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Vibrational satellite structures and properties of electronic states of transition metal complexes

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Abstract

$Pd(2\text{-}thpy)_2$, $Pt(2\text{-}thpy)_2$, $[Ru(bpy\text{-}h_8)_3]^{2+}$, $[Ru(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{2+}$, $[Ru(bpy\text{-}d_8)_3]^{2+}$, $[Os(bpy\text{-}h_8)_3]^{2+}$, $[Os(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{2+}$, and $[Os(bpy\text{-}d_8)_3]^{2+}$ were isolated in crystalline matrices in order to obtain highly resolved emission spectra. A detailed analysis of the electronic origins and of the vibrational satellite structures reveals trends, which allow the various compounds to be ordered with respect to increasing MLCT character. Interestingly, an increasing MLCT character is connected with decreasing shifts of the equilibrium positions of the potential hypersurfaces and with decreasing changes of force constants upon excitation. Presumably, this behavior is a consequence of an increasing covalency in the compounds investigated. Moreover, especially the resolved vibrational satellite structures of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ allow the conclusion that the electronic excitation in the lowest excited states is delocalized over the metal and the three (bpy)-ligands.

1. Introduction

Transition metal complexes have found an increasing interest during the past decades due to a number of possible applications.[1] These are related to the properties of the lowest excited states, which, therefore should be investigated in some detail. Especially, highly resolved spectra with resolved electronic origins and vibrational satellite structures supply a deeper insight. For example, the vibrational satellite structures of a specific electronic transition display properties like shifts of nuclear coordinates, force constants (or changes of them), and even alterations of electronic charge densities in specific spatial regions of larger molecules occurring during this transition. Highly resolved spectra are often obtainable when the chromophore of interest is isolated in a crystalline and optically inert matrix, which supplies geometrically adequate sites for the chromophore. Thus, applying the methods of site-selective excitation and site-selective detection of emission it is possible to register resolved emission and excitation spectra corresponding to the same site. Further, it is generally necessary to measure at low temperatures in order to reduce broadening effects of the electron-phonon coupling. It is subject of this paper to demonstrate the success of this procedure by discussing various compounds with respect to assignments of ligand centered or MLCT transitions and by investigating the problem of electronic localization or delocalization in excited states.

2. $Pd(2\text{-}thpy)_2$ and $Pt(2\text{-}thpy)_2$

These cyclometalated complexes [$2\text{-}thpy^-$ = ortho-C-deprotonated 2-(2-thienyl)pyridine] belong to a relatively new class of compounds with promising photochemical and photophysical properties.[1-5] The spectra of these compounds recorded in glass-forming matrices show only broad features (Fig. 1a, 2a), where the information about the electronic origins, the zero-field splittings (zfs), and the vibrational satellite structures is lost. On the other hand, if the chromo-

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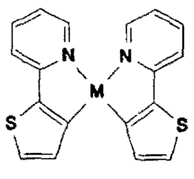


M = Pd, Pt

phores are dissolved, for example, in n-octane (using an intermediate solvent like 1,4-dioxane)[5], one obtains at low temperatures a polycrystalline matrix. In this matrix the guest molecules possess partial geometric similarities with the replaced host molecules. This Shpol'skii technique is well established for organic molecules.[6] The enormous increase of resolution which mainly results from decreases of inhomogeneous broadenings and electron-phonon couplings, is demonstrated in Fig. 1 and 2. Thus, it is possible to observe in emission and excitation the electronic origins and detailed vibrational satellite structures.

Electronic Origins.

The low extinction coefficients at the electronic origins and the long emission lifetimes of more than 10^2 μs for both compounds at low temperature display the fact that the lowest excited states are mainly of triplet character with a singlet ground state (see also [2,3]). For *Pt*(2-*thpy*)$_2$, the spectral resolution obtained allows the different electronic origins of the triplet sublevels (I, II, III in Fig. 2) to be resolved. The related total zfs is 16 cm^{-1}. On the other hand, for *Pd*(2-*thpy*)$_2$ the zfs is less than the optical resolution of 1 cm^{-1}, presumably of the order of 0.1 cm^{-1} [7,8]. Interestingly, the electronic transition $|I\rangle \leftrightarrow |0\rangle$ in *Pt*(2-*thpy*)$_2$ is strongly forbidden compared to $|II\rangle$, $|III\rangle \rightarrow |0\rangle$ (Fig. 2d). Thus, the radiative deactivation from state $|I\rangle$ is dominated by a vibronic (Herzberg-Teller) mechanism (e. g. see [5,9]). For *Pd*(2-*thpy*)$_2$, one observes similar differences in the radiative decay properties of the three (non-resolved) sublevels (details in [5]).

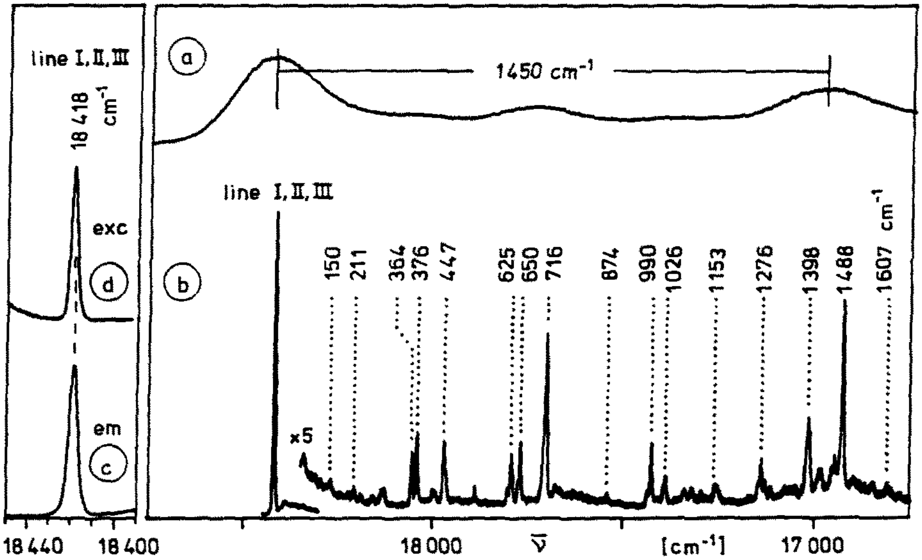


Fig. 1. Emission spectrum of *Pd*(2-*thpy*)$_2$ in butyronitrile (a) und in an n-octane Shpol'skii matrix (b). The energies of the vibrational satellites are specified relative to the electronic origin at 18418 cm^{-1}. For a better comparison the broad emission spectrum (a) is red-shifted by 200 cm^{-1}. The given number at the spectrum (a) characterizes a fictitious progression, which would appear more "clearly" when spectrum (a) is registered 1500 cm^{-1} further to the red (see [5]). (c), (d): Origins in emission and excitation ($\bar{\nu}_{det}$ = 17702 cm^{-1}); λ_{exc} = 337.1 nm; T = 1.3 K, c[*Pd*(2-*thpy*)$_2$] $\approx 10^{-5}$ M.

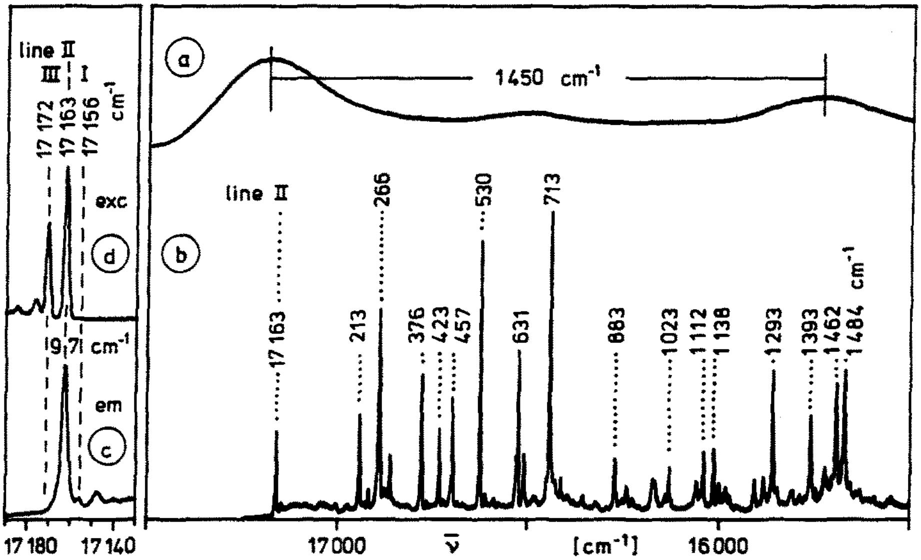


Fig. 2. Emission spectrum of $Pt(2\text{-}thpy)_2$ in butyronitrile (a) and in n-octane (b) at T = 1.3 K. The energies of the vibrational satellites are specified relative to the origin I at 17156 cm^{-1}. λ_{exc} = 337.1 nm. Spectrum (a) is red-shifted by 370 cm^{-1}. Spectral range of the origins (I, II, III) in emission (c) and in excitation (d) (T = 4.2 K, $\bar{\nu}_{det}$ = 16445 cm^{-1}) For further details see Fig. 1.

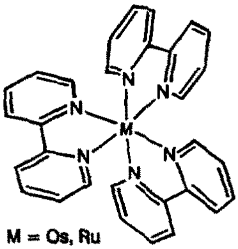
Ground State/Excited States Distortion.

It is an important fact that the vibrational satellite structures do not show any *dominating* vibrational Franck-Condon progression as might erroneously be deduced from the broad spectra.(Fig. 1a, 2a) A value, which quantitatively characterizes the magnitude of a progression is the Huang-Rhys factor S [11]. For all observable vibrational modes (and for all three sublevels) the maximum S value is 0.2 for $Pd(2\text{-}thpy)_2$ (e. g. for the 1488 cm^{-1} mode)[5] and 0.1 for $Pt(2\text{-}thpy)_2$ (e. g. for the 1484 cm^{-1} mode[10]), while the unresolved spectra would give a fictitious value of S ≈ 0.5. From the smallness of the S-values it follows (e. g. see [11]) that the excited states and the ground state have very similar equilibrium positions of the potential hypersurfaces. This holds for both compounds, but the distortion through an excitation is still smaller for $Pt(2\text{-}thpy)_2$ than for $Pd(2\text{-}thpy)_2$. Moreover, the vibrational force constants in the excited and ground states are also very similar, as is seen by comparing the vibrational energies in the emission and excitation spectra (not reproduced, see [5]). This holds also for both compounds, but the changes of the vibrational energies upon excitation are slightly smaller for $Pt(2\text{-}thpy)_2$ than for $Pd(2\text{-}thpy)_2$.

Ligand Centered Transitions/MLCT Character.

Previously it had not been clear, whether the electronic transitions described should be classified as being mainly ligand centered or whether an appreciable metal-d-*thpy*-CT admixture is of importance. A comparison of the two compounds shows obvious differences: The zfs increases from less than 1 cm^{-1} (probably ≈ 0.1 cm^{-1}) in $Pd(2\text{-}thpy)_2$ to 16 cm^{-1} in $Pt(2\text{-}thpy)_2$. Further, the ratio of the emission intensities of the M-L vibrations (say, in the range from 150 cm^{-1} to 500 cm^{-1}) compared to the total vibrational intensities (say, in the range from 150 cm^{-1} to 1700 cm^{-1}) increases from ≈ 20 % for *Pd(2-thpy)*$_2$ to ≈ 30 % for *Pt(2-thpy)*$_2$. (See also sect. 4.) Moreover, the longest decay component in the emission decreases (due to a higher spin-orbit coupling) by about one order of magnitude (at T = 1.3 K) from *Pd(2-thpy)*$_2$ to *Pt(2-thpy)*$_2$. All these results show that the lowest triplets of *Pd(2-thpy)*$_2$ are mainly ligand centered while those of *Pt(2-thpy)*$_2$ contain a distinct d-orbital admixture.

3. $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$



The electronic properties of the lowest excited states of these complexes have been reported in a large number of publications. In particular, the description of the charge distribution has been discussed very contradictorily. This is understandable, since for a long time highly resolved spectra were not available. However, after the first observation of the electronic origins with vibrational satellite structures in 1985 [12] and after the discovery of suitable and inert crystalline matrices in 1987 [13] and in 1989 [14] a more reliable description of the electronic properties was within reach.

Vibrational Satellite Structures and Partial Deuteration.

The question whether a localization or delocalization of the excited electron occurs, can clearly be answered from an investigation of the vibrational satellite structures. Already the non-occurrence of pronounced vibrational progressions (observed vibrational Huang-Rhys factors, $[Ru(bpy)_3]^{2+}$: S ≈ 0.1 [15]; $[Os(bpy)_3]^{2+}$: S $\leq$ 0.08 [16,17]) excludes [18] a localization in a deep trap of several 10^2 cm^{-1}, as frequently assumed (e. g. see [19]).

A different method allows the same conclusion to be reached: Since an isotope marking of one (or two) bpy-ligands should clearly display an electronic localization or delocalization in the vibrational satellite structure[20,21], we investigated the partially deuterated $[Os(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{2+}$ doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$. Excitation at higher energy leads to a complicated emission spectrum which consists of super-imposed multi-site spectra.[20] Therefore, we used site-selective excitation and obtained the emission spectrum shown in Fig. 3a. Fig. 3c, 3d reproduce the emission and site-selectively detected excitation spectra for the range of the electronic origins. One observes three origins, which lie 222 cm^{-1} apart. These may be assigned to represent the zfs components. At T = 1.3 K, the emission, however, results only from the lowest excited state |I⟩.

The vibrational satellite structure consists of low energy lattice modes, M-L modes and ligand modes. Here we want to focus on properties of the ligand modes. The energies of these are largely determined by the force constants of the *individual* ligands, since the heavy metal ion serves as a buffer and vibrationally decouples the ligands from each other.[22,23] A coupling through space may also be excluded.[21] Consequently, we expect to observe energies of ligand modes, which largely correspond to values known from the fully protonated[24] and the fully deuterated[24] compounds, respectively. It is an important result that the spectrum (Fig. 3a) exhibits the vibrational satellites of both of ($bpy\text{-}h_8$)- and of ($bpy\text{-}d_8$)-ligand modes. Further, these different satellites belong to the *same electronic origin* at 14238 cm^{-1}. Moreover, the emission decay is mono-exponential and exhibits the same value of $\tau = (26 \pm 1)\mu s$, when measured at the origin I or on any vibrational satellite. This τ-value lies between the values of the totally protonated (22 μs) and of the totally deuterated (46 μs) compounds. These results taken together show clearly that the lowest excited state of the partially deuterated compound and consequently also of $[Os(bpy)_3]^{2+}$ doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ is *delocalized* over the three ligands.[21]

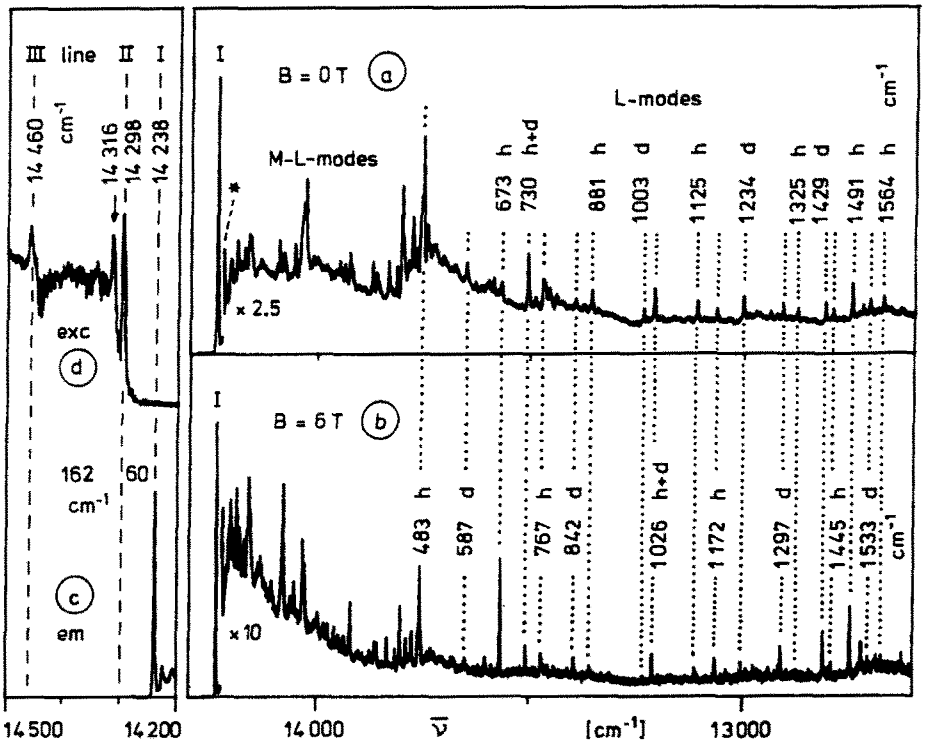


Fig. 3. Site-selectively excited emission of $[Os(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{2+}$ in $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ at B = 0 T (T = 1.3 K, λ_{exc} = 692.1 nm) (a) and at B = 6 T (T = 1.7 K, λ_{exc} = 699.3 nm) (b). The energies of the vibrational satellites are specified relative to the origin I at 14238 cm^{-1}. Ligand modes, which correspond to ($bpy\text{-}h_8$) and ($bpy\text{-}d_8$) are characterized by **h** and **d**, respectively. Most of the modes appear in both spectra (a) and (b). These satellites are connected by dotted lines but signified only once. The asterisk in (a) designates the origin of a different site which could not be totally separated. Origin range in emission(c) and excitation(d) at B = 0 T, T = 1.3 K. The arrow marks a recently discovered electronic origin which also occurs in the tris-compounds[16,17]. Concentration of the dopant ≈ 0.2 %.

The partial deuteration represents a distortion with respect to the regular $[Os(bpy)_3]^{2+}$ compounds. Obviously, this distortion is not sufficient to localize the excited electron. Therefore, it is straight forward to apply a high magnetic field ($\vec{B}$ perpendicular to the $\vec{C}_3$ axis of the regular complex) in order to test whether this additional perturbation might lead to the localization. However, Fig. 3b shows a spectrum equivalent with respect to the behavior described for the B = 0 T situation. Thus, the additional distortion is also not sufficiently strong to localize the excited electron. (The observed magnetic-field induced change of the vibrational satellite structure and the relative increase of the intensity at the origin I are explained in [9].)

An equivalent investigation of $[Ru(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{2+}$ doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ has also been carried out.[25] Tab. I gives the energies of a series of observed vibrational satellites in the energy range of ligand modes for the three relevant compounds. Again, the partially deuterated compound exhibits $(bpy\text{-}h_8)$ **and** $(bpy\text{-}d_8)$ modes to the same electronic origin at 17684 cm^{-1} (B = 0 T). The emission decay is mono-exponential $[\tau = (255 \pm 5)\mu s]$ and the decay time lies between the values of the tris-compounds. ($[Ru(bpy\text{-}h_8)_3]^{2+}$: $\tau = (230 \pm 5)\mu s$; $[Ru(bpy\text{-}d_8)_3]^{2+}$: $\tau = (310 \pm 5)\mu s$) Thus, the conclusion is the same as that drawn for $[Os(bpy)_3]^{2+}$: The excitation is delocalized over the three ligands of $[Ru(bpy)_3]^{2+}$ in the investigated system.

Table I. Vibrational satellites in the energy range of the ligand modes in the emission from the states $|I\rangle$.[cm^{-1}] (T = 1.3 K, B = 0 T) The chromophores are doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ (1 %). Experimental error: Origins ± 1 cm^{-1}; vibrational satellites: ± 2 cm^{-1}.

	$[Ru(bpy\text{-}h_8)_3]^{2+a)}$	$[Ru(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{2+}$	$[Ru(bpy\text{-}d_8)_3]^{2+a)}$
$III^{b)}$	17745	17743	17787
$II^{b)}$	17693	17693	17732
$I^{b)}$	17684	17684	17724
	667	667	
		734	734
	767	767	
		989	989
	1174	1174	
		1203	1203
	1275	1275	
	1325	1325	
		1430	1430
	1495	1495	
		1524	1524
	1559	1559	
		1572	1572

a) Data from [15]; *b*) Electronic origins.

In addition, it is important to note that $[Ru(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{2+}$ also occupies at least a second site in the discussed matrix with the lowest electronic origin at 17726 cm^{-1}. But this site does not carry an appreciable emission intensity. However, in general one has to be prudent if electronic origins of different sites are in the same energy range. In this case one might easily come to a non-conclusive interpretation regarding the problem of localization or delocalization, especially, when the vibrational satellite structure is not carefully inspected as, for example in [26].

4. MLCT Character and Covalency

The compounds considered here exhibit interesting trends with respect to the importance of an MLCT contribution. (Tab. II) For example, the lowest triplets are red-shifted with an increasing MLCT contribution compared to the triplets of the free ligands (column 2). Clear tendencies are also found for the total zero-field splittings (column 3). These values increase with the spin-orbit coupling, which is induced by an admixture of metal-d-character.[7] Moreover, an increasing spin-orbit coupling/d-character reduces also the emission decay time. (Column 4 gives the longliving components.) The increasing d-character is further displayed in the intensity ratio of the M-L modes relative to all vibrational modes (sect. 2) (column 5). (The value of ≈ 40% for $[Os(bpy)_3]^{2+}$ is determined from Fig. 3a.) This ratio goes up to ≈ 90 % for d-d transitions in $[Cr(bpy)_3]^{3+}$. Finally, column 6 gives the maximum Huang-Rhys factor, which is determined after an inspection of all observed vibrational satellites in the emission spectrum. This value is a measure of the extent of the shift along the involved normal coordinate upon excitation.[11] (See also sect. 2.) The S-values obviously decrease with an increasing MLCT character. This means that the equilibrium positions of the potential hyper-surfaces are decreasingly affected through the excitation process. Moreover, with increasing MLCT character the force constants in the excited states and in the ground state become more similar. For $Pd(2\text{-}thpy)_2$ and $Pt(2\text{-}thpy)_2$ this is directly seen by comparing the vibrational energies of the ground state and of the excited state(s) (sect. 2), while for $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ this behavior is only manifested indirectly. (See the detailed discussion in [15].)

Table II. Systematic variation of spectroscopic data with increasing MLCT character

1 Compound (protonated)	2 ΔE [cm^{-1}] = T_1(ligand) − T_1(complex)	3 zfs [cm^{-1}]	4 τ (1.3 K) [μs]	5 $\frac{I(\text{M-L vibr.})}{I(\text{all vibr.})}$	6 S	Lowest excited states
bpy, *H*(2-*thpy*)	–	≈ 0.1	$1.3 \cdot 10^6$ a)b)	–	0.3a)	LC
$Pd(2\text{-}thpy)_2$	2100 d)	< 1	$1.2 \cdot 10^3$	20 %	0.2	Increasing
$Pt(2\text{-}thpy)_2$	3400 d)	16	110	30 %	0.1	MLCT
$[Ru(bpy)_3]^{2+}$	5800 d)	61 d)	230	– c)	0.1	character
$[Os(bpy)_3]^{2+}$	9300 d)	210 d)	22	40 %	0.08	↓
$[Cr(bpy)_3]^{2+}$ e)	–	–	–	90 %	–	d-d transition

a) Value for *bpy*. b) The decay time for *H*(2-*thpy*) at T = 77 K is 34 ms.[3] c) This value has not yet been determined. d) These values depend slightly on the matrices. e) Given for comparison, see [25].

In conclusion, the results for the systems discussed here demonstrate that an increasing "MLCT" character is connected with decreasing nuclear shifts and decreasing changes of force constants upon excitation. This seems to be a consequence of an increasing covalency. Thus, the simple picture of a transfer of one electron charge from the metal to the ligand is not adequate to describe the complexes investigated. Moreover, especially the resolved vibrational structures of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ show that an electron localization on one ligand does not occur.

Acknowledgment

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