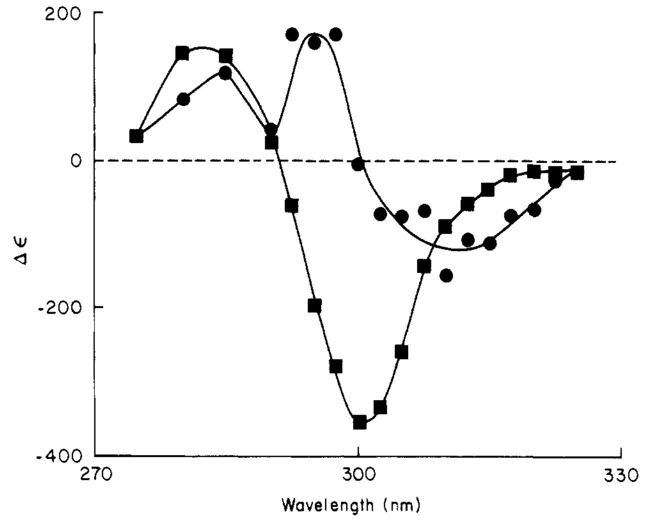

Figure 3. Ground-state (■) and excited state (●) CD spectra of (Δ)-Fe(bpy)$_3^{2+}$. Each point on the spectrum represents the average of three experiments of 256 averages. For the three experiments, the average standard deviation (in Δε) for the ground-state values is 37, while the average standard 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 $\nu(\mathrm{Mo_2})$ 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 $\nu(\mathrm{Mo_2})$ of ≈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 $\nu(\mathrm{Mo_2})$ of ≈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]

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

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

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

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.

0002-7863/86/1508-8296$01.50/0

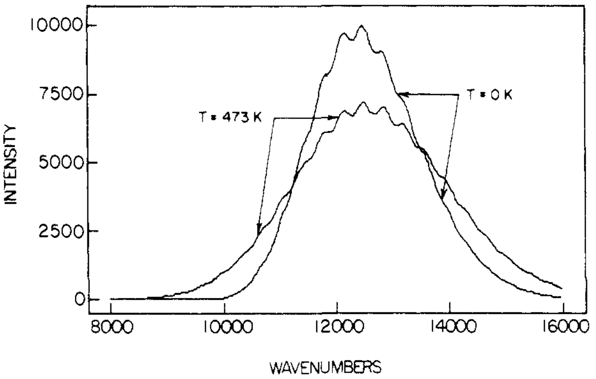

Figure 1. Calculated absorption band profiles at indicated temperatures for $\nu_i = \nu_f = 360$ cm^{-1}, $S = 7$, and a Gaussian fwhm of 400 cm^{-1} for the individual lines. The electronic origin was arbitrarily placed at 10 000 cm^{-1}.

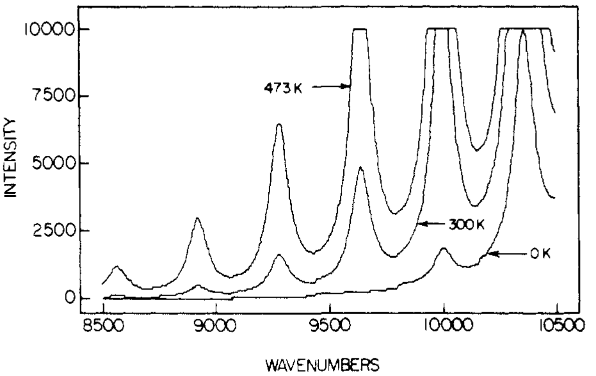

Figure 2. As for Figure 1 but with a Lorentzian fwhm of 100 cm^{-1} and showing an expanded view of the region near the origin.

units (equal to the reduced mass for a diatomic molecule), and ΔQ is the distortion in angstroms.

For nonzero temperature, the spectrum becomes a sum of spectra for the various electronic ground state thermally populated vibrational levels. For equal ground- and excited-state frequencies, we have lines at energies $E_{00} + p\nu$, where $p = n - m$ and m is some number of ground state vibrational quanta. A computationally convenient expression for the total intensity at E_{00} is[5a]

$$A(p) = |D^0|^2 Z^{-p/2} \exp\left(-S\frac{1+Z}{1-Z}\right) I_p(2SZ^{1/2}/1 - Z) \quad (3)$$

where

$$Z = \exp(-\nu/kT) \quad (4)$$

and the I_p are modified Bessel functions.

In Figures 1–3 we show some calculations for $\nu = 360$ cm^{-1}; an E_{00} of 10 000 cm^{-1} was arbitrarily assumed. A value near 6.7 eV would be correct,[1] but this does not, of course, affect relative intensity distributions.

The $T = 0$ K calculation for $S = 7$ is similar to the data and calculation of LB. However, our calculation shows that the band at 473 K (200 °C) is substantially broadened; interpreted as a $T = 0$ K spectrum, it appears to require at least nine 360-cm^{-1} quanta to maximize from the "origin" (which is actually a hot band), and it does *not* resemble the experimental data.

Insight into what is happening is provided by Figure 2, where we use a narrow line width for clarity. At higher temperatures, not only do the "normal" hot bands grow in (negative values of p in eq 3), but intensity also increases for $p = 0, 1, \ldots$, while (Figure 1) intensity decreases for p near 7 (the maximum). The integrated intensity remains constant. The important point is that the intensity at $p = 0$ is *not* temperature independent and that neglect of this point will result in serious underestimation of calculated hot band intensities if both S and T are large. The reason for this is that, for large S, vibrational overlaps for, e.g., 1 → 1 and 2 → 2, transitions are much larger than those for 0 → 0. Figure 3 shows a calculation for a much smaller value of S, that is $S = 3$. At 200 °C, the band profile between the maximum and the "origin" (which is actually a hot band) resembles the data of LB. Thus, we conclude that the $^2B_{2g}$ distortion is significantly less than estimated by LB; $S = 3$ corresponds to $\Delta Q = 0.11$ Å, according to eq 2 in the diatomic approximation.

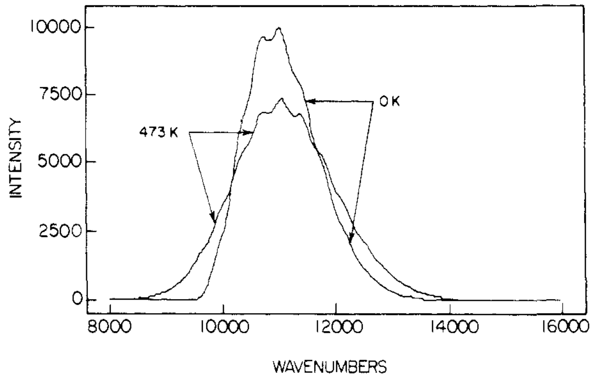

Figure 3. As for Figure 1 but with $S = 3$.

There are other effects we have not taken into account of in our calculations. One particularly important one is that the $\delta \rightarrow \delta^*$ absorption under high resolution at low temperature shows[2] many other vibronically active modes in addition to the dominant $\nu(\mathrm{Mo_2})$. These additional modes either have relatively small S values or are non-totally symmetric, but combinations of them with $n\nu(\mathrm{Mo_2})$ make important contributions to the intensity. The qualitative effect of such modes on a thermally broadened spectrum will be[7,8] to increase the apparent S for $\nu(\mathrm{Mo_2})$, as intensity due to progressions in $\nu(\mathrm{Mo_2})$ based upon other modes adds to the pure broadened $\nu(\mathrm{Mo_2})$ progression. Obviously, the apparent $\nu(\mathrm{Mo_2})$ for such a spectrum is not entirely reliable either. We think it likely that such effects indeed contribute to the δ ionization band, and our estimate of distortion should be considered as an upper limit.

We think it is safe to conclude, however, that the distortions along the metal–metal coordinate for the $^1A_{1g} \rightarrow {}^2B_{2g}$ and $^1A_{1g} \rightarrow {}^1A_{2u}$ δ excitations of $\mathrm{Mo_2(O_2CCH_3)_4}$ are *similar*, a somewhat more intuitively satisfying situation than was left by LB's original interpretation. This is the most that can be said at present. Perhaps, following the lead of LB, more highly resolved ionization spectroscopy data will become available in the future.

Calculation Details. Calculations were performed upon a PDP-11 computer using programs written by the authors. The modified Bessel functions in eq 3 were computed by standard[9] series representations. While this approach works well at the relatively high temperatures of the present calculations, for low temperatures the Bessel function series may exhibit round-off error induced computational difficulties. A calculation involving computing the spectra for individual ground-state vibrational levels (which involves[5a] calculating generalized Laguerre polynomials by a series[10] approach) and doing a Boltzmann sum is then preferable. This approach is considerably slower than that of eq 3 and may suffer from convergence errors for high temperatures because of the strongly oscillatory nature of the Laguerre polynomials.

Acknowledgment. We thank Prof. Dennis Lichtenberger for helpful comments. This work was performed at the Jet Propulsion Laboratory, California Institute of Technology, and was supported jointly by the National Aeronautics and Space Administration and Caltech through the Caltech President's Fund.

---

(7) We have confirmed this by explicit calculations of the $\delta \rightarrow \delta^*$ absorption band[2] of $\mathrm{Mo_2(O_2CCH_3)_4}$. In the absence of *experimental* parameters for other vibronically active modes in the δ ionization, band-shape calculations including additional modes would be science fiction.

(8) Experimental data showing this effect for a $\delta \rightarrow \delta^*$ transition are also available. Fanwick, P. E.; Martin, D. S.; Webb, T. R.; Robbins, G. A.; Newman, R. A. *Inorg. Chem.* **1978**, *17*, 2723.

(9) Olver, F. W. J. In *Handbook of Mathematical Functions*; Abramowitz, M., Stegun, I. A., Eds.; Dover: New York, 1965; Chapter 9.

(10) Hochstrasser, U. W., in ref 9, Chapter 22.