

Dipolar character of ligand-centered transitions in transition metal tris-bipyridyl complexes¹

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Abstract

The Stark spectra of bipyridine (bpy) and the metaltris(2,2'-bipyridine) complexes of Zn, Fe, Ru and Os have been measured in the ligand-centered region in the near UV. The results show that excitation into these ligand-centered absorption bands of the metal complexes leads to excited states with dipole moments that are substantially larger than would be expected were the transitions purely ligand-centered. The difference dipoles between ground and excited states are 4.6 ± 0.3 D/f for Ru, 3.5 ± 0.3 D/f for Os, 2.2 ± 0.2 D/f for Fe, 1.4 ± 0.2 D/f for Zn and 0.5 ± 0.5 D/f for free bpy (*f* is the local field correction: 1.1–1.3). The values of the excited state dipole moments roughly correlate with the separation between the UV ligand-centered bands and the visible MLCT bands. Possible mixing of ligand-centered excited states with MLCT states is discussed.

Keywords: Tris-bipyridyl complexes; Stark spectra; Zn complexes; UV spectroscopy

1. Introduction

The lowest energy excited singlet and triplet metal-to-ligand charge-transfer (MLCT) states of transition metal tris-diimine complexes such as $[\text{Ru}(\text{bpy})_3]^{2+}$ have been extensively characterized because they are responsible for the interesting and useful photochemistry of these complexes [1,2]. There have been only a few reports on the higher-energy, nominally ligand-centered (LC) transitions in the near UV. To a first approximation, it might be expected that these transitions would be largely like those of free bpy. A comparative study of the solvent shifts of the MLCT and ligand-centered transitions in $[\text{Ru}(\text{bpy})_3]^{2+}$ with the free ligand and anthracene showed that the shifts were similar and could be explained by dispersion interactions [3]. These results contrast with an earlier study in which a dipole moment change, $|\Delta\mu|$, upon excitation was calculated from solvent shifts of the MLCT bands [4]. In the course of our studies of the electro-optic properties of transition metal complexes using Stark effect (electro-absorption) spectroscopy [5], we investigated the ligand-

centered region for $[\text{Ru}(\text{bpy})_3]^{2+}$ and were surprised to discover that these transitions possess considerable dipolar character. In the following we report a systematic study of these transitions in a series of complexes and discuss a possible correlation between the degree of charge-transfer character and the energy of localized low-lying MLCT states.

Upon application of an external electric field to molecules that are immobilized and not oriented, e.g. in a glass or polymer film, the electronic absorption is broadened, shifted and changed in intensity due to changes in dipole moment, $\Delta\mu$, polarizability, $\Delta\alpha$, and oscillator strength, respectively. The contributions of each type of electro-optic property can be extracted by comparing the observed change in absorption in the field with the second, first and zeroth derivatives of the absorption spectrum, respectively. It is straightforward to show that for an isolated, homogeneous absorption band in a non-oriented, immobilized sample the change in absorption upon application of a electric field is given by [6,7]:

$$\Delta A(\nu, \mathcal{E}) = (f\mathbf{F}_{\text{ext}})^2 \{ A_{\chi} A(\nu) + (B_{\chi}\nu/15hc) d[A(\nu)/\nu]/d\nu + (C_{\chi}\nu/30h^2c^2) d^2[A(\nu)/\nu] d\nu^2 \} \quad (1)$$

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¹ This paper is dedicated to Professor Harry B. Gray.

where χ is the angle between the field direction of the externally applied electric field F_{ext} and the electric vector of the probing light; A_χ depends on the transition polarizability and hyperpolarizability; $B_\chi = (1/2)\{5 \text{Tr}(\Delta\alpha) + (3 \cos^2\chi - 1)[3(\mathbf{p}\cdot\Delta\alpha\cdot\mathbf{p}) - \text{Tr}(\Delta\alpha)]\}$ (neglecting the contribution from the cross term of the transition polarizability and $\Delta\mu$); and $C_\chi = |\Delta\mu|^2[5 + (3 \cos^2\zeta - 1)(3 \cos^2\chi - 1)]$. ζ is the molecular angle between $\Delta\mu$ and the transition moment \mathbf{p} associated with the transition being probed. ζ is obtained from the second derivative coefficients of the Stark spectra obtained at different values of χ when linearly polarized light is used to probe ΔA . f is the local field correction. It is generally a tensor, but is taken here as a scalar, as the $[\text{M}(\text{bpy})_3]^{2+}$ complexes do not deviate much from a spherical shape and the solvent glass is isotropic. The value of f is not known with certainty, but likely lies in the range 1.1–1.3. Whatever its value, all molecules in this study were examined under identical conditions, thus the value of f is likely to be essentially the same. To separate errors in the measurements and fitting of the data from uncertainties in the value of f , we report changes in dipole moment divided by f . In order to obtain information on the desired electro-optical properties, the coefficients A, B, and C in Eq. (1), the observed change in absorption is analyzed in terms of contributions from the zeroth, first and second derivatives of the absorption band. Details of methods for performing this decomposition are presented elsewhere [8–10]. In the following discussion we only focus on $|\Delta\mu|$ obtained from the second derivative contribution.

2. Experimental

The tris-bipyridine complexes of Zn, Fe and Os were prepared according to published procedures [11,12]. $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was purchased from Aldrich. All complexes were prepared as the PF_6 salts and were recrystallized twice from water/acetone mixtures.

The $\Delta A(\nu, \chi)$ and $A(\nu)$ spectra were recorded at 77 K in cells made from two parallel quartz slides separated by 75 mm thick Kapton spacers. The inner surfaces of the slides were coated with conductive and semitransparent layers of Ni (75 Å) and were contacted to an AC power supply. Horizontally polarized light was passed at $\chi = 90^\circ$ and 50° incidence through the cell by rotating the sample holder around a vertical axis. The Ni electrodes have a flat transmission of about 25% from 240 to 2000 nm. The solvent was a mixture of 2-methyl-THF and 20–25% acetonitrile. This mixture forms a clear glass at 77 K which is important because Stark measurements in the UV region are sensitive to glass imperfections. The Stark spectrum of the chloride salt of $[\text{Ru}(\text{bpy})_3]^{2+}$ was also measured in EtOH/MeOH (4:1). The results were the same within the signal-to-noise of the experiment. $\Delta A(\nu, \chi)$ and $A(\nu)$ were measured in a Stark spectrophotometer consisting of a 150 W xenon arc lamp, a 1/4 m

monochromator and a photomultiplier tube on which the resistor network has been altered so as to bypass the last few dynodes. The latter allows a reasonable compromise between the requirement for spectral sensitivity in the near-UV and modest amplification at low noise. The spectral resolution was 1.8 nm with a repositioning precision of better than ± 0.5 nm. A sinusoidal electric field of typically 290 Hz was applied with an AC-power supply constructed locally. The signal was detected at twice the modulation frequency using lockin detection. In order to obtain high quality absorption spectra for the computation of the derivatives the absorption, spectra were also measured on a Varian 2300 spectrophotometer with a spectral resolution of 1 nm. The accuracy of the wavelength calibration between the spectrophotometer and the Stark apparatus was better than ± 1 nm. Further details on the experimental set-up and methods of analysis can be found in Refs. [9,10].

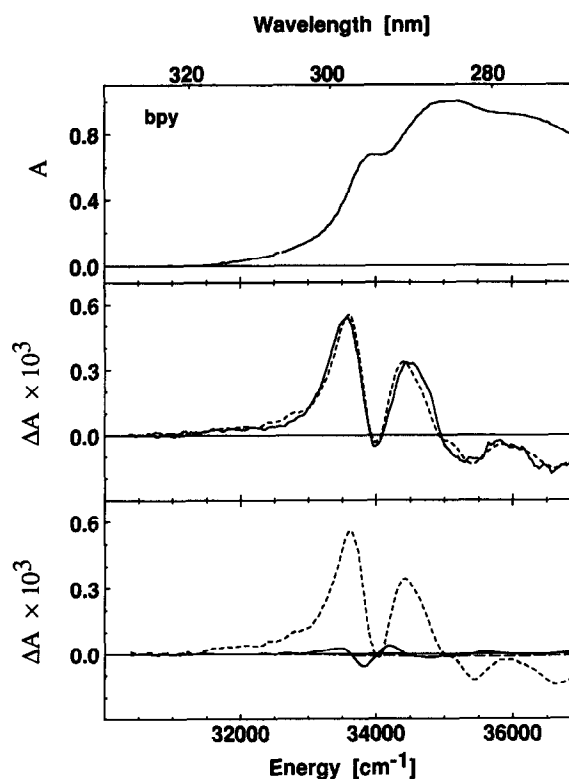


Fig. 1. Absorption, $A(\nu)$ (top), Stark effect spectra, $\Delta A(\nu)$ (middle) and components of the least square fits (bottom: long broken line, zeroth derivative; short broken line, first derivative; solid line, second derivative) of bipyridine (bpy). The middle panel also compares the best least square fits of the sum of the absorption derivatives (broken line) with the Stark data. For ease of comparison, in this figure and subsequent figures, the absorption data are presented normalized to an absorption of 1.0 at the absorption maximum (the actual sample absorption was typically less than 1), and the Stark spectra are scaled to the magnitude they would have in an applied external field of 1 MV cm^{-1} (the actual field was different for each sample, typically in the range $0.5\text{--}0.8 \text{ MV cm}^{-1}$; experimentally and theoretically, ΔA depends quadratically on the applied field strength, cf. Eq. (1)).

3. Results

Figs. 1–5 show the absorption and Stark spectra of bipyridine (bpy), $[\text{Zn}(\text{bpy})_3]^{2+}$, $[\text{Fe}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{bpy})_3]^{2+}$, and $[\text{Os}(\text{bpy})_3]^{2+}$, respectively, in the ligand-centered region. The top panels show the absorption spectra, the middle panels the Stark spectra at $\chi = 90^\circ$ (solid line) and the least square fits with a sum of the absorption derivatives (broken line, cf. Eq. (1)). The bottom panels show the components of the least square fits discussed below. The ΔA spectra recorded at $\chi = 50^\circ$ (not shown) were almost identical to those (shown) at $\chi = 90^\circ$. This implies that ζ is approximately the magic angle, 54.7° , and this value was used in the evaluation of the second derivative coefficient, C_χ to obtain $|\Delta\mu|$. For ease of comparison, the absorption data are presented normalized to an absorption of 1.0 at the absorption maximum (the actual sample absorption was typically less than 1), and the Stark spectra are scaled to the magnitude they would have in an applied external field of 1 MV cm^{-1} (the actual field was different for each sample, typically in the range $0.5\text{--}0.8 \text{ MV cm}^{-1}$; experimentally and theoretically, ΔA depends quadratically on the applied field strength (cf. Eq. (1)).

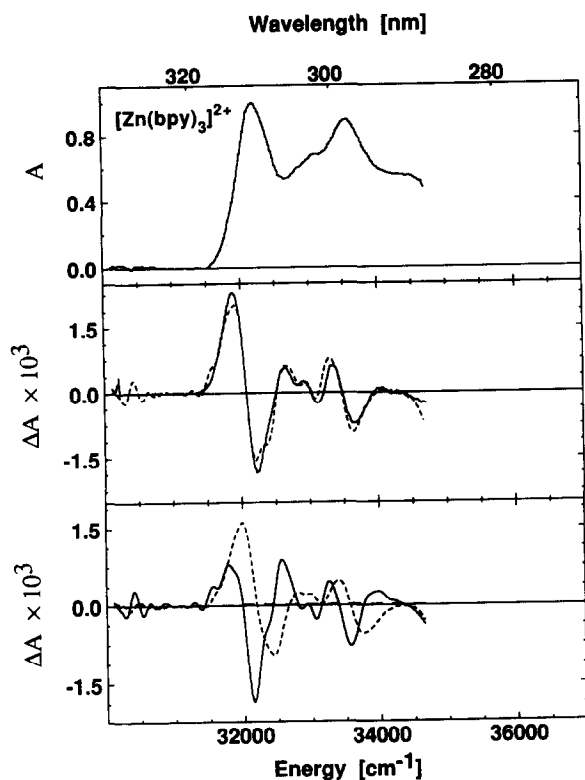


Fig. 2. Absorption, $A(\nu)$ (top), Stark effect spectra, $\Delta A(\nu)$ (middle), and components of the least square fits (bottom: long broken line, zeroth derivative; short broken line, first derivative; solid line, second derivative) of $[\text{Zn}(\text{bpy})_3]^{2+}$. The middle panel also compares the best least square fits of the sum of the absorption derivatives (broken line) with the Stark data.

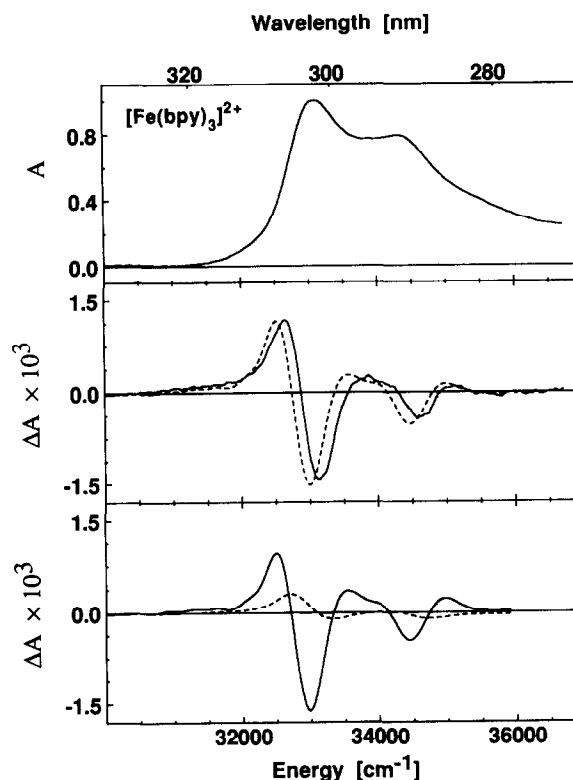


Fig. 3. Absorption, $A(\nu)$ (top), Stark effect spectra, $\Delta A(\nu)$ (middle), and components of the least square fits (bottom: long broken line, zeroth derivative; short broken line, first derivative; solid line, second derivative) of $[\text{Fe}(\text{bpy})_3]^{2+}$. The middle panel also compares the best least square fits of the sum of the absorption derivatives (broken line) with the Stark data.

For the bpy ligand itself, the Stark effect spectrum consists almost entirely of a spectral shift (first derivative of absorption), characteristic of a change in polarizability with little change in dipole moment. For $[\text{Zn}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{bpy})_3]^{2+}$ there are increasing second derivative contributions, while for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$, the Stark spectrum is dominated by the second derivative of the absorption. In most cases, we observe that the Stark effect spectra are slightly blue shifted relative to the best fit sum of derivatives of the absorption. In the case of bpy, $[\text{Zn}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$, the shifts are within experimental error ($\pm 1 \text{ nm}$), but for $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$, the shifts are larger (2 and 3 nm, respectively). The origin of this effect is not known (possible origins of this effect, which has been observed in other systems, are discussed in Ref. [8]), and good fits could not be obtained unless the sum of derivatives was shifted. The values of $|\Delta\mu|$ calculated from the least-squares fits are listed in Table 1. The results in Table 1 are the mean values and standard deviations of 2–4 independent experiments for each compound. For bpy and $[\text{Zn}(\text{bpy})_3]^{2+}$, where only two independent experiments were performed, the standard deviation is multiplied by 2.

4. Discussion

Examination of the values for the change in dipole moment in Table 1 shows that the ligand-centered transitions in these complexes exhibit substantial dipolar character. The likely origin of the dipolar character in the nominally π - π^* ligand transition is mixing with low lying dipolar states of the complex involving ligand–metal interactions. The energy differences between the lowest energy MLCT states and the ligand-centered transitions are also tabulated. It is seen that a consistent trend is that the closer in energy the ligand centered transition is to the MLCT transition, then the greater is the dipolar character of the ligand-centered transition. This trend suggests a coupling between these transitions. Such a coupling has been suggested by Myrick and DeArmond in a study of a series of $\text{Ru}(\text{bpy})_2\text{X}$ complexes [13], where different ligands (X) modify the energy of the MLCT transitions. A correlation between the energies of the lowest MLCT band and the LC band of bpy was found, with the LC transitions increasingly blue shifted the closer (higher in energy) the MLCT transitions were located to the LC transitions. The observed shifts were explained by a first order coupling between MLCT and π - π^* states. In our

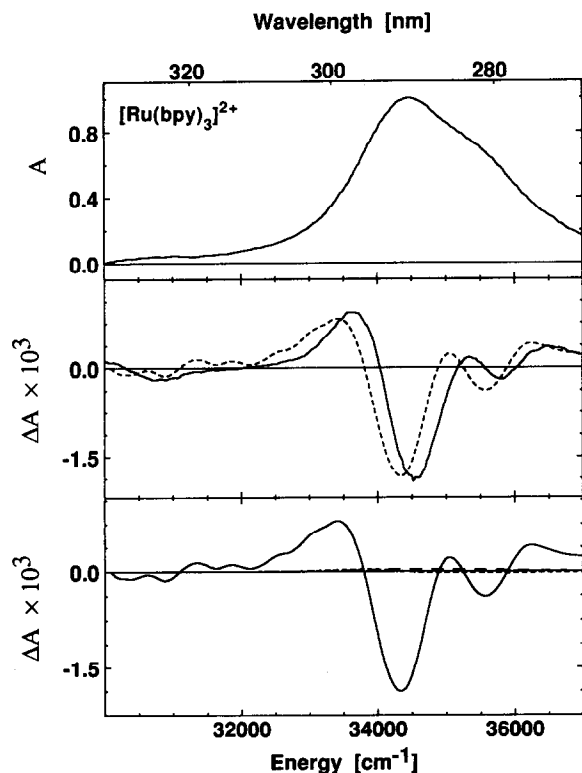


Fig. 4. Absorption, $A(\nu)$ (top), Stark effect spectra, $\Delta A(\nu)$ (middle), and components of the least square fits (bottom: long broken line, zeroth derivative; short broken line, first derivative; solid line, second derivative) of $[\text{Ru}(\text{bpy})_3]^{2+}$. The middle panel also compares the best least square fits of the sum of the absorption derivatives (broken line) with the Stark data.

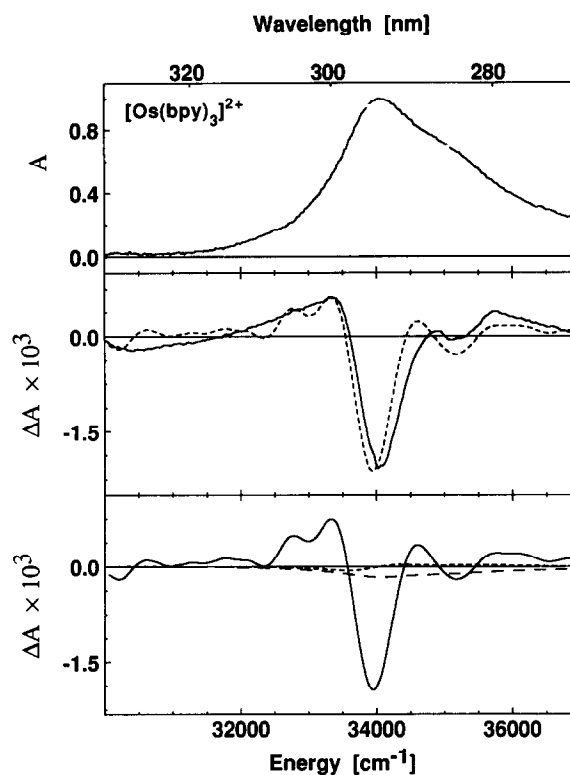


Fig. 5. Absorption, $A(\nu)$ (top), Stark effect spectra, $\Delta A(\nu)$ (middle) and components of the least square fits (bottom: long broken line, zeroth derivative; short broken line, first derivative; solid line, second derivative) of $[\text{Os}(\text{bpy})_3]^{2+}$. The middle panel also compares the best least square fits of the sum of the absorption derivatives (broken line) with the Stark data.

series of Zn-, Fe-, Os- and $[\text{Ru}(\text{bpy})_3]^{2+}$ we observe a similar correlation. Two types of MLCT transitions were distinguished in complexes with bpy ligands, classified as transitions to the $\pi^*(\chi)$ and $\pi^*(\psi)$ [14] acceptor orbitals which are symmetric and antisymmetric, respectively, relative to the C_2 axis bisecting the ligands [15]. It was suggested that the visible MLCT transitions in Fe, Ru and $\text{Os}(\text{bpy})_3$ are to the $\pi^*(\psi)$ orbitals, and that the transitions to the $\pi^*(\chi)$ orbitals are located at 7000–10 000 cm^{-1} higher energies, which would place them at 1000–2000 cm^{-1} above the LC-transitions [15]. Myrick and De Armond assumed in their treatment that of the two MLCT states, only the metal- $\pi^*(\psi)$ state couples with the ligand

Table 1

Spectral properties of ligands and complexes correlated with $|\Delta\mu|$

Ligand or complex	$\nu_{\max}(\pi-\pi^*)$ cm^{-1} (nm)	$\nu_{\max}(\text{MLCT})$ cm^{-1} (nm)	$\Delta\nu$ cm^{-1}	$ \Delta\mu $ Debye/f
bpy				0.5 ± 0.5
$\text{Zn}(\text{bpy})_3$	32000 (311)			1.4 ± 0.2
$\text{Fe}(\text{bpy})_3$	33100 (302)	18900 (529)	14200	2.2 ± 0.2
$\text{Os}(\text{bpy})_3$	34000 (294)	21000 (476)	13000	3.5 ± 0.3
$\text{Ru}(\text{bpy})_3$	34500 (290)	21900 (456)	12600	4.6 ± 0.3

centered transition. This is supported by our preliminary electroabsorption results with $[\text{Ru}(\text{NH}_3)_4(\text{bpy})]^{2+}$ which exhibit MLCT transitions at 570 nm and at 390 nm (presumably the $\pi^*(\psi)$ and $\pi^*(\chi)$ transitions, respectively) which are both associated with difference dipoles of 6 ± 1 D, while the ligand-centered absorption at 300 nm leads to a difference dipole of 3.1 ± 0.5 D, similar to $\text{Os}(\text{bpy})_3$, despite the closeness of the π - $\pi^*(\chi)$ transition. Ceulemans and Vanquickenborne predicted one peak with two minor satellites for the high energy MCLT $\pi^*(\psi)$ transition which is what is observed in the higher energy MLCT in $[\text{Ru}(\text{NH}_3)_4(\text{bpy})]^{2+}$.

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