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Outer-Sphere Charge-Transfer Effects on the Spectroscopy of the $[Ru(NH_3)_5(py)]^{2+}$ Complex

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We report here the results of a theoretical analysis of the $[Ru(NH_3)_5(py)]^{2+}$ absorption spectrum, which is known to be sensitive to media effects.[1] The intermediate neglect of differential overlap (INDO) model parametrized for spectroscopy at the configuration interaction (CI) level of theory has been used in these studies.[2] We demonstrate here that the absorption spectrum of the above complex can be reproduced only if specific outer-sphere effects are considered and, in particular, that the solvent-to-complex charge transfer is essential in lowering the energy of the metal-to-ligand charge transfer (MLCT) excitations to positions that agree with experiment.[3] A simple point-charge model we utilize in this work is shown to be a successful substitute for the explicit solvent modeling. The proposed procedure reproduces the experimental energies and provides a correct assignment of the absorption bands at substantially reduced computational cost.

In this work we examine the spectroscopy of $[Ru(NH_3)_5(py)]^{2+}$, whose structure is shown in Figure 1. Although the electronic spectra of such complexes have been known for over 25 years to be sensitive to the nature of the solvent, the reasons for this sensitivity have remained elusive.[1,3] The bond lengths we use for the model structure shown in Figure 1 are taken from X-ray experiments.[4] The INDO parametrization[2] used for the ruthenium 4d orbitals (β_d) was obtained to reproduce the observed d−d spectrum of $[Ru(NH_3)_6]^{2+}$.[1] The β_d thus obtained is −13.0 eV. The value for β for the s and p electrons has been modified slightly from that used for the first-row transition series, from $\beta_s = \beta_p = -1.0$ eV to $\beta_s = \beta_p = -2.0$ eV.

The molecular orbital (MO) diagram for the frontier orbitals of $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(py)]^{2+}$ is given in Figure 2. The pyridine-dominated π^* orbitals were found in the d−d gap as expected from the spectroscopy of similar Ru compounds and previous theoretical work.[5−8] The location of the occupied π pyridine orbitals varies slightly with the geometry and is typically 0.1 au (1 au = 27.21 eV) below the occupied Ru d orbitals, labeled in Figure 2 as d_π.

As one can expect from the MO diagram in Figure 2, the absorption spectrum of $[Ru(NH_3)_5(py)]^{2+}$ should contain contributions from weak d−d excitations and from the more intense d → π^* MLCT and intraligand $\pi \rightarrow \pi^*$ transitions. The symmetry-forbidden d−d transitions are not expected to compete in intensity with the MLCT and $\pi \rightarrow \pi^*$ transitions, and the d−d bands are hidden under the more intense bands mentioned above; see Table 1. Calculations performed on the isolated complex $[Ru(NH_3)_5(py)]^{2+}$ shown in Figure 1, however, do not agree very well with the observed bands and their intensities, as can be seen from Table 1. Excitations from $t_{2g} \rightarrow e_g$ d orbitals (O_h symmetry) yield states of $^1T_1$ and $^1T_2$, as can also be seen from Table 1. The small splittings of these $^1T_1$ and $^1T_2$ states are caused by the reduced symmetry of the complex. Small changes in geometry do not yield a marked increase in the intensity of these d−d excitations, and we do not expect spin−orbit interactions to change the calculated intensities significantly. Table 1 suggests that we can reproduce the observed transition energies, but not the observed fact that the bands at 25 000 cm^{-1} and 41 000 $^{-1}$ have equal intensities. In this assignment, the lower band, generally assumed MLCT, would be d−d.

Figure 1. Structure of $[Ru(NH_3)_5(py)]^{2+}$. The Ru−NH$_3$ bond distances are 2.144 Å, and the Ru−N(py) bond length is set to is 2.156 Å, the observed distance in similar complexes. Data are taken from ref 4.

Table 1. Calculated Transition Energies (in 1000 cm^{-1}) for $[Ru(NH_3)_5(py)]^{2+}$ in the gas phase *vs* the Experimental Spectrum from Ref 1[a]

calcd (gas phase)			exptl (soln)		
energy	OS	assignment	energy	log ϵ_{max}	assignment
24.2	0.00	d → d	24.6	3.89	MLCT
24.9	0.00				
25.0	0.00				
33.1	0.00	d → d	(nq)	(nq)	(nq)
33.6	0.00				
33.8	0.00				
37.5	0.07	$\pi \rightarrow \pi^*$			
40.5	0.20	MLCT	41.0	3.66	$\pi \rightarrow \pi^*$

[a] OS stands for the calculated oscillator strengths. MLCT is a metal to ligand (d → π^*) charge transfer band; (nq) stands for bands not quoted experimentally.

The findings in Table 1 seem, at first glance, to be unexpected given the fact that we are able to reproduce the corresponding spectra of both the pyridine and $[Ru(NH_3)_6]^{2+}$ complexes. However, complexes such as $[Ru(NH_3)_xL_{6-x}]^{2+}$ are sensitive to medium effects. It is known that these complexes do not show the spectroscopic shifts expected from dielectric continuum theory.[9] Indeed, we have examined the spectra of these complexes by using the self-consistent reaction field (SCRF) theory of Karelson and Zerner[9] that is implemented in ZINDO,[2] and a similar small red shift is observed when this method is used for all the solvents utilized. This is a consequence of the fact that most of the solvents used have a similar dielectric permittivity ϵ and index of refraction η, and the important reaction field factors,[9] $(\epsilon - 1)/(2\epsilon + 1)$ and $(\eta^2 - 1)/(2\eta^2 +$

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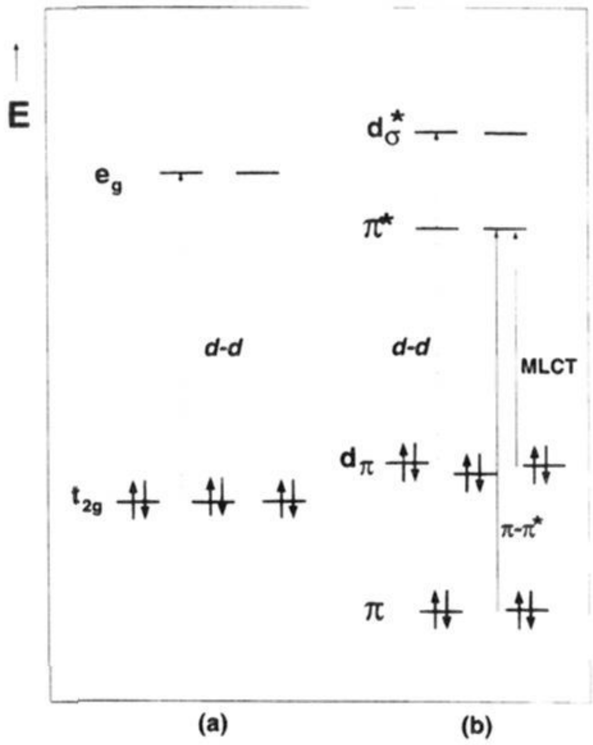
Table 2. Calculated Transition Energies (in 1000 cm^{-1}) with Different Numbers of Water Molecules around the Complex and with Two or Five Negative Point Charges behind the NH_3 Groups[a]

5 H_2O	10 H_2O	15 H_2O	2-*xy*-3.5	2-*xz*-3.5	5-*xyz*-3.5	type
34.3 (0.19)	28.5 (0.19)	25.5 (0.20)	26.7 (0.19)	24.3 (0.25)	26.5 (0.20)	MLCT
43.7 (0.20)	40.1 (0.15)	39.4 (0.11)	39.9 (0.16)	39.8 (0.15)	39.3 (0.18)	$\pi-\pi^*$

[a] The d−d transition energies are not given as they are of very low intensity (see Table 1, however). The assignments of the calculated transitions are the same for all the bands; the oscillator strengths are given in parentheses. 2-*xy*-3.5, for example, means that two negative charges have been added on the *x* and *y* axes 3.5 Å away from the Ru atom. The point charges are always equally divided and add up to −2. The Ru−N(py) bond is on the *z* axis; see also Figure 3.



(a) (b)

Figure 2. Frontier molecular orbitals as obtained in this work for (a) $[Ru(NH_3)_6]^{2+}$ and (b) $[Ru(NH_3)_5(py)]^{2+}$. The orbital labels correspond to O_h symmetry, although the actual symmetry is lower. The calculated splitting of the d_π orbitals is very small as depicted here.

1), are approximately $^1/_2$ and $^1/_5$, respectively, for all the common solvents used experimentally.[1]

We began our study of outer-sphere effects by adding a water molecule behind each of the five amino groups and optimizing the geometry until the gradient norm fell below 0.0001 au/Å. We recognize that there are many structures of nearly the same total energy, but all we have seen yield results similar to those reported in Table 2 as "$5H_2O$". The MLCT transition drops in energy from 40 500 cm^{-1} (Table 1) to 34 340 cm^{-1}, and the pyridine $\pi \rightarrow \pi^*$ band shifts from 37 540 cm^{-1} to 43 730 cm^{-1}! The subsequent addition of five more water molecules, one behind each of the NH_3 groups, followed by geometry optimization and CI calculation gives results that systematically approach the experimental ones. The "$15H_2O$" calculation is in very good agreement with experiment.

In Figure 3 we represent a "typical" structure of the complex surrounded by 15 H_2O molecules. As seen from Table 3, increased solvation leads to a shifting of electrons from the solvent to the amino groups and to the Ru atom. This, as expected, lowers the energy of the MLCT transition. We note that the INDO model leads to overbinding in H-bonding simulations, and this results in shorter O−H−X bonds than expected. This, in turn, might lead to exaggerated results, but generally the charge distribution, which is important here, is well reproduced. Note that in the 15 H_2O case, although the overall complex is +2, the solvent bears most of this charge, +1.6.

The calculations, especially $[Ru(NH_3)_5(py)]^{2+}(H_2O)_{15}$, are rather expensive, and so we attempted a simpler model to reproduce these rather dramatic spectroscopic shifts. We did this by placing negative charges summing up to −2 along the axes *x*, *y*, and *z* behind the amino groups. Table 3 reports the results obtained with two −1 charges placed behind two different NH_3 groups on the *x*, *y* and *x*, *z* axes, 3.5 Å from the Ru atom, and when five −0.4 charges are placed behind each amino group. All of these calculations reproduce the observed spectrum. We further note that the electric field at the Ru atom caused by amino groups of average charge +0.065 and a −0.4 charge at 3.5 Å (behind the amino groups) well reproduces the field at the Ru atom of amino groups with an average charge of +0.015 that we have calculated for the 15 H_2O case.

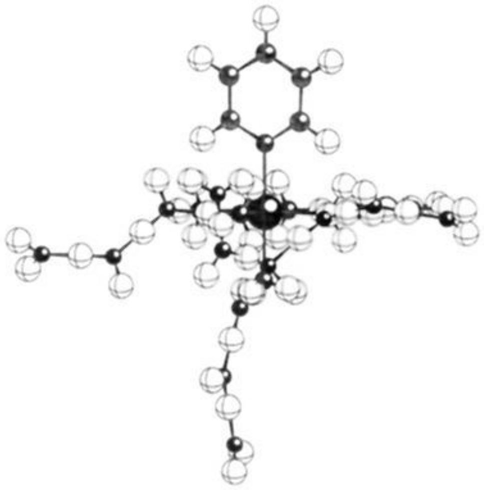


Figure 3. "Typical" structure obtained from geometry optimization of $[Ru(NH_3)_5(py)]^{2+}$ with 15 H_2O molecules. Note that sometimes additional water molecules are bonded to NH_3, but more often to one another, a consequence of the stronger H−O−H hydrogen bond.

Table 3. Charges on Fragments of the $[Ru(NH_3)_5(py)]^{2+}$ Complex in Different Environments as Obtained from the Mulliken Population Analysis[a]

fragment	no PTC	2 PTC	5 PTC	10 H_2O	15 H_2O
Ru	0.375	0.222	0.206	0.147	0.118
net py	0.290	0.081	0.161	0.194	0.165
net NH_3	1.335	1.697	1.633	0.233	0.073
net H_2O				1.426	1.642

[a] PTC stands for point charges.

These calculations clearly show that specific hydrogen bonding to the amino groups in complexes such as $[Ru(NH_3)_5(py)]^{2+}$ leads to a significant intracomplex charge redistribution (Table 3) which results in marked red shifts of the MLCT excitations and, at least in this case, yields quantitative agreement with experiment. This effect cannot be reproduced by including only the nonspecific dielectric effects of the solvent through a SCRF model. They are, however, reproduced by the use of negative point charges behind the amino groups.

The calculations have been performed within the restricted open-shell Hartree−Fock approximation, followed by a subsequent CI including, in the "15 H_2O" case, nearly 900 single excitations (CIS) from the closed-shell singlet state corresponding to the d_π^6 metal configuration. The first five H_2O molecules always "wet" the NH_3 groups. Additional waters may bind to NH_3 or H_2O (as shown in Figure 3). More complete simulations are presently underway.

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