Hydrogen bonding and wavelength dependence in time-resolved infrared spectroscopy of selective ion-sensors

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Introduction

The development of luminescent sensors for the detection of oxoanions attracts attention as an efficient means of selective analysis [1]. Our studies address oxometalates [2] since there are no selective chemosensors available for molybdate, tungstate or vanadate. The analysis of molybdate is important for environmental, biochemical and medical analysis. Oxometalates must not only compete successfully for the sensor with other oxoanions, such as SO_4^{2-} and HPO_4^{2-}, but also with metal cations, such as Fe^{3+} and Cu^{2+}.

Rhenium carbonyl bipyridine complexes have been the subject of intensive study by TRIR spectroscopy and it is now well established that MLCT excited states exhibit high frequency shifts of $\nu(CO)$ whereas photoinduced electron transfer from ligands to Re(py) causes low frequency shifts [3]. TRIR spectroscopy is the method of choice for mechanistic studies of such complexes.

We have recently reported a complex that acts as a molybdate sensor via luminescence quenching (Fig. 1). [4] The complex includes a catecholate binding unit capable of electron transfer to rhenium. Our sensor molecule is designed to signal the presence of molybdate by a change in the emission intensity.
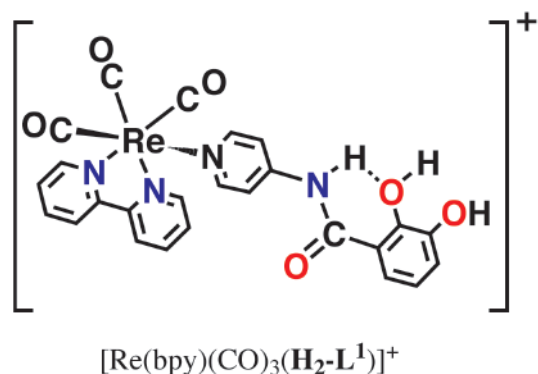

$[\text{Re(bpy)(CO)}_3(\text{H}_2\text{-L}^1)]^+$

Figure 1. Structure of the sensor molecule under investigation.

Almost complete quenching of luminescence is observed in the presence of molybdate down to pH values as low as 0.1. Figure 2 shows the Mo-complex formed upon complexation. Vanadate and tungstate may also be detected by this sensor system [4]. Absorption spectra reveal a change in the spectrum both with pH (Fig. 3) and with molybdate binding. This process is abbreviated as intra-ligand charge transfer (ILCT) from the electron rich catecholate to one of the Re-coordinated pyridine ligands).
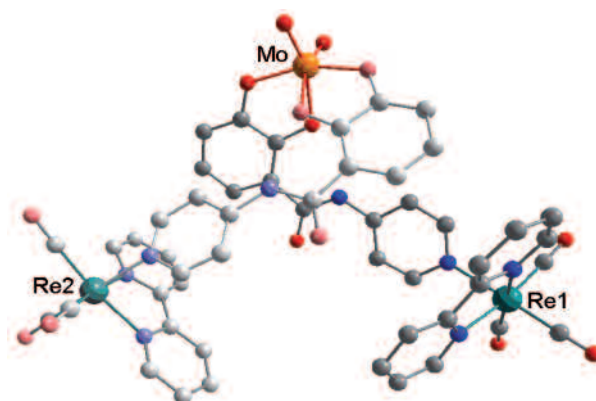

Figure 2. Molecular structure of $[\text{MoO}_2\{\text{Re(bpy)(CO)}_3(\text{L}^1)\}_2]$.

This investigation completed our previous time-resolved infrared (TRIR) investigations with PIRATE in 2005. Our earlier study provided evidence for 2-channel behavior with a switch from the emissive MLCT state to a non-emissive ILCT state as a result of deprotonation. The quenching mechanism is different with molybdate. Molybdate deprotonates both OH-groups. The ILCT absorption grows in; however, here the ILCT state is formed both by the direct route and by conversion of the MLCT state.
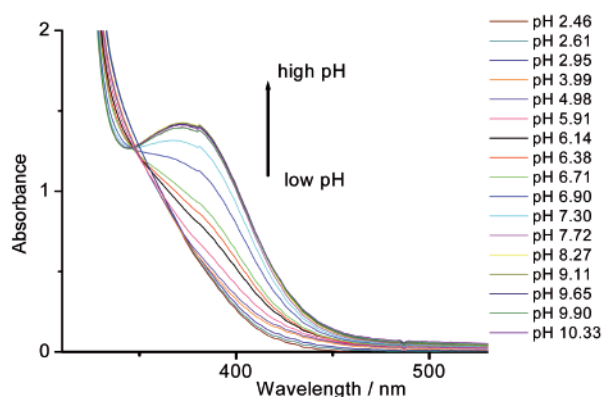

Figure 3. Absorption spectra recorded during the titration of an acidic solution of $[\text{Re(bpy)(CO)}_3(\text{H}_2\text{-L}^1)]^+$ in aqueous DMF with an aqueous tetramethylammonium hydroxide solution.

In the Mo-complex, the ILCT state exhibits three decay processes: (i) an ultrafast process of ca. 5 ps, (ii) a decay of ca. 15 ns and small proportion with a lifetime exceeding 1 μs. In order to understand the underlying photophysical

mechanism better, we had to address the following questions: (a) What is the role of hydrogen bonding in the catecholate and how does the proportion of D_2O in the solvent affect the photophysics? and (b) Can the ratio of MLCT to ILCT excitation be affected by the excitation wavelength?

Results

The results from the experiments on the PIRATE system provided the answers to both questions.

(a) What is the role of hydrogen bonding in the catecholate? How does the proportion of D_2O in the solvent affect the photophysics?

It was suggested that the enormous difference in lifetimes of the ILCT state could be associated with a change in conformation and hydrogen-bonding. We therefore investigated the effect of hydrogen bonding on the lifetimes of the ILCT state by changing the solvent system from 5% D_2O in DMF to 20% D_2O in DMF and 5% H_2O in DMF.

We collected excellent nanosecond data on the molybdenum complex of the sensor, $[MoO_2\{Re(bpy)(CO)_3(L^1)\}_2]$, in these solvent systems at pH 4. Control data sets were also collected on the protected sensor and the protonated sensor. These experiments revealed that the solvent system did not have a significant effect on the formation and lifetime of the ILCT state. Figure 4 shows the kinetics of the decay of the ILCT band at 1888 cm^{-1} obtained with 20% D_2O compared to the kinetics obtained with 5% H_2O. They are identical within experimental error. We therefore conclude that the nanosecond process is not associated with proton transfer or hydrogen bonding effects and tentatively assign the ultrafast process of ca. 5 ps as ^{1}[ILCT] to ground state and the decay of ca. 18 ns as ^{3}[ILCT] to ground state.
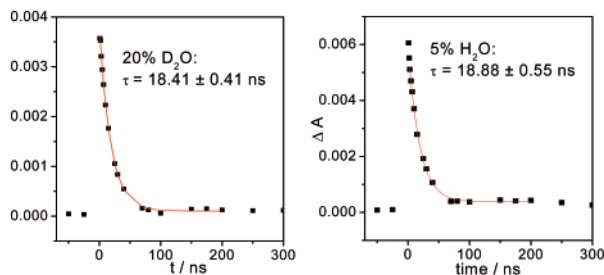

Figure 4. $[MoO_2\{Re(bpy)(CO)_3(L^1)\}_2]$: decay of the ILCT band at 1888 cm^{-1}, ns timescale, λ_{ex} 355 nm. Left: 20% D_2O in DMF Right: 5% H_2O in DMF.

(b) Can the ratio of MLCT to ILCT excitation be affected by the excitation wavelength?

Previously, our picosecond data were collected with 400 nm excitation and the ns data with 355 nm excitation. The titration of an acidic solution of $[Re(bpy)(CO)_3(H_2\text{-}L^1)]^+$ with base, however, revealed a significant pH-dependence (Figure 2) indicating that the MLCT transition overlaps with pH-dependent ligand-based transitions. The overlap of the MLCT and ILCT absorption bands may make this ratio sensitive to excitation wavelength. The addition of base leads to a significant increase in the absorbance at 400 nm due to the deprotonation of the *ortho*-OH group of the catecholamide unit and formation of $[Re(bpy)(CO)_3(H\text{-}L^1)]$. In contrast,

the absorbance at 355 nm is hardly affected. In order to investigate the effect of the excitation wavelength on the MLCT to ILCT ratio, we collected picosecond data at pH 4 with 355 nm and 400 nm excitation and compared the results obtained.

The TRIR spectra of $[MoO_2\{Re(bpy)(CO)_3(L^1)\}_2]$ at pH 4 in DMF/D_2O (20:1) obtained with 400 nm excitation are shown in Figure 5. At pH 4 both states, MLCT and ILCT, are observed. The TRIR spectra obtained are consistent with the data we collected in 2005 and confirmed that the ILCT state is formed by two mechanisms: both directly and at the expense of the MLCT state. The MLCT state converts to the ILCT state with a time constant of ca. 170 picosecond (Fig. 6), as previously observed.
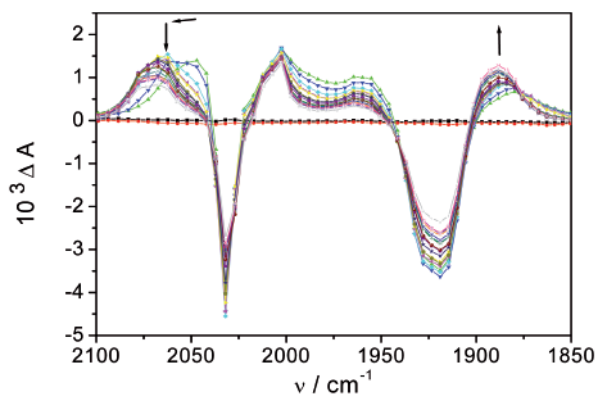

Figure 5. TRIR spectra of $[MoO_2\{Re(bpy)(CO)_3(L^1)\}_2]$ at pH 4 in DMF/D_2O (20:1) obtained with 400 nm excitation.

The TRIR spectra of the same sample were collected with excitation at 355 nm (Figure 7). The intensity of the MLCT band at around 1960 cm^{-1} is slightly lower, indicating that the MLCT to ILCT ratio has decreased compared to the ratio observed with excitation at 400 nm. This observation is consistent with the ligand-based band in the absorption spectrum of the sensor being more dominant at shorter wavelength, regardless of pH. The lifetime for the growth of the ILCT state by conversion from the MLCT state was 180 ± 13 ps, which is within the error margin of the kinetics obtained with excitation at 400 nm. However, there was a significant increase in the lifetime to 419 ± 29 ps on changing the pH to 2.
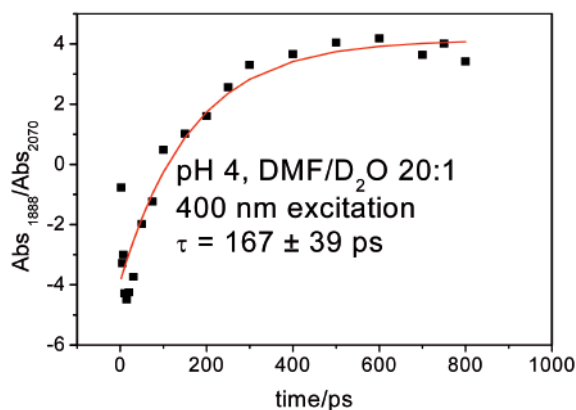

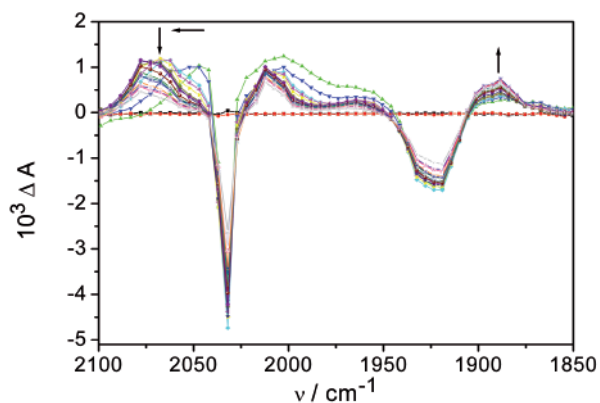**Figure 6. Kinetics of PeT conversion of MLCT to ILCT states, Re:Mo = 2:1, 400 nm excitation.**

Figure 7. TRIR spectra of [MoO$_2$\{Re(bpy)(CO)$_3$(L^1)\}$_2$] at pH 4 in DMF/D$_2$O (20:1) obtained with 355 nm excitation.

Conclusions

Our investigation showed that the lifetimes of the nanosecond component of the ILCT decay of [MoO$_2$\{Re(bpy)(CO)$_3$(L^1)\}$_2$] in 20% D$_2$O in DMF and 5% H$_2$O in DMF are exactly the same. It is therefore unlikely that this process is associated with proton transfer or hydrogen-bonding effects.

The overlap of the MLCT and ILCT absorption bands makes the MLCT/ILCT ratio sensitive to excitation wavelength. As expected from the absorption spectra, MLCT is more significant at 400 nm. The kinetics of the conversion of the MLCT to the ILCT state do not depend on the excitation wavelength

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