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Dynamics of electron solvation in methanol: Excited state relaxation and generation by charge-transfer-to-solvent

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The charge-transfer-to-solvent dynamics (CTTS) and excited state relaxation mechanism of the solvated electron in methanol are studied by time-resolved photoelectron spectroscopy on a liquid methanol microjet by means of two-pulse and three-pulse experiments. In the two-pulse experiment, CTTS excitation is followed by a probe photoejection pulse. The resulting time-evolving photoelectron spectrum reveals multiple time scales characteristic of relaxation and geminate recombination of the initially generated electron which are consistent with prior results from transient absorption. In the three-pulse experiment, the relaxation dynamics of the solvated electron following electronic excitation are measured. The internal conversion lifetime of the excited electron is found to be 130 ± 40 fs, in agreement with extrapolated results from clusters and the non-adiabatic relaxation mechanism. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922441]

I. INTRODUCTION

The solvated electron, an isolated electron in polar solution, is a species of fundamental interest to the physics of solvation and to the understanding of condensed phase reactions in the presence of ionizing radiation.¹ The solvated electron is the simplest quantum solute and is thus a fundamental model system for understanding solute-solvent interactions. As such, it has been the target of much experimental²⁻⁴ and theoretical^{5,6} study in the context of solvation. Nonetheless, many aspects of solvated electron dynamics remain unresolved, even in water and methanol, which have been studied extensively. Recently, it has become possible to couple liquid microjets to photoelectron spectroscopy^{7,8} and to measure the photoelectron spectrum (PES) of excess electrons in high vapor pressure solvents.⁹ In particular, by performing timeresolved photoelectron spectroscopy (TRPES) on electrons in liquid water jets, key dynamical issues associated with solvated electrons can be addressed that could not be explored directly by other means.^{10–13} Here, this technique is used to investigate the dynamics of solvated electrons in methanol subsequent to (a) their formation by charge-transfer-to-solvent (CTTS) excitation and (b) electronic excitation of the $s \rightarrow p$ transition.

The absorption spectra of solvated electrons in water¹⁴ and methanol¹⁵ exhibit a single broad peak in the near-infrared, 720 nm in water and 630 nm in methanol, associated with a transition from the ground "s-like" state to a quasi-degenerate manifold of "p-like" states.¹⁶ Much of the experimental work on the solvated electron in the two solvents has used this band as a probe of its solvation dynamics, primarily via transient absorption (TA)^{17–23} and resonance Raman spectroscopy.^{24,25} In TA experiments, solvated electrons are typically generated by ionization of the solvent or by photodetachment from a precursor anion. Subsequent evolution of the s \rightarrow p band probes

the time it takes the photogenerated electron to equilibrate and, depending on the experiment, the relaxation dynamics of the electron from its excited *p*-state.

Time-resolved experiments on solvated electrons generated by excitation of a precursor anion in solution, such as an atomic halide ion, have been particularly useful for elucidating the dynamics of these species.^{2,26} Gas phase halides have no bound excited states, but in solution these anions have broad CTTS bands in the ultraviolet^{27,28} corresponding to short lived excited states that rapidly decay to solvated electrons.²⁹ In contrast to photoionization or radiolysis of pure solvents, solvated electrons created by this method are generated well below the water conduction band, which can simplify the observed dynamics by limiting the excess energy of the ejected electron.³⁰ In TA experiments on water^{22,31-33} and methanol³⁴ aimed at understanding electron solvation subsequent to CTTS excitation, a UV femtosecond laser pulse generates electrons via CTTS excitation, and the subsequent recombination and solvation dynamics of these electrons are interrogated by a second broadband femtosecond pulse that probes the $s \rightarrow p$ absorption band. These experiments have stimulated theoretical efforts aimed at understanding the underlying dynamics.^{35–37}

In complementary three-pulse TA experiments, solvated electrons are generated by CTTS excitation in the UV and allowed to equilibrate. The $s \rightarrow p$ transition is then excited by a near infrared (NIR) pulse, and the resulting dynamics are probed by TA with a broadband pulse. These so-called pump-repump-probe measurements were first carried out by Barbara and co-workers²⁰ in water and, more recently, by Barbara³⁸ and Thaller *et al.*³⁹ in methanol. These measurements yield multiple time scales associated with relaxation of the electronically excited electrons. Two competing models describe the *p*-state relaxation, the "adiabatic" and "non-adiabatic" models, which differ according to whether the fastest time scale seen

in TA experiments is assigned to *p*-state relaxation or $p \rightarrow s$ internal conversion.²⁰ Identifying the most appropriate model has been the subject of considerable debate despite a large body of theoretical work on solvated electrons in water^{6,40,41} and methanol.^{42–46}

Experimentally, distinguishing between these two mechanisms requires a direct measurement of the *p*-state lifetime. Extracting this value from TA experiments is not straightforward, but it can be readily obtained from time-resolved photoelectron spectroscopy.^{47,48} In our laboratory, experiments on size-selected $(H_2O)_n^-$ and $(CH_3OH)_n^-$ anion clusters using TRPES yielded *p*-state lifetimes as a function of cluster size that extrapolated to bulk values of 60 and 150 fs for water and methanol, respectively.^{49–51} These results support the nonadiabatic model for both solvents, but one can question the validity of such extrapolations to elucidate bulk phenomena.

Since 2010, several laboratories have carried out photoelectron spectroscopy experiments on electrons in liquid jets of water and other solvents in order to explicitly "bridge the gap" between the cluster and bulk liquid regimes. These experiments have yielded the vertical binding energy of electrons in water, methanol, and acetonitrile.^{9,11,13,52–55} Time-resolved PES experiments have been carried out in liquid water jets via the two-pulse and three-pulse schemes outlined by Eqs. (1) and (2), respectively, in which the second (or third) laser pulse ejects photogenerated electrons from aqueous solution to vacuum and their kinetic energy distribution is measured,

$$I^{-}_{(aq)} \xrightarrow{h\nu_{1}} (I^{-})^{*}_{CTTS} \xrightarrow{\Delta t_{12}} e^{-}_{(aq)} \xrightarrow{h\nu_{2}} e^{-}_{(vac)}, \tag{1}$$

$$I^{-}_{(aq)} \xrightarrow{h\nu_{1},\Delta t_{12}} I_{(aq)} + e^{-}_{(aq)}(s) \xrightarrow{h\nu_{2},\Delta t_{23}} e^{-}_{(aq)}(p) \xrightarrow{h\nu_{3}} e^{-}_{(vac)}.$$

Two-pulse TRPES experiments in water provide complementary information to two-pulse TA experiments.^{10,11} Recent three-pulse TRPES experiments on hydrated electrons in liquid water jets yielded an excited state lifetime of 75 ± 20 fs, which is in agreement with the cluster extrapolation and provides further evidence for the non-adiabatic model of hydrated electron relaxation.¹²

Here, we carry out two-pulse and three-pulse TRPES experiments on methanol liquid jets based on Eqs. (1) and (2). Solvated electrons in methanol formed by CTTS excitation undergo a multistep mechanism consisting of a 550 ± 110 fs decay attributed to decay of the relaxed CTTS state, an 8 ± 3 ps thermalization of a "hot" population of electrons, and a partial decay of the ground state electron signal on a time scale of 41 ± 7 ps. The excited state solvated electron, as examined from the three-pulse experiment, is shown to undergo internal conversion to the ground state with a 130 ± 40 fs lifetime. The ground state then re-equilibrates with a lifetime of 800 ± 300 fs. The fast internal conversion lifetime is consistent with the non-adiabatic mechanism along with prior results in water and extrapolated results from methanol cluster anions.

II. METHODS

The experimental apparatus for carrying out time-resolved photoelectron spectroscopy of liquid jets is shown



FIG. 1. Main chamber of liquid microjet photoelectron spectrometer. The liquid jet (A) is crossed with a sequence of laser pulses (red arrow) that generate photoelectrons. Electrons are steered by a 1.1 T magnet (B) through a 500 μ m skimmer (C) and then drift through the 10 G solenoid (D) toward the detector (E).

schematically in Figure 1. The design of the liquid jet source is in the style developed by Faubel⁵⁶ and is unchanged from our previous work.⁵³ Iodide is introduced to solution by dissolving potassium iodide (100 mM, EMD, \geq 99% purity) in methanol (Fischer, Optima 0.2 μ m filtered). This solution is then injected into vacuum at high backing pressure (80 atm) through a fused silica capillary (20 μ m orifice diameter). The flow rate for all methanol experiments is held at 0.33 ml/min.

The jet is crossed with a sequence of two or three laser pulses following either Eqs. (1) or (2). In the two pulse experiment, the CTTS band of the iodide anion is excited with hv_1 (238 nm, 5.2 eV), and the generated electrons are detached with hv_2 (266 nm, 4.67 eV, 125 fs). To generate a time-resolved spectrum, Δt_{12} , the delay between hv_1 and hv_2 , is systematically varied in order to monitor the ensuing dynamics. In the three pulse experiments, electrons are generated with hv_1 (238 nm, 5.2 eV), excited with hv_2 (800 nm, 1.54 eV, 75 fs), and interrogated with hv_3 (266 nm, 4.67 eV, 125 fs). Δt_{12} , is held fixed at 200 ps so that only fully equilibrated electrons are excited.²² Δt_{23} is varied, and a photoelectron spectrum is taken at each delay.

Photodetached electrons are sampled through a 500 μ m skimmer to a second differentially pumped region containing a microchannel plate (MCP) detector. Typical operating pressures in the interaction and detection regions of our vacuum chamber are 3.7×10^{-4} Torr and 1.6×10^{-6} Torr, respectively. Photoelectrons are energy analyzed by time-of-flight in a magnetic bottle,⁵⁷ which offers greatly improved collection efficiency over a field-free time-of-flight analyzer. A 1.1 T steering magnet (B in Fig. 1) and 10 G solenoidal field within the flight tube direct the trajectories of the ejected photoelectrons to ward the detector, allowing in principle for ~50% of generated photoelectrons to be collected. Photoelectron flight times are measured by recording the capacitively coupled current off of the phosphor screen as a function of time. This raw photoelectron kinetic

(2)

energy (eKE) and scaled by the appropriate Jacobian transformation. For ejected photoelectrons in the kinetic energy range expected for this experiment, 1-3 eV, the electron escape depth from the surface of the microjet is a few nanometers.^{58–60} Calibration and measurement of the streaming potential associated with the microjet are based on the method described developed by Suzuki¹⁰ and are as described in our previous paper.⁵⁴

A Spectra Physics Spitfire laser system comprising a Ti:sapphire oscillator and regenerative amplifier (2.2 W, <75 fs) is used to generate all ultrafast pulses. Half of the fundamental is used to pump a Light Conversion TOPAS, and the 238 nm CTTS excitation pulse is generated by frequencydoubling the sum frequency of the signal (1175 nm) and NIR pump (800 nm). The 266 nm detachment pulse is generated from the tripled fundamental. Due to bandwidth losses from generating the UV pulses, the pulse duration of the UV beams is lengthened relative to the 800 nm fundamental. The temporal resolution in the three-pulse experiments, 115 fs as defined by the NIR/UV cross correlation (hv_2 and hv_3), is therefore much shorter than in the two-pulse experiments, 220 fs, which is determined by the cross-correlation of the two UV beams. These values are given as the average single pulse duration, defined as the full width half maximum of the cross correlation divided by $\sqrt{2}$.

Data are analyzed via two methods: by simple integration of the total signal in specified energy lanes and by a global fit assuming no spectral line shape but exponential time dynamics. This global fitting method,^{61,62} often referred to as global lifetime analysis (GLA), allows for simultaneous fitting of the entire time resolved data set which may help separate spectral contributions from overlapping features. GLA is predicated on two assumptions. First, it is assumed that the data consist of a sum of spectral components, each of which is separable into two parts: the spectrum of the component, $S_i(eKE)$, which depends only on kinetic energy, and the kinetics, $S_i(\Delta t)$, which depends only on pump-probe delay. This is expressed mathematically in Eq. (3a) with each component in the sum scaled by the relative photodetachment cross section, σ_r , and where the sum is indexed by the number of spectral components *j*. Second, the kinetics are assumed to take the form of sums of mono-exponentials (e.g., $S(\Delta t) = Ae^{-k_1t} - Be^{-k_2t}$). If both assumptions are true, the data can be represented as a sum of exponentials scaled by a constant which depends on energy,

called the decay associated spectrum (DAS),⁶² and indexed by the time constants $\tau_i = 1/k_i$, Eq. (3b),

$$S(eKE, \Delta t) = \sum_{j=1}^{n} \sigma_{r,j} \cdot S_j(eKE) \cdot S_i(\Delta t), \qquad (3a)$$

$$S(eKE, \Delta t) = \sum_{i=1}^{m} DAS_{\tau_i}(eKE) \cdot [e^{-z/\tau_i} \cdot L(z - \Delta t)](\Delta t). \quad (3b)$$

Physically, assuming energy and time are separable implies that the components do not shift on the same scale of time that they change in intensity. If this assumption is incorrect, more kinetic components than are physical will be necessary to fit the data. Analysis of the data using a method that allows for spectral shifts is detailed in the supplementary material.⁶³

To generate a fit, the spectral and temporal dimensions of background subtracted, time resolved photoelectron spectra are fit simultaneously by assuming a minimal number of kinetic rate constants, such that the three dimensional data (energy, delay, and intensity) are fit to Eq. (3b) with residuals on the order of our signal to noise. The amplitude, $DAS_{\tau_i}(eKE)$, of each exponential in each energy lane is allowed to float but the rate constants, the width of the instrument response function $L(\Delta t)$, and the zero delay time are held as a single set of fit parameters for the entire data set. The DAS are quite different from the $S_i(eKE)$'s, the delay independent spectra of the species of interest. The DAS merely gives the scale of the coefficient in front of a particular exponential in the sum at a particular energy. The shape of each DAS can be used to predict a kinetic model which can then be used to reconstruct the $S_i(eKE)$'s.

III. RESULTS

A. Two-pulse experiment

Time resolved photoelectron spectra using a 238 nm pump and 266 nm probe pulse were recorded at pump-probe delays up to 800 ps. Spectra following the background subtraction scheme $(hv_1 + hv_2) - hv_1 - hv_2$ are presented in Figure 2. Figs. 2(a) and 2(b) show the photoelectron (PE) spectra over all measured delays and over short delays, respectively. Slices through Fig. 2(a) at selected delay times are shown in Fig. 2(c). Near t₀, the PE spectrum is nearly 2 eV wide, as exemplified in



FIG. 2. TRPE spectra of methanol subsequent to CTTS excitation over two energy ranges: -1 ps to 800 ps (a) and from -1 ps to 20 ps (b). Selected spectra at various delays (c).

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the spectrum at 0.3 ps in Fig. 2(c). The data show a clear decay in the eKE range of 2.5–3.0 eV on a time scale of hundreds of femtoseconds. After this fast decay, the PE spectra are singly peaked near 1.2 eV at all delays. The PE spectrum then shifts and narrows on a few picosecond time scale. Spectral evolution appears to be complete by approximately 20 ps, after which the remaining signal decays to a steady intensity on a time scale of tens of picoseconds. The equilibrated vertical binding energy (VBE), as characterized by the peak of the binding energy spectrum beyond 20 ps, is found to be 3.4 eV ($hv_2 - eKE_{max}$), which is in good agreement with values reported previously for the ground state solvated electron in methanol.^{54,55}

Figure 3 shows plots of the integrated photoelectron intensity over the entire range of measured delays (Fig. 3(a)) and at delays less than 20 ps (Fig. 3(b)). The black curves in Figs. 3(a) and 3(b) show the integrated intensity across all electron energies, while the blue and red curves are integrated over the eKE ranges of 2.5–3.0 eV and 0.5–1.0 eV, respectively. The black curve is well fit with a triexponential decay with lifetimes of 480 ± 40 fs, 45 ± 3 ps, and ~ 4 ns, with the last decay continuing well past the fitted region. We do not find a more sophisticated functional form to be necessary to fit this data. The blue curve rises with the cross-correlation and decays bi-exponentially with decay constants of 480 ± 40 fs and 7.4 ± 0.5 ps. The red curves, representing the low eKE edge of the observed signal, are fit with a cross-correlation limited rise time convoluted with an 8 ± 1 ps rise and a 45 ± 3 ps decay. Within our time resolution, nearly 80% of the population between 0.5 and 1.0 eV appears at zero pump-probe delay. The rest is generated from the 7-8 ps component. Hence, the fast



FIG. 3. Integrated intensity at long pump-probe delays (a) and shorter pumpprobe delays (b) for the total photoelectron intensity and band extrema.

(blue) signal appears to decay to the slower (red) signal on a time scale of 7–8 ps.

The presence of overlapping features can lead to errors in lifetimes extracted from lane integration due to contamination by neighboring spectral components. Global lifetime analysis, as described in Sec. II, can be used to extract accurate lifetimes of overlapped spectral features with differing temporal characteristics. The raw two-pulse data, fit, and residuals are shown in Figures 4(a)-4(c). The data are fit using Eq. (3b) with time constants of 550 ± 110 fs, 8 ± 3 ps, and 41 ± 7 ps, along with a ~4 ns component that survives past the fitted region. The nanosecond lifetime is much longer than our window of measured delays and thus has significant error. The decay associated spectrum (DAS_{k_i}) for each kinetic component calculated from the fits is shown in Fig. 4(d). A positive going DAS is associated with a feature that decays and a negative going DAS is associated with a feature which rises. Vertical lines in the residuals are caused by noise in the delay space caused by poorer sampling in this dimension.

The three time constants extracted from GLA are in reasonable agreement with lifetimes extracted from lane integration. The DAS of the nanosecond component and the 41 ps decay, which are very similar to one another, reproduce the ground state solvated electron spectrum. The 41 ps and 4 ns time constants from GLA match the long-time decay of the total signal, i.e., the black curve in Fig. 3. The DAS of each of the two faster kinetic components shows some decay of a weakly bound (high eKE) feature and a corresponding rise of ground state signal. This trend suggests an exchange of population between the two portions of the spectrum on this time scale. DAS_{8ps} does not deplete the total integral, as the integrated intensity of the DAS is zero within error, but DAS_{500fs} has only a small negative going peak and therefore largely contributes to the fast decay of the total integral by depleting the weakly bound population of photoelectrons.

Because of the assumed separability between spectral and temporal components inherent to GLA, if there is a spectral shift on a similar time scale to the decay of a particular component, GLA gives a somewhat limited picture of the dynamics associated with that component. As a better treatment of the shifting feature, we can use the data from GLA to propose a model that explicitly allows for a shift in one or more features. In the supplementary material,⁶³ we consider the data to comprise two components each of which is allowed to shift. We demonstrate that the data are adequately fit by a model with a weakly bound feature that decays without spectral evolution and a second strongly bound feature that shifts on an 8 ps time scale. This analysis is in accord with the model presented in the main text.

B. Three-pulse experiments

The three-pulse experiments follow the excitation scheme in Eq. (2). Electrons are generated via CTTS, photoexcited after a 200 ps delay to allow for equilibration, and finally detached to vacuum. The photoelectron spectra at various delays between hv_2 and hv_3 are plotted in Figs. 5(a) and 5(b) using two background subtraction schemes, as employed in previous work.¹² The two UV photons, hv_1 and hv_3 , each



FIG. 4. TRPE spectra for the two color experiment following the subtraction method $(hv_1+hv_2)-hv_1-hv_2$: CTTS solvation data (a), four component GLA fit (b), fit residuals magnified ×15 (c), and DAS (d).

contribute a static two-photon photodetachment signal from iodide, which we treat as background. Fig. 5(a) shows results following the background subtraction method $(hv_1 + hv_2 + hv_3) - hv_1 - hv_3$. The data show a large feature near 1.2 eV eKE and a feature at higher eKE, highlighted in blue, which appears near t₀ and decays shortly thereafter. The feature at 1.2 eV is depleted as the transient feature in the blue lane appears and then recovers on a longer time scale to its initial intensity. The VBE, defined as previously, of the feature at 1.2 eV eKE is 3.4 eV and is readily identified as the ground state of solvated electrons in methanol from prior work and the results in Sec. III A.^{52,54,55}

A second background subtraction method, shown in Fig. 5(b), more clearly illustrates the evolution of the PE

spectra on the high eKE shoulder of the ground state. When the spectrum without the pump pulse hv_2 is subtracted from the three color spectrum, $(hv_1 + hv_2 + hv_3) - (hv_1 + hv_3)$, the pump-induced transient appears as positive-going and the depleted initial state as negative-going. These difference spectra more clearly demonstrate how the signal changes in the presence of hv_2 . As shown in Fig. 5(b), the high energy shoulder of the positive-going signal, 3.0-3.3 eV eKE, decays on a ~100 fs time scale, and the lower eKE portion of the positive going transient, 2.0–2.3 eV, decays on a significantly longer time scale of several hundred fs, during which time it also appears to shift toward lower eKE. The signal in this energy range is designated in red and is indicated in Fig. 5(a).



FIG. 5. TRPE spectra following two background subtraction methods: (a) $(hv_1 + hv_2 + hv_3) - hv_1 - hv_3$ and (b) $(hv_1 + hv_2 + hv_3) - (hv_1 + hv_3)$. (c) shows integrated intensity vs. time in two regions of interest.

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Plots of the integrated intensity of the signal as a function of time in the regions of interest highlighted in Figure 5(a) are shown in Figure 5(c). Integrated intensity in the blue energy lane appears within the cross correlation of the laser and decays on a time scale of 125 ± 50 fs. Above 3.0 eV eKE, the choice of integration region does not alter the lifetime of the blue lane; it thus appears this feature does not shift and that there is little overlap with any longer lived features in this integration lane. Integration between 2.0 eV and 2.3 eV eKE yields a lifetime of 690 ± 100 fs; however, this lifetime varies between \sim 850 fs and \sim 550 fs for 0.1 eV lanes between 1.9 and 2.4 eV. This variation may be due to spectral shifting in this region and significant spectral contamination of the integration region due to overlap of the features in the region. Integration of the ground state spectrum is made difficult to fit by noise at low eKE in our spectra; however, depletion and recovery of the ground state near zero pump-probe delay are clearly visible in Figs. 5(a) and 5(b).

In order to better separate the spectral contributions from each of the three features, GLA is used to globally fit the entire data set. The raw data, fit, and residuals are pictured in Figures 6(a)-6(c), respectively. The two kinetic parameters as generated from the fit are 130 ± 40 fs and 800 ± 300 fs, which reproduce both lifetimes from lane integration to within error bounds. Decay associated spectra are generated for both kinetic components and are pictured in Figure 6(d). DAS_{130fs} shows two positive going peaks: one centered at 2.7 eV and one at 1.2 eV. DAS_{800fs} has a positive component at 2.1 eV and a negative component at 1.2 eV that approximately mirrors the 130 fs component.

Analysis of the shape of each DAS can provide significant insight into the kinetics of the data being fit. A DAS with positive and negative going components suggests an exchange of population from the positive going feature to the negative going on the associated time scale. In this case, photoelectron intensity in the region of the red lane, from Fig. 5(a), exchanges with the ground state on an 800 fs time scale. Interpretation of the two positive going peaks in DAS_{130fs} is less obvious. The first peak is in the region of the blue lane and the second in the region of the red lane. In order to relate the DAS to the underlying dynamics, relations between the DAS and the static kinetic energy distributions $S_j(eKE)$ can be derived by setting Eq. (3a) equal to Eq. (3b) and invoking an explicit kinetic model to generate the expressions for the integrated rate equations, $S_i(\Delta t)$. The simplest case for this is a three step sequential kinetic mechanism ($I \xrightarrow{\tau_1} II \xrightarrow{\tau_2} III$). With the initial condition I + II + III = 0, $S_{III}(\Delta t)$ for this mechanism is

$$S_{III}(\Delta t) = \frac{A_0}{\tau_2 - \tau_1} \left[\tau_1 e^{-t/\tau_1} - \tau_2 e^{-t/\tau_2} \right].$$
(4)

Assuming $I \xrightarrow{\tau_1} II \xrightarrow{\tau_2} III$ kinetics, expressions relating the DAS_{τ_i} to the spectral components $S_j(eKE)$ are given by Eqs. (5a) and (5b),

$$DAS_{\tau_{1}}(eKE) = S_{I}(eKE) - \frac{\tau_{2}}{\tau_{2} - \tau_{1}}\sigma_{r,II}S_{II}(eKE) + \frac{\tau_{1}}{\tau_{2} - \tau_{1}}\sigma_{r,III}S_{III}(eKE),$$
(5a)
$$DAS_{\tau_{2}}(eKE) = \sigma_{r,II}S_{II}(eKE)\frac{\tau_{2}}{\tau_{2} - \tau_{1}} - \frac{\tau_{2}}{\tau_{2} - \tau_{1}}$$
(5b)

$$-\sigma_{r,III}S_{III}(eKE)\frac{\tau_2}{\tau_2-\tau_1}.$$
 (5b)

We see that $DAS_{\tau_2}(eKE)$ has a positive going component corresponding to S_{II} and a negative going component S_{III} . $DAS_{\tau_1}(eKE)$ has positive going components S_I and S_{III} but negative component S_{II} . By simply solving for S_I and S_{II} using DAS_{τ_1} , DAS_{τ_2} , and the known S_{III} , spectra for Features I and II are generated. These spectra are shown in Figure 7. Feature I peaks at 2.6 eV eKE and has a full width at half maximum



FIG. 6. GLA fit of the three color experiment showing positive going features in green to red and negative in dark blue: data (a), fit (b), residuals (c), and DAS (d).

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FIG. 7. Spectra associated with Features I, II, and III generated from analysis of the DAS and the known ground state, $DAS_{\tau_1}(eKE)$, and $DAS_{\tau_2}(eKE)$.

of 1.0 eV. Feature II peaks at 2.0 eV and comprises the high energy tail of the main peak in Fig. 5(a).

Comparing the extracted spectra for Features I and II in Fig. 7 with the integration lanes in Fig. 5(a), we see that the spectra in Fig. 7 encompass the integration lanes in Fig. 5(a). The portion of the extracted spectrum of Feature I which is not spectrally contaminated, i.e., which does not overlap Feature II, is the integration lane for the blue lane. In the absence of a spectrally pure integration lane, the region of highest intensity of the spectrum of Feature II corresponds to the red integration lane. Hence, the energy lanes in Fig. 5(a), though considerably narrower than the spectral components in Fig. 7, pick up the same dynamics as the extracted spectra from global analysis. GLA is thus an equivalent but more complete representation of the underlying dynamics.

IV. DISCUSSION

A. CTTS dynamics

The two-pulse TRPES experiments probe solvation dynamics of the electrons generated by CTTS excitation. The overall picture of these dynamics is believed to comprise several steps:^{2,36,37} (i) decay of the optically accessible CTTS state to a "contact pair," in which the I atom and electron are confined within the same solvent shell, (ii) evolution of the contact pair to an equilibrium configuration with the surrounding solvent molecules, and (iii) diffusion of the free solvated electron away from the iodine to form a solvent separated electron, which competes with geminate recombination to re-form the I⁻ anion. Based on previous work, we divide the dynamics into two parts: ejection and cavity formation dynamics in the short time regime, <20 ps (steps i and ii), and recombination dynamics in the long time regime, >20 ps (step iii).

While Vilchiz *et al.*³⁴ previously studied the CTTS dynamics of iodide in methanol with TA, their work focused on equilibration of the solvated electron and geminate recombination dynamics. Our results probe these steps along with earlier time dynamics. TRPES has been used to study the CTTS process from iodide in water,^{10,11,13} which provides a strong point of comparison to our results. Also of interest to this discussion are TA experiments of solvated electrons in neat methanol generated by photoionization of the solvent molecule.^{39,64,65} Although the photoionization scheme in these experiments generates electrons with substantially greater initial energy than in CTTS experiments, they do provide a reference point for solvation times.

1. Short time dynamics

The total photoelectron signal (black curve, Fig. 2) and the signal in the high eKE energy lane spanning 2.5-3.0 eV (blue curve, Fig. 2) rise within the laser pulse cross correlation time and exhibit fast decay constants of 480 ± 40 fs. GLA yields a DAS spanning 2.0-3.0 eV that decays in 550 ± 110 fs (Fig. 4(d)). It is reasonable to conclude that these fast time constants reflect the same process, which results in rapid depletion of photoelectron signal at high eKE but relatively little rise at low eKE.

Previously published TRPES studies in water microjets identify a 190-210 fs lifetime associated with the decay of a weakly bound hydrated electron population.^{10,11,13} This lifetime is both similar in magnitude and approximate energy range to our 550 fs lifetime in methanol; therefore, we expect these Features to be directly comparable between solvents. Early time CTTS dynamics in water have been studied in a number of laboratories. Fast dynamics on the order of 200 fs are observed in TA, in the form of a rise time in the hydrated electron absorption.^{22,33} In methanol, a rise time for TA data is also reported to be present but a lifetime for the rise is not provided.³⁴ In time resolved fluorescence monitoring, the decay of the iodine fluorescence signal in water, a two-step relaxation of 60 fs and 100-400 fs is reported.⁶⁶ Finally, using time-resolved x-ray absorption to probe the 2s-5p absorption in aqueous iodine subsequent to CTTS excitation, Galler and co-workers⁶⁷ observe a rise time of 80 fs for the neutral iodine absorption but no subsequent decay over a time scale of several hundred femtoseconds.

In water, the few-hundred fs time scale has been variously attributed to the decay of the relaxed CTTS state,⁶⁶ trapping of an iodide electron contact pair state from the CTTS state, and recombination of the electron with the iodide. In TR-PES in water, Tang *et al.*^{10,13} assigned their observed ~200 fs time scale to the decay of the CTTS state, which branches to both form the contact pair and recombine with the parent iodine. Lubcke et al.¹¹ attributed this feature exclusively to a fast recombination of the "hot" electron with the geminate iodine but allowed the possibility of a fast evolution of the photoelectron cross section. However, the absence of a \sim 200 fs decay in the iodine transient absorption data⁶⁷ provides rather convincing evidence that there is no recombination on this time scale. Therefore, assuming that the fast dynamics seen in methanol have the same origin, we conclude that the apparent decrease in the integrated photoelectron intensity is due to a rapid change in the photodetachment cross section due to evolution of the CTTS state to a solvated electron configuration.

The second lifetime extracted from the data, 6–8 ps, is seen as the longer decay component of the blue curve in Fig. 2(b) and the rise time of the red curve in the same panel. Based on the eKE ranges of the two curves, 2.5-3.0 eV and 0.5-1.0 eV, these dynamics appear to reflect exchange between the population on the weakly bound edge of the ground state spectrum with the equilibrated ground state, i.e., relaxation of the solvated electron. A similar 8 ± 3 ps time scale is observed in GLA corresponding to a DAS with decaying population centered at 2.0 eV and rising at 0.9 eV. No picosecond decay of the total signal (black curve, Fig. 2) is observed; supporting the assignment of these dynamics to solvent relaxation and not population decay.

The lifetimes for the ground state relaxation generated from lane integration and GLA, 6.0 ± 1.5 ps and 8 ± 3 ps, respectively, are in reasonable agreement despite the presence of spectral shifting. There is a clear shifting behavior in the few picosecond regime as shown in Fig. 2(b), and the residuals from GLA are highest in this region. As noted previously, shifting behavior is not well treated by GLA, and we expect significant error bounds in this lifetime. A second fitting routine which allows for spectral shifts is discussed in the supplementary material⁶³ and agrees well with the few picosecond time scale from GLA and lane integration.

In methanol, similar time scales to our 8 ps thermalization have been reported for decay of the "hot" ground state electron from TA following methanol photoionization.^{39,64,65} After CTTS excitation, Vilchiz et al.³⁴ found the spectral evolution of the solvated electron to be complete within 20 ps, in overall accord with our results. In water, Lubcke et al.¹¹ found an approximately 1 ps shift of the "hot" electron population and a corresponding sub-picosecond decay which they attributed to a fast recombination of the "hot" electron with the geminate iodine. Also in water, Tang et al.¹⁰ identified a 1.3 ps time scale which they associated with an exchange between two intermediate solvation states centered at 200 meV and 20 meV above the ground state. The general trend for these solvation times shows methanol and ethanol relaxing 3-4 times slower than water. An 8 ps solvation time for the solvated electron in methanol is therefore quite reasonable in light of prior results.

2. Long time dynamics

After ~20 ps, the population between 0.5 and 1.0 eV eKE (red curve in Fig. 3(a)) decays on a 41 ps time scale to a stable intensity for the rest of the window of measured pumpprobe delays. The DAS for the nanosecond and 41 ± 7 ps kinetic components each reproduce the relaxed ground state. Both kinetic components are also seen in the decay of the total photoelectron signal, the black curve in Fig. 3(a). Therefore, we can conclude that the 41 ps component represents a uniform depletion of the ground state photoelectron population.

In methanol, Vilchiz *et al.*³⁴ have approached the recombination problem from a number of avenues of increasing sophistication. They conclude that the total decay of the absorption signal is best fit with the numerical model allowing for an attractive potential between pairs rather than using a sum of exponentials; however, we found their simpler "competing kinetics" model to be adequate.²² In this model, the longtime behavior is represented by a branched mechanism balancing diffusive pair dissociation, k_d , and non-adiabatic (geminate) recombination with the parent, k_n . Though both the iodineelectron solvent-separated pair and the free solvated electron have the same spectrum, the geminate recombination rate can be estimated from the surviving fraction of electrons, $k_d/(k_d + k_n)$. Assuming this kinetic model and that both species have equivalent photodetachment cross sections, the fraction of electrons that survive geminate recombination is 0.71, from which we calculate $k_d = 1/(57 \text{ ps})$ and $k_n = 1/(146 \text{ ps})$. Vilchiz *et al.* find the fractional survival of electrons using the competing kinetics model to be 0.7. The 41 ps lifetime from our DAS analysis is equivalent to $1/(k_d + k_n)$. Using their exponential components to calculate a comparable rate constant yields 35 ps, which is in reasonable agreement with our reported lifetime of 41 ± 7 ps.

In water, a similar time constant was measured in TR-PES experiments monitoring the CTTS excitation from iodide. Both Suzuki and coworkers^{10,13} and Lubcke *et al.*¹¹ measured a ~20 ps decay of the total photoelectron signal. Lubcke assigned this process to geminate recombination. Suzuki and coworkers calculate a pair diffusion lifetime of 84 ps and a recombination lifetime of 28 ps. Further, their study indicated that the decay affects a population of electrons very near the ground state binding energy, in agreement with our findings in methanol.

A summary of the solvation scheme is presented in Figure 8. After CTTS excitation, electrons are formed in a range of configurations in relative proximity to the geminate iodide. The earliest process measurable with our time resolution is the 550 \pm 110 fs decay of a weakly bound population. This decay is likely due to decay of the relaxed CTTS state to a solvated electron configuration and is accompanied by a decrease in the photodetachment cross section. The solvated electron spectrum then shifts toward the equilibrated spectrum on an 8 ± 3 ps time scale as excess energy is redistributed into the solvent modes. Dynamics after this point do not affect the binding energy spectrum and consist solely of a decrease in the solvated electron population to a stable long term value. The lifetime of the decay of the total population is 41 ± 7 ps. 71% of generated solvated electrons survive geminate recombination, and thus presumably become free solvated electrons. The geminate recombination lifetime, assuming branched exponential kinetics, is 146 ps and the pair diffusion lifetime, 57 ps.



FIG. 8. Summary of charge-transfer-to-solvent dynamics from I^- to methanol after 238 nm excitation. The dynamics include a fast evolution of the photodetachment cross section, thermalization of the electron, and competitive diffusion and recombination of the relaxed electron.



FIG. 9. Schematic relaxation mechanism for the solvated electron subsequent to electronic excitation.

B. Excited state dynamics

The relaxation mechanism of the solvated electron after excitation to its *p*-state is expected to comprise three steps, as summarized in Figure 9: relaxation on the excited state, $\tau_{\rm P}$; internal conversion to the ground state, $\tau_{\rm IC}$; and solvent relaxation on the ground state, $\tau_{\rm S}$. Prior work on this system has been conducted by a number of groups using TA in methanol.38,39 From these experiments, three lifetimes were extracted, ~100 fs, ~700 fs, and 5-6 ps, but conclusive assignment of these lifetimes to a particular physical process has been a matter of some debate.⁶ The relaxation process is expected to follow one of two proposed mechanisms.²⁰ In the adiabatic mechanism, τ_p is expected to occur on a ~100 fs time scale, $\tau_{\rm IC}$ occurs on a ~700 fs time scale, and $\tau_{\rm S}$ on a few picosecond time scale. In the non-adiabatic mechanism, τ_{IC} occurs on a ~100 fs time scale, and the longer time constants involve solvent relaxation after internal conversion.

As was the case with water, the two mechanisms can be distinguished by pinning down the internal conversion lifetime. From the perspective of the work presented here, resolving this issue depends on the assignment of Features I and II in the three-pulse experiments in Fig. 7. If Feature I is the unrelaxed *p*-state and II is the relaxed *p*-state, then the mechanism is best described as adiabatic, but if Feature II is best assigned to the ground state, then the relaxation mechanism is non-adiabatic. We note that features analogous to I and II were seen in our three-pulse experiments on water liquid jets; the latter assignment in favor of the non-adiabatic mechanism was made there.¹²

Similar arguments are invoked herein. Features I and II in Fig. 7 overlap but their maxima differ by 0.6 eV. Comparison of the red energy lane in Fig. 5(a) and Feature II in Fig. 7 shows that the 800 fs relaxation affects a population on the hot edge of the ground state feature as would be expected from s-state relaxation. As mentioned in reference to Fig. 5(b), the pump-induced signal, shown in the curves from 200 to 600 fs, does appear to be shifting toward lower electron kinetic energy. Such a shift could also explain the relatively large error bars on the 800 fs lifetime extracted from GLA. A shift is suggestive of electrons in a non-equilibrated solvent environment as would be expected for *s*-state electrons just after internal conversion. Conversely, electrons in the blue lane do not appear to shift, as evidenced by the independence of the fitted lifetime from integration lane; therefore, it is not likely the result of a shift on the excited state. Finally, if 800 fs was the internal conversion

time, we would expect to observe some ground state solvation on a longer time scale; however, we find no evidence for a 5-6 ps lifetime within our 10 ps observation window. Therefore, it is logical to assign Feature I to the *p*-state and its lifetime to internal conversion. The internal conversion lifetime of the solvated electron is then 130 ± 40 fs, as extracted from GLA. The spectrum of Feature I as shown in Fig. 7 is centered at 2.57 eV eKE, yielding a vertical binding energy of 2.1 eV for the *p*state. The lifetime of the "hot" *s*-state, Feature II, is 800 fs.

Our value of 130 fs for the internal conversion lifetime and 800 fs for the ground state relaxation lifetime is in good agreement with the reported values of 105 ± 25 fs and 670 ± 100 fs by Thaller *et al.*³⁹ They narrowed the assignment of the 670 fs relaxation to either the internal conversion lifetime or ground state relaxation. Silva *et al.*³⁸ also performed TA studies of the equilibrated solvated electron in methanol. They report an internal conversion lifetime of ~300 fs; however, this discrepancy may be due to the limitations of their 300 fs time resolution, which would have made the first time constant unresolvable.

The values and assignments reported here are also in good agreement with extrapolated results from solvent cluster anions $(157 \pm 25 \text{ and } 760 \pm 25 \text{ fs})$.⁵⁰ It is interesting to note that the extrapolated results from clusters produce reasonable lifetimes considering the extrapolated ground state binding energy of 2.6 eV⁶⁸ is well off the measured value of 3.38 eV⁵⁴ in the bulk. It has been speculated that the phase of these methanol clusters may more closely resemble solids than liquids.⁶⁹ In light of the difference from the binding predicted binding energy, the correspondence between the extrapolated lifetime and the bulk measurement requires future consideration.

We next turn to a comparison of the results here to those measured in water. The solvated electron in water was shown by TRPES to sequentially undergo internal conversion and relaxation on the ground state on 75 ± 20 and 410 ± 100 fs time scales, respectively.¹² Methanol shows identical excited state dynamics to water albeit at a slower rate by nearly a factor of two for both solvents. Our results are in qualitative agreement with the results of Borgis *et al.*⁷⁰ who predict non-adiabatic transition times of <160 fs depending on the model. The 150 fs internal conversion time in methanol predicted by Zharikov and Fischer⁴⁵ also agrees well with our reported value, as it similarly does in water.

V. CONCLUSION

In the two pulse experiment, the solvated electron generated from CTTS excitation in methanol undergoes similar dynamics to the hydrated electron. The earliest dynamics include contact pair formation followed by ultrafast depletion of a weakly bound electron population with a lifetime of 550 ± 110 fs. We assign the 550 fs lifetime to decay of the CTTS state to a solvated electron accompanied by rapid decrease in the photodetachment cross section. The photoelectron spectrum then shifts on an 8 ± 3 ps time scale to the ground state solvated electron spectrum. Finally, the ground state spectrum is depleted with a 41 ± 7 ps lifetime; however, solvated electrons survive well past the measured delays. Approximately 70% of the ground state signal survives the 41 ps recombination step. Using the surviving electron fraction and the 41 ps decay, we find a 57 ps pair diffusion lifetime and 146 ps geminate recombination lifetime.

From the three pulse experiments, relaxation of the excited p-state electron in methanol is attributed to the non-adiabatic mechanism. Global lifetime analysis yields spectra associated with the p-state and hot s-state of the solvated electrons, yielding internal conversion and ground state relaxation time scales of 130 ± 40 fs and 800 ± 300 fs, respectively. This interpretation is in accord with measurements in water. The lifetimes of both solvation processes are shown to be in agreement with results from TA, and the internal conversion lifetime agrees with extrapolated results from methanol cluster anions.

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