

**SUPPLEMENTARY INFORMATION** to accompany Barthel, Martini, Keszei and Schwartz, “Solvent Effects on the Ultrafast Dynamics and Spectroscopy of the Charge-Transfer-to-Solvent (CTTS) Reaction of Sodide,” *J. Chem. Phys.*

## I. Details of DE+S Model and Fitting

In order to model the ultrafast transients presented in Figures 3–5, we need to account for the fact that electrons photodetached via CTTS excitation of  $\text{Na}^-$  can exist in immediate contact pairs, solvent-separated contact pairs, or as free solvated electrons.<sup>1</sup> We have argued previously<sup>1,2</sup> that the recombination of solvent-separated contact pairs (and of free solvated electrons with free solvated sodium atoms) takes place on time scales comparable to or longer than tens of picoseconds. Therefore, to describe the dynamics during the first  $\sim 10$  ps, it is sufficient to consider only the kinetics of detachment and the fate of immediate contact pairs, represented by Eqs. 1-6 in the main text. Since the recombination dynamics of solvent-separated pairs and free electrons with free sodium atoms (main text Eqs. 3 and 4) are indistinguishable on the  $\sim 10$  ps timescale, we can replace the branching fractions  $q$  and  $r$  with their sum,  $q' = q + r$ . In other words, the only recombination events in the first ten picoseconds occur from immediate contact pairs, and we can simply group the rest of the solvated electron/sodium containing species as a fraction  $q'$  of “non-recombining” electrons. If this approximation is made, the resulting first-order coupled kinetic differential equations can be easily solved, giving the following result for the modeled signal,  $\Delta OD(t)$ :

$$\Delta OD(t) = \varepsilon_{\text{Na}^-} [\text{Na}^-]_t + \varepsilon_{\text{Na}^{-*}} [\text{Na}^{-*}]_t + (\varepsilon_{\text{Na}^0} + \varepsilon_{e^- \text{ solvated}}) ([\text{Na}^0 \bullet e^- \text{ solvated}]_{\text{im},t} + [\text{Na}^0 \bullet e^- \text{ solvated}]_{\text{sep},t}) \quad [\text{S1}]$$

with

$$[Na^-]_t = -N_0 + N_0 p \frac{k_1 k_2}{k_2 - k_1} \left( \frac{1}{k_2} (e^{-k_2 t} - 1) + \frac{1}{k_1} (1 - e^{-k_1 t}) \right) \quad [S2]$$

$$[Na^{*-}]_t = N_0 e^{-k_1 t} \quad [S3]$$

$$[Na^0 \bullet e^-_{solvated}]_{im,t} = N_0 p \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad [S4]$$

$$[Na^0 \bullet e^-_{solvated}]_{sep,t} = N_0 (1 - p) (1 - e^{-k_1 t}) \quad [S5]$$

where  $q'$ , the fraction of electrons that do not recombine within 10 ps, is just  $1 - p$ , and  $k_i$  is  $1/\tau_i$  (as used in the main text). Due to dynamic solvation, the molar extinction coefficient of the sodium atom is time dependent:  $\epsilon_{Na^0} = \epsilon_{Na^0}(t)$ . The time evolution of this absorption cross section depends on the band shape of the spectrum at time  $t$ , the initial width and height of the spectrum, and the final shape of the spectrum. We choose to represent the  $Na^0$  spectrum as a standard Gaussian-Lorentzian (G-L) line shape,<sup>3,4</sup> with the Lorentzian line shape on the blue side of the maximum, and the Gaussian line shape on the red side. At all times, the absorption cross section of the spectrally shifting  $Na^0$ ,  $\epsilon_{Na^0}(\omega, t)$ , is given by:

$$\begin{aligned} \epsilon_{Na^0}(\omega, t) &= \frac{A_0(t)}{1 + \left( \frac{\omega - \omega_0(t)}{\gamma(t)} \right)^2}, & \omega \geq \omega_0(t); \\ \epsilon_{Na^0}(\omega, t) &= A_0(t) \exp \left[ - \left( \frac{\omega - \omega_0(t)}{\sigma(t)} \right)^2 \right] & \omega < \omega_0(t) \end{aligned} \quad [S6]$$

where  $A_0(t)$  is the maximum absorbance value at time  $t$ ,  $\omega_0(t)$  is the spectral position of the absorption maximum at time  $t$ ,  $\omega$  is the frequency of light at which the absorption cross section is evaluated, and  $\gamma(t)$  and  $\sigma(t)$  are the time-dependent Lorentzian and Gaussian widths, respectively. The amplitude and half-widths of the G-L line shape evolve from their  $t = 0$  values to the experimentally constrained  $t = \infty$  spectrum.<sup>4</sup> In the DE+S model, we choose a phenomenological

spectral evolution that follows simple exponential behavior, with a single time  $t_1$  for evolution of both the center frequency and band width:

$$\omega_0(t) = \omega_0 - (1 - e^{-t/t_1})(\omega_0 - \omega_\infty) \quad [\text{S7}]$$

$$\gamma(t) = \gamma_0 - (1 - e^{-t/t_1})(\gamma_0 - \gamma_\infty) \quad [\text{S8}]$$

$$\sigma(t) = \sigma_0 - (1 - e^{-t/t_1})(\sigma_0 - \sigma_\infty) \quad [\text{S9}]$$

In addition to the center frequency and width of the spectrum, we also allow the integrated area (oscillator strength) of the spectrum to change with a second time constant. Defining  $F(t)$  as the area under the G-L line shape, we choose:

$$F(t) = F_0 - (1 - e^{-t/t_2})(F_0 - F_\infty) \quad [\text{S10}]$$

Once the total area and half-widths of the line shape are specified at a given time, the amplitude (maximum absorbance at  $\omega_0(t)$  at time  $t$ ) is determined. We found it convenient to define the fractional areas under each side of the composite line shape:

$$f_L(t) = \frac{1}{1 + \frac{\sigma(t)}{\sqrt{\pi}\gamma(t)}}; \quad [\text{S11}]$$

$$f_G(t) = 1 - f_L(t)$$

The spectral amplitude  $A_0$  as a function of time is then given by:

$$A_0(t) = \frac{f_L(t)F(t)}{\pi\gamma(t)} \quad [\text{S12}]$$

At first it may seem unphysical to let the oscillator strength of the  $\text{Na}^0$  absorption band increase with time, but this variation was necessary in order to best fit the data. We believe that this variation may be an artifact of the phenomenological way we treat the  $\text{Na}^0$  absorption band. The Thomas-Reiche-Kuhn sum rule requires that the total oscillator strength for all transitions from

the ground state of the sodium atom (including transitions to the continuum) be conserved.<sup>5</sup> The Gaussian-Lorentzian line shape we employ, however, is intended to model only the transitions from the ground to the first few singlet excited states (possibly the solvatochromically shifted remnants of the gas-phase Na D line). It is quite likely, however, that a significant amount of the oscillator strength available to solvated  $\text{Na}^0$  comes from higher-lying electronic states that are not taken into account by our empirical single-band line shape. If this is the case, then the oscillator strength of the hot species in the visible region of the spectrum could be considerably less than that at equilibrium, as solvent dynamics bring additional electronic states into the spectral window under consideration.<sup>6</sup> For each of the equations S6-S12, the  $t = \infty$  values of each parameter are known experimentally,<sup>4</sup> and are tabulated in Table S1. With these relations in hand, the data were fit to Eq. S1 numerically convoluted with a Gaussian instrument response function. A Marquardt fitting procedure minimizing the sum of the squared residuals was employed to get the best fit.<sup>7</sup> The estimated parameters describing the solvation dynamics of  $\text{Na}^0$  in each solvent are summarized in Table S2.

We reiterate that in our picture, it takes  $\sim 700$  fs in THF for the CTTS excited state ( $\text{Na}^{-*}$ ) to decay into the "hot" sodium atom ( $\text{Na}_{\text{HOT}}^0$ ), and only after CTTS detachment does dynamic solvation of the neutral occur. Attempts to model the dynamics as only a hot sodium atom shifting to the red (i.e. without a separate  $\text{Na}^{-*}$  state) lead to poor agreement of the fits with the physical data; we referred to this type of picture as the "solvation model" in reference 1. We also point out that if the interpretation of Ruhman's group<sup>8</sup> is correct and the (first) electron detaches within 200 fs, the only way to explain the subsequent rise of the data in the IR (probe wavelengths between 1200 and 1500 nm) is via the ejection of the second electron from the  $\text{Na}^0$ , which is difficult to reconcile with the fast  $\sim 1$  ps recombination and the results of three-pulse

experiments in which a femtosecond laser pulse is used to force the detached electrons to recombine and regenerate the parent  $\text{Na}^-$ .<sup>9</sup>

## II. Addition of Polarized Hole-Burning to the DE+S Model:

One of the most striking features in the transient spectroscopy of  $\text{Na}^-$  observed by Ruhman and co-workers<sup>8</sup> (as well as by us in Figure 9 of the main text) is the strong polarization dependence in the bleach. As described in the main text, our working picture of the electronic structure of the  $\text{Na}^-$  CTTS band is that it consists of an inhomogeneous superposition of three  $s \rightarrow p$ -like transitions, which would normally be degenerate but whose energies are split by the locally asymmetric (instantaneous) environment of the solvent: this picture is very similar to that used in previous hole-burning studies of the permanganate ion<sup>10</sup> as well as the hydrated electron.<sup>11,12</sup> The basic idea behind anisotropic spectral diffusion is that excitation on one edge of the band excites only a subset of states whose asymmetry lies along the polarization of the laser; the entire band is not bleached uniformly until solvent dynamics causes all memory of the initial asymmetry to be lost. At early times, this leads to the appearance of an “excess bleach” when probing within the same sub-band and using the same polarization as the excitation light. This excess bleach then decays as solvent fluctuations spread the excitation deficit out over the entire ground state absorption profile. In this section, we describe the details of how the DE+S model can be modified to account for this type of anisotropic spectral diffusion.

We start by defining a laboratory coordinate frame wherein the pump and probe light propagate along the  $z$ -axis; the pump beam is linearly polarized along the  $x$ -direction, and the probe beam can be linearly polarized in either the  $x$  or  $y$  direction. For simplicity, we assume first that our system has only three distinct types of absorbers, as depicted schematically in Figure S1: those with their lowest-energy ( $\epsilon_1$ ) transition dipoles oriented exactly along the  $x$ ,  $y$ ,

or  $z$  axes, respectively (later, we will recover the limit of an isotropic distribution of transition dipoles by taking the appropriate orientational averages.) Statistically, we would expect that  $1/3$  of the total ensemble of molecules should have their lowest-energy transition dipoles oriented along any particular spatial axis (i.e.,  $N_1 = N_2 = N_3$ ). Moreover, since the three quasi-degenerate excited states are eigenstates of the same Hamiltonian, they must be orthogonal to each other and thus have orthogonal transition dipoles to the ground state. Thus, for the subset of molecules with the lowest-energy transition dipole moments along a particular axis, the other two transition dipole moments ( $\epsilon_2$  and  $\epsilon_3$ , which by definition occur at higher energies than the transition for  $\epsilon_1$ ) lie with equal probability along either of the remaining two axes.

For the ensemble of absorbers that can be excited at energy  $\epsilon_1$ , one-third of them will absorb  $x$ -polarized pump light (that is, a pump pulse with energy profile  $\delta(\epsilon - \epsilon_1)$ ), while the remaining absorbers will not be excited because their transition dipoles have zero overlap with the linear  $x$  polarization of the pump beam. The probe pulse then observes the deficit in the sample's absorption due to the fact that a subset of the ensemble has been excited and no longer absorbs. First, we consider the case where the probe is exactly resonant with one of the energy levels, that is, the probe energy can be  $\delta(\epsilon - \epsilon_1)$ ,  $\delta(\epsilon - \epsilon_2)$ ,  $\delta(\epsilon - \epsilon_3)$ , or  $\delta(\epsilon - \epsilon_4)$ . It has been shown for a triply degenerate excited state that is split into non-degenerate states by solvent asymmetry that the orientationally averaged dipole matrix element contributions to the anisotropic bleaching of the ground state can be categorized into diagonal and off-diagonal contributions.<sup>10</sup> The diagonal contribution is that in which the probe beam measures only the absorption deficit of absorbers whose transition dipoles were initially along the direction of the pump polarization, while the off-diagonal contribution results from those molecules whose

transition dipoles were initially orthogonal to the polarization of the pump. Under these conditions at  $t = 0$ , the observed signals will be as follows:

### 1. Diagonal

At  $\varepsilon_1$ : Transient bleach or depletion of strength  $-N_1$ ; the probe sees fewer absorbers after the pump because they have been excited;

At  $\varepsilon_2$  or  $\varepsilon_3$ : No signal – we have selectively excited only those molecules whose lowest energy absorption is along  $x$ ; by definition these higher-energy absorptions must lie in orthogonal directions.

At  $\varepsilon_4$ : bleach signal of relative strength  $-N_1$ ; the same absorbers that absorbed at  $\varepsilon_1$  also absorb at energy  $\varepsilon_4$  because absorption to the continuum is unpolarized.

### 2. Off-diagonal

At  $\varepsilon_1$ : No signal; by construction, the probe interrogates those molecules whose transition dipoles were along orthogonal directions to those excited by the pump;

At  $\varepsilon_2$  or  $\varepsilon_3$ :  $-1/2 N_1$ ; of the molecules that were excited,  $1/2$  will have their  $\varepsilon_2$  and  $\varepsilon_3$  transition dipoles along the direction of the laser propagation ( $z$  axis), and the probe will observe the absorption deficit of the remaining  $1/2$ .

At  $\varepsilon_4$ :  $-N_1$ , for the same reasons as for the diagonal case.

As  $t \rightarrow \infty$ , the fact that the solvent has scrambled all the local environments should asymptotically produce a uniform bleach of  $-1/3 N_1$  for both diagonal and off-diagonal populations and at all possible energies. We define  $s_{diag}(\varepsilon_i : \varepsilon_j)$  as the diagonal signal observed probing at  $\varepsilon_i$  after pumping at  $\varepsilon_j$ , and  $s_{off-diag}(\varepsilon_i : \varepsilon_j)$  for the corresponding off-diagonal signal. If we assume that the relaxation to equilibrium follows single exponential kinetics with time constant  $\tau$ , we have:

$$s_{diag}(\varepsilon_1 : \varepsilon_1) = -N_1 + \frac{2}{3}N_1(1 - e^{-t/\tau}) \quad [\text{S13}]$$

$$s_{diag}(\varepsilon_2 : \varepsilon_1) = s_{diag}(\varepsilon_3 : \varepsilon_1) = -\frac{1}{3}N_1(1 - e^{-t/\tau}) \quad [\text{S14}]$$

$$s_{off-diag}(\varepsilon_1 : \varepsilon_1) = -\frac{1}{3}N_1(1 - e^{-t/\tau}) \quad [\text{S15}]$$

$$s_{off-diag}(\varepsilon_2 : \varepsilon_1) = s_{off-diag}(\varepsilon_3 : \varepsilon_1) = -\frac{1}{2}N_1 + \frac{1}{6}N_1(1 - e^{-t/\tau}) \quad [\text{S16}]$$

$$s_{diag}(\varepsilon_4 : \varepsilon_1) = s_{off-diag}(\varepsilon_4 : \varepsilon_1) = -N_1 \quad [\text{S17}]$$

Next, we consider the case of pumping at  $\varepsilon_1$  but probing at some arbitrary energy  $\varepsilon'$ . We argued in the main text that the sodide ground state absorption band is well-described by a sum of four Gaussian subbands, representing the three polarized  $p$ -like excited states and a single unpolarized continuum band. If we use  $S_i(\varepsilon')$  as the absorption cross section of the  $i^{\text{th}}$  band at  $\varepsilon'$  (that is,  $S_i(\varepsilon') = a_i \exp[-(\varepsilon' - \varepsilon_i)^2 / \sigma_i^2]$ ), then the diagonal signal probed at  $\varepsilon'$  is:

$$s_{diag}(\varepsilon' : \varepsilon_1) = S_1(\varepsilon')s_{diag}(\varepsilon_1 : \varepsilon_1) + S_2(\varepsilon')s_{diag}(\varepsilon_2 : \varepsilon_1) + S_3(\varepsilon')s_{diag}(\varepsilon_3 : \varepsilon_1) + S_4(\varepsilon')s_{diag}(\varepsilon_4 : \varepsilon_1) \quad [\text{S18}]$$

which, given Eqs. S13-S17 above, reduces to:

$$s_{diag}(\varepsilon' : \varepsilon_1) = -N_1[S_1(\varepsilon') + S_4(\varepsilon')] + \frac{1}{3}N_1(1 - e^{-t/\tau})[2S_1(\varepsilon') - S_2(\varepsilon') - S_3(\varepsilon')] \quad [\text{S19}]$$

The expression for the off-diagonal signal is formally the same except for the subscripts, and reduces to:

$$s_{off-diag}(\varepsilon' : \varepsilon_1) = -N_1[\frac{1}{2}S_2(\varepsilon') + \frac{1}{2}S_3(\varepsilon') + S_4(\varepsilon')] + N_1(1 - e^{-t/\tau})[-\frac{1}{3}S_1(\varepsilon') + \frac{1}{6}S_2(\varepsilon') + \frac{1}{6}S_3(\varepsilon')] \quad [\text{S20}]$$

The expressions for excitation at either  $\varepsilon_2$  or  $\varepsilon_3$  are obtained by cyclic permutation of the subscripts on those functions  $S$  that do not have  $\varepsilon_4$ . We also note that:

$$s_{diag}(\epsilon' : \epsilon_4) = s_{off-diag}(\epsilon' : \epsilon_4) = -N_1 S_4(\epsilon') \quad [S21]$$

that is, pumping with a pulse of energy distribution  $\delta(\epsilon - \epsilon_4)$  depletes all the ground state absorbers equally because their absorption to the continuum states is unpolarized.

If we now excite at an arbitrary energy  $\epsilon''$  and probe at our arbitrary energy  $\epsilon'$ , the composite signal, within an overall normalization factor, becomes:

$$\mathbf{S}_{diag}(\epsilon' : \epsilon'') = S_1(\epsilon'') s_{diag}(\epsilon' : \epsilon_1) + S_2(\epsilon'') s_{diag}(\epsilon' : \epsilon_2) + S_3(\epsilon'') s_{diag}(\epsilon' : \epsilon_3) + S_4(\epsilon'') s_{diag}(\epsilon' : \epsilon_4) \quad [S22]$$

and similarly for the off-diagonal case. More compactly,

$$\mathbf{S}_{diag/off-diag}(\epsilon' : \epsilon'') = \sum_{i=1}^4 S_i(\epsilon'') s_{diag/off-diag}(\epsilon' : \epsilon_i) \quad [S23]$$

Finally, we need to consider the fact that the real system is not composed of perfectly aligned absorbers. If there is an isotropic distribution of absorbers, then polarized excitation selects a cosine-squared distributed subset of them. Some members of this cosine-squared sub-ensemble will have their low-energy transition dipoles oriented with significant components in directions orthogonal to the original laser polarization, so that the parallel polarized signal is not identical to the diagonal signal described above. The orientational averages to obtain the *measured* parallel and perpendicular signals in terms of the calculated diagonal and off-diagonal contributions for an isotropic distribution of transition dipoles have been calculated:<sup>13,14</sup>

$$\mathbf{S}_{\parallel}(\epsilon' : \epsilon'') = \frac{9}{5} \mathbf{S}_{diag}(\epsilon' : \epsilon'') + \frac{6}{5} \mathbf{S}_{off-diag}(\epsilon' : \epsilon'') \quad [S24]$$

$$\mathbf{S}_{\perp}(\epsilon' : \epsilon'') = \frac{3}{5} \mathbf{S}_{diag}(\epsilon' : \epsilon'') + \frac{12}{5} \mathbf{S}_{off-diag}(\epsilon' : \epsilon'') \quad [S25]$$

Using these expressions for the polarization-dependent bleach of sodide, along with the DE+S model described by equations S1-S12, all the known pump-probe data for the sodide CTTS system in ethers can be reasonably well described. In particular, we can reproduce the

salient features of both our own data, shown in Fig. 9 of the main text, and that of Ruhman and coworkers,<sup>15</sup> with only a single spectral diffusion time (2.0 ps in THP for our data in Fig. 9; ~150 fs for the short-time portion of Ruhman's data in THF<sup>15</sup>). Moreover, given the formalism presented above, it is straightforward to incorporate more complex anisotropic bleaching kinetics; we hope to make such modifications to the model once the results of simulations of the polarized pump-probe experiments on Na<sup>-</sup> become available.

### III. Microsoft Excel Spreadsheet Incorporating DE+S and Polarization:

The Excel spreadsheet included in this Supplementary Information, titled *Aniso\_Bleach\_Na<sup>-</sup>.xls*, is designed to calculate pump-probe signals for CTTS excitation of Na<sup>-</sup> using the DE+S model incorporating anisotropic bleaching as described in section II.<sup>16</sup> Values shown in boldface are to be input by the user; values in plain typeface are calculated by the spreadsheet using the input values. In "Model Data," cells in the rectangle *A1* to *F15* contain various parameters needed for the four-Gaussian fit of the Na<sup>-</sup> CTTS spectrum; the fit itself can be found on the "4-Gaussian Fit of Na<sup>-</sup> Spectrum" worksheet. The *G* and *I* columns, from *G5-I9*, contain the pump wavelength (*G5*), probe wavelength (*I5*), and single exponential time for the anisotropy decay (*G9*); we note also that as the calculations must be performed in energy or frequency space, the spreadsheet automatically converts wavelengths input in nanometers to energy units in electron volts.

Columns *B-Q* calculate, as a function of the time in column *A*, the polarization functions given in Eqs. S13–S25. The total time-dependent anisotropic bleach, in the parallel, perpendicular, and magic angle cases, is then appropriately scaled to the absolute absorption cross-section of Na<sup>-</sup> at the probe wavelength (cell *H14*) and substituted for  $\epsilon_{\text{Na}^-}$  in Eq. S1.

Columns *S* to *AB* contain the kinetic parameters for the DE+S model (rows 1-13), as well as the time-dependent shifting  $\text{Na}^0$  spectral parameters. The concentration functions for the species in Eq. S1 are calculated at each time step in columns *AD-AG*. These functions are then substituted into Eq. S1 to obtain the "instantaneous" signal as a function of time. To simulate the effect of a finite instrument response time, these "instantaneous" signals are numerically convoluted with a gaussian function (column *AL*), giving the final signals for the parallel, perpendicular, and magic angle polarization geometries (columns *AN-AP*).

### **Supplementary Information Figure Caption:**

**Figure S1:** Schematic representation of the energy levels and polarizations of a hypothetical ensemble of  $\text{Na}^-$  absorbers. The symbols  $\varepsilon_i$  represent the transition energies for each of the quasi-degenerate *p*-like CTTS states, while *x*, *y*, and *z* represent the alignment of the transition dipoles to each of these states from the 3*s* sodide ground state.

### **Supplementary Information References:**

- <sup>1</sup> E. R. Barthel, I. B. Martini, and B. J. Schwartz, *J. Phys. Chem. B* **105**, 12230 (2001).
- <sup>2</sup> I. B. Martini, E. R. Barthel, and B. J. Schwartz, *J. Chem. Phys.* **113**, 11245 (2000).
- <sup>3</sup> See, e.g., W. A. Seddon and J. W. Fletcher, *J. Phys. Chem.* **84**, 1104 (1980); W. A. Seddon, J. W. Fletcher, F. C. Sopchyshyn, and E. B. Selkirk, *Can. J. Chem.* **57**, 1792 (1979).
- <sup>4</sup> B. Bockrath and L. M. Dorfman, *J. Phys. Chem.* **77**, 1002 (1973).
- <sup>5</sup> See, e.g. J. J. Sakurai, *Modern Quantum Mechanics, Revised Ed.*, Addison-Wesley Publishing, New York, 1994, 338.

- <sup>6</sup> We also note that in HMPA, for which no visible scans were available, the Na<sup>0</sup> spectrum was simply fixed at its infinite time value in THF, thus eliminating the (as of this time) unnecessary fitting parameters.
- <sup>7</sup> D. W. Marquardt, *J. Soc. Ind. App. Math.* **11**, 431 (1963).
- <sup>8</sup> R. Sension, Z. Wang, O. Shoshana, B. Hou, and S. Ruhman, in *Ultrafast Phenomena XIII* (Springer Series in Chemical Physics, Springer-Verlag, Heidelberg, 2002), 420; Z. Wang, O. Shoshana, B. Hou, and S. Ruhman, submitted to *J. Phys. Chem.*
- <sup>9</sup> I. B. Martini, E. R. Barthel, and B. J. Schwartz, *J. Amer. Chem. Soc.* **124**, 7622 (2002); I. B. Martini, E. R. Barthel, and B. J. Schwartz, *Science* **293**, 462 (2001).
- <sup>10</sup> J. Yu and M. Berg, *J. Phys. Chem.* **97**, 1758 (1993).
- <sup>11</sup> B. J. Schwartz and P. J. Rossky, *Phys. Rev. Lett.* **72**, 3282 (1994).
- <sup>12</sup> P. J. Reid, C. Silva, P. K. Walhout, and P. F. Barbara, *Chem. Phys. Lett.* **228**, 658 (1994).
- <sup>13</sup> T. Tao, *Biopolymers* **8**, 609 (1969).
- <sup>14</sup> We note that in reference 13, Tao derived Eqs. S24 and S25 only for the polarized signal at time zero, and argued that the anisotropy should decay as a single exponential process that is a solution to the angular diffusion equation. We chose to add the single exponential decay of polarization memory (Eqs. S13-S16) as a strictly phenomenological process from the beginning of our derivation, as we expect that in addition to rotational diffusion of the CTTS excited state wave function, nonadiabatic transitions between the *p*-like states in the CTTS manifold also could lead to loss of polarization memory; a full investigation will have to wait for theoretical work underway in our group.
- <sup>15</sup> Z. Wang, O. Shoshana, and S. Ruhman, in *Ultrafast Phenomena XII* (Springer Series in Chemical Physics, Springer-Verlag, Heidelberg, 2001), 624.
- <sup>16</sup> We note that Microsoft Excel's Analysis ToolPak is required for the spreadsheet included on EPAPS to function properly. Before the spreadsheet is used, this component must be installed and activated by the user.

If the **Data Analysis** command is not on the **Tools** menu, you will need to install the Analysis ToolPak in Microsoft Excel.

To install and use the Analysis ToolPak:

1. On the **Tools** menu, click **Add-Ins**.

If **Analysis ToolPak** is not listed in the **Add-Ins** dialog box, click **Browse** and locate the drive, folder name, and file name for the Analysis ToolPak add-in, *Analys32.xll* — usually located in the Microsoft Office\Office\Library\Analysis folder — or run the Setup program if it is not installed.

2. Select the **Analysis ToolPak** check box.

**Table S1: Time-Infinity DE+S Spectral Parameters For Na<sup>0</sup> in THF<sup>a</sup>**

Parameter	Meaning	Value	Other Units
$\omega_\infty$	Max absorption frequency of Na <sup>0</sup>	1.39 eV	890 nm; 11 200 cm <sup>-1</sup>
$\gamma_\infty$	HWHM of Lorentzian Side	0.637 eV	5128 cm <sup>-1</sup>
$(\sqrt{\ln 2})\sigma_\infty$	HWHM of Gaussian Side	0.219 eV	1764 cm <sup>-1</sup>
$A_0(t = \infty)$	Max absorbance value <sup>a</sup>	24 000 L mol <sup>-1</sup> cm <sup>-1</sup>	—————
$F(t = \infty)$	Area under absorption band	29 606 eV L mol <sup>-1</sup> cm <sup>-1</sup>	2.3879×10 <sup>8</sup> cm <sup>-1</sup> L mol <sup>-1</sup> cm <sup>-1</sup>

<sup>a</sup> See reference 19 in main text for details.

**Table S2: Estimated DE+S Na<sup>0</sup> Spectral Parameters with 95% Confidence Intervals**

Solvent	A(0)/A(∞)	$\lambda_0$ (nm)	$\sigma_0 2\sqrt{\ln 2}$ (eV)	$2\gamma_0$ (eV)
THF	0.17 ± 0.47 <sup>a</sup>	645 ± 134	1.20 ± 0.78 <sup>b</sup>	0.20 ± 1.63 <sup>a</sup>
THP <sup>c</sup>	0.17 <sup>a</sup>	626	0.46	0.20 <sup>a</sup>
DEE	0.67 ± 0.80	820 ± 261	1.20 ± 0.69 <sup>b</sup>	0.41 ± 2.7
HMPA <sup>d</sup>	1.00 <sup>d</sup>	890.00 <sup>d</sup>	0.44 <sup>d</sup>	1.27 <sup>d</sup>

<sup>a</sup> Constrained to be no lower than this value.

<sup>b</sup> Constrained to be no greater than this value.

<sup>c</sup> Errors could not be estimated in THP; see main paper text for details.

<sup>d</sup> Solvation dynamics was not modeled in HMPA; see main paper text for details.

$\epsilon_4$  (continuum)

