

## Combined Use of M.c.d. and Resonance Raman Spectra for the Detection of Different Electronic Transitions in a Charge-transfer Band of $[\text{Mo}(\text{CO})_4\text{L}]$ ( $\text{L} = 2\text{-iminomethylpyridine}$ )

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**Summary** The combination of m.c.d. and resonance Raman spectra is shown to be a new and valuable tool for the detection of four different electronic transitions in one charge-transfer band of  $[\text{Mo}(\text{CO})_4(2\text{-iminomethylpyridine})]$ .

at ca. 550 nm ( $\text{CHCl}_3$ ). This band is broad and shows hardly any structure even at low temperatures, although it is expected to be composed of at least three electronic transitions from the separate Mo  $d$ -orbitals to the di-imine ligand.<sup>2,3</sup>

COMPLEXES of transition metals with ligands possessing low-lying excited states often show strong metal to ligand charge-transfer (CT) bands in the visible region. Examples of ligands which meet this requirement are molecules with conjugated double bonds such as the  $\alpha$ -di-imines which form highly coloured complexes with many transition metals.<sup>1</sup> An example is  $[\text{Mo}(\text{CO})_4(\text{impy})]$  (impy = 2-imino-methylpyridine) (Figure 1), which shows a strong CT band

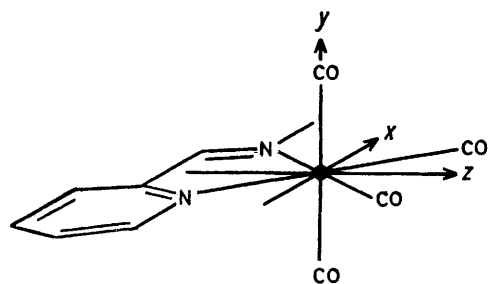


FIGURE 1. Structure of  $[\text{Mo}(\text{CO})_4(\text{impy})]$ .

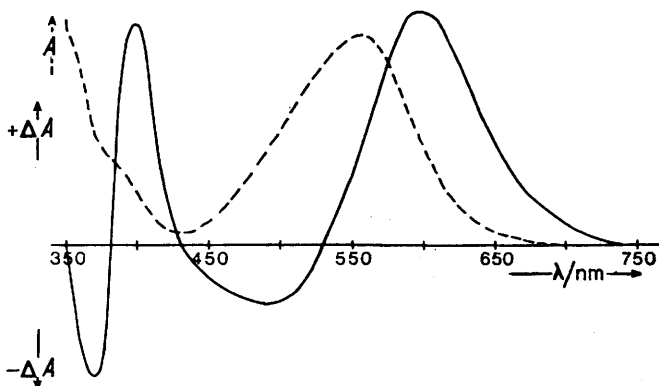


FIGURE 2. M.c.d. (—) and absorption (---) spectra of  $[\text{Mo}(\text{CO})_4(\text{impy})]$  in  $\text{CHCl}_3$ .

More information about these transitions was obtained from the m.c.d. spectra (Figure 2). This spectrum, which only possesses  $B$  terms because of the low symmetry of these compounds, clearly shows the presence of an electronic transition at the low energy side of the absorption

band. Furthermore, at least one, but probably two, transitions are found at the high energy side of this band between 450 and 500 nm. No m.c.d. effect was observed for the main electronic transition at 550 nm.

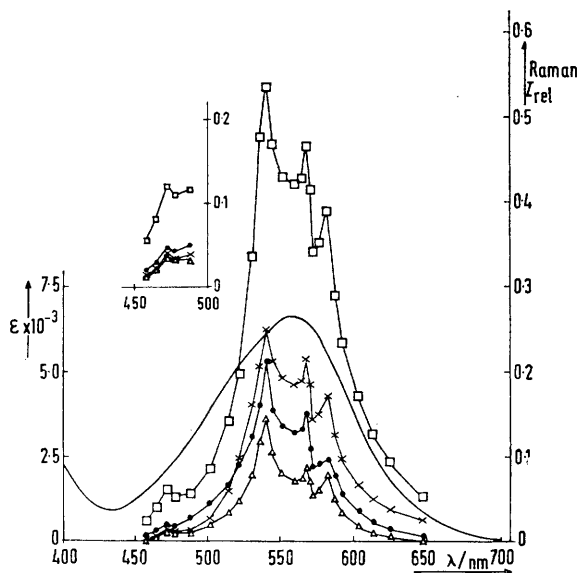


FIGURE 3. Excitation profiles of  $[\text{Mo}(\text{CO})_4(\text{imp})]$  in  $\text{CHCl}_3$ , relative to the  $758\text{ cm}^{-1}$  band of this solvent:  $\bullet$   $\nu_s(\text{CO}_{cis})$   $2023\text{ cm}^{-1}$ ;  $\triangle$   $\nu(\text{CN})$   $1610\text{ cm}^{-1}$ ;  $\square$   $\nu(\text{PyII})$   $1549\text{ cm}^{-1}$ ;  $\times$   $\nu(\text{PyIII})$   $1474\text{ cm}^{-1}$ . Inset: the 450–500 nm region for a higher concentration.

<sup>1</sup> H. tom Dieck and I. W. Renk, *Chem. Ber.*, 1971, **104**, 110.

<sup>2</sup> L. H. Staal, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1978, **26**, 255.

<sup>3</sup> R. W. Balk, D. J. Stufkens, and A. Oskam, *Inorg. Chim. Acta*, 1978, **28**, 133.

<sup>4</sup> R. J. H. Clark, in 'Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Heyden, London, 1975, vol. 1, p. 143.

The resonance Raman spectra of this compound were taken under conditions in which the frequency of the exciting laser line (nearly) coincided with the maximum of an allowed electronic transition. These spectra normally show a large increase of intensity for those vibrations which interact with a single electronic excited state.<sup>4</sup> The compound under discussion shows the largest enhancement of Raman intensity for  $\nu(\text{PyII})$ ,  $\nu(\text{PyIII})$ , and  $\nu(\text{CN})$  of the di-imine ligand, for  $\nu_s(\text{CO})$  of the carbonyl ligands, which are in the *cis*-position with respect to the di-imine ligand, and for  $\nu_s(\text{Mo-N})$ .

The intensities of these modes, with the exception of  $\nu_s(\text{Mo-N})$ , have been measured for a  $3 \times 10^{-4}\text{ M}$  solution in  $\text{CHCl}_3$  relative to the  $758\text{ cm}^{-1}$  band of this solvent and have been corrected for variation of absorption of the scattered light and for the sensitivity of the spectrophotometer. The excitation profiles in Figure 3 show the intensities of these modes as a function of the wavelength of the laser line. These excitation profiles possess four distinct maxima which coincide for the four different modes. This indicates the presence of four different electronic transitions within the CT band in close agreement with our m.c.d. results.

These results show that the combination of m.c.d. and resonance Raman spectra is a new and powerful tool for the detection of different electronic transitions in one CT band which may become of wider use in chemistry.

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