

# Photophysics of $[\text{Re}(\text{NCS})(\text{CO})_3(\alpha\text{-Diimine})]$ complexes: character of the lowest excited state

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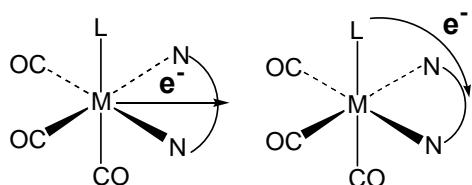
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## Introduction

Mixing of MLCT (metal to ligand charge transfer) and LLCT (ligand to ligand charge transfer) characters in electronic transitions and excited states is an intriguing topic in organometallic photochemistry. This character mixing has been inferred for complexes of the form  $[\text{Re}(\text{L})(\text{CO})_3(\text{N},\text{N})]$ , where L is an electron donating ligand (such as a halide), and N,N is a diimine ligand (Figure 1) but no direct evidence has been offered so far.



**Figure 1.** Schematic representation of MLCT (left) and LLCT (right) transitions in  $\text{fac-}[\text{Re}(\text{L})(\text{CO})_3(\text{N},\text{N})]n^+$  complexes.

Our approach was to substitute the halide by a “pseudo-halide”, in this case thiocyanate. This enabled us to study changes in the axial ligand by monitoring the NCS stretching vibration. For this purpose, two novel thiocyanate complexes,  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})]$  and  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{DAB})]$  ( $\text{bpy} = 2,2'$ -bipyridine,  $\text{DAB} = \text{N},\text{N}'$ -diisopropyl-1,4-diazabutadiene), have been synthesized and characterized. Both complexes were expected to undergo mixed MLCT/LLCT transitions upon irradiation.

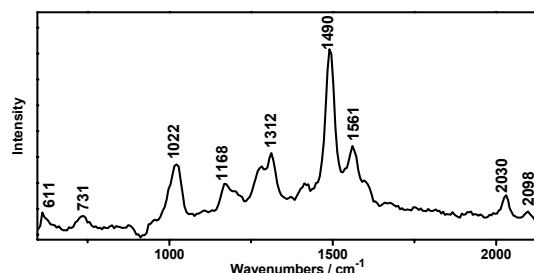
## Experimental

Both thiocyanate complexes were synthesized from the  $[\text{Re}(\text{CF}_3\text{SO}_3)(\text{CO})_3(\text{N},\text{N})]$  complex by addition of  $[\text{Bu}_4\text{N}]\text{NCS}^1$ .

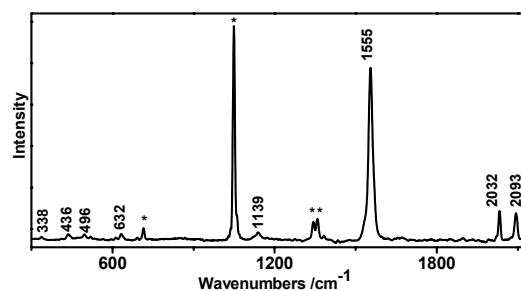
Time-resolved IR measurements used the equipment and procedures available in the CLF, which have been described in detail previously<sup>2-4</sup>. Ground-state resonance Raman spectrum of strongly emissive  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})]$  was collected during a 4 ps interval determined by a synchronized opening of an optical Kerr gate and it was, thereby, separated from the long-lived interfering emission<sup>5</sup>.

## Results and discussion

A combination of stationary (UV-Vis absorption, resonance Raman, fluorescence) and picosecond time-resolved (TRIR absorption, fluorescence) techniques have successfully generated evidence for the character of the excited state: Irradiation of the  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{N},\text{N})]$  complexes excites the molecules to a state of mixed  $\text{Re} \rightarrow \text{N}-\text{N}$  MLCT and  $\text{NCS} \rightarrow \text{N}-\text{N}$  LLCT character. This can be seen in Figures 2 and 3, by the resonance enhancement of Raman bands corresponding to the in-phase  $\text{A}'(1)$   $\nu(\text{CO})$  vibration at  $2030 \text{ cm}^{-1}$  and the  $\nu(\text{NC})$  vibration of the NCS ligand at  $2098 \text{ cm}^{-1}$ .



**Figure 2.** Resonance Raman spectrum of  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})]$  in MeCN measured using  $\sim 2$  ps, 400 nm laser pulses synchronized with a 4 ps optical Kerr gate that rejects the long lived emission. The solvent background is subtracted.

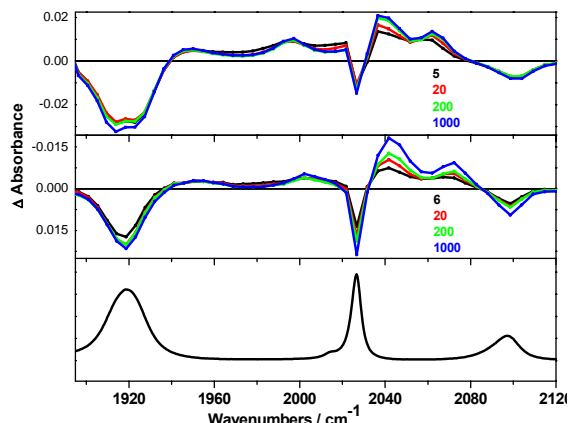


**Figure 3.** Resonance Raman spectrum of  $[\text{Re}(\text{NCS})(\text{CO})_3(i\text{Pr-DAB})]$  measured in a rotating  $\text{KNO}_3$  pellet, using continuous laser irradiation at 457.0 nm. Asterisks indicate peaks due to  $\text{KNO}_3$ .

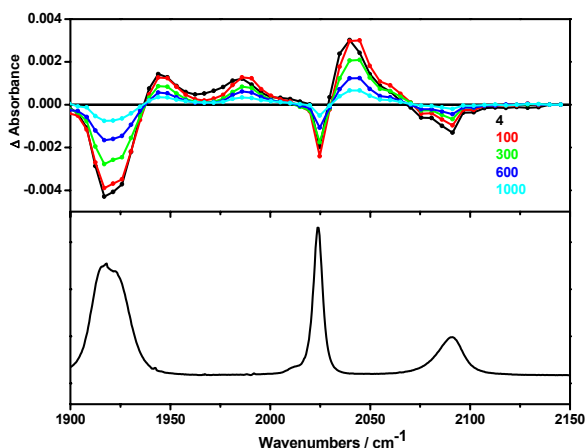
The Franck-Condon state, in both cases, undergoes intersystem crossing to the lowest triplet excited states, which were characterized using picosecond time-resolved IR spectroscopy, TRIR. The TRIR spectra are shown in Figures 4 and 5, together with the ground-state FTIR spectra. These triplet states have a lifetime of 23 ns for  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})]$  and 625 ps for  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{DAB})]$ .

In the ground state, both complexes show a broad band at *ca.*  $1920 \text{ cm}^{-1}$ , which encompasses the out-of-phase  $\text{A}'(2)$  and equatorial  $\text{A}''$   $\nu(\text{CO})$  vibrations, and bands at  $2027 \text{ cm}^{-1}$  and  $\sim 2100 \text{ cm}^{-1}$  due to the in-phase  $\text{A}'(1)$   $\nu(\text{CO})$  and  $\nu(\text{NC})_{\text{NCS}}$  vibrations, respectively. Empirically, we assign the excited-state bands of  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})]$  at 1952, 2002, and  $2072 \text{ cm}^{-1}$  to up-shifted  $\nu(\text{CO})$  vibrations, as is characteristic for MLCT excitations<sup>4, 6-8</sup>. The  $2041 \text{ cm}^{-1}$  band is assigned to the  $\nu(\text{NC})_{\text{NCS}}$  vibration. Its downward shift from the ground-state position demonstrates the LLCT contribution to the excitation, which removes electron density from an  $\text{N}=\text{C}=\text{S}$   $\pi$  bonding orbital, weakening the  $\text{N}=\text{C}$  bond and thus decreasing the  $\nu(\text{CO})$  frequency. The assignment of the  $2072 \text{ cm}^{-1}$  band as  $\nu(\text{CO})$  is corroborated by the solvent effect, Figure 4. Decreasing the solvent polarity diminishes the extent of the charge transfer from the  $\text{Re}(\text{CO})_3$  unit. This is manifested by a smaller shift of the highest  $\nu(\text{CO})$  band upon excitation;  $+32 \text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  vs.  $+46 \text{ cm}^{-1}$  in MeCN.

Excited-state TRIR spectra of  $[\text{Re}(\text{NCS})(\text{CO})_3(i\text{Pr-DAB})]$  show similar features as  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})]$ , although the shifts of the IR bands upon excitation are smaller and the highest vibration is manifested as a  $\sim 2068 \text{ cm}^{-1}$  shoulder on the most intense  $2053 \text{ cm}^{-1}$  band, Figure 5.

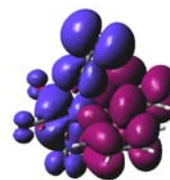


**Figure 4.** Difference TRIR spectra of  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})]$  in  $\text{CH}_2\text{Cl}_2$  (top) and MeCN (bottom) measured after 400 nm,  $\sim 150$  fs excitation at time delays (ps) specified in the insets. Experimental points are separated by  $4\text{--}5 \text{ cm}^{-1}$ . The ground-state FTIR spectrum is shown in the bottom panel.

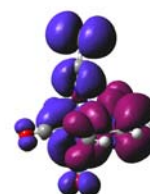


**Figure 5.** Difference TRIR spectrum of  $[\text{Re}(\text{NCS})(\text{CO})_3(i\text{Pr-DAB})]$  in THF measured after 470 nm,  $\sim 150$  fs excitation at time delays (ps) specified in the inset. Experimental points are separated by  $4\text{--}5 \text{ cm}^{-1}$ . The ground state FTIR spectrum is shown in the bottom panel.

Calculations of the electron density redistribution, Figures 6 and 7, show that electron density is transferred from the Re atom, the NCS and CO ligands to the  $\pi^*$  system of the diimine. The largest depopulation occurs at Re and NCS, accounting for the MLCT and LLCT contributions, respectively. These calculations also suggests that the excited state can be viewed as delocalized, the electron density being excited from the  $\pi$  system of the entire  $\text{Re}(\text{NCS})(\text{CO})_3$  moiety.



**Figure 6.** Change of electron density distribution upon the  $a_1A' \rightarrow a_3A'$  electronic transition of  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{bpy})]$ . Blue and violet colors correspond to a decrease and increase of electron density, respectively. Calculated by TD-DFT G03/PBE1PBE/CPCM for MeCN solution.



**Figure 7.** Change of electron density distribution upon the  $a_1A' \rightarrow a_3A'$  electronic transition of  $[\text{Re}(\text{NCS})(\text{CO})_3(\text{Me-DAB})]$ . Blue and violet colors correspond to a decrease and increase of electron density, respectively. Calculated by TD-DFT G03/PBE1PBE/CPCM for MeCN solution.

## Conclusions

The lowest allowed electronic transitions and excited states of *fac*- $[\text{Re}(\text{NCS})(\text{CO})_3(\text{N,N})]$  ( $\text{N,N} = 2,2'$ -bipyridine (bpy) di- $i\text{Pr-N,N}'$ -1,4-diazabutadiene, ( $i\text{Pr-DAB}$ )) were identified as charge transfer excitations of electron density from the whole  $\text{Re}(\text{NCS})(\text{CO})_3$  moiety to the  $\pi^*$  system of the  $\alpha$ -diimine ligand  $\text{N,N}$ . Such excited states can be described as mixed  $\text{NCS} \rightarrow \text{N,N}/ \text{Re} \rightarrow \text{N,N}$  LLCT/MLCT. Experimentally, this type of CT transition is manifested by upward and downward shifts of  $\nu(\text{CO})$  and  $\nu(\text{NC})$  vibrations upon excitation, respectively, and resonance enhancement of Raman  $\nu(\text{NC})$  and  $A'(1) \nu(\text{CO})$  bands. Moreover, the detailed excited state character was revealed by TD-DFT calculations, which reproduce well the spectral properties of the ground and excited states.

## References

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