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## Electron accommodation dynamics in the DNA base thymine

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The dynamics of electron attachment to the DNA base thymine are investigated using femtosecond time-resolved photoelectron imaging of the gas phase iodide-thymine (I<sup>-</sup>T) complex. An ultraviolet pump pulse ejects an electron from the iodide and prepares an iodine-thymine temporary negative ion that is photodetached with a near-IR probe pulse. The resulting photoelectrons are analyzed with velocity-map imaging. At excitation energies ranging from -120 meV to +90 meV with respect to the vertical detachment energy (VDE) of 4.05 eV for I<sup>-</sup>T, both the dipole-bound and valence-bound negative ions of thymine are observed. A slightly longer rise time for the valence-bound state than the dipole-bound state suggests that some of the dipole-bound anions convert to valence-bound species. No evidence is seen for a dipole-bound anion of thymine at higher excitation energies, in the range of 0.6 eV above the I<sup>-</sup>T VDE, which suggests that if the dipole-bound anion acts as a "doorway" to the valence-bound anion, it only does so at excitation energies near the VDE of the complex. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4923343]

### I. INTRODUCTION

The mechanism by which radiation causes damage to living tissue, including damage to DNA, is of considerable interest in chemistry, physics, and biology.<sup>1</sup> High-energy radiation produces secondary low-energy electrons that are capable of inducing both single and double strand breaks in DNA,<sup>2</sup> even at electron kinetic energies below the ionization potential of any of the DNA components.<sup>3-7</sup> These observations have motivated several theoretical studies aimed at identifying the site of electron attachment to DNA and the mechanism of bondbreakage.<sup>8,9</sup> Some of these find initial electron attachment to the nucleobase followed by delocalization and cleavage of the sugar phosphate backbone<sup>10</sup> or the glycosidic bond,<sup>11</sup> while others indicate that direct electron attachment and cleavage on the DNA backbone is energetically feasible.<sup>12,13</sup> In the gas phase, spectroscopic and electron scattering experiments have focused on how low-energy electrons interact with isolated molecular DNA constituents.<sup>14–17</sup> In this paper, we investigate the time-resolved dynamics of electron attachment to the DNA base thymine using UV-initiated charge transfer in iodidethymine (I-T) binary clusters and compare these results to uracil, the RNA counterpart to thymine.

Electron-nucleobase interactions in the gas phase have been probed by dissociative electron attachment (DEA),<sup>17–20</sup> negative ion photoelectron (PE) spectroscopy,<sup>14</sup> and Rydberg electron transfer (RET).<sup>15</sup> DEA experiments have shown that electrons with kinetic energy as low as 0.6 eV can break the N1–H bond in thymine (see atomic numbering in Figure 1(a)), the location of the glycosidic bond that attaches the DNA base to the sugar in nucleotides and nucleosides.<sup>17,18</sup> Sharp peaks in the DEA intensity below 1.5 eV were attributed to cross section enhancement from vibrational Feshbach resonances of the thymine dipole-bound (DB) anion coupling to the  $\sigma^*$  state of the N1–H bond,<sup>19</sup> and involvement of both dipole-bound and valence-bound (VB) orbitals of the anion has been implicated in thymine N1–H bond breakage in the gas phase.

With a dipole moment of 4.2 D,<sup>21</sup> thymine can easily support a DB anion.<sup>22</sup> Characterized by a very diffuse excess electron orbital, the DB anion of thymine has a planar geometry similar to that of neutral thymine and a very low vertical detachment energy (VDE), the energy difference between the neutral and the anion at the geometry of the anion, of 69  $\pm$  7 meV, measured with photoelectron spectroscopy.<sup>14</sup> When the thymine ring puckers, thymine can also support a VB anion in which the excess electron resides in a  $\pi^*$  orbital.<sup>23</sup> RET experiments estimate the VB anion to be only minimally adiabatically bound.<sup>15</sup> The PE spectrum of the bare VB anion of thymine has not been measured experimentally to date, but the PE spectra of  $T^{-}(H_2O)_n$  clusters yielded an extrapolated adiabatic electron affinity (AEA) for the bare thymine VB anion of  $120 \pm 120$  meV and a VDE of  $440 \pm 120$  meV.<sup>24</sup> Theoretical estimates of the AEA of the VB anion vary from  $-50 \text{ meV}^{25}$  to 18 meV,<sup>23</sup> with a VDE of 457-512 meV depending on the method of calculation.<sup>26</sup> Calculations estimate the vertical attachment energy (VAE) of thymine, the difference in energy between the neutral and the anion at the geometry of the neutral, to be about 650 meV,<sup>25</sup> and electron transmission spectroscopy estimate the  $\pi^*$  orbital to lie 290 meV higher in energy than the neutral.<sup>27</sup>

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FIG. 1. Calculated optimal geometries of (a) I<sup>-</sup>T, (b) I···T<sup>-</sup>(DB), (c) I···T<sup>-</sup>(VB), (d) I<sup>-</sup>U, (e) I···U<sup>-</sup>(DB), and (f) I···U<sup>-</sup>(VB).

In our laboratory, we have performed time-resolved experiments on electron attachment to nucleobases and other electron acceptors through femtosecond time-resolved photoelectron spectroscopy (TRPES) on binary clusters of iodide and the molecule of interest.<sup>28–31</sup> Using the scheme in (1),

$$I^{-}M \xrightarrow{h\nu_{1}} I \cdots M^{-} \xrightarrow{\Delta t, h\nu_{2}} I \cdots M + e^{-}(eKE = h\nu_{2} - eBE),$$
(1)

an ultraviolet pump pulse  $(hv_1)$  excites the excess electron, originally localized on the iodide, to form a temporary negative ion associated with the electron acceptor *M* that is photode-tached with a near-IR probe pulse  $(hv_2)$  after a known delay time. With this scheme, we can investigate the dynamics of electron attachment to *M*, as well as any ultrafast decay mechanisms occurring after electron transfer.

The nucleobase uracil, which operates in place of thymine in RNA, differs only in the exchange of the methyl group at C5 for a proton (see Figure 1(d)). In TRPES experiments on iodide-uracil (I<sup>-</sup>U) clusters, at excitation energies near the VDE (4.11 eV) of I<sup>-</sup>U complex, both the DB and VB anions of uracil were formed, while at excitation energies 550-790 meV above the VDE, only the VB anion was seen.<sup>28,31</sup> Near the VDE, the VB anion of uracil appeared more slowly than the cross correlation of the pump and probe pulses, while at excitation energies well above the VDE, the VB anion appeared on a cross correlation limited time. We concluded that the VB anion was formed directly at the higher excitation energies, while at lower excitation energies, the VB anion was being formed via another state, possibly the DB anion. However, the evidence for this transition was indirect, in contrast to experiments in our group with iodide-nitromethane and ongoing work on iodideadenine A3 tautomer where the DB anion acts as an obvious doorway state to the VB anion.<sup>30,32</sup>

In previous experiments using TRPES with I<sup>-</sup>T clusters, excitation energies 550-740 meV above the VDE of I<sup>-</sup>T, 4.05 eV, were used to initiate charge transfer.<sup>29</sup> Only the VB anion of thymine was observed, appearing on a cross

correlation limited lifetime before decaying to zero by 10 ps. In this work, we use TRPES to investigate electron attachment dynamics in I<sup>-</sup>T clusters at excitation energies near the VDE of I<sup>-</sup>T, and compare and contrast to our results from I<sup>-</sup>U. We observe both the DB and VB anions of thymine, with the VB anion appearing after the DB anion, suggesting that the VB anion is formed via the DB anion at excitation energies near the VDE of I<sup>-</sup>T. Both the DB and VB states ultimately decay bi-exponentially with similar decay lifetimes. Time-dependent density-functional theory (TD-DFT) calculations find that the optimized structures of  $I \cdots T/U_{DB}^{-}$  and  $I \cdots T/U_{VB}^{-}$  are different from those of I<sup>-</sup>T and I<sup>-</sup>U and indicate that the iodine atom perturbs the initially formed DB anion. In total, we explore how small energetic and structural differences between I<sup>-</sup>T and I<sup>-</sup>U impact their electron attachment and decay dynamics, continuing our exploration of electron attachment to biologically relevant molecules.

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

The time-resolved photoelectron spectrometer has been described elsewhere in detail.<sup>33,34</sup> Iodide-thymine clusters are formed by passing 50 psig neon over a reservoir containing methyl iodide; the resulting neon-methyl iodide mixture passes through an Even-Lavie pulsed solenoid valve operating at 500 Hz with a cartridge containing solid thymine heated to 205 °C. A ring filament ionizer ionizes the resulting supersonic expansion via secondary electron attachment. The formed negative ions are mass-selected for the species of interest, and after steering and focusing ion optics, they interact with the pump and probe laser pulses.

A KM Labs Griffin oscillator and Dragon amplifier generates pulses centered around 790 nm at a 1 kHz repetition rate. The portion of this light to be used as the probe pulse is split off, while the remainder is steered into a Light Conversion TOPAS-C optical parametric amplifier (OPA). Frequency-doubling the output of the OPA results in pump pulses between 315 and



FIG. 2. Excited state calculations for both I<sup>-</sup>T (a) and I<sup>-</sup>U (b) showing the difference in electron density prior and subsequent to electronic excitation from the neutral to the first excited state at iso-surface value 0.0015. Regions where electron density is removed with UV excitation are shown in teal, while regions where electron density increases after UV excitation are shown in purple.

300 nm that are used as the pump pulse. At the interaction region, typical pulse powers are 5-10  $\mu$ J/pulse for the pump and 80  $\mu$ J/pulse for the probe. The cross correlation of the pump and probe pulses is below 150 fs. An optical chopper is used to match the repetition rates of the Even-Lavie valve and the laser. Photoelectrons resulting from laser interaction with the iodidethymine cluster are accelerated towards a position sensitive detector using velocity map imaging (VMI).<sup>35</sup> The resulting images are reconstructed using the BASEX algorithm.<sup>36</sup>

#### **III. THEORETICAL METHODS AND RESULTS**

Calculations on the I<sup>-</sup>T and I<sup>-</sup>U complexes were conducted with long-range corrected density functional theory (LC-DFT) using the  $\omega$ B97XD functional with the Gaussian09 program package.37 For H, C, N, and O atoms, the standard aug-cc-pVDZ basis set was used, where hydrogen atoms were further augmented with additional sets of diffuse sp basis functions to describe the very diffuse nature of DB anions. The exponents of the diffuse functions were obtained from the outermost sp functions of the standard basis set by using a scaling factor of 2. For the iodine atom, we employed the aug-cc-pVDZ-pp pseudopotential basis set,<sup>38</sup> where diffuse *sp* functions were further added with the same scaling factor. Figures 1(a) and 1(d) show the optimized geometries for I<sup>-</sup>T and I-U, respectively, in their ground electronic states. The calculations show that in both the thymine and uracil cluster geometries, iodide is bound at the positive end of the nucleobase dipole moment, between the  $C_6$  and  $N_1$  positions.

Time-dependent density functional theory (TD-DFT) calculations using the same  $\omega B97XD$  functional were also performed in order to obtain the equilibrium geometries on the electronically excited state potential energy surfaces of the  $I \cdots T_{DB}^-$ ,  $I \cdots U_{DB}^-$ ,  $I \cdots T_{VB}^-$ , and  $I \cdots U_{VB}^-$  clusters, as well as to calculate electron density differences between  $I^-T/U$ and  $I \cdots T/U_{DB}^-$  at the  $I^-T/U$  geometries. The optimized geometries of the complexes for both DB and VB anions are also shown in Figure 1. The optimized structures of the  $I \cdots T_{DB}^-$  and  $I \cdots U_{DB}^-$  complexes, as shown in Figures 1(b) and 1(e), have elongated iodine N<sub>1</sub>–H and C<sub>6</sub>–H distances compared to the ground state geometries. In comparison, the  $I \cdots T_{VB}^-$  and  $I \cdots U_{VB}^-$  complexes, as shown in Figures 1(c) and 1(f), show strikingly different geometries from both the ground state anion and DB anion complexes; the iodine atom has moved above the nucleobase ring, which has undergone significant ring puckering by  $31.01^{\circ}$  and  $33.29^{\circ}$  for thymine and uracil, respectively. The electronic density differences between the ground and DB anion excited states at the optimized ground state geometries of both I<sup>-</sup>T and I<sup>-</sup>U are shown in Figure 2. Figure 2 indicates that vertical excitation from the ground state involves electron promotion from an iodide valence *p*-orbital to a diffuse orbital located outside of the nucleobase. The photo-excited electron appears to localize near the iodine atom site, in the same region where the excess electron is localized in the isolated thymine DB anion.<sup>16</sup>

The AEAs of  $I \cdot T$  and  $I \cdot U$  cluster systems and the dipole moments of the neutral  $I \cdots T/U$  clusters in the anion and neutral geometries were calculated with second-order Møller-Plesset perturbation theory (MP2) and coupled cluster singles and doubles (CCSD) with the Gaussian09 program package.<sup>37</sup> The VDEs of I<sup>-</sup>T and I<sup>-</sup>U have been reported previously.<sup>28,29</sup> The I<sup>-</sup>T and I<sup>-</sup>U and I $\cdots$ T and I $\cdots$ U neutral cluster geometries were optimized with MP2, and frequency calculations verified that they are minimum energy geometries. These geometries are included in Table S1.39 Unsurprisingly, there are slight differences between the MP2 geometries and the LC-DFT geometries, although the two methods are very similar; in the ground state anion cluster geometries, the iodide-nucleobase distances are slightly shorter with MP2. These differences carry over to comparison between the  $I \cdots T/U_{DB}^{-}$  and  $I \cdots T/U$  geometries. While the geometries are expected to be slightly different, at the MP2 level, the  $I \cdots T/U$  distances are shorter than the LC-DFT  $I \cdots T/U_{DB}^{-1}$ geometries. Using the MP2 geometries, single-point energy calculations were then done using CCSD for higher accuracy AEAs and dipole moments. All calculations used the aug-ccpVDZ basis sets for C, N, O, and H atoms and the aug-ccpVDZ-pp pseudopotential for iodine.<sup>38</sup> The calculated AEAs and dipole moments are reported in Table I.

TABLE I. Calculated adiabatic electron affinities (AEAs) and dipole moments  $(\mu)$  for neutral iodine-thymine and iodine-uracil clusters.

Cluster	AEA (eV)	$\mu$ anion geometry (D)	$\mu$ neutral geometry (D)		
Iodine-thymine	3.95	6.23	5.64		
Iodine-uracil	3.99	6.48	5.85		

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TABLE II. Calculated energies of the dipole-bound to valence-bound transition barrier height for different calculation methods and basis sets.

Method	Basis set	Uracil (meV)	Thymine (meV)	
ωB97XD	6-311+G(2d,p)	138	155	
	Aug-cc-pVDZ	116	131	
CAM-B3LYP	6-311+G(2d,p)	56	63	
	Aug-cc-pVDZ	36	44	

Calculations of the transition barrier between the DB and VB anions of thymine were carried out using the  $\omega$ B97XD and CAM-B3LYP methods of LC-DFT. LC-DFT methods can describe both DB and VB anion states, with their different excess electron binding motifs, as well as interconversion between them with reasonable computational costs.<sup>40</sup> The same basis sets were used as in the DFT calculations discussed earlier in this section. These calculated barriers are reported in Table II. These isolated base anion results suggest that the DB  $\rightarrow$  VB transformation barrier for the excited I<sup>-T</sup> complex would also be larger than that for I<sup>-</sup>U, although the calculated barrier heights do not contain the effect of iodine.

#### **IV. EXPERIMENTAL RESULTS**

All excitation energies from this point will be referred to relative to the previously determined I<sup>-</sup>T VDE of 4.05 eV,<sup>29</sup> where  $E_{relative} =$  excitation energy – VDE(I<sup>-</sup>T), and therefore pump photon energies of 3.93 eV, 4.00 eV, 4.07 eV, and 4.14 eV will be referred to as –120 meV, –50 meV, 20 meV, and 90 meV, respectively. Figure 3 shows time-resolved photoelectron spectra of the I<sup>-</sup>T binary cluster at –50 meV excitation energy and 1.58 eV probe energy. A contour plot where the x-axis is delay time, and the y-axis is electron binding energy (eBE), defined as eBE = hv<sub>probe</sub> – eKE, is shown in Figure 3(a) are plotted in Figure 3(b). Two features are present in Figure 3, labeled

feature *I* and feature *II*. Feature *I* is a narrow, high-intensity, feature that appears between 0 and 0.2 eV, and changes both in intensity as well as energy with pump-probe delay time. Feature *II* is a broad, low-intensity, feature appearing between 0.2 and 0.8 eV, and peaking around 0.5 eV. As in previous investigations of iodide-molecule binary clusters, intense near-zero kinetic energy electrons were present in the photoelectron spectra, which appear at eBEs of ~1.56-1.58 eV, and are not included in Figure 3 for clarity.<sup>28–31</sup> The dynamics of these electrons were similar to those reported previously for I<sup>-</sup>T and will not be discussed further.<sup>29</sup> Based on previous investigations, we can assign feature *I* as the DB anion of thymine and feature *II* as the VB anion of thymine, with or without the iodine atom.<sup>29–31</sup>

The peak of feature I, which represents the VDE, shifts slightly with pump-probe delay, illustrated by the dotted and dashed lines in Figures 3(a) and 3(b). The dotted line marks the VDE at initial times, and the dashed line indicates the VDE at approximately 700 fs. The peak of feature *I* eventually recovers at long times to the dotted line. This energy shifting can be quantified by fitting feature I to a Gaussian function at each pump-probe delay and plotting the peak versus pumpprobe delay as shown in Figures 4(a) and 4(b), for -50 meVexcitation energy. The VDE at initial times is slightly below but within error bars of the longtime VDE,  $75 \pm 5$  meV. Over the next several hundred femtoseconds, the VDE of feature I increases, reaching the maximum of 95 meV at approximately 700 fs, before decaying and reaching the longtime value of  $75 \pm 5$  meV by 20-30 ps. The analogous plot for I<sup>-</sup>U at 4.00 eV (-40 meV relative to the I<sup>-</sup>U VDE) is shown for comparison in Figures 4(c) and 4(d).

Time-resolved photoelectron spectra at -120 meV, 20 meV, and 90 meV are similar to that shown in Figure 3 in that they contain both features *I* and *II* as well as similar shifts in the VDE of feature *I*, with some differences in time-dynamics as well as relative intensities of the two features. These results are different from those previously reported for I<sup>-</sup>T clusters, where the excitation energy was significantly



FIG. 3. Time-resolved photoelectron spectra of I<sup>-</sup>T with 4.00 eV (-50 meV) excitation energy and 1.58 eV probe energy, where (a) shows a contour plot and (b) selected delays and where the dotted and dashed lines highlight the minimum and maximum VDEs of feature *I*, respectively.

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FIG. 4. Shifting of the VDE of feature *I* for (a) I<sup>-</sup>T at 4.00 eV (-50 meV) excitation energy at short and (b) long times, and (c) I<sup>-</sup>U at 4.07 eV (-40 meV) excitation energy at short and (d) long times. The dashed lines indicate the longtime values of feature *I* for I<sup>-</sup>T and I<sup>-</sup>U, 75 ± 5 meV and 95 ± 5 meV respectively.  $\Delta E_1$  denotes the d ifference in energy between the minimum and maximum VDE and  $\Delta E_2$  denotes the difference in energy between the maximum and the longtime VDE for I<sup>-</sup>T and I<sup>-</sup>U. The uracil data in (c) and (d) are reprinted with permission from King *et al.*, J. Chem. Phys. **141**, 224310 (2014). Copyright 2014 AIP Publishing LLC.

above the VDE of the I<sup>-</sup>T cluster.<sup>29</sup> At those excitation energies, only feature *II* was observed, similar to observations for I<sup>-</sup>U at excitation energies well above the VDE.<sup>28,31</sup>

The differences between the time-resolved PE spectra at various excitation energies can be quantified by analyzing the changing intensities of both features in time, as well as the ratios of the two features. The normalized intensities of both features at short and long times are shown for selected excitation energies in Figure 5. The normalized intensities of both features at long times for all pump photon energies from 3.93 eV to 4.14 eV are shown in the supplementary material, Figure S1.<sup>39</sup> These normalized intensities can be fit to the convolution of the Gaussian experimental response function with a multiple exponential function capturing the rise as well as decay of both features, as follows:

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

$$* \begin{cases} I_0, \quad t < 0 \\ I_0 + \sum_i A_i \exp\left(\frac{-t}{\tau_i}\right), \quad t \ge 0 \end{cases}$$
(2)

At excitation energies near the VDE of I<sup>-</sup>T, -120 meV to 90 meV, both features *I* and *II* rise more slowly than the cross correlation of the pump and probe pulses (<150 fs). Feature *I* rises on a 200-250 fs time at excitation energies -120 meV to 90 meV, and decays bi-exponentially. Feature *II* rises on



FIG. 5. Normalized intensities of feature *I* and *II* for I<sup>-</sup>T, where feature *I* is in blue and feature *II* is in red at (a) 3.93 eV, -120 meV; (b) 4.00 eV, -50 meV; (c) 4.07 eV, 20 meV; (d) 4.00 eV, -50 meV at long delay times; (e) 4.69 eV, 640 meV; and (f) 4.69 eV, 640 meV at long delay times.

a 1.5 ps time at -120 meV and 250-300 fs time at all other excitation energies and then also decays bi-exponentially. In Table III, A<sub>1</sub> and  $\tau_1$  measure the mono-exponential rise and A<sub>2</sub> and  $\tau_2$  and A<sub>3</sub> and  $\tau_3$ , the bi-exponential decay. The ratio A<sub>1</sub>/(A<sub>2</sub> + A<sub>3</sub>) reflects the degree of rising behavior in comparison to the decay of each feature. In both features,  $|A_1|/(A_2 + A_3)$  decreases with increasing excitation energy, where a ratio of ~0 means that the signal appears within the cross correlation and has no additional rising behavior.

Feature *II* displays markedly different early time dynamics at higher excitation energies. Figures 5(e) and 5(f)

TABLE III. Lifetimes, and decay coefficients, and ratios for features I and II of I<sup>-</sup>T.  $\tau_1$  is the rise time (if applicable), and  $\tau_2$  and  $\tau_3$  are decay times.  $E_{relative} = excitation energy - VDE(I^-T)$ , where the VDE of I<sup>-</sup>T is 4.05 eV.

Excitation energy (eV)	E <sub>relative</sub> (meV)	$\tau_{1}(fs)$	$\tau_2 (ps)$	$\tau_3  (ps)$	$A_1/(A_2 + A_3)$	Ratio I/II
		F	eature I			
3.93	-120	223 ± 18	$6.4 \pm 0.2$	$1000 \pm 130$	-0.60	2.25
4.00	-50	$-50$ $220 \pm 25$		$1800 \pm 200$	-0.55	2.04
4.07	7 20		$5.2 \pm 0.4$	$1100 \pm 130$	-0.49	1.63
4.14	90	$230 \pm 50$	$2.1 \pm 0.3$	33 ± 5	-0.45	1.13
		Fe	ature II			
3.93	-120	$1510 \pm 140$	25 ± 3	$400 \pm 140$	-0.68	
4.00	-50	$310 \pm 40$	$11.4 \pm 1.2$	$590 \pm 90$	-0.55	
4.07	20	$250 \pm 50$	$13.1 \pm 1.2$	$530 \pm 130$	-0.33	
4.14	90	$350 \pm 120$	$5.0 \pm 0.9$	$50 \pm 20$	-0.30	
4.60	550		$0.46 \pm 0.04$			
4.69	640		$0.61 \pm 0.04$			
4.79	740		$0.46\pm0.03$			

show feature *II* from our previously published results with I<sup>-</sup>T at 4.69 eV (640 meV) excitation energy, where feature *II* appears within the cross correlation and then decays on an ultrafast timescale.<sup>29</sup> The decay dynamics of this feature can be reasonably well fit by both mono-exponential as well as bi-exponential decays; Figure S2 of the supplementary material shows a comparison of the mono-exponential versus bi-exponential fits.<sup>39</sup> We previously reported bi-exponential decay lifetimes for I<sup>-</sup>T to maintain consistency with what were clearly bi-exponential long-time decays for I<sup>-</sup>U.<sup>29</sup> We have revisited this fitting and here report the mono-exponential decay lifetimes of the previously published thymine VB anion data at excitation energies of 4.60–4.79 eV in Table III. The mono- versus bi-exponential decay contrariety is addressed in Sec. V C.

Bi-exponential decay kinetics, like those observed in features *I* and *II* at low excitation energies, are well described by kinetic schemes like Scheme 1, as has been discussed in previous papers in our group.<sup>28–31</sup>

Using analysis by Knee *et al.*,<sup>41</sup> and detailed in our paper on I<sup>-</sup>U,<sup>31,42</sup> rate constants k<sub>1</sub>, k<sub>2</sub>, and k<sub>3</sub> can be extracted from the bi-exponential delay times,  $\tau_2$  and  $\tau_3$ , as well as the fraction of the first decay to the total decay,  $F_{A_2} = A_2/(A_2 + A_3)$ . These rate constants are summarized in Table IV.

#### **V. DISCUSSION**

In our experiments, thymine is in many ways very similar to its RNA analog uracil. Both the DB and VB anions of the iodine-thymine complex are generated at excitation energies near the VDE of I<sup>-</sup>T, while only the VB anion is formed in



SCHEME 1. Visual representation of the bi-exponential decay kinetics.

the higher excitation energy region. The rise time of the DB anion is slower than the cross correlation of the pump and probe pulses and shifts in energy at early times. In the lower energy region, the rise time of the thymine VB anion is longer than both the cross correlation and the DB anion, while in the higher energy region, it appears within the cross correlation. At excitation energies near the VDE of I<sup>-</sup>T, the DB and VB anions decay bi-exponentially with similar decay rates.

However, there are slight but noticeable differences in the dynamics in the I<sup>-</sup>T and I<sup>-</sup>U experiments. At early times, the increase in the VDE of the iodine-thymine DB anion is less than that of the corresponding species in uracil (see Fig. 4). In addition, the rise time of the thymine DB anion is 220-250 fs for all excitation energies in the lower excitation energy region, while the corresponding rise time of the uracil DB anion drops slightly with increasing excitation energy. The rise of the thymine VB anion at the lowest excitation energy, 1.5 ps at -120 meV, is considerably slower than the 200-300 fs rise times for the VB anion in uracil, while from -50 meV to 90 meV, the thymine VB anion rise time is approximately constant and comparable to these uracil values. Last, while the bi-exponential decay rates for thymine and uracil are similar at lower excitation energies, new analysis shows that at excitation energies  $\geq$  500 meV, decay of the VB anion of thymine can be fit mono-exponentially with a similar lifetime to the short lifetime of the uracil bi-exponential decay. The longer-time decay in uracil  $(\tau_3, \text{ Table S2})^{39}$  is absent in thymine. We will now explore these effects in detail.

#### A. Early time dynamics of the thymine DB anion and comparison to the uracil DB anion

Of the four pump photon energies near the VDE, two lie slightly above the VDE, and two lie below it. In addition, the four pump photon energies are at -20 meV, 50 meV, 120 meV, and 190 meV with respect to the calculated AEA of I  $\cdot$  T, 3.95 eV (Table I). The bandwidth of the pump pulse is around 40 meV, so all four excitation energies can access the

TABLE IV. Rate constants and fractions for bi-exponential decay kinetics.  $E_{relative}$  = excitation energy – VDE(I<sup>-</sup>B), where the VDE of I<sup>-</sup>T is 4.05 eV and the VDE of I<sup>-</sup>U is 4.11 eV. The uracil data are reprinted with permission from King *et al.*, J. Chem. Phys. **141**, 224310 (2014). Copyright 2014 AIP Publishing LLC.

Molecule	Erelative (meV)	$k_1(10^{10}s^{-1})$	$k_2(10^{10}s^{-1})$	$k_3(10^{10}s^{-1})$	F <sub>A2</sub>	$k_1(10^{10}s^{-1})$	$k_2(10^{10}s^{-1})$	$k_3(10^{10}s^{-1})$	F <sub>A2</sub>	
			Feature I				Feature <i>II</i>			
	-120	13	2.8	0.10	0.82	3.4	0.6	0.24	0.84	
Thymine	-50	9.5	5.5	0.06	0.63	6.4	2.4	0.17	0.72	
	20	13	6.5	0.10	0.66	6.1	1.6	0.19	0.79	
	90	36	11	3.0	0.74	16	4.0	1.9	0.78	
Uracil <sup>31</sup>	-110	6.0	5.6	0.05	0.52	3.5	2.6	0.22	0.55	
	-40	7.1	6.9	0.08	0.50	4.1	3.0	0.22	0.56	
	30	15	5.8	0.20	0.71	11	6.4	1.2	0.61	
	100	35	23	3.2	0.58	13	7.3	1.3	0.63	

electron detachment continuum, even at the lowest energy when accounting for the laser bandwidth. Hence, direct detachment is in principle accessible at all four pump photon energies and should be particularly facile above the VDE because of good Franck-Condon (FC) overlap between the initial and accessible final states of the complex. Nonetheless, at all four photon energies, we observe evidence for long-lived dipolebound states.

The presence of DB states is not overly surprising, since the calculated dipole moment of the  $I \cdot T$  complex in the FC geometry, 6.23 D, lies well above the critical 2 D dipole moment needed to support a dipole-bound state. It also lies well above the dipole moment of bare thymine, 4.2 D. This enhancement of the dipole moment by addition of an I atom was also reported by Mabbs and co-workers<sup>43</sup> in their work on iodide-pyrrole complexes. The more interesting question is why the onset of photoelectron signal associated with feature I exhibits a clear rise time of  $\sim 250$  fs, as seen in Figs. 5(a)-5(c), given that photoexcitation to a dipole-bound state should be an instantaneous process within the time-resolution of our experiment. This delay was not seen in analogous experiments on  $I^{-}(CH_{3}CN)$  and  $I^{-}(CH_{3}NO_{2})$ , where the increase in VDE compared to bare iodide, 0.49 eV and 0.55 eV, respectively, was about half of the  $\sim 1 \text{ eV}$  increase for I<sup>-</sup>T and I<sup>-</sup>U.<sup>29,30</sup>

The intensity of feature *I* and the increase in the VDE of feature *I* both peak at similar times, at approximately 600-800 fs. It is therefore reasonable to assume that these two effects have a common dynamical origin. Given the geometric differences between the I<sup>-</sup>T ground state and the equilibrium structure of the I  $\cdots$  T<sub>DB</sub><sup>-</sup> state, as shown in Fig. 1, these early time dynamics most likely comprise motion of the I atom relative to the nucleobase.

We first consider the effect of I atom motion on the VDE of feature *I*. In both I<sup>-</sup>T and I<sup>-</sup>U, the VDE initially increases and reaches its maximum value at approximately 700-800 fs, before decreasing within tens of ps to that of the bare DB anion VDE, 75 meV for T<sup>-</sup> and 95 meV for U<sup>-</sup>.<sup>14,24</sup> Figure 6 shows one-dimensional potential energy curves for the neutral complex and the DB anion state as a function of iodine-thymine distance that are consistent with these data and the calculated energetics presented in this paper. The experimentally determined VDE and the calculated AEA of the iodine-thymine neutral cluster are connected along the iodine-nucleobase reac-

tion coordinate for the neutral potential energy curve. The DB anion potential energy curve is displaced from the neutral curve taking into account the changing VDE of the DB anion observed in the data. These curves show that there are repulsive iodine-nucleobase interactions for both the DB anion as well as the neutral at the FC geometry. For the VDE to increase as the iodine atom moves toward the optimized  $I \cdots T/U_{DB}$  geometry, the interaction between the iodine and the nucleobase in the anion excited state at shorter distances must be more repulsive than in the open-shell neutral complex, an effect that can be attributed to the repulsive interaction between the iodine atom and the dipole-bound state, due to excluded volume effects.<sup>43–47</sup> There is also an attractive interaction, leading to the slight minimum in the potential energy curve, due to van der Waals and ion-induced dipole interactions between the DB state and the neutral iodine atom. At longer times, the subsequent drop in the VDE is attributed to the iodine atom leaving the cluster. This VDE drop reflects the significantly larger dipole moment of the iodine-nucleobase complex compared to that of the bare nucleobase (see Table I), resulting in stronger dipolar binding of the excess electron in the presence of the I atom.



FIG. 6. Energy schematic illustrating how the energies of the neutral and DB anion of thymine change with iodine distance. Plain text indicates an experimental value, while italicized text indicates a calculated energy at the CCSD level of theory. The shape of the curves is determined from the experimental VDE of feature I, 70 meV at initial delay times, 95 meV at approximately 1 ps, and 75 meV at long delay times.

One notable difference between I<sup>-</sup>T and I<sup>-</sup>U is that  $\Delta E_1$ , the VDE difference between the minimum and maximum VDE of feature I as shown in Figure 3, is approximately half as large in thymine as in uracil, 25 meV versus 40 meV, respectively, suggesting that the iodine repulsion is less steep for the thymine DB anion than the uracil DB anion. Comparison of the optimized  $I \cdots T_{DB}^{-}$  and  $I \cdots U_{DB}^{-}$  geometries to those of the I<sup>-</sup>T and I<sup>-</sup>U ground anion states in Figure 1 offers a possible explanation for this effect. After UV excitation, iodine moves away from both the N1-H and C6-H atoms in thymine and uracil, changing angles with both hydrogens. However, the iodine moves farther relative to the center of the  $N_1$ - $C_6$  bond in uracil than in thymine. Transitioning from the FC geometry to the  $I \cdots B_{DB}^{-}$  equilibrium geometry, iodine moves 0.467 Å away from the  $N_1$ – $C_6$  bond in uracil, but only 0.449 Å in thymine. At long-times,  $\Delta E_2$  is the same for the two nucleobases, indicating that the iodine atom leaving the relaxed binary cluster has approximately the same energetic effect on the DB orbital VDE in both nucleobases.

We now return to the issue of the rise time of feature *I*, which we attribute to an increasing photodetachment cross section correlated with I atom motion just after photoexcitation. A similar effect was observed previously in I<sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> clusters,<sup>44,48</sup> although in that case, the collective motion of the H<sub>2</sub>O molecules was believed to play a role as well.<sup>46,47</sup> In those studies, the increase in photodetachment cross section was attributed to increased localization of the dipole-bound electron, and a similar effect is expected here. When the de Broglie wavelength of the detached electron is smaller than the spatial extent of the orbital from which it was detached, the photodetachment cross section is exceptionally sensitive to the spatial extent of the orbital.<sup>49</sup> The kinetic energy of the photodetached electrons in the current experiment is approximately 1.57 eV, corresponding to a de Broglie wavelength of  $\sim 10$  Å. We can estimate the spatial extent of the dipole-bound electron in thymine at different points in time by using a crude model that approximates the distance between a point charge from a point dipole for a given binding energy, Equation (3) in atomic units where  $E_b$  is the binding energy of the electron,  $\mu$  the dipole moment, and r is the mean radius of the dipolebound orbital,

$$E_b = \mu/r^2 \tag{3}$$

as used by Lineberger and Johnson to estimate the spatial extent of dipole-bound electrons of acetaldehyde enolate<sup>50</sup> and acetonitrile.<sup>51</sup>

At the FC geometry, the dipole moment of the iodinethymine complex is 6.22 D and the VDE of the electron, an excellent estimate of the electron binding energy, is approximately 70 meV. We can solve Eq. (3) for *r* and find that the mean radius of the dipole-bound orbital at the FC geometry is 16 Å. If we do the same calculation at the peak in the VDE of feature *I* at ~1 ps, where the VDE is ~95 meV and the iodinethymine complex has relaxed to that of the optimized neutral geometry with a dipole moment of 5.65 D, the approximate size of the dipole-bound orbital is only 13 Å. This increase in DB orbital localization is consistent with the increase in photodetachment cross section that we observe in the DB anion of thymine. Of course this model does not take into account the other atoms in the cluster system, quantum mechanical effects, or the excluded volume of the iodine atom, but it does give an estimate for the extent of the DB orbital as a function of both the dipole moment and binding energy of the DB electron. This model is probably better suited for evaluating the change in the local extent of the DB orbital with dipole moment and electron binding energy rather than the absolute size of the DB orbital, which has been calculated for bare uracil and thymine by Adamowicz and coworkers.<sup>16</sup>

This model also explains why we do not see a corresponding rise in the DB anion signal in nitromethane. The DB anion of nitromethane does not exhibit VDE shifting. The change in cluster dipole moment between the iodinenitromethane FC geometry and the relaxed neutral geometry is 4.62 D versus 4.51 D,<sup>30,52</sup> a much smaller dipole moment change than observed in thymine and uracil. This results in a negligible change in the spatial extent of the DB orbital and an apparently instantaneous rise time in the DB anion of nitromethane at early times.

At 30 and 90 meV excitation energies, where we are above the VDE of I<sup>-</sup>T, "dipole scattering (DS) states" could in principle also participate in the observed dynamics. Gianturco and co-workers<sup>53,54</sup> calculated scattering of strongly polar molecules with low-energy electrons and found strong similarities between the real part of the scattering wavefunction and the extremely diffuse electronic wavefunction for a DB state lying below the detachment threshold. Therefore, one might expect facile coupling between a DS state and a DB state with conversion of a small amount of electronic energy to vibrational energy of the molecular core. This DS to DB state conversion is essentially the inverse of vibrational autodetachment<sup>55</sup> that would take place to form a vibrationally excited DB state whose electronic energy lies below the detachment threshold. Iodine motion could be the primary sink of the vibrational energy.

#### B. Thymine VB anion formation mechanism

As was the case in uracil, we observe two distinct dynamical regimes for the formation of the VB anion state of thymine, feature *II* in our time-resolved spectra. At energies well above the VDE, as shown in Figure 5(e) at 640 meV excitation energy, the VB state appears within the cross correlation of the two laser pulses, and the photoelectron spectra show no evidence for feature *I*. The calculated VAE of the VB anion of thymine is approximately 650 meV above the neutral, while electron transmission spectroscopy experiments estimate that the energy of the first  $\pi^*$  orbital is 290 meV above the neutral,<sup>25,27</sup> in the range of our pump photon energies at 550-740 meV above the I<sup>-</sup>T VDE. Therefore, these dynamics are attributed to direct formation of the VB state by the pump pulse in which the scattered electron is captured by the VB orbital of thymine.

At excitation energies near the VDE, formation of both DB and VB anion states is observed for I<sup>-</sup>T. The rise time of the VB state,  $\tau_1$ , is slower than that of the DB state at -120 and -50 meV, with the rise times being nearly identical within error bars at 20 and 90 meV. The slower rise time of the VB state is particularly noticeable at -120 meV (Fig. 4(a)). Similar but not

identical trends were seen for I<sup>-</sup>U at excitation energies near the I<sup>-</sup>U VDE, with  $\tau_1$  for the VB state always being slightly longer than for the DB state. One interpretation of these trends, as discussed in our previous work, is that the DB state acts as a gateway to the VB state at excitation energies near the VDE. Depending on the excitation energy, a small population of the DB anions formed by electron capture convert over a small barrier to VB anions on a hundred(s) of fs time scale.

This sequential picture for VB formation has several positive aspects. It is consistent with the VB state never appearing before the DB state and with the decreasing rise time for the VB state as the excitation energy increases, corresponding to more rapid passage over the DB to VB state barrier. Moreover, the DB to VB anion calculated barrier is slightly higher for thymine than uracil at all levels of theory (Table II). This is in accordance with the considerably longer 1.5 ps rise time for the VB state at -120 meV in the I<sup>-</sup>T experiments compared to the 260 fs VB anion rise time at a comparable excitation energy in our I<sup>-</sup>U studies, as well as the increased DB anion signal relative to the VB anion signal in thymine compared to that observed in uracil, shown in Tables III and S1.<sup>39</sup> Additionally, the higher barrier and reduced production of the VB anion in thymine is also consistent with the relatively constant DB anion rise time and prominence in thymine contrary to what was observed in uracil. Finally, as discussed above, any dipole scattering states created by the pump pulse should easily convert to vibrationally excited DB states, making a DB state a reasonable gateway state for subsequent dynamics.

The primary negative aspect of the sequential mechanism is that we do not observe a depletion of the DB signal with a time constant that mirrors the rise of the VB signal. Such a correspondence would offer unambiguous evidence for a DB-to-VB anion conversion and was observed in our previous time-resolved work on iodide-nitromethane,<sup>30</sup> as well as in ongoing work on iodide-adenine complexes (for the A3 conformer of adenine).<sup>32</sup> The DB to VB anion transition is calculated to be slightly endothermic for thymine and uracil, by 52 and 53 meV respectively,<sup>23,56</sup> while it is exothermic in both nitromethane<sup>57</sup> and the A3 conformer of adenine, enabling complete conversion and a clear depletion of the DB state. While one can rationalize the absence of a depleted DB signal for I<sup>-</sup>T and I<sup>-</sup>U based on these energetic considerations, more sophisticated theoretical treatments may be required to sort out the VB formation mechanism in the low excitation energy regime.

# C. Decay mechanisms and differences between thymine and uracil

In the low excitation energy region, near the I<sup>-</sup>T VDE, both the DB and VB anions of the iodine-thymine complex decay bi-exponentially with similar decay lifetimes. Biexponential decay has been observed previously in our experiments with uracil, nitromethane, and acetonitrile<sup>28–31</sup> and can be represented with a kinetic scheme like Scheme 1, shown earlier. As shown by Knee *et al.*,<sup>41</sup> rate constants  $k_1$ ,  $k_2$ , and  $k_3$  can be calculated from the bi-exponential decay rates and amplitudes, shown in Table IV.

Iodine loss was invoked previously to explain biexponential decay kinetics in thymine and uracil.<sup>28,29,31</sup> In such a mechanism,  $k_1$  corresponds to autodetachment from the binary complex of iodine and the nucleobase,  $k_2$  to the rate of iodine leaving the complex, and  $k_3$  to the rate of autodetachment from the nucleobase, where some of the internal energy of the complex has been transferred to iodine kinetic energy. A comparison between  $k_1$ ,  $k_2$ , and  $k_3$  for uracil versus thymine finds that  $k_2$  for thymine is systematically slightly smaller than for uracil, while  $k_1$  and  $k_3$  are more or less the same between the two molecules. This is consistent with the VDE shifting for thymine and uracil shown in Figure 3. In thymine, the VDE of feature I reaches that of the bare thymine DB anion by approximately 20-30 ps, while in uracil, the VDE reaches that of the bare uracil DB anion by ~10 ps. That iodine loss may take longer in thymine than in uracil is in agreement with the larger number of degrees of freedom in thymine than in uracil, assuming that iodine loss is an evaporative process. In contrast, the values of  $k_3$  are almost the same for the two systems, consistent with the iodine binding energy, measured by  $\Delta E_2$ , being approximately the same in the VDE shifting of feature I for both systems. Iodine loss thus appears to be a reasonable primary mechanism for bi-exponential decay of both the DB and VB anions of thymine and uracil in the lower excitation energy region.

At the higher excitation energy, the decay of the VB anion of thymine can be fit with either a mono-exponential or a bi-exponential decay function. In previous publications, the thymine VB anion was fit bi-exponentially, consistent with the bi-exponential decay of the uracil VB anion.<sup>28,29</sup> However, the VB state of thymine can be well fit using a single exponential decay and, as shown in Table III, the resulting decay lifetime is similar to the first decay constant of uracil, Table S1.<sup>39</sup> The thymine mono-exponential decay rate is  $\sim 200 \times 10^{10} \text{ s}^{-1}$  and this is very comparable to  $k_1$  for uracil at excitation energies 550-790 meV above the I<sup>-</sup>U VDE, which ranges from 140 to  $290 \times 10^{10} \text{ s}^{-1}$ , depending on excitation energy.<sup>31</sup> Regardless of the choice of the number of exponential decays, the thymine VB anion decays to zero intensity by approximately 5-10 ps, while the uracil VB anion still has population intensity at 100 ps. Hence, at high excitation energies, there is a long-lived component of the uracil VB anion that is absent for thymine.

The bi-exponential decay of the uracil VB anion in the high excitation energy region was attributed to a combination of the same iodine loss mechanism discussed above as well as the difference in non-statistical versus statistical autodetachment rates before and after intermolecular vibrational energy redistribution (IVR), where  $k_1$  is autodetachment from a subset of vibrational modes, the IVR is rate  $k_2$ , and traditional statistical autodetachment is rate  $k_3$ . The absence of a long lifetime in thymine in the higher excitation energy region implies that in thymine, the initial autodetachment rate,  $k_1$ , competes more effectively with IVR or iodine loss,  $k_2$ . In the lower excitation region, the rate of iodine loss from  $I \cdots B_{VB}^{-1}$ was slightly slower for thymine than uracil, while the rate of  $I \cdots B_{VB}^{-}$  autodetachment was approximately the same. If these trends continue in the high-energy region, comparative rates of autodetachment to iodine loss would be consistent with the lack of long-time thymine VB anion decay. In contrast, the

rate of IVR would be expected to increase in thymine with the presence of the methyl rotor and higher density of vibrational modes.<sup>58,59</sup> Therefore, we conclude that faster initial autodetachment compared to iodine loss is the primary decay mechanism leading to mono-exponential decay for the thymine VB anion in the higher excitation energy region.

#### **VI. CONCLUSION**

Overall, the electron attachment dynamics in thymine are similar to those in uracil. At excitation energies -120 meVto 90 meV from the VDE of I<sup>-</sup>T, both the dipole-bound and valence-bound anions of thymine are formed. The DB anion photoelectron signal has a consistent 200-250 fs rise time and shifting VDE with pump-probe delay, while the VB anion has a rise time that varies with excitation energy but appears after the DB anion. These dynamics are attributed to initial formation of a vibrationally excited DB state and rapid formation of the VB anion from the DB anion. At excitation energies significantly above the VDE of I<sup>-</sup>T, the VB anion of thymine is formed directly upon pump excitation and appears within the cross correlation of the pump and the probe pulses. The work on I<sup>-</sup>T presented here supports our previous interpretation of a DB to VB anion transition in I<sup>-</sup>U.<sup>31</sup> The slight differences between the DB and VB anion rise time trends and ratios between thymine and uracil are consistent with the calculated higher DB to VB anion barrier for thymine.

We also find that the bi-exponential decay lifetimes of both the DB and VB anions of thymine formed with excitation energies near the VDE of I<sup>-</sup>T are very similar to those previously reported for uracil.<sup>31</sup> This suggests the same bi-exponential decay mechanism, most likely changing rates of autodetachment prior to and subsequent to iodine loss. However in the higher excitation energy region, ~550 – 740 meV above the VDE of I<sup>-</sup>T and I<sup>-</sup>U, the VB anion of thymine has no long-time decay lifetime, suggesting that autodetachment from I · · · T<sub>VB</sub><sup>-</sup> is essentially complete before the I atom leaves.

While this study was done in the gas phase and is therefore not directly analogous to *in vivo* radiation damage, the subtle differences between thymine and uracil have larger implications for the stability of DNA versus RNA in the presence of ionizing radiation. Not only is the barrier to formation of the VB anion of thymine higher than in uracil but also the decay mechanisms to eliminate the excess charge in thymine are more efficient, possibly decreasing the likelihood that an electron attaching to thymine will transfer throughout a nucleoside and lead to DNA damage. This issue and others will be addressed in planned experiments on more complex nucleic acid constituents.

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