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# Time-resolved dynamics in iodide-uracil-water clusters upon excitation of the nucleobase

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#### ABSTRACT

The dynamics of iodide-uracil-water ( $I^-U \cdot H_2O$ ) clusters following  $\pi \cdot \pi^*$  excitation of the nucleobase are probed using time-resolved photoelectron spectroscopy. Photoexcitation of this cluster at 4.77 eV results in electron transfer from the iodide moiety to the uracil, creating a valence-bound anion within the cross correlation of the pump and probe laser pulses. This species can decay by a number of channels, including autodetachment and dissociation to  $I^-$  or larger anion fragments. Comparison of the energetics of the photoexcited cluster and its decay dynamics with those of the bare iodide-uracil ( $I^- \cdot U$ ) complex provides a sensitive probe of the effects of microhydration on these species.

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#### I. INTRODUCTION

DNA damage has been shown to proceed directly from UV photoexcitation as well as indirectly from the attachment of lowenergy electrons to its constituent nucleobases.<sup>1–4</sup> DNA bases exhibit strong absorption cross sections for UV radiation, particularly near 260 nm (4.77 eV),<sup>5,6</sup> and the interaction of nucleobases with the surrounding solvent water molecules plays a key role in the relaxation and photostability of nucleobases in this excitation energy regime.<sup>43</sup> The attachment of low-energy electrons induces strand breaks in DNA,<sup>2-4</sup> and it has been proposed that the initial site of electron attachment is the nucleobase followed by electronic coupling that facilitates fragmentation at the backbone.<sup>9-16</sup> Photoelectron spectroscopy has shown that the addition of water increases the electron affinity of nucleobases,<sup>17,18</sup> while molecular dynamics simulations find that solution-structure fluctuation likely promotes attachment of bulk hydrated electrons to nucleobases.<sup>19</sup> Our group has previously examined the ultrafast dynamics of electron attachment to nucleobases using time-resolved photoelectron spectroscopy<sup>20</sup> (TRPES) of various iodide-nucleobase (I<sup>-</sup>·N) complexes<sup>21-</sup> and related model systems.<sup>28,29</sup> The present study uses TRPES to examine iodide-uracil-water (I $^-$ ·U·H<sub>2</sub>O) clusters photoexcited at 260 nm

and compares these results to those of iodide-uracil ( $I^-\cdot U$ ) to understand the role of water in the mechanisms of excitation and charge transfer in these anionic clusters in this UV excitation regime.

I-N complexes have been previously studied by photofragment action spectroscopy<sup>26,30,31</sup> and electronic structure calculations<sup>26,30,32</sup> in addition to TRPES. Two regimes of UV photoabsorption have been measured for these complexes.<sup>26,30,31</sup> The first is centered near the vertical detachment energy (VDE), the difference in energy between the anion and the neutral clusters at the equilibrium geometry of the anion, which is approximately 4 eV for most I-N clusters.<sup>21,22,25</sup> The second region of UV photoabsorption is a broad band spanning ~4.6-5.0 eV. Excited state calculations for  $I^- \cdot U$ ,<sup>26</sup> iodide-thymine ( $I^- \cdot T$ ),<sup>30</sup> and  $I^- \cdot U \cdot H_2 O^{32}$  show that photoexcitation near the VDE corresponds to optical excitation from the iodide (5p) orbital to a dipole-bound (DB) state of the nucleobase. The nucleobase DB state arises from capture of the excess electron by the relatively large dipole moment of the base.<sup>33–37</sup> In contrast, these same calculations indicate that photo excitation near 4.7-4.8 eV primarily corresponds to base-centered  $\pi$ - $\pi^*$  excitation. The dynamics resulting from near-VDE photoexcitation of I-U·H<sub>2</sub>O and the effects therein of the water molecule have already been considered in detail,<sup>32</sup> so we focus here only on the effect of the addition of water on the dynamics ensuing  $\pi$ - $\pi$ <sup>\*</sup> photoexcitation.

TRPES of I<sup>-</sup>·N clusters probes the dynamics of photoinduced electron attachment and electronic excitation in nucleobases and traces the time evolution of nascent transient negative ions (TNIs) and anionic decay photofragments. Our TRPES studies with pump excitation energies from 4.60 to 4.90 eV are expected to create a  $\pi$ - $\pi$ <sup>\*</sup> excited state of the nucleobase, as in the following equation:

$$I^{-}(5p^{6}) \cdot N(\pi^{4}\pi^{*0}) \xrightarrow{hv_{pump} \sim 260 \text{ nm}} I^{-}(5p^{6}) \cdot N(\pi^{3}\pi^{*1}).$$
(1)

Time-resolved studies in this pump excitation regime have found instantaneous formation of the cluster valence-bound (VB) anion with no evidence for the presence of DB states.<sup>21,22</sup> The VB state corresponds to electron attachment to a valence orbital, the  $\pi^*$  orbital of the base.<sup>14,17,38</sup>

We have previously proposed<sup>21,27</sup> for I<sup>-</sup>·U and I<sup>-</sup>·T complexes that, subsequent to  $\pi$ - $\pi^*$  excitation of the nucleobase, charge transfer from iodide to the empty  $\pi$  orbital creates the VB anion. While this overall mechanism is consistent with experimental results and electronic structure calculations,<sup>27</sup> it still awaits theoretical confirmation.

Photofragment action spectroscopy in conjunction with TRPES has identified autodetachment as well as formation of I<sup>-</sup> as the major cluster decay pathways in both photoexcitation regimes for I<sup>-</sup>·U binary clusters,<sup>26</sup> although the nature of the time-resolved dynamics of these channels has been found to be clearly different for each set of pump energies.<sup>27</sup> Autodetachment refers to the spontaneous emission of an electron from photoexcitation of an anion resonance embedded within the neutral plus free electron continuum;<sup>39–41</sup> these electrons can be very slow if randomization of vibrational energy occurs prior to electron emission (the thermionic emission limit).<sup>42</sup>

In the present study, we employ TRPES to excite I<sup>-</sup>·U·H<sub>2</sub>O complexes near the peak of the base-centered  $\pi$ - $\pi^*$  excitation<sup>32</sup> at 260 nm (4.77 eV) and track the resulting dynamics with 1.58 eV or 3.18 eV probe pulses. These experiments, which complement previous work<sup>32</sup> on near-VDE excitation of I<sup>-</sup>·U·H<sub>2</sub>O complexes, probe the dynamics of electronically excited uracil as well as the interaction of low-energy electrons with the nucleobase. TRPES can identify and trace the dynamics of nascent TNIs (eBE ~ 0 eV-1 eV)<sup>18</sup> with 1.58 eV probe pulses, while the higher energy probe is capable of detecting anionic photofragments such as I<sup>-</sup> (neutral electron affinity = 3.059 eV).<sup>47</sup> Here, we observe prompt formation of the VB anion, with autodetachment and the formation of I<sup>-</sup> as the major decay channels for the photoexcited clusters. The lifetimes of the VB anion and autodetachment features reflect the stabilizing effect of the presence of water, while the I<sup>-</sup> rise dynamics suggest that additional water-associated fragmentation channels may be active here.

#### **II. EXPERIMENTAL METHODS**

The experimental apparatus employed in this study has been described in detail previously<sup>48,49</sup> and is briefly summarized here.

I<sup>−</sup>·U·H<sub>2</sub>O clusters were generated by passing 515 kPa helium buffer gas over a reservoir of distilled water and a reservoir of methyl iodide (CH<sub>3</sub>I). The reservoirs and the connecting gas line were wrapped in heating tape; the water reservoir was heated to approximately 30 °C, while the CH<sub>3</sub>I reservoir and gas line were heated to approximately 40 °C. The gas mixture was then passed through an Even-Lavie pulsed valve operating at 500 Hz, which contained a sample cartridge of uracil (Sigma-Aldrich, ≥99%) heated to 240 °C. The gas mixture was expanded into vacuum through a ring-filament ionizer to create anionic clusters, which were then extracted orthogonally into a Wiley-McLaren time-of-flight mass spectrometer.<sup>50</sup> The I<sup>−</sup>·U·H<sub>2</sub>O clusters were mass-selected and then intersected by the pump and probe laser pulses.

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To generate the pump and probe laser pulses, a KMLabs Griffin oscillator and a Dragon amplifier were used to produce 45 fs pulses centered at approximately 785 nm (1.58 eV) with 1.8 mJ/pulse. The fundamental was frequency tripled with two  $\beta$ -barium borate (BBO) crystals to produce ~10  $\mu$ J/pulse of 260 nm (4.77 eV) pump pulses. The residual 785 nm pulses were recovered from the frequency-tripler set-up and were sent to a delay stage to serve as probe pulses of ~80  $\mu$ J/pulse. Alternatively, this recovered 785 nm light was frequency-doubled in a BBO to produce ~60  $\mu$ J/pulse of 390 nm (3.18 eV) probe pulses. In either case, the pump and probe pulses were combined at the chamber in a dichroic beam splitter. The cross correlation of 260 nm/785 nm was  $\leq$ 180 fs, and that of 260 nm/390 nm was <300 fs; the latter cross correlation, measured outside the chamber, is obscured by residual 390 nm light, and the actual cross correlation is expected to be as much as 50-100 fs shorter than this measured value.20

The resultant photoelectrons were analyzed by a velocity-map imaging assembly<sup>51</sup> comprising three electron optical elements and a chevron-stacked microchannel plate detector coupled to a phosphor screen imaged by a charge-coupled device camera. Basis-set expansion (BASEX) reconstruction methods were used to reconstruct the 3D photoelectron kinetic energy (eKE) distributions.<sup>52</sup>



**FIG. 1.** Single-photon photoelectron spectrum of I<sup>-</sup>.U-H<sub>2</sub>O at 4.74 eV and calculated ground state I<sup>-</sup>.U-H<sub>2</sub>O structure (inset). The spectrum and structure are adapted with permission from A. Kunin, W.-L. Li, and D. M. Neumark, J. Chem. Phys. **149**, 084301 (2018). Copyright 2018 AIP Publishing LLC.



**FIG. 2.** Photoelectron spectra of  $I^-$ .U.H<sub>2</sub>O at 4.77 eV pump excitation energy and 1.58 eV probe energy at selected delay times.

#### III. RESULTS

Figure 1 presents a laser noise-subtracted, single-photon photoelectron spectrum of I-U·H2O clusters photodetached at 4.74 eV as well as an image of the calculated ground state structure of the cluster.<sup>32</sup> The photoelectron spectrum is provided as a function of eKE as well as electron binding energy (eBE) (eBE =  $hv_{photon} - eKE$ ). Two features appear in this spectrum: feature A, peaked at approximately  $4.69 \pm 0.05$  eV eBE (0.05  $\pm$  0.05 eV eKE), and feature B, peaked at 4.40  $\pm$  0.05 eV eBE (0.37  $\pm$  0.05 eV eKE). As has been previously determined,<sup>32</sup> feature A corresponds to autodetachment of ~0 eV eKE electrons from the photoexcited I-U·H<sub>2</sub>O clusters and feature B corresponds to direct detachment to the lower iodine spin-orbit state  $({}^{2}P_{3/2})$  from the I<sup>-</sup>·U·H<sub>2</sub>O anion, yielding a VDE of 4.40 eV for I<sup>-</sup>·U·H<sub>2</sub>O. As both of these features arise from single-photon (pump-only) processes at the pump energy employed in our TRPES experiments, they are also present in all of the TRPE spectra here at these same eKEs.

Figure 2 presents photoelectron spectra at selected time delays for  $I^-$ ·U·H<sub>2</sub>O at 4.77 eV pump excitation energy and 1.58 eV probe



**FIG. 3.** Representative background-subtracted time-resolved photoelectron spectra for feature C at short pump-probe delays for  $I^-$ ·U·H<sub>2</sub>O at 4.77 eV pump excitation energy and 1.58 eV probe energy.



**FIG. 4.** Photoelectron spectra of  $I^-$ .U-H<sub>2</sub>O at 4.77 eV pump excitation energy and 3.18 eV probe energy at selected delay times.

energy; here and in other TRPE spectra, eBE =  $hv_{probe} - eKE$ . Feature A exhibits nonzero intensity at negative times and increases in intensity over approximately 10 ps before decreasing back to its initial intensity. Feature B exhibits noisy but similar time dynamics as feature A, likely due to the spectral overlap between the two features in this region. Feature C, covering the region from approximately 0.1 eV-0.9 eV eBE, is enlarged in the inset. Based on our previous results on I<sup>-</sup>·U clusters photoexcited at excitation energies in the range of 4.69–4.90 eV,<sup>21,22</sup> we can assign feature C as the VB anion of photoexcited I<sup>-</sup>·U·H<sub>2</sub>O. Time-resolved photoelectron spectra for feature C, background-subtracted with respect to the most negative delay time, are shown in Fig. 3 for time delays up to 5 ps.

Figure 4 presents photoelectron spectra at selected time delays for  $I^-$ ·U·H<sub>2</sub>O at 4.77 eV pump excitation energy and 3.18 eV probe energy. Features A and B are the same features shown in Fig. 2. The prominent new feature in these spectra, feature D, is located at 3.06  $\pm$  0.05 eV eBE, and this narrow feature grows monotonically in intensity over the course of the experiment. Based on the binding energy, spectral shape, and time-dynamics of feature D,



**FIG. 5.** Representative background-subtracted time-resolved photoelectron spectra for features A (near maximum eBE, eKE  $\sim$  0–0.07 eV) and D (eBE = 3.06 eV) for I<sup>-</sup>·U·H<sub>2</sub>O at 4.77 eV pump excitation energy and 3.18 eV probe energy.



FIG. 6. Concatenated normalized integrated intensities for features A (black, autodetachment) and C (red, VB anion) at (a) early time delays, (b) 10 s of ps, and (c) long time delays from excitation at 4.77 eV and probed with 1.58 eV. Feature A rises in  $11.3 \pm 2.2$  ps and decays in  $285 \pm 70$  ps. The rise time for feature C is cross correlation limited, and the decay is  $540 \pm 240$  fs and  $220 \pm 70$  ps.



FIG. 7. Comparison of concatenated normalized integrated intensities for (a) the VB anion at early times and (b) long times and (c) autodetachment dynamics for I<sup>-</sup>·U·H<sub>2</sub>O (green) at 4.77 eV pump excitation energy and 1.58 eV probe energy and I<sup>-</sup>·U (purple) at 4.79 eV pump excitation energy and 1.57 eV probe energy.

we assign feature D to photodetachment of atomic iodide to the  ${}^{2}P_{3/2}$  iodine spin-orbit state. Background-subtracted time-resolved photoelectron spectra for features A and D are presented in Fig. 5.

#### **IV. ANALYSIS**

The normalized, integrated intensities for the VB anion (red, feature C) and the autodetachment feature (black, feature A) are shown at early, intermediate, and long time delays in Fig. 6. The integrated signals are fit to the convolution of a Gaussian instrumental response function with i exponential functions as in the following equation:

$$I(t) = \frac{1}{\sigma_{CC}\sqrt{2\pi}} \exp\left(\frac{-t^2}{2\sigma_{CC}^2}\right) \cdot \begin{cases} I_0, \quad t < 0, \\ I_0 + \sum_i A_i \exp\left(\frac{-t}{\tau_i}\right), \quad t \ge 0. \end{cases}$$
(2)

In this equation,  $\sigma_{cc}$  is the Gaussian full width at the half-maximum given by the cross correlation of the pump and probe laser pulses,  $I_0$  is the signal background,  $A_i$  are the coefficients for each exponential function, and  $\tau_i$  are the corresponding rise or decay lifetimes for each exponential. These fits are shown in Fig. 6 as solid red and black lines for the VB anion and autodetachment features, respectively. The VB anion is found to appear within the cross correlation of the pump and probe laser pulses and decay biexponentially. The fits for the I<sup>-</sup>·U·H<sub>2</sub>O VB anion decay are 540 ± 240 fs and 220 ± 70 ps. The autodetachment feature was found to remain relatively constant in intensity at negative times. At positive delay times, this feature rises to a maximum in 11.3 ± 2.2 ps followed by decay to the negative-time intensity in approximately 285 ± 70 ps. For ease of comparison to our previous work on  $I^- \cdot U$  clusters, the normalized, integrated intensities for the VB anion and autodetachment produced from  $I^- \cdot U$  photoexcited at 4.79 eV are presented in Fig. 7 in purple, overlaid with the corresponding  $I^- \cdot U \cdot H_2O$  features (green) from Fig. 6. Figure 8 presents the normalized integrated intensity and fitted rise for the  $I^-$  signal observed here. The  $I^-$  formation was found to be biexponential, with rise time constants of 32.5 ± 2.6 ps and 230 ± 20 ps. Table I summarizes the fit rise and decay lifetimes for the VB anion, autodetachment, and  $I^-$  feature for  $I^- \cdot U \cdot H_2O$  in the present study and for  $I^- \cdot U$  photoexcited at 4.79 eV from our past work.<sup>21,26</sup>



**FIG. 8**. Normalized integrated intensity for feature D at 4.77 eV pump excitation energy and 3.18 eV probe energy. Feature D rises biexponentially with time constants of  $32.5 \pm 2.6$  ps and  $226 \pm 20$  ps.

<b>TABLE I.</b> Lifetimes for the VB anion, autodetachment feature, and I <sup>-</sup> feature for 4.77
eV pump $I^- \cdot U \cdot H_2O$ and comparison to previous $I^- \cdot U$ studies. The $I^- \cdot U$ data for the
VB anion and autodetachment dynamics are from Ref. 21, and for the I <sup>-</sup> feature, the
data are from Ref. 26.

VB anion				
Cluster	$h\nu_{pump}~(eV)$	$ au_{decay,1}$ (fs)	$ au_{decay,2}$ (ps)	
$I^- \cdot U \cdot H_2O$	4.77	$540 \pm 240$	$220 \pm 70$	
$I^- \cdot U$	4.79	$390\pm80$	$37\pm20$	
	Autodet	achment		
Cluster	hv <sub>pump</sub> (eV)	$\tau_{rise}$ (ps)	$ au_{decay}$ (ps)	
$\overline{I^- \cdot U \cdot H_2 O}$	4.77	11.3 ± 2.2	$285\pm70$	
$I^- \cdot U$	4.79	~5	~50	
	I			
Cluster	hv <sub>pump</sub> (eV)	$ au_{rise,1}$ (ps)	$ au_{rise,2}$ (ps)	
$I^- \cdot U \cdot H_2O$	4.77	32.5 ± 2.6	$230 \pm 20$	
$I^- \cdot U$	4.72	$36 \pm 3$		

#### V. DISCUSSION

This work explores the dynamics of I<sup>-</sup>·U·H<sub>2</sub>O clusters photoexcited at 4.77 eV, resonant with the base-centered  $\pi$ - $\pi$ <sup>\*</sup> transition for uracil. We observe instantaneous formation of the VB anion of the cluster following photoexcitation, and biexponential decay of this species with time constants of 540 fs and 220 ps. Autodetachment and I<sup>-</sup> re-formation are observed as decay channels in this photoexcitation regime. These experiments show that to the first order, the dynamics of photoexcited I-U·H<sub>2</sub>O are similar to those of I<sup>-</sup>·U following  $\pi$ - $\pi$ <sup>\*</sup> photoexcitation. However, the addition of a water molecule noticeably affects the rise time of the I<sup>-</sup> signal as well as the decay dynamics of the VB state, as shown in Fig. 6 and Table I. As summarized in Eq. (3), we have previously proposed that the initial  $\pi$ - $\pi^*$  iodide-associated photoexcited state decays by two pathways: the  $\pi$ - $\pi$ <sup>\*</sup> excited nucleobase state internally converts to the ground state of the cluster and subsequently evaporates iodide, or iodide transfers a valence electron to fill the hole in the nucleobase  $\pi$  orbital, creating a VB anion that then decays by autodetachment,<sup>2</sup>

$$I^{-}(5p^{6}) \cdot N(\pi^{4}\pi^{*0}) \xrightarrow{\text{hv}_{pump} \sim 260 \text{ nm}} I^{-}(5p^{6}) \cdot N(\pi^{3}\pi^{*1}),$$

$$I^{-} \cdot N(\pi^{3}\pi^{*1}) \xrightarrow{\text{Internal Conversion}} I^{-} \cdot N \to I^{-} + N \to I \cdot N^{-}(\pi^{4}\pi^{*1})$$

$$\xrightarrow{\text{Autodetachment}} I \cdot N + e^{-}.$$
(3)

TRPES on  $I^- \cdot U \cdot H_2O$  at this pump energy is sensitive to each of these decay channels. In Subsections V A–V C, we consider the iodide formation, VB anion, and autodetachment dynamics and the effect of the added water to expand on the basic framework previously set forward.

#### A. lodide formation dynamics

 $I^- \cdot$ 

TRPES of  $\pi$ - $\pi^*$  photoexcited I<sup>-</sup>.U·H<sub>2</sub>O clusters finds biexponential I<sup>-</sup> formation in 32.5 ps and 230 ps, in contrast to I<sup>-</sup>.U clusters for which I<sup>-</sup> was found to appear monoexponentially in 36 ps.<sup>26</sup> As in Eq. (3), we have suggested that due to the previously observed strong connection between the VB anion and the autodetachment dynamics in this pump energy regime, the base-centered  $\pi$ - $\pi^*$  excitation is followed by internal conversion to the ground state and subsequent dissociation to produce iodide monoexponentially.<sup>27</sup> While this mechanism is likely the source of the fast I<sup>-</sup> rise signal, it alone cannot fully explain the origin of the biexponential I<sup>-</sup> appearance observed here for I<sup>-</sup>.U·H<sub>2</sub>O clusters.

Several energetically accessible dissociation channels have been previously calculated for I<sup>-</sup>·U·H<sub>2</sub>O clusters, including dissociation to yield I<sup>-</sup>·H<sub>2</sub>O clusters.<sup>32</sup> I<sup>-</sup>·H<sub>2</sub>O produced as a dissociation product upon photoexcitation could also then further dissociate to yield a second source of the I<sup>-</sup> signal with a delayed rise time, contributing to the biexponential rise dynamics observed here, as depicted in the following equation:

$$I^{-} \cdot U \cdot H_2O \xrightarrow{hv_{pump} \sim 260 \text{ nm}} I^{-} \cdot U(\pi^3 \pi^{*1}) \cdot H_2O,$$

$$(4)$$

$$U(\pi^3 \pi^{*1}) \cdot H_2O \xrightarrow{\text{Internal Conversion}} I^{-} \cdot U \cdot H_2O \rightarrow I^{-} + U \cdot H_2O$$

$$\rightarrow I^{-} \cdot H_2O + U \rightarrow I^{-} + H_2O + U.$$

TRPES experiments of I<sup>-</sup>.U·H<sub>2</sub>O clusters photoexcited at 4.77 eV pump energy and probed by 4.0 eV and by 4.77 eV probe energies were unable to conclusively identify the formation of I<sup>-</sup>.H<sub>2</sub>O (VDE =  $3.51 \pm 0.02$  eV)<sup>53,54</sup> due to poor overall signal levels at these probe energies. However, the existence of this dissociation channel could be verified in future experiments by photofragment action spectroscopy, for example.

#### B. VB anion formation and decay dynamics

As shown in Fig. 3, the VB anion of  $I^- \cdot U \cdot H_2O$  exhibits the strongest intensity near eBE = 0.8-0.9 eV, which is approximately 0.2-0.3 eV higher than the strongest intensity for the I<sup>-</sup>·U VB anion from our past work in this  $\pi$ - $\pi$ <sup>\*</sup> pump excitation energy regime.<sup>21,22</sup> This finding indicates that the presence of water stabilizes the VB anion. In our past work on near-VDE photoexcited  $I^- \cdot U$  and  $I^- \cdot U \cdot H_2O$  clusters, we previously observed that the addition of water also caused an increase of approximately 0.2-0.3 eV eBE in the TNI binding energies.<sup>32</sup> The width of the VB anion photoelectron spectrum is commensurate with the VB anion measured in our past work in this photoexcitation regime as well as our near-VDE photoexcitation studies.<sup>21–23,32</sup> This breadth arises due to the geometric distortion of the VB anion in the ring puckering coordinate relative to the neutral;<sup>55,56</sup> thus, the presence of water does not significantly affect the uracil ring puckering as reflected by the VB anion spectral width.

In the present study, the VB anion is found to appear within the cross correlation of the pump and probe laser pulses and decay biexponentially, as is the case for I<sup>-</sup>·U photoexcited in this excitation energy regime. The fast decay of the I<sup>-</sup>·U·H<sub>2</sub>O VB anion is similar to that of the I·U<sup>-</sup> VB anion formed at 4.79 eV pump energy

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(Table I), while the long decay is an order of magnitude longer in the water-associated complex. This long-lived VB anion stabilization induced by the addition of water is commensurate with the dynamics that were previously observed in near-VDE photoexcited  $I^-.U.H_2O$  clusters, in which the VB anion long-time decay was found to be significantly longer than in  $I^-.U.^{32}$ 

In our previous results for  $\pi$ - $\pi^*$  photoexcited I<sup>-</sup>·U and I<sup>-</sup>·T clusters, we proposed that the VB anion decays by autodetachment because the measured autodetachment signals for both clusters were found to exhibit prompt depletion and recovery near to that mirrored the appearance and fast decay of the VB anion at early times, although the I-U VB anion exhibited a somewhat longer-lived biexponential decay.<sup>22,27</sup> Given the similarities between the I<sup>-</sup>·U and I-U·H<sub>2</sub>O complexes observed here, it is likely that the biexponential decay mechanism for the I-·U·H<sub>2</sub>O VB anion in the present study is by autodetachment as well. Previously, we have attributed the biexponential nature of the VB anion decay to the loss of neutral iodine from the cluster, causing a reduction in the internal energy and resulting in two autodetachment decay components.<sup>24</sup> Neutral iodine loss was implicated in our past studies of near-VDE photoexcited I<sup>-</sup>·U, I<sup>-</sup>·T, and I<sup>-</sup>·U·H<sub>2</sub>O complexes and is therefore expected to be a reasonable decay pathway.  $^{23,24,32}$  In the  $\pi$ - $\pi^*$  photoexcitation regime, the  $I{\cdot}T^-$  VB anion exhibits monoexponential decay dynamics, and it has been suggested that the initial autodetachment may be faster compared to iodine loss than in I<sup>-</sup>·U.<sup>24</sup> The biexponential I-U·H<sub>2</sub>O VB anion decay here further indicates that the biexponential or monoexponential nature of the VB anion decay is sensitive to the electronic structure of the specific nucleobase species.

#### C. Autodetachment dynamics

This section considers the nature of the time-resolved autodetachment signals observed in our TRPES studies. Figure 1 shows that autodetachment signal occurs in the 4.74 eV single-photon PES of  $I^-U H_2O^{32}$  and therefore clearly arises from a one-photon (pumponly) process. As shown in Figs. 2 and 4, the autodetachment signal exhibits considerable intensity at all times, including negative times where the probe pulse precedes the pump pulse. Therefore, the normalized, time-resolved signals in Fig. 6 show that the autodetachment intensity exhibits little to no decrease below its intensity level at negative times. At positive probe pulse arrival times, the autodetachment signal is found to rise in intensity within 11.3 ps and then decay in approximately 285 ps. Note that our experiment does not directly measure time-resolved autodetachment dynamics since the autodetachment electron signal is generated spontaneously and not by the probe pulse. Instead, the observed time-dependent integrated intensities associated with the autodetachment signal arise from probe-based interactions that affect the amount of autodetachment signal that is detected for a given probe arrival time.

Let us compare our past measurements of the autodetachment signal arising from I-N complexes to the results here for  $\pi$ - $\pi^*$  photoexcited I<sup>-</sup>·U·H<sub>2</sub>O. Our work on both I<sup>-</sup>·U·H<sub>2</sub>O and I<sup>-</sup>·U clusters has measured autodetachment arising from near-VDE photoexcitation,<sup>23,32</sup> as well as from photoexcitation in the region of the base-centered  $\pi$ - $\pi^*$  transition [shown for both I<sup>-</sup>·U·H<sub>2</sub>O and I<sup>-</sup>·U in Fig. 7(c)].<sup>21,22,26</sup> Each of these past studies, regardless of photoexcitation energy, has shown autodetachment that exhibits depletion at t<sub>0</sub> followed by recovery to or beyond its initial intensity. Near-VDE photoexcitation in both clusters yields the autodetachment signal that appears to at least qualitatively mirror the respective TNI dynamics; an example for the I-·U·H<sub>2</sub>O near-VDE pump autodetachment signal is shown in Fig. S1. Concomitant autodetachment signal depletion and recovery at  $t_0$  with time constants that mirror the TNI appearance, and fast decay indicates that the probe pulse at early times photodetaches the nascent TNI population that would otherwise decay to produce the autodetachment signal in the absence of the probe. At later times, the probe laser interacts with a decreased population of anions that have not already undergone autodetachment, so one expects less depletion of the autodetachment signal and eventually no depletion at all. Under these circumstances, the recovery of the autodetachment signal yields the lifetime of the autodetaching state.

In Fig. 7(c), it can be seen that  $\pi$ - $\pi^*$  photoexcitation for both I<sup>-</sup>·U·H<sub>2</sub>O and I<sup>-</sup>·U clusters yields an unexpected "overshoot" of the autodetachment intensity beyond the negative-time intensity in tens of picoseconds. The autodetachment intensity overshoot, therefore, is uniquely associated with the VB anion generated following  $\pi$ - $\pi^*$  photoexcitation. Moreover, the similar autodetachment dynamics for I<sup>-</sup>·U and I<sup>-</sup>·U·H<sub>2</sub>O stand in contrast to those of  $\pi$ - $\pi^*$  photoexcited I<sup>-</sup>·T clusters, which do not show any autodetachment intensity overshoot,<sup>22</sup> suggesting that the overshoot is also nucleobase-specific and likely related to the presence of the long-lived VB state.

This overshoot may arise if the probe pulse is absorbed by the VB anion and excites the TNI to a higher-lying excited state that subsequently decays by autodetachment, as in the following equation:

$$I^{-} \cdot U(\pi^{4}\pi^{*0}) \cdot H_{2}O \xrightarrow{hv_{pump}} I^{-} \cdot U(\pi^{3}\pi^{*1}) \cdot H_{2}O \rightarrow I \cdot U^{-}(\pi^{4}\pi^{*1}) \cdot H_{2}O,$$

$$I \cdot U^{-}(\pi^{4}\pi^{*1}) \cdot H_{2}O \xrightarrow{Autodetachment} I \cdot U \cdot H_{2}O + e^{-}$$

$$\xrightarrow{hv_{probe}} \left[I \cdot U^{-}(\pi^{4}\pi^{*1}) \cdot H_{2}O\right]^{*} \xrightarrow{Autodetachment} I \cdot U \cdot H_{2}O + e^{-}.$$
(5)

The autodetachment intensity overshoot is only observed in  $I^- \cdot U$ and  $I^- \cdot U \cdot H_2O$  clusters, which both exhibit longer-lived, biexponentially decaying VB anions.  $I^- \cdot T$  clusters in this pump energy region, in contrast, do not exhibit autodetachment intensity overshoot, and the VB anion decays monoexponentially in only  $\sim$ 500 fs.<sup>24</sup> As shown in Table I, the long decay lifetimes for the VB anions of  $I^- \cdot U$  and  $I^- \cdot U \cdot H_2O$  clusters are in agreement with the decay lifetimes of the excess autodetachment signal. Thus, we believe a mechanism as in Eq. (5) that is operative here for both  $I^- \cdot U$  and  $I^- \cdot U \cdot H_2O$ photoexcited in this pump energy regime.

The presence of water appears to somewhat slow the rise of the autodetachment feature (Table I), and, notably, the autodetachment signal decay lifetime is an order of magnitude longer for  $I^- \cdot U \cdot H_2O$  than  $I^- \cdot U$ . As has been observed for the  $I^- \cdot U \cdot H_2O$  VB anion both in the  $\pi$ - $\pi^*$  pump energy regime and the near-VDE excitation regime, the interaction of water may stabilize the excited cluster to decay by autodetachment, increasing the observed lifetime. The autodetachment signal resulting from I<sup>-</sup>·U·H<sub>2</sub>O also does not appear to have depletion near  $t_0$  as was observed in both I<sup>-</sup>·U and I-T clusters.<sup>21,22</sup> As noted earlier, the autodetachment depletion at early probe arrival times arises due to photodetachment of the VB excited state, which would otherwise be the spontaneous source of autodetached electrons. Lack of notable depletion in the early-time autodetachment signal of  $I^- \cdot U \cdot H_2 O$  as compared to  $I^- \cdot U$ may therefore indicate that the I<sup>-</sup>·U·H<sub>2</sub>O VB anion is more strongly stabilized relative to autodetachment than I<sup>-</sup> U clusters in this photo excitation regime. Finally, it is interesting to note that the observed autodetachment dynamics in  $\pi$ - $\pi^*$  photoexcited I<sup>-</sup>·U·H<sub>2</sub>O clusters are approximately the same in both the 1.58 eV and 3.18 eV probe energy studies (Fig. S2). It is possible, given the relatively high power of the 1.58 eV probe pulses employed in the present study, that the 1.58 eV autodetachment dynamics arise from the absorption of two probe photons by the VB anion, particularly if absorption of the first photon is resonant. This would yield similar autodetachment overshoot dynamics for each probe energy. We consider this possibility in more detail in the supplementary material (Fig. S3).

#### **VI. CONCLUSIONS**

TRPES has been used to examine TNI formation and photo dissociation in  $\pi$ - $\pi^*$  photoexcited I<sup>-</sup>·U·H<sub>2</sub>O clusters. Production of I<sup>-</sup> is measured as a major dissociation channel of the photoexcited clusters with biexponential formation in 32.5 ps and 230 ps. We suggest that the unique biexponential rise dynamics measured in I<sup>-</sup>·U·H<sub>2</sub>O clusters in this photoexcitation regime are the result of additional dissociation channels arising from the presence of water. For example, internal conversion of the  $\pi$ - $\pi$ <sup>\*</sup> excited state and subsequent cluster dissociation is expected to yield I<sup>-</sup>, with the long-time rising signal that may be produced by dissociation of  $\pi$ - $\pi^*$  photoexcited I<sup>-</sup>·U·H<sub>2</sub>O to yield I<sup>-</sup>·H<sub>2</sub>O that can subsequently decay to yield iodide. We observe instantaneous formation of the VB anion of the complex and propose that this state arises from charge transfer from iodide to fill the empty  $\pi$  orbital that remains on uracil after the nucleobase is photoexcited, consistent with the proposed mechanism for I-U binary clusters. The VB anion of I-U·H<sub>2</sub>O exhibits increased binding energy compared to the VB anion of I-U clusters in this photoexcitation regime. The VB anion is found to decay biexponentially, as in  $I^- \cdot U$ , but the long decay lifetime is an order of magnitude longer in I<sup>-</sup>·U·H<sub>2</sub>O clusters and is expected to reflect the stabilization of the VB state relative to decay by autodetachment. Autodetachment is also measured as a dissociation channel of the photoexcited I<sup>-</sup>·U·H<sub>2</sub>O complexes. Overshoot of the measured autodetachment intensity beyond the

negative-time autodetachment signal indicates that the absorption of the probe pulse by the long-lived VB anion produces additional autodetachment.

#### SUPPLEMENTARY MATERIAL

See the supplementary material for additional figures of the normalized integrated intensity for the autodetachment signal arising from I<sup>-</sup>·U·H<sub>2</sub>O clusters at 4.38 eV pump excitation energy and 3.14 eV probe energy, a comparison of the autodetachment signal arising from I<sup>-</sup>·U·H<sub>2</sub>O clusters at 4.77 eV pump excitation energy and 1.58 eV probe energy vs 3.18 eV probe energy, a power-dependent study of the autodetachment dynamics as a function of the 1.58 eV probe power, and a comment on uracil tautomerization.

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