J. Am. Chem. Soc. **2000,** *122,* 11541−11542

Measurement of Electromagnetic Radiation Emitted during Rapid Intramolecular Electron Transfer

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Received May 9, 2000
Revised Manuscript Received September 29, 2000

We report direct observation of intramolecular electron transfer (ET) by measuring the electromagnetic (EM) waveform broadcast by the charge-transfer process itself. Intermolecular and intramolecular ET each have a rich history and play a central role in chemistry, biology, and physics. For example, photosynthesis, artificial photosynthesis, redox chemistry, photography, xerography, and other processes all rely on ET. By directly monitoring the emitted waveform, both forward and back charge-transfer rates may be measured on a time scale of 0.1−10 ps *without* relying on the photoluminescent properties of the donor or acceptor species.

It is known that an accelerating charge generates EM radiation.[1] This is the underlying basis for light sources as specialized as free-electron lasers and synchrotrons, or as mundane as radio transmitters. This is, in fact, the basis for generation of terahertz (THz) pulses by photoconductive antennas.[2] THz pulses are nearly half-cycle pulses of EM radiation that are a few hundred femtoseconds in duration. A photoconductive antenna is created by applying an electric field across the face of a semiconductor wafer such as GaAs. Upon photoexcitation, electrons are promoted into the conduction band and accelerated by the bias field, thereby generating EM radiation. It has been shown that pulses generated from biased GaAs in this fashion are related to the dynamics of the charge carriers.[3] It follows that molecules undergoing coherent ET will radiate an EM pulse that is directly related to the dynamics of the charge-transfer event.

The method described here involves orienting a solution of polar molecules with an electric field and photoinitiating ET with a short (~100 fs) laser pulse. Each molecule then acts as a tiny antenna, broadcasting its dynamics by emitting an EM transient as charge moves between donor (D) and acceptor (A) sites. Dynamical information is contained in the resulting time dependent electric field, which is measured with subpicosecond temporal resolution by free-space electrooptic sampling.[4] The EM transients are measured in the far-field with no focusing elements to avoid pulse reshaping. The experimental setup is described elsewhere,[5] and only minor modifications have been made.

To probe ET in this manner, the only fundamental requirements are that the molecule can be oriented (most easily if it possesses a ground state dipole moment), and that upon photoexcitation there is a change in dipole moment along the molecular axis of orientation. One expects the signal strength to increase linearly with the degree of orientation, number of photoexcited molecules, and change in dipole moment. It should also vary as the cosine of the angle between the molecular orientation axis and excited state dipole. The sign of the radiated field depends on whether the change in dipole is positive or negative, and thus the direction of the ET can be obtained directly from the measurement.

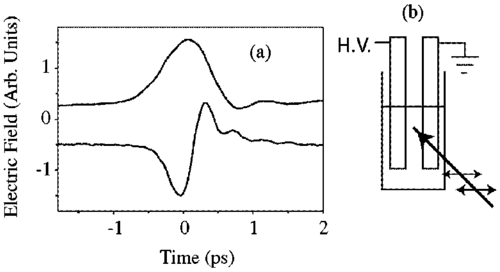

Figure 1. (a) EM generation from biased GaAs (upper curve) and betaine-30 (× 100) dissolved in $CHCl_3$ (lower curve). For both betaine-30 and GaAs the applied field was in the same direction; however, the emitted fields have opposite polarities. (b) Experimental setup. Polarization of laser pulse (thick arrow) is parallel to applied field, as is polarization of generated pulse.

We report EM generation from betaine-30 and compare it to generation from biased GaAs (Figure 1). Betaine-30, [2,6-diphenyl-4-(2,4,6-triphenylpyridinio)-phenolate] also known as Reichardt's dye, was purchased from Aldrich, dissolved in $CHCl_3$, and used without further purification. Its dipole moment decreases and changes direction upon photoexcitation (15 D in the ground state to −6 D in the excited state).[6]

Dye solutions with concentrations of roughly 4 mM were placed in a 1 mm path length quartz cuvette. High voltage pulses (~0.1 ms duration, 500 V to 3 kV) were applied across 0.75 mm thick metal electrodes inside the cuvette with 3 to 4 mm separation to generate fields from 1.25 to 10 kV/cm. Typically, a laser pulse energy of 100 μJ/pulse was used.

Figure 1 compares the THz pulses generated from biased GaAs and betaine-30. In each case the applied field is in the same direction. The pulse generated from betaine-30 has a polarity opposite that of the EM pulse generated from biased GaAs, which is a direct result of the fact that the ET in this molecule is in the opposite direction of the applied field. Furthermore, the shapes of the resultant pulses are different, reflecting their respective dynamics.

In contrast, upon photoexcitation at 400 nm of the dye 4-dimethylamino-4′-nitrostilbene (DMANS) dissolved in toluene, the dipole moment *increases*. We have verified that the signal generated from photoexciting DMANS in an applied field has the same general characteristics as the signal generated from betaine-30, but with *opposite* polarity.

The time-dependent properties of betaine-30 have been well studied[7] and can be used to characterize our new technique. In the ground state, S_0, an electron has already been transferred form the donor (D) pyridinium group to the acceptor (A) phenolate group. Upon photoexcitation at 800 nm, ET occurs instantaneously from $A^- \rightarrow D^+$. The first excited state, S_1 (D − A), has a smaller dipole moment than the ground state and points in the opposite direction (Scheme 1). Relaxation from $S_1 \rightarrow S_0$ proceeds via internal conversion with rate constant k_2 and results in movement of the electron from D back to A. This back ET rate is highly solvent-dependent, with rate constants[7] ranging from 0.2 to 1 ps^{-1}.

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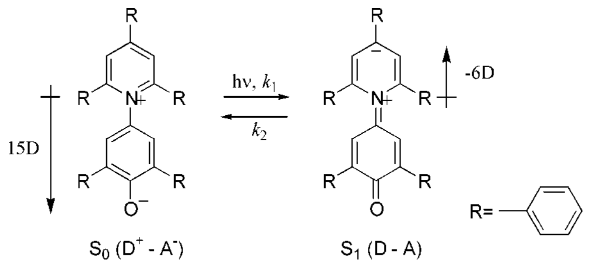
10.1021/ja001581v CCC: $19.00

Scheme 1. Betaine-30



Internal conversion mechanisms are generally referred to as "radiationless" transitions as the excess energy is transferred from the excited electronic state to hot vibrational states in S_0, and then dispersed into solvent modes as the molecule relaxes further. However, we have shown here that radiation *is* emitted from transitions that involve charge transfer.

The finite-difference time-domain (FDTD) method[8] was used to model the data to allow EM generation during simultaneous propagation of the visible and generated EM pulses through the solvent. The FDTD method is a numeric solution of Maxwell's equations in the time domain. Since the polarization enters Maxwell's equations through the displacement field we are able to quantitatively determine the time-dependent ET dynamics via a least-squares fit to the data. Numeric propagation through the cuvette walls and detector crystal was included in the simulation to account for reshaping of the pulse.[9] The absorption of the visible pulse by the dye solution is also included.

The time dependent polarization is given by[10−12]

$$P(t) = \frac{N_0 k_1}{(k_2 - k_1)}[\exp(-k_1 t) - \exp(-k_2 t)] \times (\mu_e^2 - \mu_g^2)\frac{E_l}{3k_B T} \tag{1}$$

where k_1, and k_2 are the forward and back ET rate constants, μ_e and μ_g are the excited and ground-state dipole moments, E_l is the local electric field, k_B is the Boltzmann constant, N_0 is the initial density of excited molecules, and T is the temperature in Kelvin.

The result of the nonlinear least-squares fit to EM generation in betaine-30 is shown in Figure 2, and the underlying dynamics are shown in the inset. The rate constants are $k_1 = 3.37$ ps^{-1} and $k_2 = 0.67$ ps^{-1}.

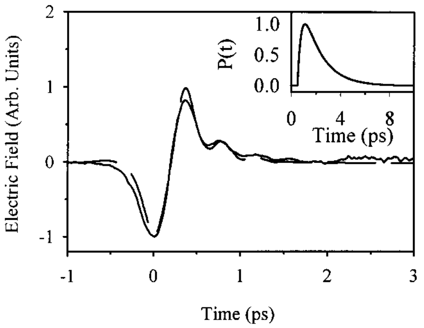


Figure 2. Results of nonlinear least-squares fit to EM generation in betaine-30: solid line is measured data, and dotted line is the best fit. Inset shows the extracted time dependent polarization with rate constants $k_1 = 3.37$ ps^{-1} and $k_2 = 0.67$ ps^{-1}. The polarization has been normalized to unity.

The signal was found to vary linearly with the applied field and visible intensity. In addition, the signal varies as a function of angle between the applied field direction and the laser polarization axis (see Figure 1b). More precisely, it varies as the convolution of two $\cos^2 \theta$ distributions whose axes are at an angle of ζ with respect each other. The interaction of the static electric field with a dipolar molecule in solution results in fractional alignment of the molecules along the field direction. This fractional alignment can be calculated by considering the $V = \boldsymbol{\mu} \cdot \boldsymbol{E} = \mu E \cos \theta$ interaction in comparison to $k_B T$, and is given by[10]

$$f(\theta) = \frac{e^{-V/k_B T}}{4\pi} \approx \frac{(1 - \mu E \cos \theta / k_B T)}{4\pi} \tag{2}$$

where θ is the angle between the applied field and molecular dipole moment. Higher order terms have been neglected as well as terms resulting from polarizability anisotropy. An additional $\cos \theta$ contribution to the generated signal results from the projection of the ground-state dipoles onto the applied field axis. The visible pulse introduces a $\cos^2 \theta$ anisotropy to the excited-state distribution relative to the laser's polarization, which is at an angle ζ with respect to the field direction. The above considerations describe the EM amplitude, A_{EM}, as a function of ζ as,

$$A_{EM}(\zeta) \propto \int_0^{2\pi} f(\theta) \cos(\theta) \cos^2 (\theta - \zeta) d\theta \tag{3}$$

We have confirmed that the signal varies with angle in this manner.

In conclusion, an EM pulse radiated from an ET event has been measured for the first time. The EM pulse generation results from rapid charge separation that occurs upon photoexcitation of roughly 10^{14} dye molecules in solution which are weakly oriented in an electric field. By measuring the emitted EM field in the time domain, charge-transfer processes may be measured on a time scale of 100 fs to 10 ps.

In addition to intermolecular and intramolecular ET dynamics in classical systems, this type of study should lend significant insight into charge transfer processes that are currently under intense investigation, such as photosystem II, reaction centers, and DNA. The fact that the electron motion itself generates the field that is measured makes this a very general probe.

Acknowledgment. We thank J.T. Kindt for suggesting this experiment. This work was supported by the Sloan Foundation and by a National Science Foundation CAREER award.

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(12) (a) The width of the visible pulse was accounted for by convoluting a Gaussian function (150 fs full width half-maximum) with the time-dependent polarization. (b) The calculated EM transient was scaled to obtain the best fit. Thus, the absolute value of the polarization is not obtained. However, the rate constants and the direction of ET are obtained unambiguously. (c) The "forward" rate constant in betaine-30 is instantaneous when exciting at 800 nm. Therefore, k_1 represents the solvent polarization in these studies. However, for other systems where photoexcitation occurs to an excited state before undergoing ET, we would measure the forward rate constant.