Temperature dependence of the hydrated electron's excited-state relaxation. II. Elucidating the relaxation mechanism through ultrafast transient absorption and stimulated emission spectroscopy

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The structure of the hydrated electron, particularly whether it exists primarily within a cavity or encompasses interior water molecules, has been the subject of much recent debate. In Paper I [C.-C. Zho *et al.*, J. Chem. Phys. **147**, 074503 (2017)], we found that mixed quantum/classical simulations with cavity and non-cavity pseudopotentials gave different predictions for the temperature dependence of the rate of the photoexcited hydrated electron's relaxation back to the ground state. In this paper, we measure the ultrafast transient absorption spectroscopy of the photoexcited hydrated electron as a function of temperature to confront the predictions of our simulations. The ultrafast spectroscopy clearly shows faster relaxation dynamics at higher temperatures. In particular, the transient absorption data show a clear excess bleach beyond that of the equilibrium hydrated electron's ground-state absorption that can only be explained by stimulated emission. This stimulated emission component, which is consistent with the experimentally known fluorescence spectrum of the hydrated electron, decreases in both amplitude and lifetime as the temperature is increased. We use a kinetic model to globally fit the temperature-dependent transient absorption data at multiple temperatures ranging from 0 to 45 °C. We find the room-temperature lifetime of the excited-state hydrated electron to be 137 ± 40 fs, in close agreement with recent time-resolved photoelectron spectroscopy (TRPES) experiments and in strong support of the "non-adiabatic" picture of the hydrated electron's excited-state relaxation. Moreover, we find that the excited-state lifetime is strongly temperature dependent, changing by slightly more than a factor of two over the 45 °C temperature range explored. This temperature dependence of the lifetime, along with a faster rate of ground-state cooling with increasing bulk temperature, should be directly observable by future TRPES experiments. Our data also suggest that the red side of the hydrated electron's fluorescence spectrum should significantly decrease with increasing temperature. Overall, our results are not consistent with the nearly complete lack of temperature dependence predicted by traditional cavity models of the hydrated electron but instead agree qualitatively and nearly quantitatively with the temperature-dependent structural changes predicted by the non-cavity hydrated electron model. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4985906]

I. INTRODUCTION

Solvated electrons, the simplest quantum objects one can study in liquids, serve as archetypal systems for benchmarking our understanding of quantum mechanics in the condensed phase.[1,2] Because solvated electrons lack nuclear degrees of freedom, their properties are extremely sensitive to the local liquid environment, making them ideal models for understanding electron transfer, photodetachment, and solvation.[3,4] Hydrated electrons, solvated electrons in water, are of particular interest since they are responsible for a large fraction of the damage to DNA caused by ionizing radiation[5] and are also responsible for much of the exotic chemistry found in strongly reducing or highly radioactive aqueous environments.[6]

The standard structural paradigm of the hydrated electron is that it occupies a quasi-spherical cavity in which the water molecules are repelled from the center of electron density.[7–14] Several years ago, we challenged this view based on the results of mixed quantum/classical molecular dynamics simulations using a new pseudopotential; our calculations predicted a hydrated electron that exists in the interstitial spaces between water molecules, with little to no central cavity and a significant radial overlap of the electron's wavefunction with the nearby waters.[15–17] In both the cavity and non-cavity pictures, however, the electronic structure of the hydrated electron is that of a particle in a finite roughly spherical box (formed by repulsive interactions with the surrounding water in the cavity model and attractive polarization interactions with interior waters in the non-cavity model) and thus has an *s*-like ground state and three quasi-degenerate *p*-like excited states.

As discussed in Paper I,[18] our suggestion of a non-cavity structure for the hydrated electron has been controversial.[19–24] Indeed, our potential, dubbed Larsen-Glover-Schwartz (LGS) in the literature, predicts that the electron is overly bound energetically[19,20,25] and has a negative molar volume of solvation,[26] in contrast to what is known from experiment.[27,28]

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On the other hand, our non-cavity picture provides many qualitatively and even quantitatively correct predictions that are missed by the more standard cavity model, including the shape of the O–H stretching band in the hydrated electron's resonance Raman spectrum,[16,17] the temperature-dependence of the electron's ground-state absorption spectrum,[16,17] the hydrated electron's time-resolved photoelectron spectroscopy,[29] and the behavior of hydrated electrons at the air/water interface.[26] Other recent theoretical calculations, which suggest a "hybrid" model with an electron that has only a small central cavity, still require a significant electron–water overlap like that in our non-cavity model to reproduce experimental findings.[30,31]

Because of the great interest in this object, there has been a significant amount of work addressing the excited-state relaxation of the hydrated electron. Early ultrafast transient absorption (TA) experiments explored the relaxation of newly created electrons injected into water's conduction band by multiphoton ionization.[32,33] Subsequently, pioneering work by Barbara and co-workers explored the pump-probe spectroscopy of equilibrated hydrated electrons in a series of 3-pulse experiments: the first pulse was used to create hydrated electrons, and after a suitable equilibration delay, the second two pulses were used to excite the equilibrated electron and probe its dynamics.[34–37] This work, along with subsequent ultrafast experiments from several other groups, identified three time scales involved in the relaxation of the photoexcited hydrated electron: a rapid, ≤100 fs component plus two slower dynamical components of ~400 fs and ≥1 ps.[38–41] Two different kinetic models were found to fit the ultrafast spectroscopy data about equally well.[2,36] In one model, termed the "adiabatic" picture, excited-state solvation takes place in ≤100 fs, and the electron lives on the excited state for ~400 fs, after which it rapidly cools upon return to the ground state so that only the small-amplitude ≥1-ps time scale is associated with ground-state relaxation dynamics.[37,42,43] In the other model, termed the "non-adiabatic" picture, the electron returns to the ground state in ≤100 fs and the subsequent cooling is relatively slow so that both the ~400 fs and ≥1 ps time scales occur on the electronic ground state.[35,40,44]

It was not until the past few years, with advances in vacuum liquid microjet technology, that direct measurements of the hydrated electron's excited-state lifetime using time-resolved photoelectron spectroscopy (TRPES) became possible. TRPES experiments on the hydrated electron measured a decay of the p-state photoelectron peak of 60–80 fs,[45–47] although we have argued that, based on simulations that indicate non-Condon effects in the photoionization cross section, the underlying lifetime of the hydrated electron is closer to ~100 fs.[29] These bulk TRPES findings are also consistent with previous TRPES experiments on water anion clusters when the anion excited-state lifetime is extrapolated to infinite cluster size.[48–51] Taken together, the majority of experiments suggest a p-state lifetime of the photoexcited hydrated electron around 100 fs and thus support the "non-adiabatic" relaxation picture discussed above.

Despite all this attention, there has been almost no work directed at exploring the temperature dependence of the photoexcited hydrated electron's relaxation dynamics. We are aware of only a single previous study in which the authors compared pump-probe transients at a single wavelength and two temperatures and concluded that there is little effect of temperature on the excited-state relaxation.[52] Large shifts in the ground-state spectra take place as the temperature (and pressure) of water is varied,[53–55] however, and Paper I makes clear that at least for the non-cavity picture, the ground-state structure of the hydrated electron could change significantly with temperature.[18] If there are temperature-dependent changes in the equilibrium structure, this suggests that the excited-state relaxation dynamics of the hydrated electron could also be temperature dependent. Indeed, in Paper I,[18] we found a large temperature dependence of the p-state relaxation dynamics for photoexcited simulated non-cavity hydrated electrons, although simulated cavity hydrated electrons showed little change in structure with temperature and thus almost no temperature dependence to their p-state lifetime.

The purpose of this paper is to experimentally determine the temperature dependence of the relaxation dynamics of the photoexcited hydrated electron. Our goals are both to determine the best experimentally-based kinetic model for understanding the photoexcited hydrated electron's transient spectroscopy and to use the measured temperature dependence as a means to help distinguish between cavity and non-cavity simulation models of the hydrated electron. We find that a version of Barbara's non-adiabatic relaxation model, modified to include stimulated emission (SE) from the electronic excited state, appropriately fits the temperature-dependent transient absorption (TA) data. The p-state lifetimes extracted from the model are strongly temperature dependent, varying by a factor of roughly two over the experimental temperature range of 0–45 °C. At room temperature, the best-fit lifetime is 137 ± 40 fs. Our temperature-dependent lifetime results are in excellent agreement with what is predicted by non-cavity hydrated electron models in Paper I,[18] and the room-temperature lifetime is in good accord with that estimated from recent TRPES experiments.[29,45–47] Overall, our results make clear that any model of the hydrated electron should predict a significant temperature dependence to the excited-state lifetime, something that the current generation of cavity models does not do.

II. METHODS

All of our 3-pulse TA experiments were performed using transform-limited 45-fs duration pulses (75-fs cross correlation time at the sample) from a commercial (Coherent, Inc.) Ti:sapphire regenerative amplifier. Briefly, 800-nm seed pulses from a passively mode-locked Ti:sapphire oscillator running at 80 MHz were stretched, amplified, and compressed at 1 kHz to create amplified pulses with ~3 mJ of energy. All of our experiments were carried out in a 3-pulse synthesis-pump-probe scheme in which electrons were first created, allowed to relax for ~100 ps, excited with an 800-nm pulse, and then probed with a broadband continuum. The 266-nm synthesis pulse was created by selecting a 1.5-mJ portion of the fundamental beam to make 500 μJ of the second harmonic of 800 nm by doubling in a β-barium borate (BBO) crystal and then mixing the

800 and 400-nm pulses in a second BBO crystal to generate 15-μJ pulses of the third harmonic at 266 nm. For exciting the s-to-p transition of the relaxed hydrated electrons, a small portion of the 800-nm fundamental beam was selected; the energy of this pulse was kept just below the threshold for multiphoton excitation of the hydrated electron.[36] For the broadband probe pulse, a small portion of the fundamental light was selected with a beam splitter and used to generate a monofilament white-light continuum by focusing through a sapphire plate, yielding probe pulses whose bandwidth spanned from ~480 nm to wavelengths redder than 800 nm. This continuum had a chirp of ~1 ps across this wavelength range, and in all the data presented below, we corrected the zero of time for this chirp at each probe wavelength by calibrating with the non-linear coherences in a jet of pure water.

The time delay between pump and probe pulses was controlled by double-passing the probe beam through a translation stage that could produce variably-controlled time delays from 10 fs to 3 ns. The change in transient absorption [$\Delta(\Delta OD)$] was measured on a one-dimensional diode array by taking the difference between consecutive probe pulses while synchronously chopping the 800-nm pump beam at 500 Hz (Helios from Ultrafast Systems). Typical ΔOD values of the ground-state hydrated electron near its 720-nm absorption maximum in 2-pulse experiments were 100–200 mOD; the subsequent bleaching of the ground-state absorption in our 3-pulse experiments was kept below 15% of the 2-pulse ΔOD, ensuring that the change in transient absorption was in the linear regime. We averaged the transient spectra at each time delay over at least 10 s per scan and 2 independent scans, yielding noise below 10^{-4} $\Delta(\Delta OD)$.

For all of our experiments, we kept the pump and probe pulses' relative polarizations at the magic angle (54.7°). Although it has been well established that there is no polarized hole-burning or other polarization-dependence to the hydrated electron's transient spectroscopy,[38,40,56] we wanted to ensure that none of the TA dynamics we observed, including the stimulated emission/excess bleach component, could possibly have resulted from polarization effects. This choice of relative polarization also helped minimizing the presence of "coherent artifacts" that can take place during the pump-probe overlap at early delay times.

The samples for all our experiments consisted of solutions of de-ionized (18 MΩ) water which were made 100 mM in $K_4Fe(CN)_6$ (Sigma-Aldrich); at this concentration, ionic strength effects should not play a role in the p-state relaxation dynamics.[35] Samples did not degrade over the measurement period but were nonetheless replaced each day. We measured the TA of the samples in a flowing gravity-fed wire-guided liquid jet,[57] which consisted of a stainless steel tube with a loop of tungsten wire crimped on one end. A laminar flow with a thickness of ~200 μm created between the wires constituted the optically accessible portion of our sample; we chose a flow rate high enough to provide a new sample volume for each pulse, but low enough to be effectively stationary on sub-ns time scales. To modulate the sample temperature, we placed in the sample reservoir a nichrome wire with a variable AC controller for heating and hollow glass condensing coils for chilling. The chiller mixture consisted of equal parts of water,

ethylene glycol, and ethanol, reaching temperatures of −40 °C and easily allowing for super-cooling or freezing of our sample in the reservoir; the nichrome wire allowed heating of the reservoir to boiling. At 0 °C, condensation would cause the jet to become unstable; this was resolved with a collapsible housing erected around the liquid jet with ports for the beam and a slight positive pressure of dry argon or nitrogen gas. We could only maintain a laminar flow of the liquid jet for a limited set of conditions, restricting our TA results to the temperature range between 0 and 45 °C.

Finally, we also performed a set of 3-pulse transient absorption scavenging experiments, the full results of which are described in more detail in the supplementary material. Briefly, KNO_3 was used to selectively scavenge a fraction of the excited p-state electrons; the scavenging yield is dependent on the wavefunction overlap with scavengers (which is different for the ground and excited states), the rate of scavenging, and the excited-state lifetime. By measuring scavenging yields when varying the KNO_3 concentration in the range of 0–400 mM and using a formalism introduced by Barbara and co-workers,[58] we were able to obtain independent upper limits of the effective excited-state radius (~7.5 Å) and scavenging rate constant (5.7×10^{-13}); details may be found in the supplementary material. Unfortunately these upper limits provide little additional information primarily due to high correlations between fitting parameters, as well as myriad other assumptions.

III. RESULTS AND DISCUSSION

A. Modeling the hydrated electron's lifetime with transient absorption spectroscopy and scavenging experiments

In pump-probe TA spectroscopy, the observed signal consists of a sum of negative components due to bleaching of the equilibrium ground state and stimulated emission from the excited state and positive components arising from absorption by electronic excited states or out-of-equilibrium species newly returned to the electronic ground state. Because all of these components spectrally overlap, it is usually not straightforward to determine whether any particular time scale observed in an ultrafast TA experiment corresponds to dynamics on the ground or excited electronic states. Thus, the standard approach is to fit the TA data to a kinetic model with as few adjustable parameters as possible and then interpret the data in terms of the model.

The first such model developed for interpreting the pump-probe TA signals for the hydrated electron was by Barbara and co-workers.[34,35] They started with the fact that the transient absorption at each time t and wavelength λ can be described by a sum of ground-state (g) and excited-state (e) spectral contributions,

$$\Delta OD_{tot}(t, \lambda, \Delta T) = \Delta OD_g(t, \lambda, \Delta T) + \Delta OD_e(t, \lambda). \quad (1)$$

They then broke the contributions from the ground and excited electronic states into sub-components,

$$\Delta OD_g = f(t) \otimes (\Delta OD_{GSB}(t, \lambda) + \Delta OD_{HGS}(t, \lambda, \Delta T)), \quad (2)$$

$$\Delta OD_e = f(t) \otimes (\Delta OD_{ESA}(t, \lambda) + \Delta OD_{SE}(t, \lambda)), \quad (3)$$

where the ground-state contribution includes both the equilibrium ground-state bleach (GSB) and the out-of-equilibrium absorption from "hot" ground-state (HGS) electrons that have relaxed from the excited state, and the excited-state contribution is from excited-state absorption (ESA); these contributions are convoluted with the experimental instrument response function, $f(t)$, which for our apparatus we measured to be roughly Gaussian with a 75-fs FWHM. The model then assumes a simple exponential interconversion from the excited state produced at $t = 0$ to the ground state with time constant τ_1. Barbara and co-workers chose not to include the component due to stimulated emission (SE) in their model.

The challenge with this type of model is that each spectral component can have a shape that changes arbitrarily with time, leading to far too many parameters to be physically meaningful. To avoid this difficulty, Barbara and co-workers made several simplifying assumptions.[35] First, they assumed that the GSB component was the same as the equilibrium absorption spectrum and did not change with time. This assumption has been tested by multiple TA,[56,59] photon echo,[38,60] and resonance Raman[61–63] experiments, all of which verify that the ground-state absorption of the hydrated electron is homogeneously broadened so there indeed should be no spectral diffusion in the GSB. Second, Barbara and co-workers assumed that the spectrum of the HGS electron was the same as that of an equilibrium hydrated electron but at a higher effective temperature and that this effective temperature relaxed exponentially with time. In this way, they were able to model the HGS contribution using the known temperature-dependence of the hydrated electron's equilibrium absorption spectrum, allowing the dynamics of the HGS electron to be described by only two parameters: ΔT, the jump in temperature characterizing the initially produced HGS and an exponential relaxation time τ_2 (or if needed, also a second relaxation time τ_3) for the hot ground-state electron to return to equilibrium. Finally, although Barbara and co-workers also attempted to model the electron's excited-state absorption contribution, there is, unfortunately, no simple way that we are aware of to make physically reasonable simplifying assumptions about this component. However, we know from both previous experimental[35,40,59] and simulation[18,43] studies (including that in Paper I[18]) that the photoexcited hydrated electron's ESA lies primarily to the red of its ground-state absorption and thus there should be little ESA contribution to the blue of 700 nm. Therefore, in this work, we focus only on this spectral region as a means to neglect the ESA component and thus further simplify the kinetic model used to fit the data.

Another difficulty with using this type of model to fit experimental transient absorption data is that the τ_1 excited-state lifetime and ΔT temperature-jump parameters are highly anti-correlated: the model can fit the data about equally well with a small τ_1 and large ΔT (the so-called "non-adiabatic" picture)[35] or a longer τ_1 and smaller ΔT (the so-called "adiabatic picture").[42,43] Barbara and co-workers eventually preferred the adiabatic picture because it was supported by molecular dynamics simulations using a cavity model for the hydrated electron.[42,43] However, in both Paper I[18] and in previous studies,[15,29] we saw that a non-cavity hydrated model predicts the non-adiabatic picture, in agreement with recent TRPES

experiments.[45–47,64–66] This dichotomy between the predictions of the cavity and non-cavity models is why we have chosen to revisit the topic of the hydrated electron's excited-state relaxation in this work. In particular, our goal is to use temperature dependence to provide sufficient experimental constraints to nail down all of the kinetics of the hydrated electron's excited-state relaxation.

We started by performing broadband TA experiments on the equilibrated hydrated electron at room temperature following excitation at 800 nm. A selected portion of our data is shown in the center panel of Fig. 1; the full dataset extends past 30 ps, a time long after the excited electron has fully recovered to equilibrium. The data, which are qualitatively similar to what has been observed by others,[35–37,39,59] have a better
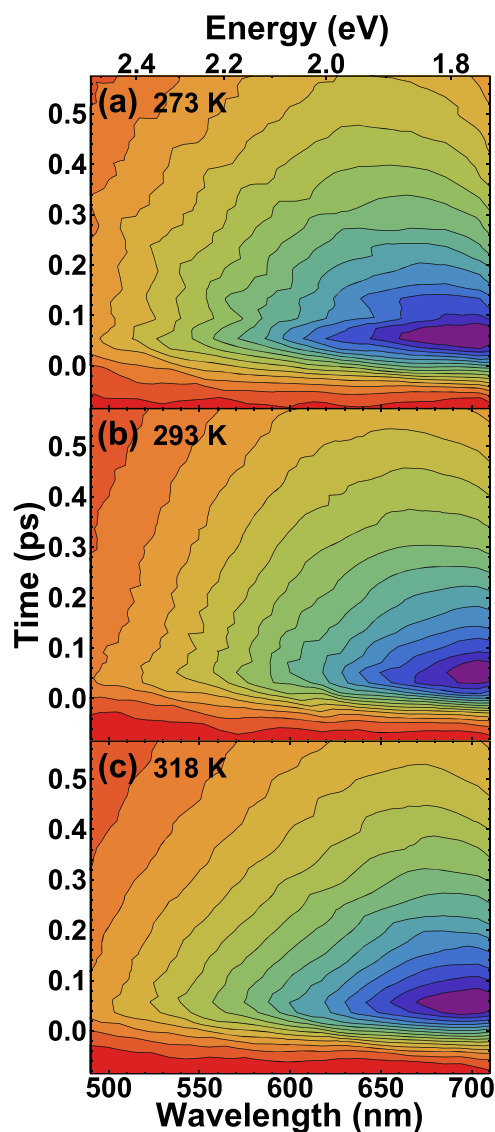

FIG. 1. Topographical plots of the raw TA data for photoexcited hydrated electrons after excitation at 800 nm at bulk temperatures T of 273, 293, and 318 K. The data are normalized between -1 and 0 (at late times) with equally spaced contours. The T-dependence of the ground-state absorption spectrum (and therefore the bleach maximum at early times) can be seen as the overall red-shift at higher temperatures. It is also clear by observing the contour lines that there is an appreciable dynamic spectral shift, which continues past the 0.6 ps shown out to several ps on the full dataset.

signal-to-noise ratio than most previous work and time resolution that is as good or better than all but a few previous experiments.[40]

When we fit this data with their original model, we find similar results to Barbara and co-workers, with the minimum least-squares error in the fit corresponding to parameters $\tau_1 \approx 100$ (or 450 fs) for the *p*-state lifetime, $\tau_2 \approx 1$ ps for the cooling of the hot ground state (or *p*-state lifetime), and $\Delta T \approx 350$ K (or 50 K) for the HGS temperature jump. Despite our improved signal-to-noise ratio, it is clear that this fit still has a great deal of associated errors. Although we know of no general procedures to quantify the additional error associated with highly correlated parameters, when we tabulate the root-mean-squared error with various fixed *p*-state lifetimes, we estimate that the reported standard errors should be adjusted upwards by a factor of 2 or 3. This uncertainty comes primarily from a correlation between the *p*-state lifetime and ΔT (correlation coefficient -0.95) that is so high that these parameters fall into the category of practical non-identifiability. This leads to a very broad and shallow error surface and multiple local minima. This can be clearly observed in the root-mean-square-error for the fit of our room temperature data to Barbara's original model, which is plotted as the orange-colored curve/squares in Fig. 2. The fact that there are multiple minima with similar overall errors but very different physical interpretations is what led to the original debate about the adiabatic and non-adiabatic pictures of the photoexcited hydrated electron's relaxation dynamics. We will show below, however, that when considering the bulk temperature dependence of the excited electron's relaxation, the interpretation of the model becomes clear.

We also estimated the electron's excited-state lifetime by repeating scavenging experiments that were first carried out by Barbara and co-workers[58] and later improved upon by Lu and co-workers.[67] The details of these experiments and the model used to extract the excited-state lifetime by fitting the results are described in the supplementary material. What we find is that the parameters in the scavenging model are even more highly correlated than those in the transient absorption model. Thus, we are able to fit a range of lifetime values that span several orders of magnitude with about equal fitting error; in particular, lifetimes of both 100 fs, consistent with "non-adiabatic" relaxation, and 400 fs, consistent with "adiabatic" relaxation, fit the data about equally well, as shown in the supplementary material. Thus, time-resolved concentration-dependent scavenging experiments are simply unable to differentiate adiabatic or non-adiabatic relaxation and thus a cavity or non-cavity structure for the hydrated electron.

B. Stimulated emission from the excited hydrated electron: Extending the kinetic model

As mentioned above, one thing potentially missing in Barbara's model is stimulated emission from the hydrated electron's excited state.[35,40,42,43,68] Simulations, including those in Paper I,[18] have predicted that there should be stimulated emission from the photoexcited hydrated electron with an oscillator strength that is comparable to (although smaller than) that of the ground-state bleach.[38,42,43,59] Indeed, fluorescence from the photoexcited hydrated electron has been observed,[68] which in conjunction with simulations that show a rapidly decreasing ground-to-excited-state energy gap following excitation indicates that the hydrated electron should exhibit SE with a rapid (<100-fs) dynamic Stokes shift. Previous TA experiments on this system by others, most notably that by Wiersma and co-workers with 5-fs pulses, found signs of an SE component, and although these workers used a kinetic model that included an SE feature, it was not deeply explored.[40,41,44]

To better investigate the possible role of SE in the excited-state TA spectroscopy of the hydrated electron, in the center panel of Fig. 3, we show our room-temperature data normalized to match the (negative of the) equilibrium absorption spectrum (black curve) between 480 and 580 nm. It is clear that at early times, there is an excess negative signal on the red side of the displayed spectra that goes beyond that expected for a simple ground-state bleach. This excess bleach component, which has an amplitude that is 30%–40% of the maximum bleach at the earliest times, decays rapidly, in ~90 fs. Since we know that the hydrated electron has a homogeneously broadened absorption spectrum and thus no spectral diffusion in the bleach,[38,56,59,61–63] that there should be a negligible excited-state in this spectral region, particularly at early times, and that the simulations in Paper I predicted that stimulated emission should produce a feature almost exactly like this,[18] we are confident in assigning this excess bleach component to stimulated emission.

The rapid decay of the SE component that we observe comes from a combination of several factors, including the following: (1) a short *p*-state lifetime that leads to direct decay of the SE; (2) the dynamic Stokes shift that moves the stimulated emission past the red edge of our probe window; and (3) the dynamic blue-shifting of the HGS spectrum that
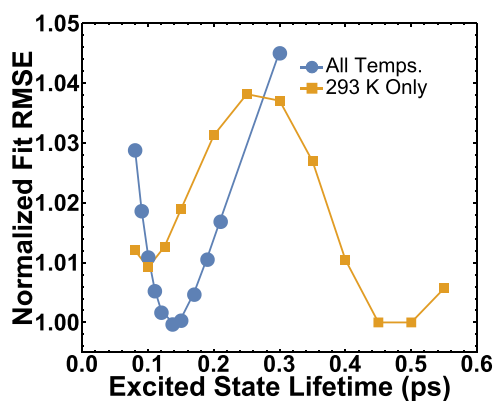
FIG. 2. Root-mean-square error (RMSE) for fitting various models to the photoexcited hydrated electron TA data in Fig. 1; in these plots, the minimum error when holding the excited-state lifetime parameter fixed at various values is normalized to 1. Using only the room temperature data along with Barbara's original model (orange curve/squares) produces an error surface with two distinct local minima of nearly equal depth. The relative RMSE of these two minima is variable depending on precisely how the data are weighted and how many early time or longer-time data points are included. Clearly, the model cannot differentiate adiabatic (longer lifetime) and non-adiabatic (shorter lifetime) pictures when only a single TA dataset is used. When a model including stimulated emission is fit simultaneously to multiple TA datasets from various bulk temperatures *T* and realistic constraints are imposed on how the different parameters should vary with *T*, the resulting error surface (blue curve/circles) has only a single global minimum, corresponding to a short lifetime that fits well with that observed by time-resolved photoelectron spectroscopy.[45–51]
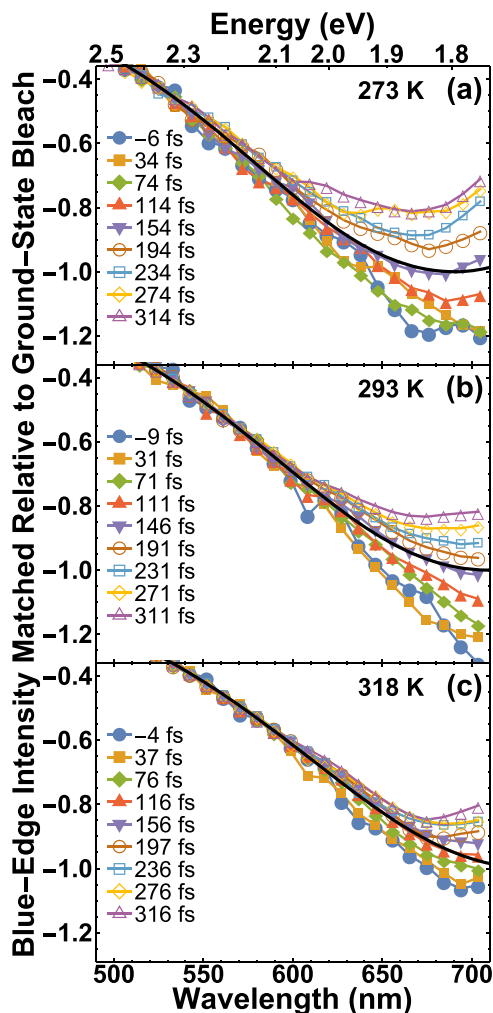
FIG. 3. Pump-probe TA data for the photoexcited hydrated electron (same data as in Fig. 1) but with the spectra at selected times normalized in the spectral region of 500–550 nm: the solid black curve represents the negative of the electron's known equilibrium absorption spectrum normalized in the same wavelength region. In this way, even without a model, it is clear that there is an excess bleach component at early times that must correspond to stimulated emission (SE). The SE decays more rapidly at higher bulk temperatures, reflecting the temperature dependence of the *p*-state lifetime, the dynamic Stokes shift of the SE out of our spectral window, and the absorption of the hot ground state shifting into our spectral window from the near-infrared (NIR). The data show unambiguously that there must be population in the excited state until the time at which there is no longer an excess bleach, placing a lower limit on the *p*-state lifetime.

overlaps and masks the component of the TA signal due to SE. Whatever the cause of the experimentally observed SE component decay, it is clear that it is significant enough that is must be included in any kinetic model of the early time TA dynamics of the hydrated electron. Moreover, the presence of SE is a clear indicator that the excited hydrated electron still occupies the excited state; for our room temperature data, this means that the excited-state lifetime must be ≳100 fs or about what our previous simulations estimated should be the case based on the 60–75 fs decay observed in the TRPES experiments.[29]

In order to address the presence of stimulated emission in the TA data, we have extended previous kinetic models for understanding the relaxation dynamics of the photoexcited hydrated electron. We begin by following the framework

established by Barbara and co-workers but add the possibility for different bulk equilibrium temperatures for each part of the model. We assume that the excited-state relaxation can be treated as a single exponential with lifetime τ_1. We note that simulations predict a more sigmoidal decay of the hydrated electron's excited state since the decay rate increases as the energy gap closes,[15,42] but we believe that the exponential assumption is reasonable for our data as our instrumental response is longer than the inertial dynamics that cause the gap to close, similar to that of the recent TRPES experiments.[45–47]

We also follow previous work in assuming that the hydrated electron's Gaussian-Lorentzian absorption spectrum, $\epsilon_{eqb}(T)$, at both the different bulk temperatures and at all stages during the ground-state cooling as the electron returns to equilibrium, can be described by the electron's known equilibrium temperature dependence.[54] Further, we assume that the temperature that describes the HGS' spectral shape decays exponentially towards equilibrium,

$$T(t) = T_{eqb} + \sum \Delta T_i \cdot e^{-\frac{t}{\tau_i}}. \tag{4}$$

We find that only one HGS cooling exponential is needed to model times ≲1 ps but two are required when longer-time data are included. Finally, we model the ground-state bleach using the known equilibrium spectrum at the bulk temperature,

$$\Delta OD_{GSB}(\lambda, T) = -\epsilon_{eqb}(\lambda, T_{eqb}). \tag{5}$$

Because electrons form on the hot ground state at different times (a direct consequence of the assumed exponential relaxation of the excited state), the HGS spectral dynamics in the model are described with a convolution,

$$\Delta OD_{HGS}(t, \lambda, T, \Delta T) = \epsilon_{eqb}(\lambda, T(t)) \otimes e^{-\frac{t}{\tau_1}}. \tag{6}$$

With our deliberately limited probe window, we can safely ignore any contributions from ESA. As shown below, this has the advantage of constraining the ΔT and τ_2 parameters, which when free of ESA are nearly directly inferred from the delayed appearance of the HGS in our probe window; the excited-state lifetime is then also determined by both the decay of the SE component, described next, and the appearance of the HGS through the convolution in Eq. (6).

Finally, given that we have a clear SE component in our data, we add an SE component to the model,

$$\Delta OD_{SE}(t, \lambda, T) = \epsilon_{SE}(\lambda, T) \cdot e^{-\frac{t}{\tau_1}}, \tag{7}$$

which decays with the same τ_1 lifetime that is used to produce the hot ground state. We model the SE spectrum in our probe window, ϵ_{SE}, as a Gaussian with a time-invariant center and width. Thus, our model does not include any dynamic Stokes shift of the hydrated electron's SE, but we believe this is justified in that it reduces the number of fitting parameters given that our time resolution and spectral range are both too limited to resolve this shift. It is worth noting, however, that both Wiersma and co-workers[40] and Tauber and Mathies[68] see a tail in the electron's SE/fluorescence that extends to the blue of the excitation wavelength. This observation, which also matches our data in Fig. 3, offers further evidence that the hydrated electron's absorption and emission spectra are homogeneously broadened.

We can compare our SE component with the previously observed fluorescence[68] from the photoexcited hydrated electron through a crude model that takes into account inertial (Gaussian decay, 25 fs) and diffusive (exponential decay, ~400 fs) components to the time-dependent energy gap between the ground and electronic excited states; details are given in the supplementary material. When we apply this model, we find that we are able to simultaneously predict both the SE dynamics we observe and the fluorescence spectrum measured by Tauber and Mathies[68] reasonably well. Figure 4(a) shows the predicted SE dynamics from the model when convoluted with an 75-fs instrument response; the results are very similar to what we observed experimentally in Fig. 3 at room temperature. Panel (b) of this figure shows the fluorescence spectra predicted by the model at different bulk temperatures (colored curves); the agreement with the experimental fluorescence spectrum (black curve)[68] at room temperature is excellent. (The structure superimposed on the experimental fluorescence spectrum is resonance Raman scattering that is not included in our model.) Thus, within the limits of our crude model, the SE dynamics we observe are entirely consistent with the known fluorescence spectrum of the hydrated electron.

C. Temperature dependence of the hydrated electron's transient absorption dynamics

Even with the SE component and additional convolution, if we fit our room-temperature TA data to the extended kinetic model described above, the results differ only slightly from previous TA experiments:[35] the fitting parameters remain highly correlated, leaving the excited-state lifetime and magnitude of the HGS temperature jump uncertain (Fig. 2). Thus, in this section, we show how we can experimentally pin down these parameters by simultaneously considering the same experiment at multiple bulk temperatures.

The upper and lower panels in Fig. 1 show TA data taken following photoexcitation of the hydrated electron at temperatures of 0 and 45 °C, respectively. When comparing the TA data at different temperatures, the most obvious feature is the red-shift of the GSB maximum with increasing temperature, which reflects the known red-shift of the ground-state absorption,[54] but closer inspection reveals that there are also changes in the kinetics at different temperatures. To more easily discern the temperature dependence of the TA kinetics, in Fig. 5, we compare normalized single wavelength slices of the TA data; the particular wavelengths for this comparison were chosen to lie at the same energy relative to the ground-state absorption spectral maximum at each temperature.

As predicted by the simulations in Paper I, there is a clear temperature dependence to the hydrated electron's excited-state recovery, with faster relaxation dynamics at higher equilibrium temperatures.[18] If we crudely fit these single-wavelength traces to single exponential decays, we find decay constants that change by a factor of roughly 1.5 between 0 and 45 °C. This experimentally observed temperature dependence to the hydrated electron's TA dynamics is at odds with the one previous experiment we are aware of[52] we attribute this discrepancy to the poorer signal-to-noise ratio and lack of broadband probing in the previous work.

To determine how the observed changes in TA dynamics with temperature correspond to changes in the excited-state
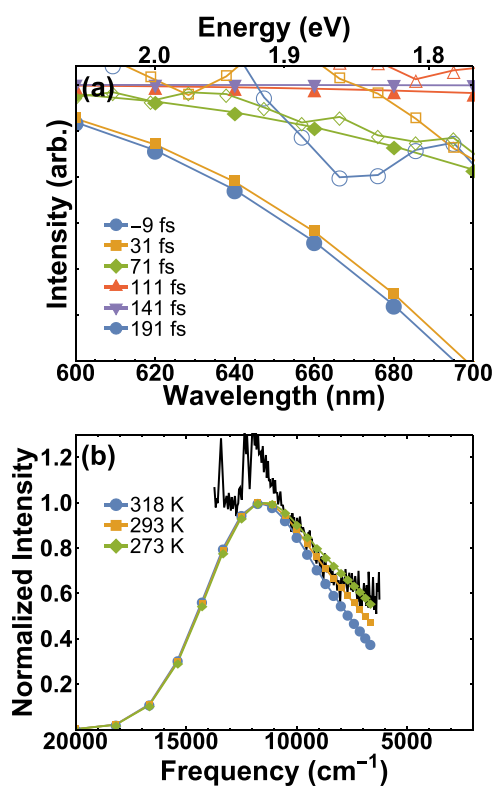

FIG. 4. (a) Shown in solid symbols are the predicted decay of the SE component of the photoexcited hydrated electron's transient absorption in the visible region of the spectrum from the crude model described in the text and supplementary material. By 141 fs, the predicted stimulated emission decay (solid inverted triangles) is mostly complete with an amplitude of 0 at all wavelengths. This model is in reasonable agreement with the excess bleach component shown as hollow symbols, which are simply the difference between the black curve and data from Fig. 3 at room temperature. The major trend is cleanly resolved and the discrepancies between the prediction and data appear to be random noise. (b) Fluorescence spectrum of the photoexcited hydrated electron as a function of temperature, predicted from the same model used in (a), along with a digitized reproduction of the experimental room temperature fluorescence spectrum.[68] The structure in the experimental spectrum is due to resonance Raman scattering that is not included in the model.
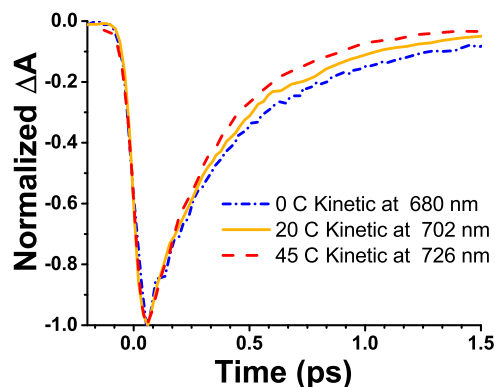

FIG. 5. Single wavelength TA kinetics for the photoexcited hydrated electron different bulk temperatures; the wavelengths were chosen to be at the same energy relative to the equilibrium absorption maximum at each temperature. The single wavelength kinetics show a clear trend, with the overall decay time decreasing with increasing temperature.

lifetime and/or ground-state cooling time(s), we globally fit the data at all three equilibrium temperatures to the extended kinetic model described in Sec. III B. We note that a second HGS cooling time was needed to fit the data at times ≥1 ps, but this slow cooling component has a small enough amplitude as to not affect the other fitting components, which are largely determined by the data prior to 1 ps. In our fits, the ≥1-ps HGS cooling component is strongly dependent on the bulk temperature, decreasing from ~3 ps at 0 °C to ~1 ps at 45 °C. The small ΔT amplitude associated with this long component (~20-50 K) is about what is expected for the temperature increase that an 800-nm photon would induce in the local solvent around a hydrated electron once the photon energy was statistically dissipated to the solvent.

In order to globally fit all the data in Fig. 1 to the model summarized in Eqs. (1)–(7), we made a few additional assumptions. First, based on the data in Fig. 3, we constrained the SE spectrum to have the same spectral width and same shift of its spectral maximum relative to the spectral maximum of the ground-state absorption at all three bulk temperatures. For our best fit, the SE spectral width was 448 ± 51 meV and the SE peak shift relative to the ground-state absorption maximum was 17 ± 3 meV. Second, when performing the fits to the early time data, we found that the HGS temperature jump (ΔT) was largely invariant across the different equilibrium temperatures. This is a result of the fact that the HGS spectrum initially appears in the near-IR (where it overlaps heavily with ESA), giving us little means to pull out fine differences in ΔT at different equilibrium temperatures. Thus, to reduce the number of parameters in our global fit, we constrained ΔT to a single value at all three equilibrium temperatures and we verified that small variations in this parameter did not significantly alter the fitted values for either the excited-stated lifetime or the HGS cooling rate. Similarly, we found that τ_2 was only weakly temperature dependent (depending roughly on $1/T$) so that we could get equally good fits by assuming a single parameter, τ_2/T, to describe the HGS cooling dynamics across all three bulk temperatures. Finally, we weighted the data as described in the supplementary material; moderate changes in our weighting procedure, however, produced a negligible effect on the outcome.

With these constraints, we were able to robustly fit the three-temperature TA dataset with the largest correlation parameter being less than 0.7, yielding a robust fit with clear assignment of a short p-state lifetime. The blue circles in Fig. 2 show the RMSE of our simultaneous fit of the data at all three temperatures, yielding a single well-defined and fairly narrow minimum. This is in stark contrast to the broad basin and multiple local minima obtained when using only a single dataset. The best fit parameters at the single global minimum to the three-temperature dataset are summarized in Table I. The most

striking result is that the p-state lifetime, τ_1, changes by a factor of slightly over two over our modest 0 to 45 °C temperature range. The fitted lifetime of 73 fs at the highest temperature, 45 °C, is comparable with our instrument response function, but the lifetimes at the two lower temperatures are cleanly resolved.

Our fitted room-temperature lifetime of 137 fs is significantly shorter than that reported in previous TA studies,[34–39,59] with the notable exception of the 50-fs estimate by Wiersma and co-workers.[40] It is worth noting that the 5 fs error bar reported in Table I for the room-temperature p-state lifetime is the standard error from the fitting procedure; our best estimates for a 95% confidence interval accounting for inherent errors and parameter correlations are closer to ±40 fs but are qualitative in nature due to the estimation of parameter correlation. Our fit unambiguously gives τ_1 excited-state lifetimes that are shorter than the τ_2 ground-state cooling times at each equilibrium temperature, strongly supporting the non-adiabatic relaxation mechanism; this is a direct result of including the SE component and simultaneously fitting the model to the data from all three equilibrium temperatures. In fact, our fitted room-temperature lifetime of 137 fs and cooling time of 401 fs are in very good agreement with the results of recent time-resolved photoelectron spectroscopy experiments, which determined a lifetime of ~100 fs (when non-Condon effects are accounted for)[29] and a cooling time of 410 fs.[45–47] Thus, the data and fitting presented here provide the first unification of the kinetics measured by TA and TRPES and give us confidence in both our kinetic model and the additional assumptions we made to fit it to the data.

Even more importantly, with the global fit in hand, we can now compare the experimental temperature dependence of the kinetic parameters to the simulation results from Paper I.[18] We reiterate that the simulations rely on a surface-hopping algorithm that does not give accurate absolute values of the excited-state lifetime but still should allow us to compare the temperature dependence of the lifetime between simulation and experiment. Our simulations showed that the traditional cavity model of the hydrated electron predicts very little change in structure and thus lifetime over the temperature range we have investigated (<10%), a result that is not consistent with the raw data in Fig. 5 let alone the global fit parameters. The non-cavity model of the hydrated electron, on the other hand, shows a significant change in structure with temperature, which in turn leads to a predicted change in lifetime of a factor of ~1.8 over the temperature range we have investigated, in excellent agreement with the data in Fig. 5 and the global fit parameters in Table I.

The other important parameter extracted from our global fit is the temperature jump associated with the hot ground state, ΔT, which we constrained to be the same at all three bulk temperatures. Although the value we extract for this parameter of 244 K may seem quite large, we argued in Paper I[18] that the nascent hot ground state hydrated electron is nowhere close to equilibrium so that the best equilibrium approximation to its spectrum requires a high temperature.[18] In fact, both the cavity and non-cavity hydrated electron simulations predict values for ΔT of a few hundred K, with the non-cavity model providing a better match to the experimentally determined

TABLE I. Global fit parameters of the data in Fig. 1 to Eqs. (1)–(7).

T_{eqb} (K)	τ_1 (fs)	τ_2 (fs)	ΔT (K)
273 ± 1	158 ± 9	430 ± 21	279 ± 10
293 ± 1	137 ± 5	401 ± 20	279 ± 10
318 ± 1	73 ± 6	369 ± 18	279 ± 10

parameter. Given that the hydrated electron's excited-state relaxation unambiguously follows the non-adiabatic picture,[29,45–47] a ΔT of only a few tens of K, like that reported previously,[35] does not make physical sense.

With the temperature-dependent lifetimes in hand, we can return to our crude model relating SE and fluorescence from the photoexcited hydrated electron to offer a prediction for the temperature dependence of the hydrated electron's fluorescence spectrum. Given that the *p*-state lifetime is significantly more *T*-dependent than both the Gaussian (which should vary as $\frac{1}{\sqrt{T}}$) and slower exponential portions of the Stokes shift, the parameters from our best-fit TA results predict that there should be significant changes in the electron's fluorescence spectrum as a function of temperature, as shown in Fig. 4(b). This crude model predicts that the fluorescence spectrum of the hydrated electron[68] to the red of 10 000 cm^{-1} should show a strong decrease in intensity with increasing bulk temperature. With these predictions in hand, it should be possible to verify the temperature dependence of the photoexcited hydrated electron's relaxation through a separate experimental avenue.

Finally, as mentioned above, previous workers have tried to estimate the excited-state lifetime of the photoexcited hydrated electron from scavenging experiments[58,67] but fits to the scavenging data rely on a model with highly correlated parameters: in this case, the excited-state lifetime and scavenging reaction rate. There is also the issue as to whether or not the hot ground state is scavenged at a rate more like that of the excited state or more like that of the equilibrium ground state; this is important since we know that the hot ground state persists for a time scale of at least ~400 fs.[38–41,45–47] In the supplementary material, we present results repeating this type of scavenging experiment at room temperature. We find that we can get equally good fits with numbers similar to the adiabatic picture reported in previous studies,[58,67] as well as with the ~137-fs lifetime we extracted from the TA data above, all with physically reasonable values of the reaction velocity. Thus, our conclusion is that model fits to a single dataset, whether it is transient absorption or scavenging, are insufficient to determine the excited-state lifetime of the hydrated electron, particularly since most such models have highly correlated parameters. The combination of datasets at multiple temperatures, in conjunction with the observation of stimulated emission, is what allows us to extract a unique lifetime from transient absorption that is in excellent agreement with the results of TRPES experiments.[29,45–47]

IV. CONCLUSION

In summary, we have performed a detailed set of transient absorption experiments on the photoexcited hydrated electron as a function of temperature. The data unambiguously show kinetics that decay more quickly at higher temperatures. Additionally, the data display an excess bleach component at early times due to stimulated emission that becomes smaller and decays more quickly as the bulk temperature is increased. We were able to construct a simple model showing that the SE component we observe by TA is consistent with the experimental fluorescence spectrum of the hydrated

electron observed in previous work.[68] By simultaneously fitting the TA data at all three temperatures with a model that explicitly includes stimulated emission, we were able to avoid the highly correlated parameters that led to multiple minima in previous models, allowing us to rigorously extract a set of lifetimes and ground-state cooling rates as a function of temperature. The results clearly indicate the excited-state lifetime at room temperature is ~137 fs, for the first time in decent agreement with the results of time-resolved photoelectron spectroscopy experiments.[45–51] Moreover, this lifetime changes by slightly over a factor of 2 over the relatively narrow temperature range of 0 to 45 °C. The change in lifetime with temperature stands in contrast to the predictions of the standard cavity picture of the hydrated electron but is in excellent agreement with the structural changes predicted by the non-cavity hydrated electron simulation model explored in Paper I.[18] Our TA data, in conjunction with our simple model, predict a significant decrease in the hydrated electron's fluorescence on the red side of the emission maximum with increasing temperature, a result that should also be testable by future experiments.

Overall, the results in this paper indicate that any model of the hydrated electron, be it cavity, non-cavity, or hybrid, must predict significant changes in the photoexcited electron's excited-state relaxation dynamics as a function of temperature. As seen in Paper I,[18] to date, only non-cavity models have been able to do this. We emphasize that our LGS non-cavity potential does slightly overestimate the temperature dependence of various ground-state properties of the hydrated electron, but this is clearly an improvement over the complete lack of temperature dependence in nearly every property predicted by traditional cavity models. Hybrid models of the hydrated electron, which predict a small central cavity but still have a significant overlap of the electron's wavefunction with the surrounding first-shell water molecules, may have a temperature dependence that falls between those of the cavity and non-cavity extremes and thus might possibly be in better agreement with experiment, but so far there have been no calculations of temperature-dependent ground-state properties for such models, let alone any calculations of excited-state non-adiabatic relaxation dynamics at even a single temperature. Given the results presented here, the non-cavity model currently offers the best prediction of the measured temperature dependence of the hydrated electron's excited-state lifetime. Thus, we urge future simulators of the hydrated electron to directly confront the experimental results presented here as part of building the most complete microscopic picture of this simple but elusive quantum solute.

SUPPLEMENTARY MATERIAL

See supplementary material for further details on the global fitting, scavenging experiments, and spontaneous and stimulated emission modeling procedures.

ACKNOWLEDGMENTS

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Erratum: "Temperature dependence of the hydrated electron's excited-state relaxation. II. Elucidating the relaxation mechanism through ultrafast transient absorption and stimulated emission spectroscopy" [J. Chem. Phys. 147, 074504 (2017)]

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Our original article[1] contained an error in Fig. 4 in which the experimental data (hollow points) were incorrectly plotted. This plotting error in Fig. 4 does not change any of the tabulated results, fits, or conclusions of the article. Note the better agreement between the experimental and modeled results in the corrected Fig. 1 as it appears below.
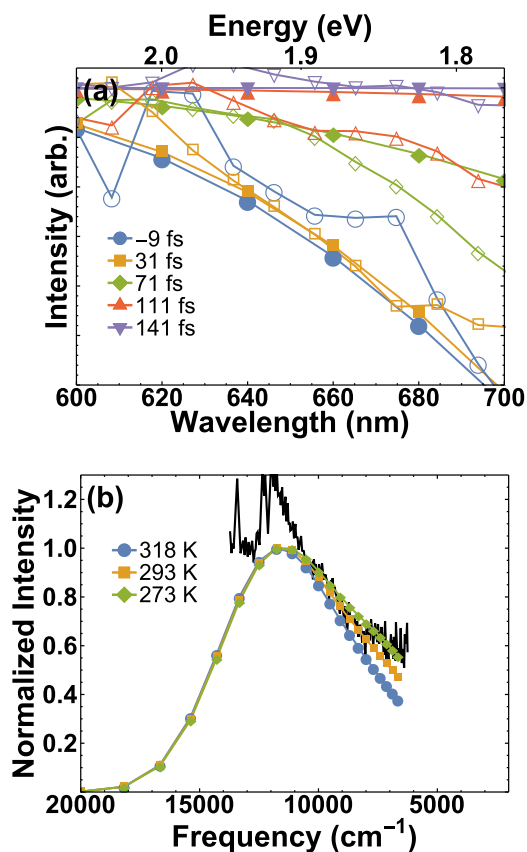

FIG. 1. Corrected Fig. 4 from the original article.

[1] E. P. Farr, C.-C. Zho, J. R. Challa, and B. J. Schwartz, J. Chem. Phys. **147**, 074504 (2017).

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