Communications to the Editor

Toward a Quantitative Understanding of Dipole-Moment Changes in Charge-Transfer Transitions: Electroabsorption Spectroscopy of Transition-Metal Complexes

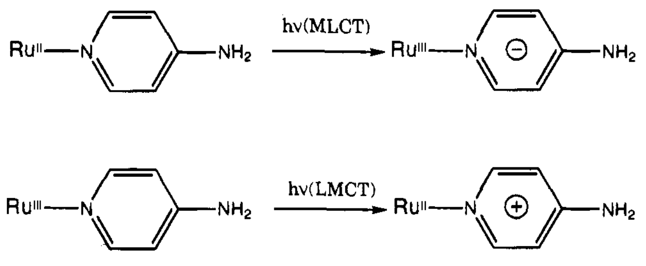
Yeung-gyo K. Shin, Bruce S. Brunschwig,*
Carol Creutz,* and Norman Sutin*

Chemistry Department, Brookhaven National Laboratory
P.O. Box 5000, Upton, New York 11973-5000

Received March 6, 1995

Electroabsorption (Stark) spectroscopy, the study of the effects of externally applied electric fields on the shapes of absorption bands,[1-3] is a powerful probe of the electronic redistribution that occurs upon charge-transfer excitation in a donor-acceptor molecule or complex. Boxer and colleagues[4-6] have recently applied the technique of electroabsorption spectroscopy to $Ru^{II}(NH_3)_5L$ with L = pyrazine and 4,4′-bipyridine complexes and to their binuclear mixed-valence counterparts, and Reimers and Hush have attempted to model the results.[7,8] While the earlier work revealed significant dipole-moment changes between the ground- and excited-state complexes, the values determined experimentally were systematically smaller than those predicted by simple models and the set of complexes studied was limited. Here we report results for metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT) absorption bands of Ru(II) and Ru(III) complexes and show that the dipole-moment changes can be understood in terms of a two-state model which considers polarization, induced-dipole, and delocalization effects.

We have studied the pair of pyridyl-bound complexes $Ru^{II}(NH_3)_5L^{2+}$ and $Ru^{III}(NH_3)_5L^{3+}$ with L = 4-aminopyridine.[9] At 77 K, in 50% aqueous glycerol glass, the Ru(II) complex exhibits MLCT absorption with λ_{max} 389 nm (oscillator strength, $f_{os} = 0.18$), while the Ru(III) complex exhibits LMCT absorption with λ_{max} 493 nm ($f_{os} = 0.049$). INDO SCF calculations[10] on L^-, L^0, and L^+ indicate both anion and cation radicals to be delocalized, with very similar negative charge centers 1.91 Å from the ligating N atom. Thus, at a naive level of modeling, the two transitions should exhibit equal, but opposite, dipole-moment changes of 18.8 D since the Ru(II)-N and Ru(III)-N bond distances are essentially the same (2.00 Å).[11,12] Analysis of the electric-field dependences of the charge-transfer bands[13] yields $f_{int}\Delta\mu_{obsd} = -(8 \pm 1)$ and $+(18 \pm 3)$ D for the MLCT and LMCT transitions, respectively, which corresponds to $\Delta\mu_{obsd} = -(6 \pm 1)$ and $+(14 \pm 3)$ D after correction for the reduction of the external field in the medium.[14] In contrast to the expectation, the measured values differ by a factor of 2 and even that for LMCT is smaller than predicted. To understand these observations, contributions to the dipole-moment change are now considered.



Since the complexes are charged, their dipole moments are undefined. However, $\Delta\mu = \mu_e - \mu_g$, the difference between the excited- and ground-state dipole moments, is a meaningful quantity. Here a two-state model, in which the polarization of the ligand electrons by the metal center is included in the description of the localized (diabatic) ground and excited states, serves as a basis for discussion.[15] For convenience, the metal center is taken as the origin of the coordinate system and, following a widely used definition, the direction of the dipole-moment vector is from the negative to the positive charge. To predict the zero-order dipole-moment difference between the localized ground and excited states, a and b, we take, as model, a ligand (L^+, L^0, or L^-) with a 2+ or 3+ point charge placed 2.00 Å from the ligating (pyridyl) ligand for Ru(II) and Ru(III), respectively, and use an INDO SCF method to determine r_-^{a} and r_-^{b}, the distances between the point charge and the negative charge center of the ligand in the localized states.[16] The model is depicted below.

The zero-order dipole-moment differences between the localized ground and excited states are then obtained from eq 1, where *n* is the number of valence electrons in L (36 for 4-aminopyridine). The values $(\mu_b - \mu_a)'_{ML} = -13.4$ D and $(\mu_b - \mu_a)'_{LM} = 17.1$ D are obtained. The first term in eq 1 is the product of a unit charge and the distance between the (oxidized) metal center and the negative center of the reduced ligand (L^- for MLCT and L^0 for LMCT). This term can be viewed as the

$$(\mu_b - \mu_a)'_{ML} = -er_-^{b} + ne(r_-^{b}) \tag{1a}$$

$$(\mu_b - \mu_a)'_{LM} = +er_-^{a'} - (n-1)e(r_-^{b'} - r_-^{a'}) \tag{1b}$$

---

(1) Liptay, W. In *Excited States:* Lim, E. C., Ed.; Academic Press: New York, 1974; Vol. 1, pp 129-229.

(2) Labhart, H. *Adv. Chem. Phys.* **1967**, *13*, 179-204.

(3) Baumann, W. In *Physical Methods of Chemistry:* Rossiter, B. W., Hamilton, J. F., Eds.; Wiley: New York, 1989; Vol. IIIB, pp 45-131.

(4) Oh, D. H.; Boxer, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 8161-8162.

(5) Oh, D. H.; Sano, M.; Boxer, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 6880-6890.

(6) Oh, D. H. Ph. D. Thesis, Stanford University, June 1991.

(7) Reimers, J. R.; Hush, N. S. *J. Phys. Chem.* **1991**, *95*, 9773-9781.

(8) Reimers, J. R.; Hush, N. S. In *Mixed Valency Systems: Applications in Chemistry, Physics and Biology:* Prassides, K., Ed.; Kluwer Academic Publisher: Dordrecht, 1991; pp 29-50.

(9) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 4021-4023.

(10) Zerner, M. The ZINDO Quantum Chemistry Package, University of Florida.

(11) Gress, M. E.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* **1981**, *20*, 1522-1528.

(12) Chou, M. H.; Szalda, D. J.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1994**, *33*, 1674-1684.

(13) The instrumentation and sample handling are similar to procedures given by Oh and Boxer[4-6] and will be described in the full publication. The glassing medium was 50% aqueous glycerol, and the cell/electrode material was indium tin oxide coated glass separated by 25-75 μm Kapton spacers. The hexafluorophosphate (Ru(II)) and chloride (Ru(III)) salts of the complexes were used. In studies of related systems, the electroabsorption results were found to be insensitive to the nature and concentration of the anion. The dipole moment was obtained by fitting the data to equations developed by Liptay[1-3] as applied to glassy media by Oh and Boxer.[4-6]

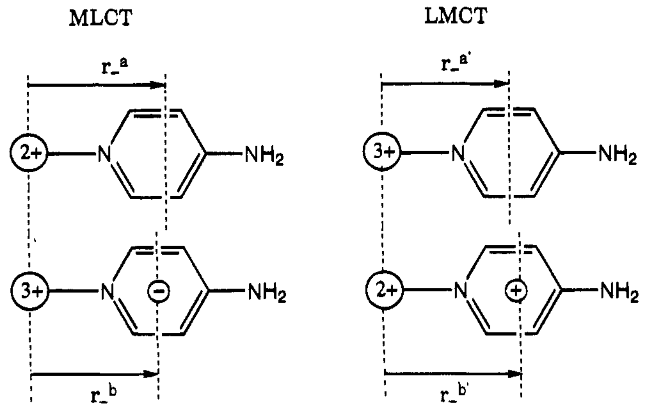
(14) The dielectric constant of the water/glycerol glass was estimated to be 3.9 by measuring the capacitance of a calibrated cell charged with the frozen glass. Thus the internal field correction was $f_{int} = 3\epsilon/(2\epsilon + 1) = 1.33$.

(15) Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol. A: Chem.* **1994**, *82*, 47-59.

(16) Here, contributions from changes at the $Ru(NH_3)_5$ center are neglected. Although dipole moments are vector quantities, only their components along the M-L axis are considered, and consequently vector notation is not used.

(17) Because of the choice of origin for the coordinate system, the distances to the positive-charge center in eq 1 cancel.

0002-7863/95/1517-8668$09.00/0



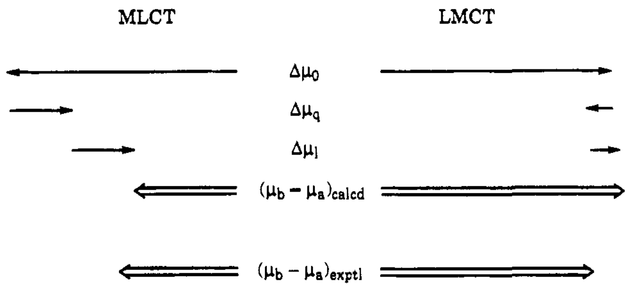
dipole-moment change $\Delta\mu_0$ due to the transferring electron. The value of $|\Delta\mu_0|$, 18.5 D, calculated from eq 1 for both types of transitions may be compared with the value 18.8 D given above for the naive model. The second term in eq 1 reflects the response (polarization) of the remaining ligand valence electrons. This term will be denoted $\Delta\mu_q$ and contributes 5.1 and −1.4 D to the MLCT and LMCT values, respectively. (Note that $\Delta\mu_0$ and $\Delta\mu_q$ have opposite signs.) The contribution of the second term is not negligible, particularly for the MLCT transition.

As discussed by Reimers and Hush,[7,8] the effect of the permanent dipoles of the NH_3 ligands also needs to be considered; the NH_3 ligands will induce dipoles (μ_l) along the M−L axis that are of different magnitudes in the ground and excited states. We model this contribution to $(\mu_b - \mu_a)$ in terms of a point dipole approximation with the induced dipole centered at $r^0_{ab}/2$ where $r^0_{ab} = |\Delta\mu_0/e|$.[18,19] This procedure yields $\Delta\mu_l^{ML} = 4.2$ D and $\Delta\mu_l^{LM} = 1.9$ D. Accordingly, the values of $(\mu_b - \mu_a)$ calculated from eq 2 are −9 and 19 D for the MLCT and LMCT transitions, respectively.

$$(\mu_b - \mu_a)_{calcd} = \Delta\mu_0 + \Delta\mu_q + \Delta\mu_l \qquad (2)$$

Finally, in order to compare the dipole-moment changes for the localized states calculated above with the measured dipole-moment changes (for the adiabatic states), the delocalization arising from the mixing of the localized ground and excited states (π-back-bonding for the Ru(II) complex and π-bonding for the Ru(III) complex) needs to be included. Employing values for the change in dipole moment, $\Delta\mu_{obsd}$, and for the transition dipole moment, μ_{ge}, determined in the spectroscopic studies, $(\mu_b - \mu_a)_{exptl}$ is calculated from eq 3.[20,21] The $(\mu_b - \mu_a)_{exptl}$ values are −(10 ± 1) and (15 ± 3) D for the MLCT and LMCT transitions, respectively, in rather good agreement with the $(\mu_b - \mu_a)_{calcd}$ values.[20,22]

$$(\mu_b - \mu_a)_{exptl} = [(\Delta\mu_{obsd})^2 + 4(\mu_{ge})^2]^{1/2} \qquad (3)$$



To summarize, the change in the charge of the metal center produced by charge-transfer excitation results in a change in ligand polarization which reduces the expected dipole-moment change. Here we have shown that including this effect, together with the effect of the permanent dipoles of the NH_3 ligands, results in encouragingly good agreement with the predictions of a two-state model for MLCT and LMCT transitions. The parameter $(\mu_b - \mu_a)$, the dipole-moment change for the diabatic states, is an important quantity: it is required, either directly or indirectly, for the calculation of electronic coupling elements (H_{ab}) from spectroscopic parameters.[15,20] The coupling elements, in turn, are fundamental to interpreting the rates and distance dependence of a variety of electron transfer processes.[15] Detailed observations and applications to a range of systems will be reported in the near future.

Acknowledgment. We thank Robert J. Cave, Noel S. Hush, and Marshall D. Newton for helpful discussions. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Supporting Information Available: The Liptay equation adapted for the glassy medium and a table of fitted coefficients and electroabsorption spectra and fitted curves (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950725G

---

(18) The ground−excited state polarizability differences are required for the calculation of the induced dipole moments. The polarizability differences were obtained from the transition dipole moment and energy using the two-state expression[19] $\Delta\alpha = -4[(\mu_{ge})^2/(E_e - E_g)]$ where $\mu_{ge} = 304\ (f_{os}/\bar{\nu}_{max})^{1/2}$ is the transition dipole moment, f_{os} is the oscillator strength, and $\bar{\nu}_{max}$ is the band maximum in cm^{-1}. These expressions yield $\mu_{ge} = 3.99$ and 2.26 D, and $\Delta\alpha = -1.2 \times 10^{-39}$ and -0.57×10^{-39} Cm^2/V for MLCT and LMCT, respectively. The value of r^0_{ab} calculated from $|\Delta\mu_0/e|$ is 3.85 Å for the MLCT and LMCT transitions. Note that the $\Delta\alpha$ values are the polarizability differences between the adiabatic ground and excited states; the corresponding quantities for the diabatic states will be more negative.[22] Note further that the simple two-state model yields $\Delta\alpha$ values that are always negative. Agreement with the experimental dipole-moment differences would be improved if $\Delta\alpha$ were less negative, but would become poorer, particularly for the MLCT, as $\Delta\alpha$ became positive.

(19) Atkins, P. W. *Molecular Quantum Mechanics*, 2nd ed.; Oxford University Press: New York, 1983; p 351.

(20) Cave, R. J.; Newton, M. D. *J. Am. Chem. Soc.*, submitted.

(21) Equation 3, which is implied by eqs 10b and B1 of ref 15, is closely related to eq 17 of ref 7. It is derived in ref 20 in the context of a generalized Mulliken−Hush model.

(22) The degree of delocalization (c_b^2) calculated from $^1/_2[1 - [\Delta\mu_{obsd}^2/(\Delta\mu_{obsd}^2 + 4\mu_{ge}^2)]^{1/2}]$ is 20% for the MLCT transition and 2% for the LMCT transition.