACs show no evidence for intermediate states in relaxation from the $S_1(^1\pi\pi^*)$ state. The thymine NAC studies revealed a substantially longer lifetime for the S_1 excited state in TMP compared to T and Thd; the source of this discrepancy was attributed to conformational changes from Thd to TMP that could impact the excited state relaxation pathway. Finally, new tabletop XUV light sources will enable carrying out LJ-TRPES experiments on a much wider variety of solutes and afford access to more information in an experiment through ionization of all valence states of a solute.

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Notes

The authors declare no competing financial interest.

Biographies

Zachary N. Heim was born in 1994 in Sartell, Minnesota. He carried out his undergraduate studies at the University of Wisconsin—Madison, graduating with a B.S. in chemistry in 2017. Since then, he has been working as a graduate student researcher in Daniel Neumark's group at the University of California at Berkeley, studying the ultrafast dynamics of solutes in high vapor pressure solvents.

Daniel M. Neumark was born in 1955 in Chicago, IL. He was an undergraduate at Harvard, then went to graduate school at UC Berkeley. There, he worked in Yuan Lee's research group and received his Ph.D. in 1984. After spending two years at the University of Colorado, Boulder as a postdoctoral fellow with Carl Lineberger, he joined the Berkeley Chemistry Department as an Assistant Professor in 1986 and has been there ever since. His research interests encompass gas phase studies of reaction dynamics via negative ion photodetachment, spectroscopy and scattering experiments involving liquid microjets, and attosecond dynamics of atoms, molecules, and solids.

ACKNOWLEDGMENTS

This research is supported by the National Science Foundation Division of Chemistry under Grant No. CHE-2154629.

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