

## Charge-Transfer Complexes and Energetic Disorder in Amorphous Organic Solids

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In many practical applications, photochemical processes take place in amorphous organic solids such as polymeric glasses, where molecular motion of the medium is largely frozen on the reaction time scale.<sup>1</sup> The disorder in such media makes it difficult to analyze the kinetics quantitatively, beyond fitting data to empirical formulas.<sup>2</sup> Photoinduced electron-transfer (ET) reactions are very sensitive to their host medium, and previous work has shown that the limited ability of the medium to relax or fluctuate during electron transfer affects the relative free energies, relaxation energies, and available reaction pathways for the species involved.<sup>3</sup> The frozen-in randomness of the medium should also give rise to a sizable energetic disorder for these reactions.<sup>3c</sup> The consequences of such disorder for photoinduced ET have received relatively little attention,<sup>3c</sup> however, and no experimental estimates of its magnitude have been reported.<sup>4</sup> Here we describe an experimental method to determine the extent of this energetic disorder for a simple ET reaction. The approach described here not only provides a quantitative measurement of the disorder but also shows how the reactions in the amorphous solid state can be understood in terms of a previously tested absolute theory for electron-transfer reactions in solution, using parameters whose meanings are well understood.

The ET reactions studied here are the interconversions of ground-state charge-transfer (CT) complexes and excited-state contact radical-ion pairs (CRIP).<sup>5</sup> The usual theory describes the rate constant for nonradiative decay of a CRIP (return electron transfer) in a fluid solution,  $k_{-et}$ , as a function of the following

parameters: a reorganization energy  $\lambda_s$  for low-frequency (mainly solvent) motions, a reorganization energy  $\lambda_v$  and an averaged vibrational frequency  $\nu_v$  for intramolecular vibrational displacements of the reactants, the reaction free energy  $\Delta G_{-et}$ , an electronic coupling matrix element  $V$ , and a Franck–Condon-weighted density-of-states function  $FC$ , eq 1.<sup>5,6</sup>

$$k_{-et} = \frac{4\pi^2}{h} V^2 FC(\Delta G_{-et}, \lambda_s, \lambda_v, \nu_v) \quad (1)$$

Here  $\Delta G_{-et} = -\Delta G$ , where  $\Delta G$  is the free energy for charge separation. The corresponding CT emission and absorption spectra can be described by similar formulas, with  $\Delta G_{-et}$  replaced by  $\pm(\Delta G_{-et} + h\nu)$ .<sup>5a</sup> Previously we showed that all of the parameters of eq 1, which describe the electron-transfer reactions in fluid solution, could be obtained from the CT emission spectra, and that  $k_{-et}$  values varying by almost 3 orders of magnitude could be predicted absolutely to within a factor of 2–3.<sup>5a</sup> Here we show how this approach can be extended to the more complex situation of reaction in the amorphous solid state.

The starting point is a recognition that certain conformational degrees of freedom, such as the orientations of the dipoles, of a solid medium are frozen for the lifetime of a CRIP,<sup>3a,b</sup> whereas others may relax rapidly, just as in fluid solution. The frozen degrees of freedom in a glassy amorphous solid result in energetic disorder, so that CT complexes in different environments have different individual free energies for CRIP formation,  $\delta g$ .<sup>3c</sup> The (mobile) degrees of freedom that relax rapidly result in a low-frequency reorganization energy,  $\lambda_s^m$ , analogous to the  $\lambda_s$  in fluid solution. For each complex,  $k_{-et}$  and the CT spectra should be given by the usual formulas, with  $\Delta G$  and  $\lambda_s$  being replaced by  $\delta g$  and  $\lambda_s^m$ . The overall distribution of conformations of the medium around a CT complex, involving both frozen and mobile degrees of freedom, should be like that for the complex in its ground state in a fluid solvent.<sup>3a,b</sup> The usual model for electron transfer reactions in solution assumes a parabolic configuration–coordinate plot or, equivalently, a Gaussian distribution of rapidly interconverting reaction energies around some mean value.<sup>6d</sup> In the solid state, the frozen degrees of freedom presumably result in a similar Gaussian distribution of  $\delta g$ , which we describe in terms of a mean value  $\bar{\delta g}$  and rms width  $\sigma$ .<sup>7</sup> For simplicity, we assume that each complex has the same value for  $\lambda_s^m$ .

An observed CT emission, excitation, or absorption spectrum is thus interpreted as a suitably weighted average of individual spectra with different ET free energies.<sup>8</sup> CT excitation produces CRIP with a distribution of free energies that depends on the excitation wavelength in addition to the overall distribution of individual environments. Consequently, the shape of a CT emission spectrum should depend on the excitation wavelength, and a CT excitation spectrum should depend on the monitoring wavelength, unlike the case for a fluid solution.

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(7) A Gaussian distribution of energies in disordered media is often assumed for the interpretation of experiments or found as a theoretical approximation.<sup>4</sup>

(8) (a) The detailed equations are provided as Supporting Information. (b) For the TCB:HMB CRIP in fluid solution, nonradiative return transfer,  $k_{-et}$ , is much faster than the corresponding radiative process, CT emission.<sup>5</sup> In the solid, however, the two processes are competitive. (c) The possibility of energy transfer from a higher-energy excited complex to a lower-energy one can be excluded by concentration experiments. A decrease in the CT complex concentration by more than an order of magnitude did not affect the individual emission and excitation spectra, and the same excitation wavelength dependency was observed as from that at the higher CT concentration.

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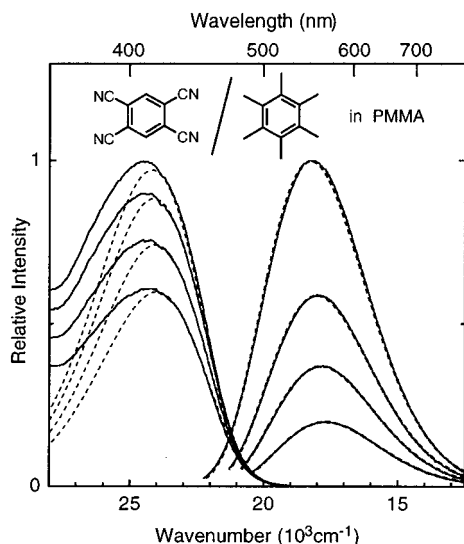
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**Figure 1.** Emission spectra (photons/second/cm<sup>-1</sup>) measured at various excitation wavelengths ( $\lambda_{\text{ex}}$ ) and excitation spectra measured at various detection wavelengths ( $\lambda_{\text{det}}$ ) for the charge-transfer complex of 1,2,4,5-tetracyanobenzene and hexamethylbenzene in a poly(methyl methacrylate) film at room temperature. From top to bottom,  $\lambda_{\text{ex}}$  is 430, 450, 460, and 470 nm, and  $\lambda_{\text{det}}$  is 560, 580, 600, and 620 nm, respectively. The dashed curves are theoretical fits to the spectra (see text and Table 1), rescaled vertically by no more than 7% to facilitate comparison of the shapes. A second CT absorption band,<sup>10g</sup> not included in the theoretical model, is responsible for the discrepancy between simulated and measured excitation spectra at high excitation energies.

The system chosen for study was the CT complex of the electron acceptor 1,2,4,5-tetracyanobenzene (TCB, 1 wt %) and the donor hexamethylbenzene (HMB, 2 wt %), dissolved in  $\sim 10 \mu\text{m}$  films of poly(methyl methacrylate) (PMMA).<sup>9,10</sup> Excitation of the complex yields a CRIP,  $\text{TCB}^{\cdot-}/\text{HMB}^{\cdot+}$ . The CRIP undergoes return electron transfer, either nonradiatively or radiatively with the emission of a photon, to regenerate the ground-state complex.<sup>5a,8c</sup>

Typical experimental spectra are shown in Figure 1. The influence of disorder is evident in an 18 nm shift of the emission maximum (from 547 to 565 nm) as the excitation wavelength is varied by 40 nm (from 430 to 470 nm). Similarly, but more subtly, the maximum of the excitation spectrum shifts from 412 to 415 nm as the monitoring wavelength is varied from 560 to 620 nm.<sup>11</sup>

Also shown in Figure 1 are simulations of the spectra, obtained using the method described above, with fitting parameters summarized in Table 1. The simulations reproduce not only the band shapes and shifts, but also the relative intensities of the different spectra. Although the solid-state spectra require one more parameter,  $\sigma$ , than did the previous solution-phase studies,<sup>5a</sup> the parameters are actually better determined, since the model requires that the same set be used, globally, to fit *all* of the different spectra.<sup>12</sup>

The average free energy for ET in the TCB/HMB/PMMA system is  $\bar{\delta}g = 2.61 \pm 0.05 \text{ eV}$ . This is comparable to  $\Delta G$  in the

(9) Samples were prepared by drop-coating a solution of HMB (5 mg), TCB (2.5 mg), and PMMA (250 mg) in 5 mL of  $\text{CH}_2\text{Cl}_2$  onto 1-in. diameter fused silica windows, which were covered to allow slow evaporation of the solvent. The samples were then purged with nitrogen overnight.

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(11) For emission spectra in photons/sec/nm, the maximum of the emission spectrum varies from 537 to 554 nm as the excitation wavelength is varied from 430 to 470 nm.

**Table 1.** Spectral Fitting Parameters

Variable Parameters	
$\bar{\delta}g$	$2.61 \pm 0.05 \text{ eV}$
$\sigma$	$0.108 \pm 0.005 \text{ eV}$
$\lambda_s^{\text{m}}$	$0.180 \pm 0.005 \text{ eV}$
$\lambda_v$	$0.270 \pm 0.005 \text{ eV}$
Fixed Parameters	
$\nu_v^a$	0.174 eV
$T$	298 K
$n^b$	1.49
$\Delta\mu^c$	13 D

<sup>a</sup> See ref 5. <sup>b</sup> See ref 13. <sup>c</sup> From solvatochromism on similar CRIP.<sup>14</sup>

least polar fluid solvents (e.g., 2.57 eV in cyclohexane<sup>5a</sup>). Presumably, the CRIP are not stabilized by orientation of the dipoles in PMMA after excitation (PMMA has a small low-frequency dielectric constant, 2.6<sup>13</sup>). The residual low-frequency reorganization energy,  $\lambda_s^{\text{m}} = 0.180 \pm 0.005 \text{ eV}$ , is comparable to  $\lambda_s$  in nonpolar solvents (0.14 and 0.16 eV in cyclohexane and carbon tetrachloride, respectively<sup>5a</sup>), presumably for similar reasons. The free-energy distribution has a significant rms width,  $\sigma = 0.108 \pm 0.005 \text{ eV}$ . This energy distribution is equivalent to a “frozen-in” component of the solvent reorganization energy,  $\lambda_s^{\text{f}} = \sigma^2/2k_B T = 0.23 \text{ eV}$ .<sup>8</sup> If the dipoles in PMMA *were* actually able to reorient and stabilize the CRIP, the corresponding value of  $\Delta G$  would be  $\bar{\delta}g - \lambda_s^{\text{f}} = 2.35 \text{ eV}$ , and the total reorganization energy would be  $\lambda_s^{\text{f}} + \lambda_s^{\text{m}} = 0.41 \text{ eV}$ . The  $\Delta G$  is somewhat lower than that for a TCB:HMB CRIP<sup>12</sup> in a comparable polar liquid such as butyl acetate (2.47 eV<sup>5a</sup>). The total reorganization energy is comparable to  $\lambda_s$  for that CRIP in butyl acetate (0.43 eV<sup>5a</sup>).

One particularly useful aspect of the present approach is that the apparently complex solid state CT spectroscopy is quantitatively understandable by using a theory that is well-established from corresponding solution-phase studies. To the best of our knowledge, such an absolute approach has not previously been described for electron-transfer processes in a disordered matrix such as these. It will be of interest to investigate how bulk properties or the specific molecular structure of the polymer matrix affects the parameters, which describe the solvation of ion pairs in glasses and, thereby, control the shapes of the spectra. An additional consequence of the distribution in free energies is that the CRIP decay kinetics should be nonexponential and vary with detection wavelength. In principle, these kinetics should also be quantitatively explained in terms of the same solution-phase parameters which describe the spectra, and preliminary experiments indicate that this is indeed the case. This is particularly interesting because nonexponential<sup>4c</sup> relaxation processes in glasses can usually be described only by using the purely empirical stretched exponential formalism.<sup>2b</sup> These issues will be discussed in detail in a future publication.

**Supporting Information Available:** Derivations of equations used to analyze spectral data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) (a) In solution, moreover, one cannot expect a single set of parameters to fit both the emission and the excitation spectra, because the initially photogenerated CRIP relaxes rapidly to a different CRIP species that dominates the emission. Evidence for this relaxation comes from transient absorption<sup>12b</sup> and time-resolved emission experiments<sup>5a</sup> and from differences in the CT emission spectra obtained by excitation into CT absorption bands and by reaction of alkylbenzene donors with freely diffusing excited TCB.<sup>5a,12c</sup> No fast relaxation comparable to that observed in solution is observed in time-resolved emission experiments in the polymer, from which we conclude that the relaxation does not occur in this case. (b) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4147. (c) Prochorow, J. *J. Lumin.* **1974**, *9*, 131.

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