of a 20-min dark-adapted PSII sample (Figure 2). The active to resting state transition has a half-time of 3.5 ± 0.7 h at 0 °C, a rate which is consistent with the results of Beck et al.;[1] in that case, the half-time was determined to be 30 ± 2 min at 25 °C.

We now consider the contributions of S states other than the S_1 active state to the relaxation enhancement of $Y_D^{\bullet}$ in short dark-adapted PSII. The long time course of the change (Figure 2) shows that there are no significant contributions from the short-lived S_2 and S_3 states to the time-dependent change of the spin-lattice relaxation behavior of $Y_D^{\bullet}$. The S_0 state is longer-lived and has been found to be slowly oxidized by $Y_D^{\bullet}$ to the S_1 state during dark incubation.[9] The conversion of S_0 to S_1 has been followed[9b] by measuring the fast phase of decay of $Y_D^{\bullet}$ ($t_{1/2}$ = 14 min at pH 6.0 and 21 °C). We have measured the decrease of the $Y_D^{\bullet}$ EPR signal as a function of dark incubation time at 0 °C in order to assess the rate of the $S_0 \rightarrow S_1$ conversion (data not shown). The fast phase of $Y_D^{\bullet}$ decay is over within 1 h and involves 20–30% of $Y_D^{\bullet}$. These results are consistent with earlier measurements[9] and indicate that the S_0 to S_1 conversion occurs much more rapidly than the changes shown in Figure 2. Therefore, we conclude that the time-dependent change in spin-lattice relaxation of $Y_D^{\bullet}$ is due mainly to the conversion of the S_1 active state, which has a paramagnetic ground state, to the S_1 resting state, which has a diamagnetic ground state.

Our conclusion that the ground spin state of the S_1 resting state is diamagnetic and that the ground spin state of the S_1 active state is paramagnetic is also consistent with several previous experimental results. The noncyclical behavior in the magnetic susceptibility measurements at room temperature[10] can be explained by the generation of the paramagnetic S_1 active state after four laser flashes, while the initial S_1 resting state has a lower level of magnetism since it has a diamagnetic ground state. Variable temperature magnetic susceptibility measurements[11] showed that "the net paramagnetism of the OEC in the dark-adapted state is low and may be zero." Finally, EPR studies of the variation of $P_{1/2}$ of $Y_D^{\bullet}$ with S state[6] showed a larger value of $P_{1/2}$ when the S_1 state was produced on the fourth flash compared to the initial dark-adapted sample.

A new EPR signal from the S_1 state in long dark-adapted PSII has been detected[12] at $g = 4.8$ in the parallel mode. The signal was very weak, which could be explained if it arises from the S_1 active state. However, we have not been able to detect a perpendicular-mode EPR signal in the difference spectrum of the S_1 active minus the S_1 resting state.

Our results have significant implications on the structure of the Mn cluster. In particular, the arrangement of a manganese trimer plus a mononuclear manganese center is ruled out because a single Mn ion is expected to be paramagnetic in all of its possible oxidation states. Our results, together with past studies,[10,13-16] point to a tetrameric Mn cluster as the most probable structure. We account for the different magnetic properties of the S_1 active and resting states by a change in the ferro- and antiferromagnetic couplings between the four Mn ions due to a structural change in the cluster.

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Comparison of Experimental and Theoretical Absolute Rates for Intervalence Electron Transfer

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Recently, direct time-resolved measurements on optical metal-metal charge-transfer (MMCT) bands have been performed, yielding the first kinetic data and other dynamical information on this important class of electron-transfer (ET) reaction.[1,2] In this paper we report ultrafast pump-probe measurements on the MMCT band of reaction 1 in various solvents over a range of temperatures.[3]

$$(NH_3)_5Ru^{III}NCRu^{II}(CN)_5^- \underset{k_{ET}}{\overset{h\nu}{\rightleftharpoons}} (NH_3)_5Ru^{II}NCRu^{III}(CN)_5^- \qquad (1)$$

Typical pump-probe transient signals for reaction 1 pumped at ~800 nm and probed at ~800 or 700 nm are shown in Figure 1. The data are well described by a biexponential decay function convoluted with the instrument response function (see Table I). There is an initial transient bleach, which recovers in ~0.1–0.7 ps depending on solvent and temperature,[4] that we assign to ground-state recovery, i.e., reverse ET.

Subsequent to the initial bleach there is a slower kinetic component, which is either a bleach or increased absorption, depending on the wavelength of the probe beam relative to the maximum of the MMCT band. The MMCT band immediately after ground-state recovery is apparently shifted toward longer wavelength, relative to the equilibrated band, as a result of excess energy content in the solute and, potentially, the solvent.[7] The second component is assigned to relaxation in the electronic ground state. An analogous effect has been reported for the betaines, an organic compound class that exhibits intervalence electron transfer.[5] Furthermore, this assignment is consistent with the visible pump/IR probe measurements of Doorn et al., who concluded that the reverse ET of reaction 1 takes place in <0.5 ps followed by vibrational relaxation of the solute in the ground state.[2]

Interestingly, the ET rate shows a pronounced, temperature-dependent hydrogen/deuterium solvent isotope effect in glycerol, indicating that hydrogenic vibrational modes of the solvent, such as librations, are significantly involved in the ET reaction, especially in frozen media.[6]

One of the main goals of this work is to evaluate absolute rate models for ET. The comparison is limited to water, the only solvent for which the necessary parameters are available.[6,7] The input for the theoretical calculations was obtained by combining MMCT resonance Raman data[8] with an MMCT band shape analysis, and in some cases only two representative solute vibrational modes were employed to limit the size of the rate calculation. Further detail will be given in a future paper. The parameters

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Table I. Biexponential Fit Parameters for the Transient Pump–Probe Signal of $(NH_3)_5Ru^{III}NCRu^{II}(CN)_5^-$ in Various Solvents

solvent	λ_{max}/nm	pump/probe[a]	T/°C	τ_1/ps (A_1)[b]	τ_2/ps (A_2)
H_2O	683	792/792	1	0.10 (0.88)	1.66 (−0.12)
			20	0.09 (0.89)	1.46 (−0.11)
		800/700	20	≤0.1 (0.95)	0.4 (0.05)
		800/640	20	1.1 (1.0)	*c*
		700/700	20	≤0.1 (1.0)	*c*
NMF[d]	779	792/792	−8.5	0.12 (0.77)	0.52 (0.23)
			20	0.11 (0.86)	0.91 (0.14)
		800/640	20	3.5 (1.0)	*c*
formamide	771	792/792	4	0.10 (0.85)	0.60 (0.15)
			20	0.09 (0.90)	0.68 (0.10)
		800/740	20	0.1 (0.91)	3.2 (0.09)
		800/700	20	0.1 (0.88)	3.5 (0.12)
ethylene glycol	730	792/792	20	0.27 (0.96)	5.64 (−0.04)
			71	0.11 (0.72)	0.41 (0.28)
glycerol	715	792/792	−100	0.74 (1.0)	*c*
			−6	0.43 (0.90)	~6 (−0.10)
			20	0.33 (0.95)	~5 (−0.05)
		700/700	20	0.3 (0.92)	~5 (0.08)
		792/792	50	0.27 (0.97)	~5 (0.03)
glycerol-d_3	711	792/792	−100	1.26 (1.0)	*c*
			20	0.40 (0.95)	~5 (−0.05)
		700/700	20	0.5 (0.91)	~5 (0.09)

[a] The wavelengths of the pump and probe beams in nanometers. [b] A_1 and A_2 are the amplitudes of each exponential in the model decay function. Plus and minus signs correspond to a bleach and an increased absorption, respectively. [c] Single exponential fit parameters. [d] *N*-Methylformamide.

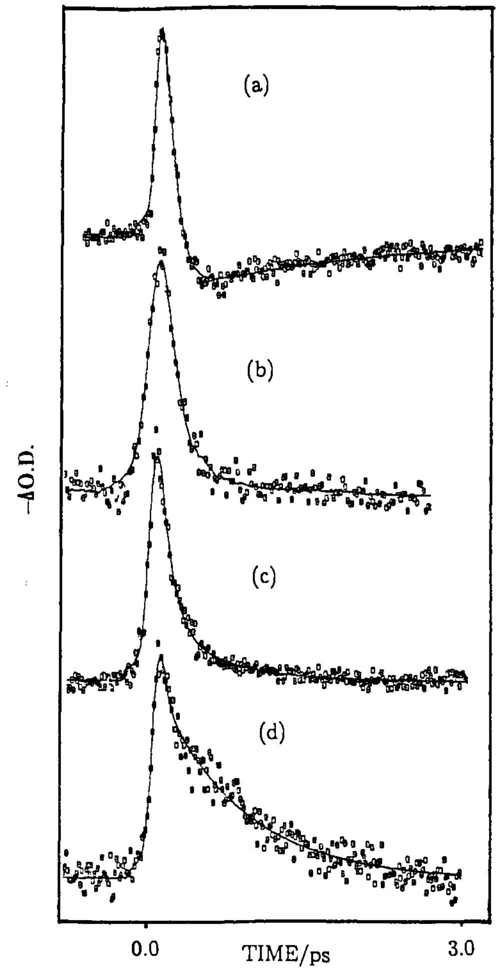

Figure 1. Change in absorption as a function of time delay between the pump and probe pulses for reaction 1 in H_2O at 20 °C (a and b), *N*-methylformamide at 20 °C (c), and glycerol at −100 °C (d). The pulse width was 70 fs and $\lambda_{pump} = \lambda_{probe} = 792$ nm for a, c, and d, and $\lambda_{pump} = 800$ nm and $\lambda_{probe} = 700$ nm for b. A positive signal indicates a bleach. The points are the experimental data, and solid curves show biexponential fits to the data.

are as follows: vibrational frequencies, 2109 and 456 cm^{-1}; vibrational reorganization energies, 619 and 1551 cm^{-1}; solvent reorganization energy, 3700 cm^{-1}; electronic matrix element, 1500 cm^{-1}; and reaction free energy, −7880 cm^{-1}. To be consistent with molecular dynamics calculations, the solvent-coordinate dynamics (D_2O) was modeled by a sum of a fast Gaussian decay (50 fs) to represent inertial solvent motion and a slower exponential decay (0.5 ps) for diffusive motion along the solvent coordinate.[7]

To simplify the calculation and take advantage of the order of magnitude time separation between the inertial and diffusive solvent motion, we have employed a Sumi/Marcus framework for the calculation using the 0.5-ps solvation component as the diffusive motion.[9] The ET rate as a function of diffusive coordinate displacement, z, was calculated by three procedures: model A (simple nonadiabatic) assumes that the inertial component relaxation is immediate on all relevant time scales, and model B (Jortner and Bixon[10]) and model C (Mukamel et al.[11]) include the effect of solvation dynamics. The instantaneous ET rate is a convolution of rates, $k(z)$, with a time-dependent distribution, $P(z)$, of displacement of the diffusive component of the solvent coordinate. This procedure is similar to that described by Walker et al.[5] Although the ET reaction in this model is not simply first-order, the simulations are reasonably well approximated by exponential decays of reactant concentration with the time constants reported below as mean relaxation times.

Model A is analogous to the standard, weak-coupling, multimode, semiquantum expression (Fermi golden rule). Eight quantized solute vibrational modes were employed, using Raman data and absorption spectral simulations to determine frequencies and reorganization energies. For the bath degree of freedom, only the inertial contribution of solvation was included. The diffusive solvent contribution was assumed to be frozen during the ET event, which is consistent with the Sumi–Marcus expression invoked.[5] For models B and C, the eight vibrational modes were grouped into two effective modes with frequencies and reorganization energies given above. The nuclear degrees of freedom were again decomposed into a diffusive mode and an inertial mode with a correlation time of 50 fs.

The theoretical predictions for the reverse ET rate are 12–240 fs for model A, 24–270 fs for model B, and 120–300 fs for model C. The range of values is due to a range (20–80%) for the assumed inertial fraction of the total dynamical response of the solvent.

Alternative theoretical models, which do not treat the vibrational modes quantum mechanically and/or assume that the solvent

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response lacks a fast inertial component, predict rates that are orders of magnitude slower than experiment.[3] Qualitatively, these results indicate that absolute ET rate theory is in good agreement with experiment for reaction 1, if vibrational modes and solvation dynamics are treated in a realistic fashion.

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Through-Space Intramolecular Triplet Energy Transfer: The Cinnamyl Esters of ω-Benzoyl Carboxylic Acids[†]

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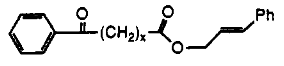
Closs has been very successful in recent years in interpreting intramolecular electron and energy transfer in relatively rigid cyclic "bichromophoric" molecules in terms of through-bond interactions.[1] Rate constants for triplet energy transfer drop approximately 1 order of magnitude for each additional bond between a benzophenone group and a naphthalene. In more flexible systems, it is to be expected that through-space transfer would become competitive as connecting chains become longer. We wish to report a clear example of this behavior that represents an extension to longer spacers of some of the earliest quantitative measurements on intramolecular energy transfer.[2]

Cowan and Baum reported sharp decreases in triplet energy transfer rate constants as the number of methylenes connecting a benzoyl group to the β-carbon of styrene increases from two to four.[2] In this case energy transfer from ketone (E_T = 72 kcal/mol[3]) to styrene (E_T = 62 kcal/mol[4]) is at least 10 kcal/mol exothermic, and the corresponding bimolecular reaction is diffusion limited.[5] We have extended the number of connecting atoms in a synthetically simple way by preparing the cinnamyl esters **1–4** of four ω-benzoylalkanoic acids.



1 - 4 : x = 1 - 4

Irradiation of the compounds at 365 nm, where the styrene group barely absorbs, produces efficient trans → cis isomerization, with quantum yields of 0.49–0.59 for **2–4**, just as was observed for the shorter analogs.[2] The cis compounds separate cleanly on GC columns and also give distinctive ^{1}H NMR signals for both the methylene and vinyl protons. Identical cis/trans ratios were measured by GC and by NMR. No other products were detectable by either analytical method except in the case of **4**, where a small amount of acetophenone was detected at high conversions.

Compound **1** is a special case, since it exists in a 2:1 equilibrium with its enol form **1′** in benzene. Its quantum yield of isomerization is only 0.06, since the enol absorbs more strongly than the ketone at 365 nm, but only the keto form undergoes trans → cis isomerization. NMR spectra at 10% conversion clearly show formation of the cis keto form with only a trace of cis enol. The cis ketone gradually is converted thermally to the cis enol until a 2:1 equilibrium is attained. The enol is a hydroxycinnamate with a lower excitation energy than the simple styrene, so that it is not surprising that excitation of the enol is not followed by triplet energy transfer to the styrene moiety.

1 **1′**

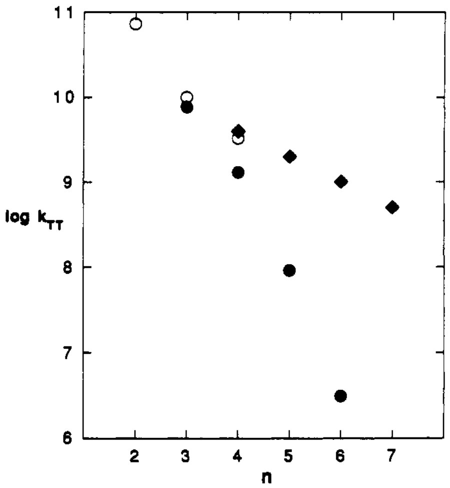


Figure 1. Rate constants for triplet energy transfer as a function of the number of atoms connecting the donor triplet benzoyl group and the acceptor: ●, ref 1; ○, ref 2; ◆, compounds **1–4**.

Triplet lifetimes of the ketones were determined by Stern–Volmer quenching of the trans → cis isomerization with added 2,5-dimethyl-2,4-hexadiene. Quantum yields of cis formation were first corrected for reversibility;[6,7] the slopes of the linear Stern–Volmer plots provided $k_q\tau$ values. Reciprocal lifetimes were calculated from the known k_q value of 6×10^9 M^{-1} s^{-1}.[8] The ester functionality near the γ-carbon in **3** and **4** is known to markedly depress rate constants for γ-hydrogen abstraction.[9] This fact and the lack of competing reaction allow us to equate k_{TT} with $1/\tau$ for these compounds: $k_{TT} = 4 \times 10^9$, 2×10^9, 1×10^9, and 5×10^8 s^{-1} for x = 1–4, respectively. Any contribution of bimolecular energy transfer to the observed decay rates is $< 5 \times 10^7$ s^{-1} since the ketone concentrations were kept below 10^{-2} M.

Figure 1 compares our results with those of Cowan[10] and Closs. Energy-transfer rate constants are plotted as a function of the number of atoms in the chain linking the two chromophores. We have chosen Closs' data only for benzophenone and naphthalene occupying equatorial positions on cyclohexane or decalin so that all of the connecting bonds have staggered conformations. This arrangement results in the fastest energy transfer in Closs' system and should correspond to the most stable conformation of the short polymethylene links in **1–4**, where $n = x + 3$. Closs' cyclic compounds of course are constrained to transfer energy through the intervening bonds, whereas the flexible acyclic tethers that we and Cowan studied potentially allow through-space transfer from partially coiled conformations to compete with through-bond transfer from stretched out conformations.

Considering Cowan's data first, we see that only the $n = 2/n = 3$ pair lies on the same curve as Closs' results and shows the order of magnitude decrease observed for each additional intervening bond in the Closs system. The similarity of actual rate constants in the two systems is not surprising, given that they both represent highly exothermic energy transfer to conjugated π-

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[†] This paper is dedicated to the memory of Gerhard Closs, whose lively brilliance made things easier for the rest of us.

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