$\mu_2{:}\eta^2$-acetyl (4) IR absorption[18,19] falls within the regime of these proposed surface species. The course of oxygenate production may utilize H_{ads} or proton transfers from Rh/support H_2O and $ZrOH$[22] functionalities in effecting acyl reductive elimination. Compensation for the loss of the Zr–O link in **4** is ultimately provided by the X of the electrophile. The corresponding oxygenate release in a heterogeneous system could be accompanied by the formation of a new Zr–O bond arising from a similar carbonyl-derived intermediate, a neighboring zirconium oxide/hydroxide,[22] or water.

Acknowledgment. Support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Cornell University is gratefully acknowledged. We thank the ARCO Foundation for a fellowship (G.S.F.) and the NIH and NSF Instrumentation Programs for support of the Cornell NMR Facility.

Circular Dichroism of a Subnanosecond State: (Δ)-$Fe(bpy)_3{}^{2+}$*

Steven J. Milder, Jon S. Gold, and David S. Kliger*

Department of Chemistry, University of California
Santa Cruz, California 95064

Received July 21, 1986

We recently presented the first time-resolved circular dichroism (CD) spectrum of a molecular excited state in a report on the CD of the luminescent (MLCT) state of (Δ)-$Ru(bpy)_3{}^{2+}$.[1] The small CD observed in the bpy^- $\pi\pi^*$ transition at 370 nm ($\Delta\epsilon \approx -3$) is consistent with a single-ligand localized model for the transferred electron in the excited state. We report here the excited-state absorption and CD spectra of (Δ)-$Fe(bpy)_3{}^{2+}$. Like $Ru(bpy)_3{}^{2+}$, the ground state of $Fe(bpy)_3{}^{2+}$ is low-spin d^6. Yet unlike $Ru(bpy)_3{}^{2+}$, its lowest excited state is a metal-centered d–d state.[2-5] Thus, differences are expected in excited-state absorption and CD spectra of these two molecules. We found a large CD in the ligand $\pi\pi^*$ transitions of the excited (Δ)-$Fe(bpy)_3{}^{2+}$, consistent with a metal-centered excited state. Since the excited-state lifetime of $Fe(bpy)_3{}^{2+}$ is 800 ps at room temperature in water,[2,6] this is the first report of a CD spectrum of a state that lives for less than a nanosecond.

Creutz et al. previously obtained the absorption spectrum of excited $Fe(bpy)_3{}^{2+}$ in the visible and near-UV regions down to approximately 310 nm and observed no significant charge-transfer transient absorptions.[2] Figure 1 shows the transient absorption spectrum extended to 280 nm.[7] Because of the short lifetime of the excited state, it was not possible to achieve saturation of the excited state with excitation energies of up to 30 mJ/pulse. We thus used the degree of bleaching observed at 488 nm, a wavelength with no significant excited-state absorption,[2] to correct for ground-state bleaching and produce the true excited-state spectrum. This absorption has slightly lower intensity and exhibits a small red shift relative to the ground-state $\pi\pi^*$ absorption. Clearly, this excited-state absorption can be assigned as primarily ligand $\pi\pi^*$.

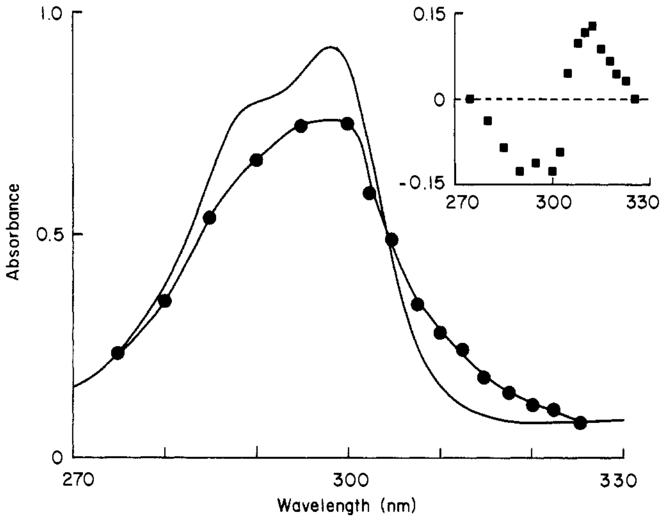

Figure 1. Ground-state absorption spectrum (—) and excited state absorption spectrum (●) of $Fe(bpy)_3{}^{2+}$ in the $\pi\pi^*$ region. Inset: The transient difference spectrum extrapolated to complete ground-state depletion (excited-state production).

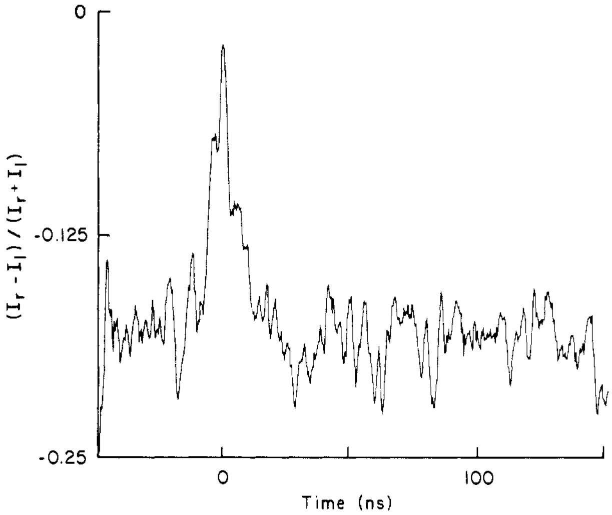

Figure 2. An example of the transient CD signal, representing the average of 256 measurements, seen at 297.5 nm. The signal $(I_r - I_l)/(I_r + I_l)$ is equal to $\Delta\epsilon(2.3cl/\delta)$, where the concentration of (Δ)-$Fe(bpy)_3{}^{2+}$ in water is 4.0×10^{-5} M, the path length is 0.2 cm, and the retardation in the probe beam strain plate, δ, is 0.018 rad (see ref 8). Excitation was with a 532-nm, 30-mJ, 4-ns pulse. A maximum of 0.5 of the chromophores within the probe beam were excited at any time during the laser pulse.

The excited-state CD of (Δ)-$Fe(bpy)_3{}^{2+}$ was obtained by using the laser photolysis apparatus used for transient absorption work with the probe beam optics modified for CD measurements as described in ref 8. Figure 2 shows a typical signal when half of the (Δ)-$Fe(bpy)_3{}^{2+}$ within the probe beam is excited at the maximum of the laser pulse. The width of the transient signal is a function of the excited-state lifetime, the excitation pulse width, and the response time of the detection system.

The actual CD signal of the excited state, rather than the change in CD upon excitation, was determined by applying a correction to the change in the signal obtained at the maximum of the laser excitation. The degree of ground-state depletion (excited-state production) at the maximum of the laser pulse was determined, and the change in the CD signal was divided by this value and then added to the ground-state CD to give the excited-state CD. The ground state racemizes quickly,[9,10] with a

---

(1) Gold, J. S.; Milder, S. J.; Lewis, J. W.; Kliger, D. S. *J. Am. Chem. Soc.* **1985**, *107*, 8285.

(2) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(3) Bergkamp, M. A.; Brunschwig, B. S.; Gutlich, P.; Netzel, T. L.; Sutin, N. *Chem. Phys. Lett.* **1981**, *81*, 147.

(4) Decurtins, S.; Felix, F.; Ferguson, J.; Gudel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4102.

(5) Reeder, K. A.; Dose, E. V.; Wilson, L. J. *Inorg. Chem.*, **1978**, *17*, 1071.

(6) Kirk, A. D.; Hoggard, P. E.; Porter, G. B.; Rockely, M. G.; Windsor, M. W. *Chem. Phys. Lett.* **1976**, *37*, 199.

(7) Excitation was with a short pulse of a Quanta Ray DCR-2 Nd:YAG laser ($\tau \approx 4$ ns) at 532 nm. Detection of the pulsed xenon probe beam was through a Pacific Precision 0.45-m monochromator by an EMI 9876QB photomultiplier (rise time ≈ 1.8 ns). The signal was recorded and analyzed on a Tektronix 7912AD/4041 data acquisition system (500-MHz bandwidth).

(8) Lewis, J. W.; Tilton, R. F.; Einterz, C. M.; Milder, S. J.; Kuntz, I. D.; Kliger, D. S. *J. Phys. Chem.* **1985**, *89*, 289.

0002-7863/86/1508-8295$01.50/0

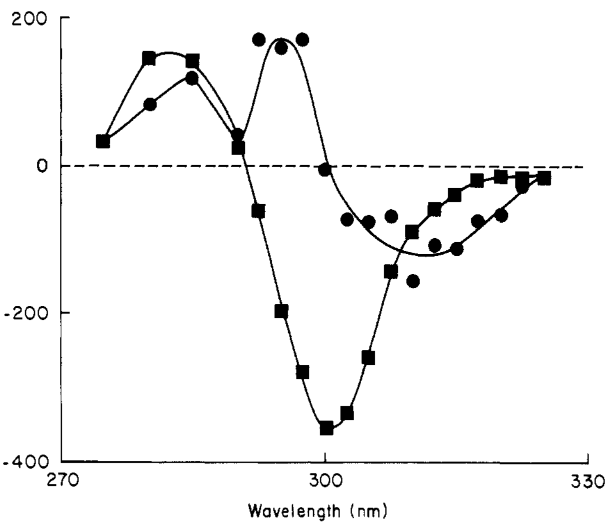

Figure 3. Ground-state (■) and excited state (●) CD spectra of (Δ)-Fe(bpy)$_3^{2+}$. Each point on the spectrum represents the average of three experiments of 256 averages. For the three experiments, the average standard deviation (in Δε) for the ground-state values is 37, while the average standard deviation for the excited state values is 44. The difference in the absolute ground-state CD compared to previously reported values[9,10] is probably due to differences in the optical purity of the samples. The experimental conditions were the same as described in Figure 2.

half-life of 18 min under our conditions. Thus, measurements at all wavelengths were made within 5 min of sample preparation.[11] Repeated laser excitation of the sample (532 nm, 2 Hz, 30 mJ/pulse, 0.15-cm^3 sample volume) did not noticeably accelerate the racemization. The ground- and excited-state CD spectra are shown in Figure 3. The ground-state spectrum is in agreement with the reported shape of the ground-state CD spectrum taken on a conventional spectrometer.[10] The excited-state CD spectrum is red shifted and somewhat diminished in magnitude relative to the ground-state CD. The dip seen in the positive band below 300 nm in the excited-state CD spectrum is reproducible, but we do not yet understand its origin.

Both the absorption and CD spectra of the $\pi\pi^*$ bpy transitions red shift and decrease in intensity in the excited-state relative to the ground state. Unlike in the ground state, there is a lack of observed visible CT states with which the $\pi\pi^*$ states can interact and be shifted to higher energy.[2,10] Thus, a red shift in the $\pi\pi^*$ absorption in the excited state is expected. Though excitation at 532 nm is into an MLCT state, it has been shown that ligand field states are populated within 10 ps of excitation.[2,3] Both $^3T_1$ and $^5T_2$ states lie at lower energy than the lowest MLCT states,[2] and both could be important in the excited-state dynamics and spectroscopy. The ligand field nature of the metastable excited state(s) should not inhibit exciton coupling among the three $\pi\pi^*$ transitions in the bipyridyl ligands, so one expects[10,12] (and observes) a strong CD in the red-shifted $\pi\pi^*$ transitions.[13] Thus, the excited-state absorption and CD is consistent with a d–d excited-state description for Fe(bpy)$_3^{2+}$.

Acknowledgment. We thank J. W. Lewis for his major role in the continuing development of the time-resolved CD technique used in this work. This work was supported by Grant GM35158 from the National Institutes of Health.

---

[9] Hidaka, J.; Douglas, B. E. *Inorg. Chem.* **1964**, *4*, 1180.

[10] Mason, S. F.; Peart, B. J.; Waddell, R. E. *J. Chem. Soc., Dalton Trans.* **1973**, 944.

[11] [(Δ)-Fe(bpy)$_3$]Br$_2$ was made by a procedure slightly modified from that described in: Dwyer, F. P.; Gyarfas, E. C. *Proc. R. Soc. N. S. W.* **1951**, *85*, 135.

[12] Bosnich, B. *Acc. Chem. Res.* **1969**, *2*, 266.

[13] A single-ligand-localized MLCT state would leave two unreduced ligands to participate in coupling in the $\pi\pi^*$ transition. One expects the decrease in the magnitude of the CD transition in such a situation to be much greater than that observed.[9,10,14]

[14] Gold, J. S.; Milder, S. J. *Inorg. Chem.* **1986**, *25*, 4611.

On the Estimation of Metal–Metal Distortions for Metal–Metal Orbital Electronic Ionizations and Excitations

Vincent M. Miskowski* and David E. Brinza

Chemical and Mechanical Systems Division
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

Received July 11, 1986

In an experimental tour de force, Lichtenberger and Blevins (LB) were recently able[1] to resolve a $\nu(Mo_2)$ vibronic structure in the metal–metal δ-orbital photoelectron ionization band ($^1A_{1g} \rightarrow {}^2B_{2g}$) of $Mo_2(O_2CCH_3)_4$ in the gas phase at 200 °C. LB performed a Franck–Condon (FC) analysis of the observed band profile. They noted the band to maximize at seven (or more) quanta of the excited state $\nu(Mo_2)$ of $\approx$360 cm^{-1} and concluded that the $^2B_{2g}$ metal–metal distortion is 0.13–0.18 Å as calculated in various approximations. This value is much greater than that for the $\delta \rightarrow \delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$) excitation previously[2] characterized at liquid helium temperature (0.08–0.11 Å in an equivalent approximation).

A larger distortion for the δ ionization than for the $\delta \rightarrow \delta^*$ excitation was unexpected; since the δ^* orbital is formally metal–metal antibonding, molecular orbital arguments would predict just the opposite trend. LB were led to suggest that the change in metal oxidation state in the ionization was of significance. However, recent Hartree–Fock–Slater calculations[3] for $Mo_2(O_2CCH_3)_4$ fail to indicate a large distortion for $^2B_{2g}$ (0.04 Å calculated). LB explicitly excluded "hot bands" as having any important effect on the FC results (footnote 27 of ref 1). This seemed surprising to us, as about 30% of the molecules should be in metal–metal vibrationally excited states at 200 °C, assuming a ground-state $\nu(Mo_2)$ of $\approx$400 cm^{-1}. We now show that the thermal effects are indeed significant.

Assume an electronic absorption transition with energy E_{00} and a single vibrationally active harmonic vibrational mode, which has equal ground- and excited-state frequencies.[4] At zero temperature, the intensity $A(n)$ of the vibronic electronic transition involving n quanta of the excited-state vibrational mode, appearing at an energy $E_{00} + n\nu$, is[5,6]

$$A(n) = |D^0|^2 \exp(-S)(S^n/n!) \qquad (1)$$

where $|D^0|^2$ is the pure electronic transition intensity and S, the Huang–Rhys factor, is the $(0 \rightarrow 1)/(0 \rightarrow 0)$ intensity ratio. For harmonic oscillators, S is generally related to distortion along the vibrational coordinate by

$$\Delta Q = 8.209\left(\frac{S}{M\nu_f}\right)^{1/2}\left(\frac{\nu_i + \nu_f}{2\nu_i}\right) \qquad (2)$$

where ν_i and ν_f are the initial and final state vibrational frequencies in reciprocal centimeters, M is the effective mass in atomic mass

---

[1] Lichtenberger, D. L.; Blevins, C. H. II *J. Am. Chem. Soc.* **1984**, *106*, 1636.

[2] (a) Trogler, W. C.; Solomon, E. I.; Trajberg, I.; Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1977**, *16*, 828. The electronic transition was unfortunately misassigned in this work. (b) Martin, D. S.; Newman, R. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2511.

[3] Ziegler, T. *J. Am. Chem. Soc.* **1985**, *107*, 4453.

[4] LB allowed for different ground- and excited-state frequencies and for $^2B_{2g}$ anharmonicity but indicated these effects to be minor, and we agree. Allowing the ground-state frequency to be slightly (10%) larger than the excited-state value will tend to smear hot band absorption to the red, accentuating the effect of the hot bands, but will not greatly affect the band shape for such a small frequency difference.

[5] (a) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill: New York, 1979; pp 109–116. (b) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951. (c) Equations 1 and 3 are the same, outside of some temperature-independent factors, as those employed for electron-transfer reactions: Jornter, J. *Biochim. Biophys. Acta* **1980**, *594*, 193.

[6] A small correction for the "Einstein" frequency dependence of the transition probability must also[5b] be applied.