

Ultrafast Vibrational Stark-Effect Spectroscopy: Exploring Charge-Transfer Reactions by Directly Monitoring the Solvation Shell Response

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Abstract: We present the first implementation of transient vibrational Stark-effect spectroscopy as an ultrafast probe of solvation dynamics. The method is applied to the phototriggered intramolecular charge-transfer reaction of Betaine-30, where the vibrational Stark shifts of the nearby solvent molecules—arising from the change in the electrostatic environment—are measured using a three-pulse photon echo probe. This new experiment provides a direct subpicosecond measure of the chromophore's excited-state dynamics and back electron transfer as viewed from the solvent's perspective. We develop a simple *ab initio* model that offers semiquantitative prediction of the experimental Stark shifts.

Charge transfer reactions—ubiquitous in chemistry and biology—present particular experimental and theoretical challenges due to the strong coupling to the environment, such as a liquid, polymer, or protein. These reactions are especially sensitive to structural rearrangements of the solvent, as the energy fluctuations of the donor and acceptor states ultimately determine the coordinate as well as the rate of the reaction; thus, separating the molecular response from the solvent degrees of freedom can be difficult.^{1,2} In this Communication we present a new approach that leverages recent advances in ultrafast spectroscopy to directly probe the solvent response during a phototriggered intramolecular charge-transfer reaction. Using a three-component system comprised of a dye, Betaine-30 (Figure 1), surrounded by a polarizable and strongly infrared-active solvation shell (Na^+SCN^-), all embedded within a supporting solvent (ethyl acetate), we demonstrate that it is possible to track ultrafast charge transfer by monitoring the infrared response of the nearest solvent molecules.

A key feature of our work is that, by probing the first solvation shell, the transient measurements interrogate only those solvent molecules that respond to and guide the charge-transfer reaction. The essential physical interaction that enables the spectroscopic observation of the electronic excitation is a dynamic vibrational Stark effect³ (VSE) that shifts the nearest solvent vibrations by a few wavenumbers in response to the changing electric field caused by the reaction, effectively shining a light on the charge-transfer process. An added advantage of the dynamic VSE method lies in the fact that Stark tuning rates, or frequency shifts as a function of field strength, can be nearly quantitatively calculated using standard electronic-structure methods,⁴ thus turning each solvent vibration into a structure-sensitive dynamical probe of the electrostatic potential. Alternative methods rely on detecting differences in low-frequency Raman^{5,6} or coherent terahertz emission⁷ spectra of the solvent, and although these transient measurements have yielded much insight into charge-transfer reactions in solution, they typically lack the chemical specificity of a resonant infrared probe.

The main challenge associated with probing the solvent during a charge-transfer reaction—an experiment first attempted by Hochstrasser and co-workers⁸—arises from the large difference in the number of

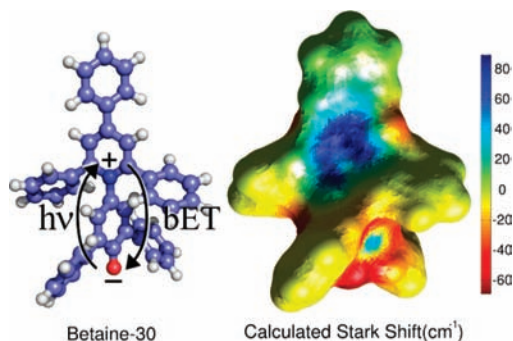


Figure 1. (Left) Molecular structure of Betaine-30 in the ground-state electronic configuration, showing the positive and negative charges on the oxygen and nitrogen atoms. The arrows represent the phototriggered charge-transfer and back electron-transfer (bET) reactions. (Right) Stark map of NaSCN frequency shifts at the solvent-accessible surface of Betaine-30.

solute and solvent molecules, causing a significant mismatch in the absorption at the UV/vis and IR wavelengths. In typical solutions, dyes are present at the level of several millimolar, while the solvent is 4–5 orders of magnitude higher in concentration. To circumvent this problem, we have implemented a three-component system consisting of two strongly interacting highly polar components, a chromophore and a spectroscopic solvent, surrounded by a less polar supporting solvent. In such a construct, it is necessary to establish that the NaSCN actually solvates the dye molecule. Measurements of the shift in absorption maximum of Betaine-30, a solvatochromic dye often used as an indicator of solvent polarity,⁹ in the presence of NaSCN provide strong evidence that NaSCN interacts with the chromophore. Descriptions of the experimental methods are provided in the Supporting Information. From the absorption shifts, the polarity of this unusual solvation environment can be estimated to be similar to that of butanol. Betaine-30 features a decrease in dipole moment⁹ as well as significant geometric rearrangements upon photoexcitation into the lowest excited singlet state. The ultrafast radiationless return to the ground state¹⁰ (<5 ps) indicates rapid dynamics following excitation as well as large solvation energies,^{11,12} making this an ideal system to study with dynamic VSE spectroscopy. A discussion of the equilibrium vibrational structure of NaSCN along with a two-dimensional spectrum is included in the Supporting Information.

A detailed description of the optical setup and modeling methods is provided in the Supporting Information. In brief, a two-stage non-collinear optical parametric amplifier generates broadband pulses (~100 fs) centered at 580 nm used to excite the dye. Three infrared pulses (~100 fs) are used to measure the homodyned infrared echo signal of the $\text{C}\equiv\text{N}$ stretch in NaSCN. As a background-free technique, transient infrared echo spectroscopy affords improved signal-to-noise ratios compared to transient infrared absorption without the need for referencing, but the information content is very similar (see Supporting Information). Transient spectra are obtained by subtracting the excited- from the ground-state infrared echo spectra. Nonequilibrium structural

and dynamical information can be extracted from the lineshapes and time evolution of the transient spectra, respectively (Figure 2). The bleach at 2058 cm^{-1} and the positive Stark-shifted peak at 2039 cm^{-1} arise from a local change in electric field at the positions of the nearby solvent molecules, induced by the dipole moment change of the chromophore upon optical excitation. The observed 19 cm^{-1} red-shift can be used to map the electric field change induced by the reaction. The Stark tuning rate of SCN is $\sim 0.7\text{ cm}^{-1}/(\text{MV}/\text{cm})$;¹³ thus, a shift of 19 cm^{-1} represents a change in electric field of approximately $27\text{ MV}/\text{cm}$. To obtain a molecular-level interpretation of the results, we computed the expected Stark shifts of the NaSCN molecules in the first solvation shell. The procedure is straightforward: starting with the Betaine-30 ground- and excited-state atomic charges,¹⁴ we computed the difference in electric field (excited – ground) at the solvent-accessible surface of the dye; a map of the C≡N frequency shifts at the surface was then calculated using the NaSCN Stark tuning

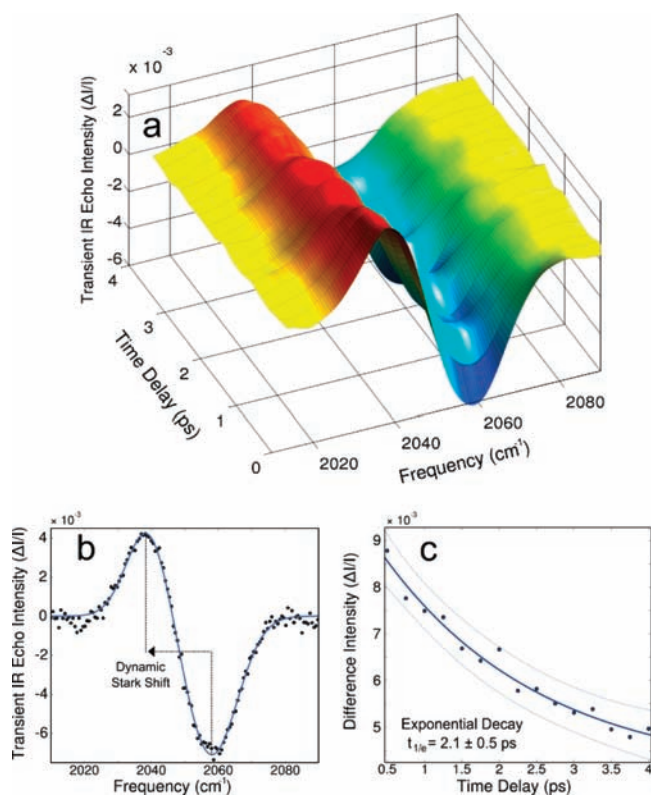


Figure 2. (a) Vibrational Stark-effect spectra of the thiocyanate C≡N stretch at various delays after excitation of Betaine-30. (b) Single VSE spectrum at zero time delay with a dual-Gaussian fit (solid line), showing the 19 cm^{-1} red-shift of the solvent C≡N stretching frequency induced by the change in electrostatic environment. (c) VSE difference amplitude (induced signal – bleach) versus delay after excitation with a single-exponential fit (solid line) and 95% confidence bounds (dashed). The Betaine-30 and NaSCN concentrations are 2 and 50 mM, respectively.

rate.¹³ Though the Stark shifts are orientation dependent, as a first approximation we computed the maximum magnitude of the shift at various points within the surface. The results (Figure 1) show that molecules lying near the nitrogen or oxygen atoms shift by as much as 80 cm^{-1} , but molecules near the phenyl rings only shift by $\sim 20\text{ cm}^{-1}$ or less, in general agreement with the experimental observations. The change in electric field can be thought of as adding an extra inhomogeneity into the system; thus, randomly oriented solvent molecules would not show an overall shift but only a broadening of the C≡N stretch band. The experimental red-shift thus indicates a degree of alignment between the chromophore and solvent molecules.

Polarization-sensitive VSE experiments also suggest that the dye and NaSCN molecules are somewhat aligned (see Supporting Information). Finally, our simple *ab initio* model highlights one of the main advantages of dynamic VSE spectroscopy, namely the ability to semiquantitatively predict the Stark shifts from first principles. The Stark map can be further combined with classical dynamics simulations to test the intermolecular interactions and underlying nonequilibrium dynamics that give rise to the observed spectra.

In general, the time evolution of the Stark lineshapes reports on the excited-state dynamics of the chromophore/solvent system and can be related to more traditional solvation measurements, such as transient absorption or dynamic Stokes shifts. The amplitude of the Stark spectra immediately following photoexcitation (Figure 2) shows a single-exponential decay with a time constant of $2.1 \pm 0.5\text{ ps}^{-1}$. The decay can be attributed to the back electron transfer (bET) reaction that returns Betaine-30 to its ground-state electronic configuration. In full agreement with our results, transient absorption measurements also suggested a bET rate of $<5\text{ ps}^{-1}$ in polar solvents.^{10,15,16} Orientational relaxation and vibrational energy transfer to the solvent may also contribute to the signal decay, but these processes are generally slower (additional discussion provided in the Supporting Information). To minimize the contributions from these processes, only the short-delay data ($<4\text{ ps}$) were analyzed. Future experiments will be aimed at probing both the impulsive and the diffusive solvent orientational contributions to the overall solvation of the charge-transfer state.

In conclusion, the vibrational Stark-effect measurements demonstrated here have the potential to elucidate nonequilibrium dynamics in charge-transfer processes, where a clean separation of system and bath consisting of molecule and solvent may not be applicable because the solvent fluctuations guide the reaction, which in turn causes a further response in the solvent. This general method may be used to characterize charge-transfer reactions from the solvent's perspective in many chemical and biological processes. Dynamic modeling methods should provide a microscopic interpretation of the observed Stark lineshapes.

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Supporting Information Available: Description of the optical setup and simulation methods; *ab initio* energies and structures; equilibrium 2D spectrum of NaSCN; discussion of NaSCN solvation shell; orientational and energy transfer effects on the VSE measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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