

group 5 and 6 elements with d^2 configuration.⁶ The bonding properties of the latter are well understood in terms of a MO description. Despite the structural similarities, the electronic properties of **2** are distinctly different and the MO description of the group 5 and 6 trimers is not applicable to **2**.

Assignment of oxidation states II to Ir1 and Ir2 and I to Ir3 (consistent with the preferred coordination geometries of the respective oxidation states)⁷ leads to an 18-electron count for each of the three Ir centers if a bonding interaction is assumed to take place between Ir1 and Ir3 as well as Ir2 and Ir3 but not between Ir1 and Ir2. This view is consistent with the observed bond distances of 3.002 (1), 2.660 (1), 2.663 (1) Å for Ir1–Ir2, Ir1–Ir3, and Ir2–Ir3, respectively.

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Transient Circular Dichroism of the Luminescent State of Ru(bpy)₃²⁺

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We have recently developed a new technique capable of measuring transient circular dichroism (CD) spectra on a nano-second time scale.^{1,2} In this report we describe the application of this technique to the measurement of the CD spectrum of the excited-state absorption of (Δ)-Ru(bpy)₃²⁺. While CD spectra of a few very long-lived triplet excited states of chiral organic molecules have been measured with modifications of standard steady-state photoelastic modulation methods,³⁻⁵ this is the first report of a time-resolved excited-state CD spectrum.

CD spectra have been useful for assigning ground-state spectral transitions in Ru(bpy)₃²⁺.^{6,7} The excited-state spectrum of Ru(bpy)₃²⁺ has not been completely assigned.⁸⁻¹⁰ We have

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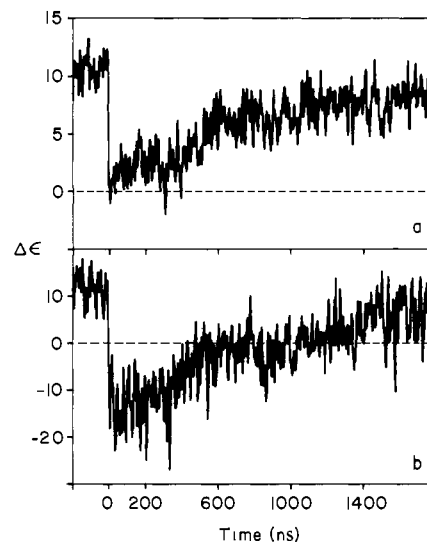


Figure 1. Time-resolved CD signal of Ru(bpy)₃²⁺ in H₂O at 20 °C excited with a 7-ns, 355-nm pulse from a Nd:YAG laser: (a) signal at 420 nm, note a positive CD before the laser fires and subsequent disappearance upon excitation; (b) signal at 315 nm, note the initial positive ground-state CD and subsequent negative CD of the excited state. The kinetics at both wavelengths are consistent with the previously reported lifetime of the luminescent state.¹¹

measured the CD spectrum of this state to address issues concerning the nature of this state. This state is amenable to CD spectroscopy as the lifetime is approximately 640 ns at 20 °C in water¹¹ and the quantum yields for racemization and decomposition are low.^{12,13}

The transient CD technique used here has been described previously.^{1,2} CD is determined by measuring the change in eccentricity of an elliptically polarized probe beam produced by passing linearly polarized light from a xenon flash lamp through a strained, fused quartz plate. A solution of Ru(bpy)₃²⁺ in water is excited with a 355-nm, 7-ns light pulse from a Nd:YAG laser. The sample, resolved in the manner described by Dwyer and Gyarfás,¹⁴ is flowed through a 2-mm path-length cell with strain-free quartz windows.

The ground-state circular dichroism of metal tris(bipyridyls) has been studied in detail.^{15,16} Qualitatively, for ligand-centered transitions the magnitude of the CD can be explained in terms of the degree of coupling between the transition moments on the different ligands. For example, the coupled interligand transition of ground-state M(diimine)₃, centered near 300 nm exhibits a large CD ($\Delta\epsilon > 100$).^{16,17} For this transition in Co(bpy)₂(NO₂)₂³⁺ $\Delta\epsilon \approx 20$,¹⁷ and in Co(bpy)(ethylenediamine)₂³⁺ $\Delta\epsilon \approx 10$.¹⁸ Hence for the absorption of Ru(bpy)₃²⁺ a very small CD would be expected ($\Delta\epsilon \approx 10$) for a $\pi^*\pi^*$ transition localized on a single bipyridyl ligand, while a larger CD would be expected from a transition coupled between two or more ligands.

Figure 1 shows representative CD signals as a function of time. At 420 nm (Figure 1a) there is a positive CD signal before the laser fires (ground-state signal) and subsequent disappearance of the signal upon photolysis (complete ground-state depletion). At 315 nm (Figure 1b) there is a positive CD in the ground state and then a negative CD in the excited state. The lifetime of the signal is the same within our experimental resolution as that previously reported for the luminescence (640 ns).¹¹

Figure 2a shows the ground-state CD of Ru(bpy)₃²⁺ from 310 to 480 nm obtained by averaging the signal for 50 ns before photolysis for 64 averages. This is in excellent agreement with

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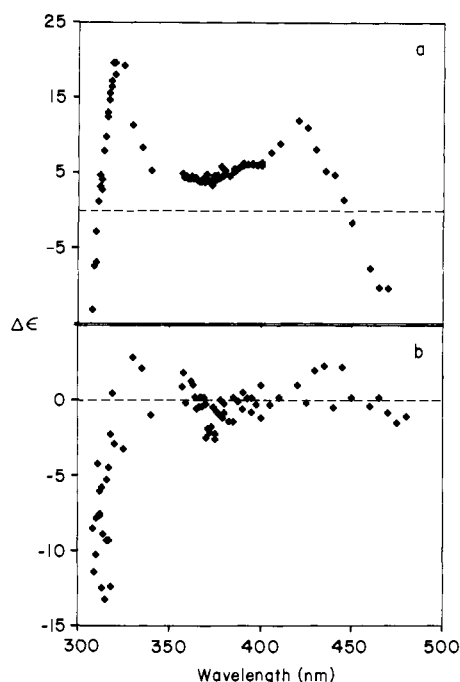


Figure 2. Ground-state (a) and excited-state (b) CD spectra of Ru-(bpy)₃²⁺ taken with the transient CD apparatus.¹ The ground-state spectrum is in excellent agreement with the previously reported spectrum taken with a conventional CD spectrometer.¹⁹ The excited-state spectrum is the average of 64 measurements of signals in a window from 10 to 70 nm after the laser pulse. Sufficient laser power was used to ensure complete ground-state depletion.

a spectrum taken on a conventional CD spectrometer.¹⁹ Note that each point in the spectrum represents a total of 3.2- μ s exposure time. The comparable spectrum taken on a conventional CD spectrometer would require a time constant on the order of 1 s. Work is now proceeding to incorporate a photodiode array detection system to facilitate more efficient collection of CD spectra.

Figure 2b is the excited-state CD spectrum obtained by averaging signals for 60 ns after the laser pulse. Sufficient laser power was used to ensure complete depletion of the ground state as determined by the laser power dependence of the signal. There is no postlaser CD signal within experimental error ($|\Delta\epsilon| \leq 2$) from 450 to 480 nm, a region that lacks significant excited-state absorption. The transient absorption reported by Creutz et al.¹⁰ at 420 nm shows no significant circular dichroism. The CD of the 370-nm transient absorption is very small ($\Delta\epsilon \approx 3$), while a moderate CD is observed centered at 312 nm ($\Delta\epsilon \approx -15$).^{9,10}

The near-zero magnitude of the 370-nm band is consistent with a single ligand localized $\pi\pi^*$ transition. This CD is even less than that reported for the single phen localized $\pi\pi^*$ transition of Co(en)₂(phen)⁺ ($\Delta\epsilon \approx 10$).¹⁸ The moderate CD at 315 nm does not persist into the red, though the excited-state absorption is reported to go as far as 330 nm.¹⁰ Hence the CD implies that the absorption band consists of at least two transitions, one being much more strongly CD active than the other. The magnitude of the $\Delta\epsilon$ of this CD-active band is on the order of the interligand $\pi\pi^*$ CD of the ground-state absorption of Co(bpy)₂(NO₂)₂.¹⁷ Moreover, the transition occurs in a region in which bipyridyl ligand $\pi\pi^*$ transitions are seen. Hence, we tentatively assign this band as interligand $\pi\pi^*$ absorption of the two unreduced ligands. However, a LMCT $d^5\pi^* \rightarrow d^6\pi\pi^*$ transition is also expected to occur in the transient spectrum and this assignment cannot be ruled out. Taken together, our assignments support previous descriptions of the lowest MLCT excited state of Ru(bpy)₃²⁺ as having the transferred electron localized on a single ligand.^{10,20-23}

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Electron Transfer through Aromatic Spacers in Bridged Electron-Donor-Acceptor Molecules

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Recently, linked electron-donor-acceptor systems¹ have been shown to be useful for a critical test of mechanisms and theories of electron-transfer processes.² Among the factors, which determine the rates of electron-transfer processes, are the exothermicity of the reaction, the distance between donor and acceptor, and the nature of the medium or of the spacer between them.

The question of interest in this paper is the potential influence of the spacer between electron donor and electron acceptor on the electron transfer.³

With this goal we synthesized⁴ four linked donor-acceptor compounds (1-4), in which dimethylaniline acts as the donor and (excited) pyrene or anthracene as the acceptor.

Because of the possible rotations around the σ -bonds at the methylene groups, the absolute distance between donor and acceptor is not fixed,⁵ whereas the difference of the distances in the biphenyl bridged (2, 4) compared with the phenyl bridged compounds (1, 3) is definite (4 Å).

The fluorescence lifetimes of the compounds (1-6, Figure 1) were measured by time-resolved photon counting. The pyrene or anthracene moiety was excited at a wavelength of 337 nm by using a flashlamp (ORTEC 9362) with a pulse width of 2.7 ns (fwhm). At this wavelength, the absorption of the dimethylanilino group and of the spacers is negligible. Singlet energy transfer from excited pyrene or anthracene to the dimethylanilino group is impossible for energetic reasons. In time-resolved experiments, the fluorescence light was not spectrally resolved except by the

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