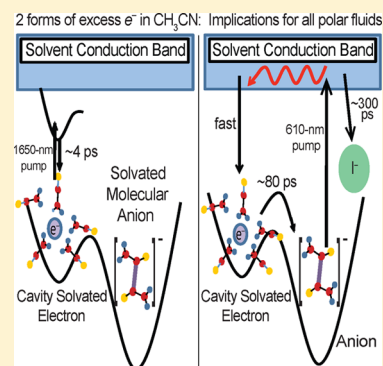


# Nature of Excess Electrons in Polar Fluids: Anion-Solvated Electron Equilibrium and Polarized Hole-Burning in Liquid Acetonitrile

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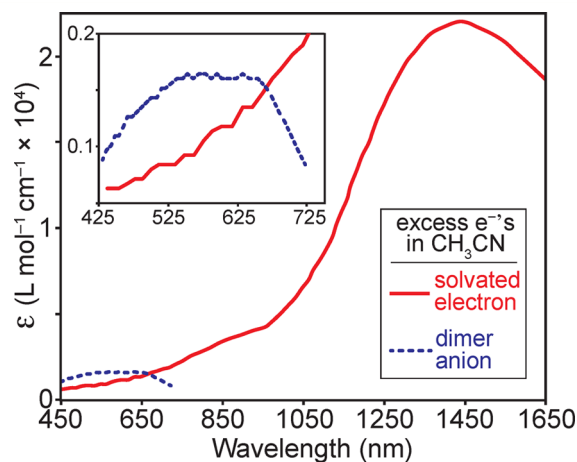
**ABSTRACT:** Unlike most polar liquids, excess electrons in liquid  $\text{CH}_3\text{CN}$  take on two distinct forms – solvated electrons ( $e_{\text{solv}}^-$ ) and solvated molecular anions – that are in equilibrium with each other. We find that excitation of  $e_{\text{solv}}^-$  leads to a short-lived excited state that has no effect on the equilibrium but that excitation of the molecular anion instantaneously leads to the production of new  $e_{\text{solv}}^-$ . We also find that  $e_{\text{solv}}^-$  produced by excitation of dimer anions relocate to places far enough from their original location to alter their recombination dynamics. Finally, we show using polarized transient hole-burning that  $e_{\text{solv}}^-$  in liquid  $\text{CH}_3\text{CN}$  have an inhomogeneously broadened spectrum, demonstrating that these electrons almost certainly reside in a cavity. Because there is no polarized hole-burning for  $e_{\text{solv}}^-$  in water or methanol, these results have important implications for the nature of excess electrons in all polar liquids.



**SECTION:** Liquids; Chemical and Dynamical Processes in Solution

What happens when an extra electron – one more than is needed to ensure electrical neutrality – is injected into a typical polar liquid? It is easy to imagine two possible fates for such an electron. One possibility is that the excess electron is ‘captured’ by one or more solvent molecules, producing a solvated molecular anion or multimer anion. Even though the solvent molecules in most liquids are closed-shell and will not bind an extra electron in isolation, extra electrons can bind to multiple solvent molecules, and in a liquid environment, the free energy of solvation makes it possible for solvated anions to be stable in solution. The second possibility is that excess electrons are expelled by the closed-shell solvent molecules, creating solvated electrons ( $e_{\text{solv}}^-$ ) that effectively reside between the solvent molecules. Understanding the detailed nature of how excess electrons behave in polar liquids is important because these species play a fundamental role in radiation chemistry and charge-transfer reactions.

Liquid acetonitrile ( $\text{CH}_3\text{CN}$ ), a polar solvent with a dielectric constant and solvation properties similar to those of methanol, provides one of the more interesting environments for excess electrons. Although straight  $\text{CH}_3\text{CN}$  molecules will not bind an excess electron, the electron affinity of acetonitrile increases as the molecule bends. The result is that an excess electron can form a covalent bond between the cyano carbons of two bent, antiparallel acetonitrile molecules to make a  $(\text{CH}_3\text{CN})_2^-$  molecular dimer anion.<sup>1,2</sup> Thus, when excess electrons are introduced into liquid  $\text{CH}_3\text{CN}$  (or become part of gas-phase  $(\text{CH}_3\text{CN})_n^-$  clusters,<sup>3,4</sup>) two species are formed, one which has a weak visible absorption spectrum (high binding energy in clusters) and the other which absorbs more intensely in the near-IR (and has a weak binding energy in clusters); the spectra of these species in liquid  $\text{CH}_3\text{CN}$  are shown in Figure 1. We<sup>5</sup> and others<sup>6,7</sup> have investigated the nature of these two

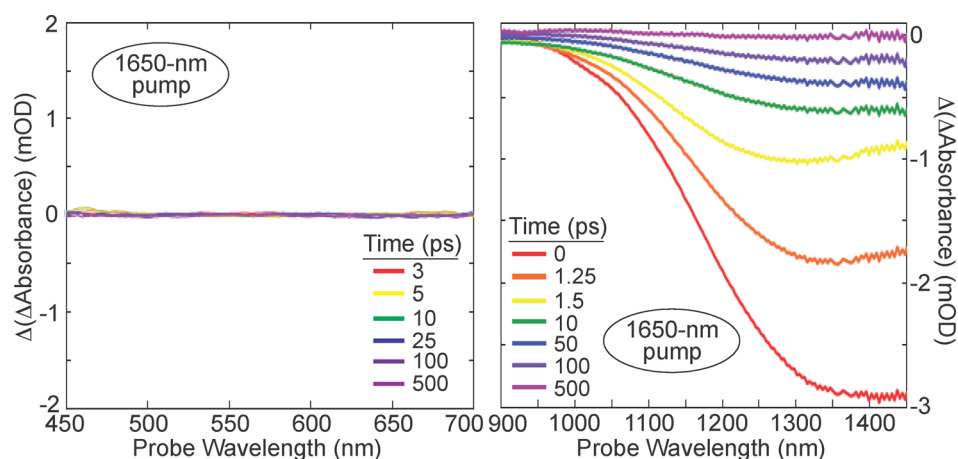


**Figure 1.** UV–visible absorption spectra of the two excess electron species in liquid  $\text{CH}_3\text{CN}$ , as measured in ref 5. The blue dashed curve shows the spectrum of the visible-absorbing species, assigned to the solvated dimer anion, and the red curve shows the spectrum of the IR-absorbing species, assigned to the solvated electron. The inset shows the visible portion of the spectra on an expanded scale with the same units as the main figure.

excess electron species in liquid acetonitrile using ultrafast spectroscopy and concluded that the visible absorption results from the solvated  $(\text{CH}_3\text{CN})_2^-$  molecular dimer anion and that the near-IR band arises from a solvated electron. These two excess electron species are in equilibrium with each other, with

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**Figure 2.** Results of three-pulse transient absorption experiments on excess electron species in liquid  $\text{CH}_3\text{CN}$ . Excess electrons were created via 266 nm CTTS excitation of  $\text{I}^-$  (cf. ref 5), and after a 1 ns equilibration period, the IR-absorbing species was excited at 1650 nm. The left panel shows the results of probing in the visible region of the spectrum as a function of time after the re-excitation pulse, and the right panel shows the results in the near-IR. On the basis of the magnitude of the bleach signal in the right panel and the known cross sections for the two species in Figure 1, our signal-to-noise ratio precludes the possibility of any changes in the population of the visible-absorbing species greater than  $\sim 5\%$ .

the solvated molecular dimer anion favored at room temperature by a factor of  $\sim 4$ .<sup>5</sup>

In this work, we examine how photoexcitation of the excess electron species in liquid  $\text{CH}_3\text{CN}$  perturbs the equilibrium between them. We find that photoexcitation of the IR-absorbing species does not measurably affect the visible-absorbing species and that the excited-state dynamics associated with IR excitation matches well with the behavior of  $e_{\text{solv}}^-$  seen in other polar solvents. In contrast, photoexcitation of the visible-absorbing dimer anion species leads to instantaneous production of more IR-absorbing solvated electrons, demonstrating a one-way photoconversion that results from the different nature of the local solvent environment around each species. We also find that the  $e_{\text{solv}}^-$  produced from photoconverted dimer anions appear a significant distance away from where the anions originally resided, indicating that such electrons can undergo photoinduced relocalization.<sup>8,9</sup> Finally, we show that the IR absorption band is inhomogeneously broadened, a feature that is unambiguously associated with the presence of a solvated electron that resides in a roughly spherical cavity between the solvent molecules.<sup>10</sup> All of this work has important implications not only for the nature of solvated electrons in liquid  $\text{CH}_3\text{CN}$  but also for the nature of  $e_{\text{solv}}^-$  in other solvents such as water and methanol.

In previous work, we<sup>5</sup> and others<sup>7</sup> found that excess electrons could be injected into liquid  $\text{CH}_3\text{CN}$  by excitation of the charge-transfer-to-solvent (CTTS) band of  $\text{I}^-$  in the near-UV. Immediately following excitation of  $\text{I}^-$  in liquid  $\text{CH}_3\text{CN}$ , there is a strong preference for the newly injected excess electrons to localize as  $e_{\text{solv}}^-$ . Subsequently, most of the solvated electrons convert into solvated molecular dimer anions, attaining equilibrium on an  $\sim 80$  ps time scale.<sup>5</sup> This observation indicates that even though solvated molecular anions are the favored species at equilibrium the natural solvent structure of liquid  $\text{CH}_3\text{CN}$  is more like that around a solvated electron, so that  $e_{\text{solv}}^-$  are kinetically favored when electrons are first introduced into the liquid. We also found that the excess electrons could diffusively recombine with the iodine atoms present in solution and that this recombination took place on a

hundreds-of-picoseconds time scale, depending on the I atom concentration.<sup>5</sup>

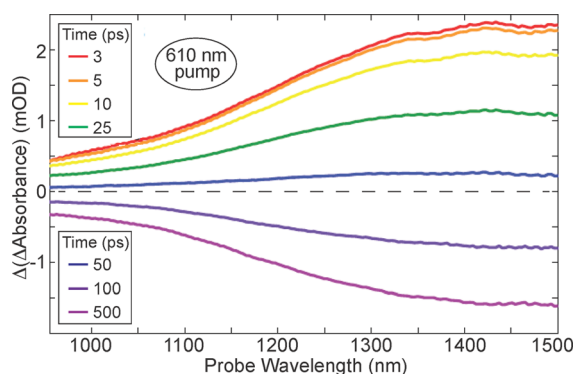
To understand how the equilibrium between solvated electrons and solvated molecular anions in liquid  $\text{CH}_3\text{CN}$  is perturbed when one of the two species is photoexcited, we used an experimental setup similar to that in our previous work,<sup>5</sup> except that three laser pulses were used instead of two. We dissolved 50 mM *t*-butylammonium iodide in dry liquid acetonitrile and then applied a first laser pulse at 266 nm to photoexcite the CTTS band of  $\text{I}^-$ , creating excess electrons. We then let the system age for a time of  $\sim 1$  ns to ensure that the equilibration between the two species and any subsequent recombination reactions were complete before applying a second laser pulse to the system that was tuned to excite either the IR-absorbing solvated electron or the visible-absorbing solvated dimer anion. We then applied a third, broadband pulse to the system after a variable time delay to measure the change in the absorption spectra of the two species. The details of our experimental apparatus and how we performed these three-pulse experiments are given elsewhere.<sup>11,12</sup>

The right panel of Figure 2 shows the results of an experiment in which the solvated electron in liquid  $\text{CH}_3\text{CN}$  was excited at 1650 nm, and the effect of this excitation was probed throughout the near-IR. It is clear that immediately following excitation of the solvated electron its IR absorption is reduced in intensity, or photobleached. It is well known that the excited-state absorption of  $e_{\text{solv}}^-$  in polar liquids occurs to the red of the ground-state absorption. For electrons in liquid  $\text{CH}_3\text{CN}$ , this excited-state absorption likely occurs beyond the red edge of our probe window, which extends only to  $\sim 1500$  nm because of the limitations of our detector, so that all we are able to see is the bleach of the ground-state absorption spectrum. This bleach recovers fully on a time scale of just a few picoseconds. This indicates that the excited state of the solvated electron is short-lived and that whatever process leads to de-excitation simply returns the solvated electron back to its original ground state.

The left panel of Figure 2 shows the results of the same experiment exciting the solvated electron in liquid  $\text{CH}_3\text{CN}$  at 1650 nm but probing in the visible to see the effects on the solvated dimer anion. The data show no observable effect:

photoexcitation of  $e_{\text{solv}}^-$  in liquid acetonitrile does not affect the  $(\text{CH}_3\text{CN})_2^-$  anions. Because we know the cross sections of the two species from our previous work<sup>5</sup> and we also know the number of  $e_{\text{solv}}^-$  we excited from the magnitude of the bleach seen in the right panel of Figure 2, we can conclude that for every solvated electron we excited there must be less than a  $\sim 5\%$  change in the number of solvated dimer anions or we would have been able to observe the change given the signal-to-noise ratio of our measurements. The fact that there is no observable change in the dimer anion population can be rationalized based on our previous work. We know that the time for ground-state solvated electrons to convert into solvated dimer anions is  $\sim 80$  ps and that the equilibrium between the two species favors the dimer anion by a factor of  $\sim 4$ .<sup>5</sup> A simple detailed balance argument thus implies that the rate at which ground-state solvated molecular anions can convert into solvated electrons must be  $\sim 320$  ps. Because the excited state of the solvated electron lasts for only a few picoseconds, there simply is not time for the solvated molecular anions to ‘notice’ the excitation, which recovers on a time scale that is fast compared with the interconversion rate: in other words, any photochemical reactions involving the dimer anion are slow enough that this species is effectively decoupled from the solvated electron.

Figure 3 shows the results of the reverse experiment, where we excite the solvated molecular anion in liquid  $\text{CH}_3\text{CN}$  at 610 nm



**Figure 3.** Results of three-pulse transient absorption experiments on excess electron species in liquid  $\text{CH}_3\text{CN}$ . Following the same preparation as in Figure 2, the visible-absorbing species was excited at 610 nm. Exciting the visible species initially creates more of the IR-absorbing species, but as time progresses, the net result of visible excitation is an overall reduction in the population of the IR-absorbing species.

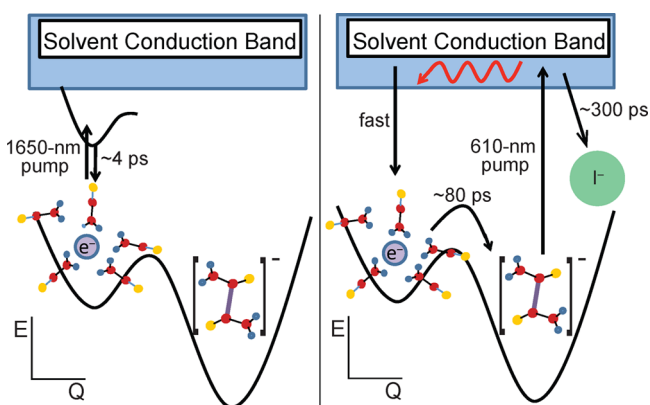
nm and probe the effects of this excitation on the solvated electron in the near-IR. Unlike the previous case, excitation of the molecular anion leads to a dramatic effect on the population of solvated electrons. We see that immediately ( $\leq 1$  ps) following excitation of the dimer anion there is an increased population of solvated electrons: there is a one-way photoconversion process that allows  $e_{\text{solv}}^-$  to be created from solvated dimer anions but not vice versa. Moreover, the excess electrons that are created from the solvated molecular anions start to disappear on a tens to hundreds of picosecond time scale. Even more interesting is that at long times we see that there are fewer  $e_{\text{solv}}^-$  present than before the excitation of the dimer anion, so that some of the original solvated electrons are also made to disappear by exciting the dimer anion.

How can we explain all of these observations? We argued in our previous work that the low absorption cross-section of the solvated  $(\text{CH}_3\text{CN})_2^-$  anion indicates that its absorption spectrum likely consists of bound-to-continuum transitions.<sup>5</sup> This would suggest that when this band is photoexcited the excess electron is placed into the conduction band of the liquid, in much the same way as if it had been injected by pulse radiolysis or by CTTS excitation of  $\text{I}^-$ . Because we also know that kinetics favors the production of  $e_{\text{solv}}^-$  from newly injected excess electrons, it is perhaps not surprising that there is a strong preference for the excited electrons from photoexcited dimer anions to relax back into the liquid as solvated electrons. This idea makes sense based on what we expect for the local solvent configurations that stabilize the two forms of excess electron in liquid acetonitrile. The solvated molecular dimer anion has two, bent antiparallel  $\text{CH}_3\text{CN}$  molecules covalently bound together by the excess electron. When this electron is photodetached, one of the  $\text{CH}_3\text{CN}$  molecules is known to dissociate via cyanide elimination, a process that likely takes place in at most a few hundreds of femtoseconds.<sup>6</sup> Once this process is complete, there is no way for the excited electron to return to reform the original dimer anion, so the kinetics proceeds as if the excited electron was injected freshly into the liquid.

Why do the  $e_{\text{solv}}^-$  that were created by photoexciting solvated dimer anions subsequently disappear, leading ultimately to a net reduction in the number of solvated electrons? We believe that are two processes that cause the decay of the newly created solvated electron population. The first process is simply the same re-equilibration that we observed in our previous work.<sup>5</sup> The act of photoexciting the dimer anion creates excess  $e_{\text{solv}}^-$  relative to what is present at equilibrium. Thus, most of the newly created  $e_{\text{solv}}^-$  should turn into solvated dimer anions on the same  $\sim 80$  ps interconversion time scale that we observed previously, and indeed, the initial decay of the excess solvated electron population seen in Figure 3 does occur on a roughly  $\sim 80$  ps time scale. Second, we believe that the  $e_{\text{solv}}^-$  created by photoexcitation of dimer anions can localize in places in the liquid far from their original location. We already argued above that the local molecular environment where the dimer anion was originally located is not a favorable place for the electron to return. This means that the newly excited excess electrons can explore a large range of solvent environments until they find one conducive to localizing as a solvated electron. Thus, the act of photoexciting the dimer anion not only changes the identity of the excess electrons but also *relocalizes* the position of the excess electron, as has been observed for excited solvated electrons in other solvents.<sup>8</sup> Therefore, even though all of the excess electrons in our experiment were initially located far from any iodine atoms (which we know because these  $e^-$  were the ones that did not recombine on subnanosecond time scales), the relocalized  $e_{\text{solv}}^-$  created by photoexciting the dimer anions can appear near enough to an I atom to undergo recombination on a  $\sim 300$  ps time scale in our 50 mM solution. When we increased the  $\text{I}^-$  concentration, we found that both the rate and yield of the observed decay increased, verifying that these dynamics indeed result from enhanced recombination.<sup>13</sup> Because this recombination changes the total number of excess electron species present, once re-equilibration is complete there are fewer total excess electrons – both dimer anions and solvated electrons – than there were before the photoexcitation. Thus, the  $e_{\text{solv}}^-$  created by photoconversion of dimer anions disappear due to both equilibration and



recombination, two processes that occur on similar enough time scales that they are difficult to separate. The way in which the photoconversion, equilibration, and recombination processes occur in this system is summarized in Figure 4.



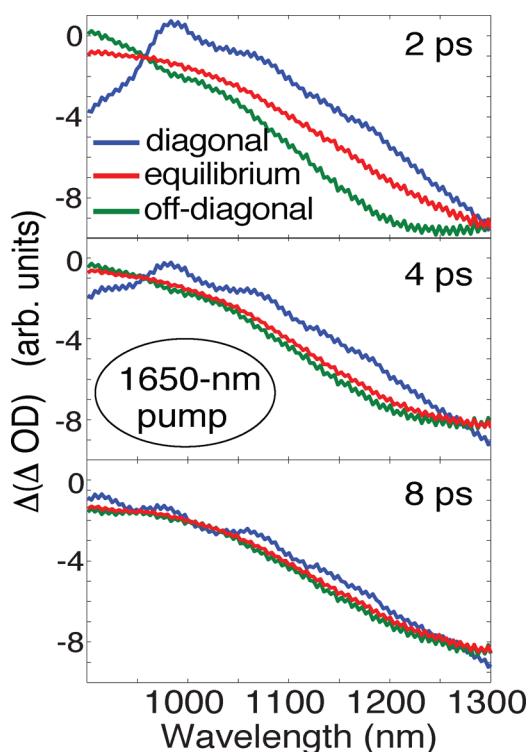
**Figure 4.** Schematic of the one-way photoconversion of the excess  $e^-$  species in liquid  $\text{CH}_3\text{CN}$ ; the  $x$  axis denotes the solvent motions ( $Q$ ) that interconvert the  $e^-_{\text{solv}}$  and  $(\text{CH}_3\text{CN})_2^-$  anion, and the  $y$  axis represents the free energy ( $E$ ). At 300 K, the dimer anion is favored at equilibrium by a factor of  $\sim 4$ , so it has lower free energy.<sup>5</sup> The left panel shows that 1650 nm excitation of the  $e^-_{\text{solv}}$  produces a localized excited  $e^-$  that relaxes in  $\sim 4$  ps to its original location; this relaxation is fast compared with the interconversion, so the excitation does not perturb the equilibrium between the two species (cf. Figure 2). The right panel shows that 610 nm excitation of the dimer anion likely promotes the  $e^-$  directly to the solvent conduction band, where it can relocalize as a  $e^-_{\text{solv}}$  in a different place in the liquid. The kinetically favored  $e^-_{\text{solv}}$  interconvert back to dimer anions on an  $\sim 80$  ps time scale. Some of the relocalized  $e^-$  recombine with I atoms, so the net result is that excitation reduces the total population of excess  $e^-$  species (cf. Figure 3).

Now that we have learned a great deal about the nature of the equilibrium solvent structures that define solvated electrons and solvated dimer anions, we next examine the precise nature of the  $e^-_{\text{solv}}$  in liquid  $\text{CH}_3\text{CN}$ . Most of the theoretical work examining  $e^-_{\text{solv}}$  in polar fluids has concluded that they reside in cavities. We recently performed calculations that challenged this viewpoint for the hydrated electron,<sup>14</sup> and the cavity or noncavity nature of the hydrated electron remains the subject of much debate.<sup>15–20</sup> One of the key features predicted by simulations in which  $e^-_{\text{solv}}$  reside in a cavity is that the absorption spectrum is inhomogeneously broadened.<sup>10</sup> This is because the zeroth-order picture of a cavity solvated electron is that of a particle in a quasi-spherical box, with an electronic structure that consists of an s-like ground state and three p-like excited states. If the cavity was a perfect sphere, then the three p-like excited states would be degenerate, but the fluctuations in a typical liquid environment cause the cavity in such simulations to be aspherical on average, leading to a splitting of the three excited states. Cavity simulations further predict that the three excited states only interchange roles when the long and short-axes of the cavity reorient, which occurs on a time scale of a few picoseconds, so that the width of single electronic transition is roughly half of the full width of the  $e^-_{\text{solv}}$  absorption spectrum.<sup>10</sup> For noncavity electrons, simulations suggest a homogeneously broadened absorption spectrum because small motions of the solvent molecules within the electron's wave function rapidly interchange the roles of the three excited states, so that each has a width that is comparable to the full absorption spectrum.<sup>14</sup>

Nearly 20 years ago, we proposed an experiment that could reveal the width of the electronic states underlying a solvated electron's spectrum, providing a way to distinguish between cavity and noncavity solvated electron models.<sup>10</sup> The idea was that the three excited states have transition dipoles oriented in orthogonal directions so that exciting with polarized light and probing with light of the same polarization leads to a bleach of the electronic transition that was excited but not of the other transitions with orthogonally oriented dipoles. In addition, probing with light of the perpendicular polarization leads to a bleach of the electronic transitions that were *not* originally excited and no bleach of the originally excited state. The details of precisely how this experiment works have been discussed elsewhere; what is typically done is to plot linear combinations of the parallel and perpendicular polarized spectra, known as the diagonal (effectively same-state probe) and off-diagonal (effectively other-state probe) spectra, to enhance the ability to pick out any polarization anisotropy in the measured pump-probe signals.<sup>21,22</sup> Simulations predict that there should be a clear polarized hole-burning signature for some cavity models of the hydrated electron,<sup>10</sup> but the prediction is less clear for other models.<sup>22–24</sup> Some initial experiments reported seeing polarized hole-burning with a signature that matched well with what was predicted,<sup>25</sup> but subsequent experiments found no polarized hole-burning and concluded that the absorption spectrum of the hydrated electron is indeed homogeneously broadened.<sup>11,26</sup> We note that  $e^-_{\text{solv}}$  in methanol also have a homogeneously broadened spectrum,<sup>11</sup> and that there are no experimental reports in the literature of polarized hole-burning observed for  $e^-_{\text{solv}}$  in any solvent.

Figure 5 shows the results of the polarized transient hole-burning experiment on  $e^-_{\text{solv}}$  in liquid acetonitrile following excitation on the red edge of their absorption spectrum at 1650 nm. It is clear that when probing the states to the blue of what we originally excited we see a definite polarized hole-burning effect: there is an enhanced bleach in the off-diagonal spectrum and a reduced bleach of the diagonal spectrum relative to the shape of the equilibrium ground-state spectrum. The anisotropy decays on a  $\sim 4$  ps time scale. This signature is *exactly* what is predicted by simulations for a cavity-bound solvated electron,<sup>10</sup> so we can conclude from these data that  $e^-_{\text{solv}}$  in liquid  $\text{CH}_3\text{CN}$  unambiguously occupy a cavity. This idea fits well with our arguments above that excitation of the solvated electron did not lead either to photoconversion into dimer anions or to enhanced recombination due to relocalization, because the ground-state electron occupies a cavity, photoexcitation produces an excited state that occupies the same cavity. The  $\sim 4$ -ps excited-state lifetime does not provide sufficient time for solvent molecules to fill in the cavity, so when the  $e^-$  returns to its ground state the most logical place for it to go is the pre-existing cavity from which it came. Thus, after a few picoseconds, excited  $e^-_{\text{solv}}$  in liquid acetonitrile relax to their original configurations, leading to no net change in the spectroscopy of this system.

This observation of polarized hole-burning for  $e^-_{\text{solv}}$  in liquid acetonitrile has important implications for the nature of solvated electrons in other solvents. The fact that polarized hole-burning is *not* observed for solvated electrons in water and methanol<sup>11</sup> strongly suggests that the nature of  $e^-_{\text{solv}}$  is different in different polar liquids. The polarity and solvation dynamics of liquid  $\text{CH}_3\text{CN}$  are quite similar to those of liquid methanol, yet the homogeneity of the electronic absorption spectrum of  $e^-_{\text{solv}}$  in these two solvents is undoubtedly different, suggesting



**Figure 5.** Polarized transient hole-burning of  $e_{\text{solv}}^-$  in liquid  $\text{CH}_3\text{CN}$ . Following the same preparation as in Figures 2 and 3,  $e_{\text{solv}}^-$  were excited with polarized light at 1650 nm and probed throughout the near-IR with light polarized both parallel and perpendicular to the excitation light. Following the work in refs 11, 21, and 22, we combined the measured parallel and perpendicular transient spectra to produce the diagonal (blue curves) and off-diagonal (green curves) spectra at each time. The fact excitation on the red side of the absorption band (cf. Figure 1) leads to an enhanced off-diagonal bleach, and weaker diagonal bleach relative to the equilibrium spectrum (red curves) at bluer wavelengths is an inhomogeneously broadened spectral signature that has been predicted by simulation for  $e_{\text{solv}}^-$  that occupy a cavity.<sup>10</sup>

that the nature of the solvated electrons themselves is also different. We believe that it is entirely possible that solvated electrons may occupy cavities in some solvents but not in others or possibly live in an equilibrium between cavity and noncavity states with an equilibrium constant that depends sensitively on the nature of the solvent. In particular, H-bonding solvents may prefer noncavity motifs because the entropic cost of breaking up the H-bond network to form a cavity is simply too high, explaining why the nature of  $e_{\text{solv}}^-$  in  $\text{CH}_3\text{CN}$  and methanol are so different even though the two solvents have similar macroscopic properties. Thus, there is no single universal picture that describes excess electrons in polar liquids.<sup>20</sup> Excess electrons may be attached to specific molecules in some solvents and reside between molecules in other solvents, or, as in the case of liquid acetonitrile, do both at the same time in equilibrium.

In summary, we have examined the equilibrium between solvated dimer anions and  $e_{\text{solv}}^-$  in liquid acetonitrile. We have found that photoexcitation of dimer anions produces solvated electrons but not vice versa, indicating that there is a one-way photoconversion process that connects these two excess electron species. In addition to photoconversion, photoexcitation of dimer anions leads to relocalization, moving the excess electron far enough to allow for recombination to take place in under a few hundred picoseconds even though

diffusion from the original location would not have led to recombination on a nanosecond time scale. We were able to rationalize all of these observations by considering the details of the local solvent environment around each species, as summarized in Figure 4. Finally, we showed that the solvated electron in liquid  $\text{CH}_3\text{CN}$  exhibits polarized hole-burning, a signature that definitively shows that these electrons reside in a cavity. The fact that such signatures are not observed for  $e_{\text{solv}}^-$  in other solvents provides a strong indicator that the nature of solvated electrons in different solvents may be different, including between polar liquids with similar dielectric properties and solvation dynamics.

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### Notes

The authors declare no competing financial interest.

## REFERENCES

- (1) Takayanagi, T.; Hoshino, T.; Takahashi, K. Electronic Structure Calculations of Acetonitrile Cluster Anions: Stabilization Mechanism of Molecular Radical Anions by Solvation. *Chem. Phys.* **2006**, *324*, 679–688.
- (2) Timerghazin, Q. K.; Peslherbe, G. H. Electronic Structure of the Acetonitrile and Acetonitrile Dimer Anions: A Topological Investigation. *J. Phys. Chem. B* **2008**, *112*, 520–528.
- (3) Mitsui, M.; Ando, N.; Kokubo, S.; Nakajima, A.; Kaya, K. Coexistence of Solvated Electrons and Solvent Valence Anions in Negatively Charged Acetonitrile Clusters,  $(\text{CH}_3\text{CN})_n^-$  ( $n = 10\text{--}100$ ). *Phys. Rev. Lett.* **2003**, *91*, 153002.
- (4) Young, R. M.; Griffin, G. B.; Kammrath, A.; Ehrler, O. T.; Neumark, D. M. Time-resolved Dynamics in Acetonitrile Cluster Anions  $(\text{CH}_3\text{CN})_n^-$ . *Chem. Phys. Lett.* **2010**, *485*, 59–63.
- (5) Doan, S. C.; Schwartz, B. J. Ultrafast Studies of Excess Electrons in Liquid Acetonitrile: Revisiting the Solvated Electron/Dimer Anion Equilibrium. *J. Phys. Chem. B* **2013**, DOI: 10.1021/jp303591h.
- (6) Shkrob, I. A.; Sauer, M. C., Jr. Electron Localization in Liquid Acetonitrile. *J. Phys. Chem. A* **2002**, *106*, 9120–9131.
- (7) Xia, C.; Peon, J.; Kohler, B. Femtosecond Electron Ejection in Liquid Acetonitrile: Evidence for Cavity Electrons and Solvent Anions. *J. Chem. Phys.* **2002**, *117*, 8855–8866.
- (8) Martini, I. B.; Barthel, E. R.; Schwartz, B. J. Optical Control of the Electron During Electron Transfer. *Science* **2001**, *293*, 462–465.
- (9) Bedard-Hearn, M. J.; Larsen, R. E.; Schwartz, B. J. Moving Solvated Electrons with Light: Nonadiabatic Mixed Quantum/Classical Molecular Dynamics Simulations of the Relocalization of Photoexcited Solvated Electrons in Tetrahydrofuran (THF). *J. Chem. Phys.* **2006**, *125*, 194509.
- (10) Schwartz, B. J.; Rossky, P. J. Hydrated Electrons as a Probe of Local Anisotropy: Simulations of Ultrafast Polarization-Dependent Spectral Hole Burning. *Phys. Rev. Lett.* **1994**, *72*, 3282–3285.
- (11) Cavanagh, M. C.; Martini, I. B.; Schwartz, B. J. Revisiting the Pump-probe Polarized Transient Hole-burning of the Hydrated Electron: Is its Absorption Spectrum Inhomogeneously Broadened? *Chem. Phys. Lett.* **2004**, *396*, 359–366.
- (12) Bragg, A. E.; Glover, W. J.; Schwartz, B. J. Watching the Solvation of Atoms in Liquids One Solvent Molecule at a Time. *Phys. Rev. Lett.* **2010**, *104*, 233005.
- (13) Doan, S. C. Ultrafast Broadband Spectral Studies of Electron Motion in Condensed-Phase Molecular Systems. Ph.D. Thesis, UCLA, Los Angeles, CA, 2011.
- (14) Larsen, R. E.; Glover, W. J.; Schwartz, B. J. Does the Hydrated Electron Occupy a Cavity? *Science* **2010**, *329*, 65–69.
- (15) Turi, L.; Madarsz, A. Comment on ‘Does the Hydrated Electron Occupy a Cavity?’. *Science* **2011**, *331*, 1387–c.

(16) Jacobsen, L. D.; Herbert, J. M. Comment on 'Does the Hydrated Electron Occupy a Cavity?'. *Science* **2011**, *331*, 1387–d.

(17) Larsen, R. E.; Glover, W. J.; Schwartz, B. J. Response to Comments on 'Does the Hydrated Electron Occupy a Cavity?'. *Science* **2011**, *331*, 1387–e.

(18) Herbert, J. M.; Jacobsen, L. D. Structure of the Aqueous Electron: Assessment of One-Electron Pseudopotential Models in Comparison to Experimental Data and Time-Dependent Density Functional Theory. *J. Phys. Chem. A* **2011**, *115*, 14470–14483.

(19) Casey, J. R.; Larsen, R. E.; Schwartz, B. J. Resonance Raman and Temperature-dependent Electronic Absorption Spectra of Cavity and Noncavity Models of the Hydrated Electron. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 2712–2717.

(20) Uhlig, F.; Marsalek, O.; Jungwirth, P. Unraveling the Complex Nature of the Hydrated Electron. *J. Phys. Chem. Lett.* **2012**, *3*, 3071–3075.

(21) Yu, J.; Berg, M. Local Anisotropy and Structural and Phonon Dynamics of Permanganate ( $\text{MnO}_4^-$ ) in Glassy and Liquid Lithium Chloride Hexahydrate by Ultrafast Transient Hole Burning. *J. Phys. Chem.* **1993**, *97*, 1758–1764.

(22) Shkrob, I. A. Pump-probe Polarized Transient Hole-Burning (PTHB) Dynamics of the Hydrated Electron Revisited. *Chem. Phys. Lett.* **2008**, *467*, 84–87.

(23) Bratos, S.; Leicknam, J.-C. Pump-probe Absorption Anisotropy of the Hydrated Electron. A Theory. *Chem. Phys. Lett.* **1998**, *291*, 496–500.

(24) Jacobson, L. D.; Herbert, J. M. A One-electron Model for the Aqueous Electron that Includes Many-Body Electron-Water Polarization: Bulk Equilibrium Structure, Vertical Electron Binding Energy, and Optical Absorption Spectrum. *J. Chem. Phys.* **2010**, *133*, 154506.

(25) Reid, P. J.; Silva, C.; Walhout, P. K.; Barbara, P. F. Femtosecond Absorption Anisotropy of the Aqueous Solvated Electron. *Chem. Phys. Lett.* **1994**, *228*, 658–664.

(26) Baltuska, A.; Emde, M. F.; Pshenichnikov, M. S.; Wiersma, D. A. Early-Time Dynamics of the Photoexcited Hydrated Electron. *J. Phys. Chem. A* **1999**, *103*, 10065–10082.