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(CN)$_4$] in water and acetone were determined by picosecond transient absorption spectroscopy.[8,11] In both solvents transient absorption kinetics were pulse-width limited, indicating excited-state lifetimes shorter than 25–30 ps. Although the decay kinetics for the complex in the two solvents appeared similar, the spectra of the transient species were not. The difference spectrum recorded during 532-nm (25-ps) excitation of $Fe(bpy)(CN)_4^{2-}$ in H_2O is shown in Figure 1a and that recorded during 532-nm excitation of the same complex in acetone is shown in Figure 1b; similar results were observed for excitation at 650 nm.[12]

Approximate absorption spectra of the transient species generated from the difference spectra are shown in Figure 2.[13] The excited-state absorption spectrum for $Fe(bpy)(CN)_4^{2-}$ in water (Figure 2a) exhibits only weak, featureless absorption from 360 to 800 nm. By contrast, the spectrum of the transient formed in acetone (Figure 2b) has two major absorption features: a sharp band at 370 nm and a weaker one maximizing near 525 nm. The spectrum in Figure 2b bears a close resemblance to that of the 2,2′-bpy radical anion[1,14] and is very strong evidence that the transient generated by 532- or 650-nm excitation of $Fe(bpy)(CN)_4^{2-}$ in acetone is an MLCT ($Fe^{III}(bpy^-)$) state.[15] The absence of bands at 370 and 525 nm in Figure 2a and the resemblance to the transient spectra of $Fe(bpy)_3^{2+}$ and $Fe(bpy)_2(CN)_2$ demonstrate that a LF state is produced when $Fe(bpy)(CN)_4^{2-}$ is excited at 532 nm in water.

These results demonstrate the dramatic effect of solvent on the photophysical properties of a solute molecule.[16] The coarse tuning of MLCT excited-state energies by modifying the ligands has been fairly widely exploited.[4,11,16,17] The additional dimension of solvent variation permits a continuous fine tuning of MLCT state energies over a comparable range. When used together, ligand and solvent tuning of excited-state energies creates an extraordinary degree of flexibility in selecting the properties of a photosensitizer.

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(11) (a) $H_2Fe(CN)_4(bpy)$ was prepared using the procedure described by Schilt[11b] and the complex was converted to its tetrabutylammonium salt as described by Toma and Takasugi.[3] (b) Schilt, A. A. *J. Am. Chem. Soc.* **1960**, *82*, 3000.

(12) Although similar difference spectra were obtained for both 532-nm and 650-nm excitation of $Fe(bpy)(CN)_4^{2-}$ in acetone, complete recovery of the initial absorbance was only observed with 650-nm excitation, perhaps because of photochemistry or multiphoton effects with 532-nm excitation.[8] The 650-nm excitation was of lower intensity and was predominantly into the lower energy MLCT band of $Fe(bpy)(CN)_4^{2-}$ (Figure 2b). By contrast, excitation with 532 nm was into both the higher and the lower energy MLCT bands.

(13) The absorption spectra of the transient species were estimated from their difference spectra by adding to the latter sufficient ground-state absorption to produce nonnegative, smoothly varying molar absorptivities throughout the observation region.[2]

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(15) (a) The molar absorptivities of the 370- and 525-nm bands in Figure 2b are about half as great as the values reported for the corresponding transitions in $Ru(bpy)(CN)_4^{2-}$.[10] A low molar absorptivity for the MLCT state of $Fe(bpy)(CN)_4^{2-}$ would be calculated if the difference spectrum in Figure 1a does not arise solely from the MLCT state but rather from two excited states (MLCT and LF) which decay serially or in parallel with comparable rates. If this is the case the MLCT state need not necessarily be lower in energy than the LF state, but the two states must be close enough in energy to retard the MLCT to LF transition. (b) The very short lifetime of the MLCT state in acetone could be due to the proximity of the LF state and/or the fact that the MLCT state is relatively low lying[9] (energy-gap law).

(16) (a) To our knowledge this is the first transient measurement demonstrating solvent tuning of the excited state. However, Malouf and Ford[16b] discussed the possibility of solvent tuning in steady-state photolyses of the comparably solvent-dependent $Ru(NH_3)_5L^{2+}$ (L a pyridine derivative) series. In addition, the solvent-sensitive carbonyls[16c] afford the same opportunity for certain metal–ligand combinations. (b) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213. (c) See: Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 572 and references cited therein.

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A Novel Method for Determining Internuclear Distances and Correlation Times from NMR Cross-Relaxation Rates

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The development of NMR techniques for determining proton–proton distances, r_{ij}, from cross-relaxation rates, σ_{ij}, or NOE's has greatly enhanced our knowledge of the three-dimensional structure of molecules in solution.[1] To obtain quantitative distances from such experiments, however, one must also know the correlation time, τ_c, for the relaxation processes since $\sigma_{ij} = (\gamma^4\hbar^2/r_{ij}^6)f(\omega_0,\tau_c)$. Although τ_c may be obtained by measuring σ at different field strengths, $B_0 = \omega_0/\gamma$, a more common practice is to determine $f(\omega_0, \tau_c)$ by measuring σ for a pair of protons whose separation is known a priori. Unknown distances may then be calculated from the relation $r_{ij} = r_{std}(\sigma_{ij}/\sigma_{std})^{1/6}$. This approach requires that $f(\omega_0,\tau_c)$ is the same for all pairs of protons and that there is some proton pair suitably resolved for calibration purposes.

Here we show how τ_c, and thus internuclear distances, may be determined by a novel method involving measurements of both longitudinal ($\sigma_\parallel$) and transverse[2,3] ($\sigma_\perp$) cross-relaxation rates. The experiments may be done at a single field strength and require no calibration pair nor assumptions about $f(\omega_0,\tau_c)$ for different protons. The method is based on the fact that $\sigma_\parallel$ and $\sigma_\perp$ have different dependencies on τ_c.

As Bothner-By and co-workers first showed[2a] $\sigma_\perp$ for a pair of nonequivalent protons separated by r_{ij} which undergoes isotropic reorientation can be expressed as

$$(\sigma_\perp)_{ij} = (\gamma^4\hbar^2/10r_{ij}^6)(3/(1 + \omega_0^2\tau_c^2) + 2)\tau_c \qquad (1)$$

This equation may be compared with the well-known expression for $\sigma_\parallel$

$$(\sigma_\parallel)_{ij} = (\gamma^4\hbar^2/10r_{ij}^6)(6/(1 + 4\omega_0^2\tau_c^2) - 1)\tau_c \qquad (2)$$

For short τ_c ($\omega_0\tau_c \ll 1$), the ratio $\sigma_\parallel/\sigma_\perp$ has a limiting value of 1, while for long τ_c ($\omega_0\tau_c \ll 1$), the limit is –0.5. At intermediate values of τ_c in the range $-1 \leq \log \omega_0\tau_c \leq 1$, there is a smooth transition between these limits such that one can determine τ_c uniquely from the ratio of $\sigma_\parallel$ to $\sigma_\perp$. Once τ_c is known, r_{ij} can be calculated directly from eq 1 or 2.

Transverse cross-relaxation is observed in the rotating frame with the spins oriented along an effective spin-locking field, $\omega_e = \gamma B_{eff} = \gamma(\Delta^2 + B_{SL}^2)^{1/2}$, which makes an angle, $\beta = \sin^{-1}(B_{SL}/B_{eff})$ with the longitudinal component, Δ, of the applied field in the rotating frame.[2,4] In practice offsets, Δ cannot be ignored so that the cross-relaxation rate as observed in the rotating reference frame must be expressed as[5]

$$(\sigma_{RF})_{ij} = \cos\beta_i \cos\beta_j(\sigma_\parallel)_{ij} + \sin\beta_i \sin\beta_j(\sigma_\perp)_{ij} + (\gamma^4\hbar^2/10r_{ij}^6)\sin^2\beta_i \sin^2\beta_j((1 + 4\omega_e^2\tau_c^2)^{-1} - 1)\tau_c \qquad (3)$$

In solutions, $\omega_e^2\tau_c^2 \ll 1$ so the last term in eq 3 can safely be ignored. Clearly, when $B_{SL} \gg |\Delta|$, $\beta \approx \pi/2$ and $\sigma_{RF} \approx \sigma_\perp$.

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Table I. Longitudinal and Transverse Cross-Relaxation Rates for $^{Pro}C_{\delta}H_2$ and ^{Phe}NH–$^{Leu}C_{\alpha}H$ Protons in Gramicidin S in Me_2SO-d_6

proton pair	temp, °C	$\sigma_{\parallel}$, s^{-1}	σ_{RF}, s^{-1}	$\sigma_{\perp}$, s^{-1}[b]	τ_c, ns	$f_{\parallel}/\sigma_{\parallel}$, 10^{-9} s^2[c]	$r_{\parallel}$, Å[d]	$f_{\perp}/\sigma_{\perp}$, 10^{-9} s^2[e]	$r_{\perp}$, Å[f]
$C_{\delta}H \rightarrow C_{\delta}H'$[a]	20	−1.8	4.0	4.4	1.9	0.96	1.9	0.98	1.9
	30	−1.3	3.4	3.6	1.5	0.98	2.0	0.98	1.9
	40	−0.79	2.8	3.0	1.2	1.0	2.0	0.97	2.0
	60	−0.27	2.0	2.1	0.77	1.0	2.0	1.1	2.0
$^{Phe}NH \rightarrow {}^{Leu}C_{\alpha}H$[a]	20	−0.75	1.6	1.9	1.8	2.1	2.2	2.1	2.2
	30	−0.40	1.4	1.6	1.1	1.7	2.1	1.8	2.1
	40	−0.20	1.0	1.2	0.8	1.9	2.2	1.9	2.2
	60	~0	0.9	1.0	0.6			1.9	2.2

[a] Offsets from rf carrier: $^{Pro}C_{\delta}H$, −357 Hz; $^{Pro}C_{\delta}H'$, −662 Hz; ^{Phe}NH, 1302 Hz; $^{Leu}C_{\alpha}H$, −50 Hz; γB_{SL} = 2174 Hz. [b] From eq 3. [c] $f_{\parallel} = (6/(1 + 4\omega_0^2\tau_c^2) - 1)\tau_c$. [d] From eq 2. [e] $f_{\perp} = (3/(1 + \omega_0^2\tau_c^2) + 2)\tau_c$. [f] From eq 1.

To test this we measured $\sigma_{\parallel}$ and $\sigma_{\parallel}$ as a function of temperature for different pairs of protons in the cyclic decapeptide Gramicinin S in Me_2SO-d_6. The experiments were done at 300 MHz by using one-dimensional difference techniques. To determine $\sigma_{\parallel}$, a weak 180° pulse (20 ms) from the decoupler was used to selectively invert one of the proton lines in the spectrum. Following a delay 10–100 ms for cross-relaxation, a strong nonselective 90° pulse was applied and the FID was collected. On alternate scans, the frequency of the decoupler pulse was offset by ~50 Hz and the FID was subtracted from memory. Fourier tranformation of the difference FID yielded a spectra containing only the inverted line and "cross-peaks" from cross-relaxation. For σ_{RF}, the pulse sequence was modified by replacing the delay and 90° pulse with a 90° pulse followed immediately by a spin-locking pulse (γB_{SL} = 2100 Hz) shifted in phase by 90° and applied for times ranging from 10 to 100 ms.[6] The cross-relaxation rates were taken as the initial slope of the ratio of the "cross-peak" to inverted peak intensities vs. the delay or the spin-locking time.[7] The transverse cross-relaxation rate $\sigma_{\perp}$ was calculated by using eq 3 and the observed values of $\sigma_{\parallel}$ and σ_{RF}.

Cross-relaxation rates for the geminal pair of proline C_{δ} protons and for the phenylalanine NH-leucine $C_{\alpha}H$ pair are listed in Table I, together with the correlation times and internuclear distances derived from these rates. In view of the fact that no a priori assumptions were made about distances or correlation times, these results are quite acceptable. The PheNH–Leu$C_{\alpha}H$ distance is in excellent agreement with that predicted by minimum-energy calculations and molecular models.[8] Even the apparent lengthening of the distance between the C_{δ} geminal protons by 0.2 Å is consistent with what is known about the internal dynamics of proline-ring deformations. According to the "model free" approach,[9] internal molecular motion occurring at rates much faster than the overall rotational tumbling of the molecule leads to a diminution of $\sigma_{\parallel}$ and σ_{RF} by a factor, $\mathcal{S}^2$. Consequently, $r_{app}^{-6} = \mathcal{S}^2 r_{true}^{-6}$. Assuming r_{true} = 1.8 Å, we calculate a value for $\mathcal{S}$ of 0.6. This agrees well with the value of 0.57 calculated by using parameters of London[10] for proline ring dynamics and ^{13}C relaxation.

Our results also show that the correlation times for cross-relaxation of the $NHC_{\alpha}H$ pair are approximately 0.7 times shorter than those for the C_{δ} geminal pair. Such differences could arise if there are internal modes with correlation times comparable to the rotational correlation time or if the rotational motion is anisotropic and the internuclear vectors have significantly different orientations with respect to the axis of the diffusion tensor.

We also note that if one calculates $r_{NHC_{\alpha}H}$ using the accepted separation of the C_{δ} protons for calibration, one finds $r = 2.1 \pm 0.1$ Å. Although this procedure is clearly invalid for gramicidin S, it yields a perfectly acceptable result owing to a fortuitous cancellation of two erroneous asssumptions.

Recently, Mirau and Bovey[11] described a method for determining τ_c on the basis of the ratio of the nonselective and selective spin–lattice relaxation rates, and it is applicable over the same range of τ_c as ours (i.e., for molecules of MW = 1–3 kdaltons). It differs in that one must assume that spin–lattice relaxation is purely dipolar in origin; an assumption that may not be generally valid. Nonetheless, both methods provide useful access to internuclear distances which are unencumbered by a priori assumptions.

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Coordination Chemistry of Semiconductor Photoelectrodes: Reactions of Etched n-GaAs with Co(III) Complexes

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We report studies of the reactivity of n-GaAs surfaces with transition-metal complexes. Generally, adsorption of metal ions at semiconductor junctions has been observed to increase carrier trapping rates.[1] A notable exception is the improved performance of n-GaAs interfaces after exposure to acidic aqueous solutions of Ru(III) ions and other metal cations,[2] but little information is available regarding the chemistry of these surface treatments. Except for systems in which metal ions act as precursors for the deposition of metals or metal alloys,[3] no information is available regarding the oxidation state or chemical environment of chemisorbed transition-metal complexes on semiconductor electrodes. Possible but undocumented mechanisms of metal ion attachment to the semiconductor surface include electrostatic binding, ligand substitution processes, and redox reactions. To explore the various

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