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# Detection and Assignment of Different Electronic Transitions within the First CT Band of $M(CO)_4L$ (M = Cr, Mo, W; L = 1,4-diazabutadiene (DAB) and pyridine-2-carbaldehydeimine (PyCa)) with the Use of Resonance Raman and MCD Spectra

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*The magnetic circular dichroism (MCD) together with the electronic absorption spectra of $Mo(CO)_4$-pyridine-2-carbaldehyde-(N-phenyl)-imine revealed that the first Mo to L CT band consists of different electronic transitions which could be assigned with the help of resonance Raman spectra.*

*The excited states of $M(CO)_{4-x}L(PR_3)_x$ complexes (M = Cr, Mo, W; x = 0, 1; L = 1,4-diazabutadiene and pyridine-2-carbaldehyde-($R_1$)-imine, $R_1$ = i-prop, phenyl; R = phenyl and n-butyl) are investigated with the resonance Raman effect and interpreted with the help of electronic absorption spectra and CNDO/S calculations.*

*The resonance Raman spectra gave detailed information about the properties of the excited states of the various complexes.*

## Introduction

During the last few years much attention has been paid in our laboratory to the coordinating properties of nitrogen donor ligands with cumulated or conjugated double bonds [1–3]. It has been found that the bonding properties of bidentate sulfurdiimines (R–N=S=N–R) and α-diimines ($R_1$–N=C($R_2$)–C($R_2$)=N–$R_1$) in the complexes $M(CO)_4L$ (M = $Cr^0$, $Mo^0$ and $W^0$) are very much alike. Both types of complexes show a strong π-backbonding from the metal to the ligand L and possess a very intense CT band in the visible region.

For some of the diimine complexes we investigated the resonance Raman (RR) spectra which showed the presence of at least three different electronic transitions within this CT band. Furthermore, apart from metal and diimine orbitals also orbitals of the carbonyls in the *cis* position with respect to the diimine ligand appeared to be involved in the first excited state. We now present a combined study of the M.C.D. and RR spectra of $Mo(CO)_4$(PyCa-Ph) (PyCa-Ph = pyridine-2-carbaldehyde-(N-phenyl)-imine), the structure of which is shown in Fig. 1. Furthermore, the relative enhancement of Raman intensities for the different modes of the diimine and carbonyl ligands in dependence of metal and diimine ligand is described and discussed**.

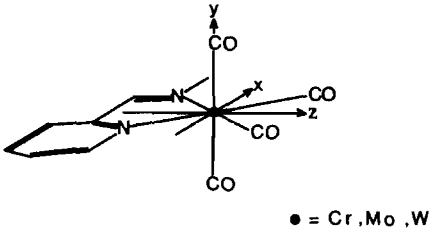

Fig. 1. Structure of $M(CO)_4$pyridine-2-carbaldehydeimine.

## Experimental

All compounds were prepared by methods described earlier [3–5]. The electronic absorption spectra were recorded on Cary 14 and Beckman model 25 spectrophotometers.

Resonance Raman spectra were recorded on Coderg PH 1 and Jobin Yvon HG 2 S Raman spectrophotometers, using Krypton CR 500 K, Argon CR 8 lasers and a model CR 490 tunable dye-laser with Rhodamine 6 G and sodium fluoresceine in ethyleneglycol as dyes and cyclooctatetraene as photosensitizer. The spectra were recorded with a spinning cell according to Kiefer [6] from 1–8 × $10^{-4}$ *M* solutions in chloroform and benzene, while the 758 $cm^{-1}$ band of $CHCl_3$ and the 606 $cm^{-1}$ band of $C_6H_6$ were used as internal standards. Band intensities were measured with a Hewlett Packard model 10 calculator with a 9864 A Digitizer and corrected for the sensi-

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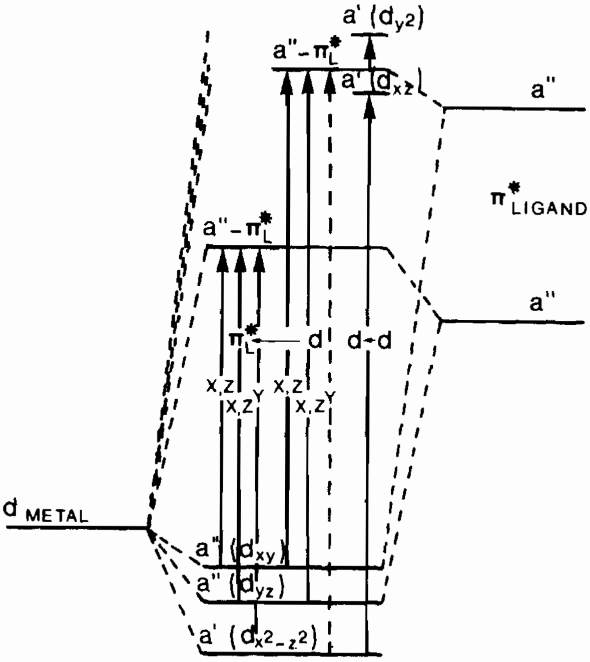

Fig. 2. Relevant part of the M.O.-diagram; possible transitions and polarization characteristics are shown.

tivity of the spectrophotometer, the absorption of the scattered light and decomposition in the laser beam.

The MCD spectra were recorded at the Laboratorium voor Algemene Chemie of the Rijksuniversiteit van Utrecht by Dr Hezemans and co-workers with a home-made instrument. The concentrations were chosen such that the optical density was about 0.75. The spectra were measured with a band pass of 3 nm at a magnetic field strength of 7.0 tesla and were corrected for the base-line.

Gaussian analyses were carried out on a Du Pont curve resolver model 310.

Molecular Orbital calculations were performed with the CNDO/S method in the parametrization of Jaffé and Del Bene [7], in which the repulsion integrals were approximated by the method of Nishimoto and Mataga [8]. Bond lengths and angles of the ligands are taken from ref. [9] and [10].

## Electronic Absorption Spectra

According to the tentative M.O. diagram of the $Mo(CO)_4$(PyCa-Ph) complex with symmetry $C_s$ (Fig. 2) six CT transitions are expected from the metal to the lowest excited states of PyCa-Ph. Only the three transitions to the first orbital have been observed in the visible region [2, 3].

The second $a''^* \leftarrow a''$ transition will be most intensive because it occurs between orbitals which strongly overlap giving rise to the strong π-backbonding from Mo to PyCa-Ph.

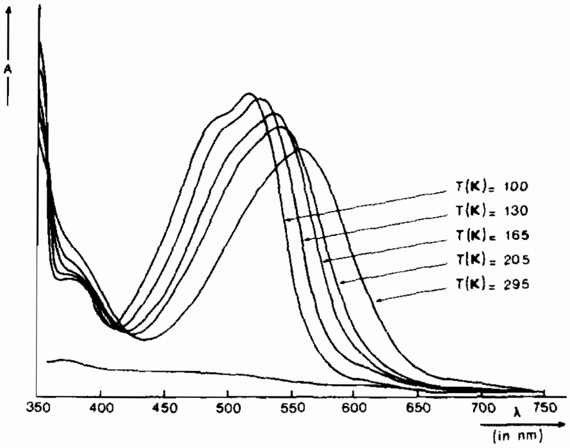

Fig. 3. Low-temperature absorption spectra of $Mo(CO)_4$-PyCa-pH in EPA.

The absorption spectrum in n-hexane (Fig. 4f) indeed shows the presence of more electronic transitions within the band at 595 nm. Apart from an intensive transition in the middle of the band, which is assigned to the second $a''^* \leftarrow a''$ transition according to the reasoning above, a second transition is observed as a shoulder at the high energy side.

In order to visualize the transitions within this band we recorded the low temperature spectra in an EPA glass. Apolar glasses cannot be used for this purpose because the spectra in such solvents show drastic changes below 200 K (ref. 3, 11).

The spectra in EPA (Fig. 3) show a strong thermochromic blue shift due to strengthening of the dipole–dipole interaction between the complex ($\mu \cong 9$ D) and solvent molecules. Furthermore, the band becomes structured showing the presence of at least two electronic transitions.

Apart from a sharpening of the bands, however, also a change of relative intensities is observed going from 295 to 100 K. The high energy shoulder increases in intensity with respect to the other transition. Apparently, the transition probabilities are affected by the electron shift in the complex which is accompanied by the thermochromic blue shift of the band. This effect may be due to the same conformational change which has been found for this type of complexes in alkane glasses [11].

### *Magnetic Circular Dichroism*

Further evidence for the existence of several electronic transitions in the CT band appeared from the MCD spectra.

The magnetic circular dichroism can be expressed in the molecular parameters A, B and C according to $\theta_m = -21.3458\{f_1A + f_2[B + C/kT]\}$ in which $\theta_m$ represents the molar ellipticity per unit magnetic

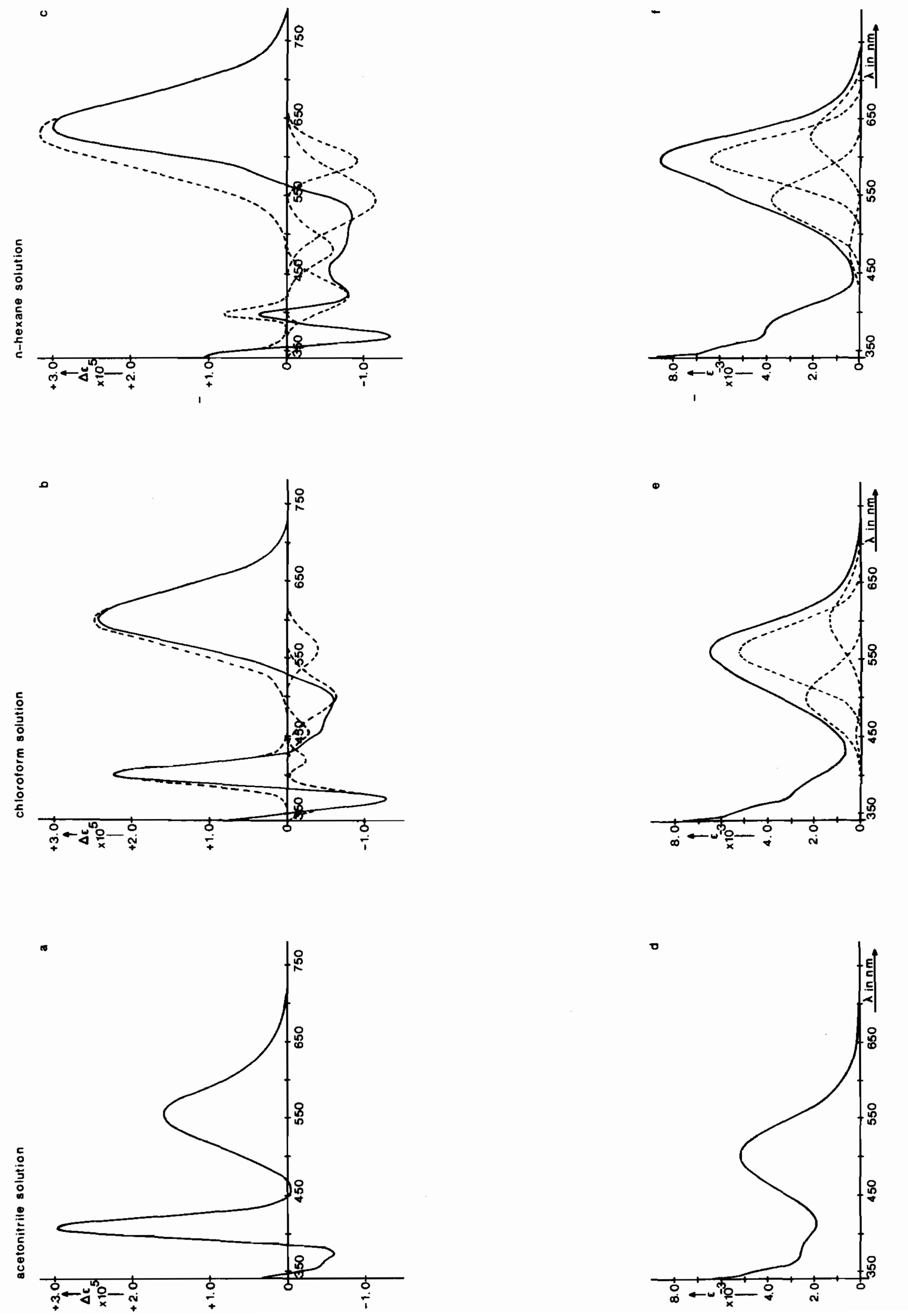

Fig. 4. MCD and electronic absorption spectra of Mo(CO)$_4$PyCa-Ph in CH$_3$CN(a, d), CHCl$_3$(b,e) and n-C$_6$H$_{14}$(c, f).

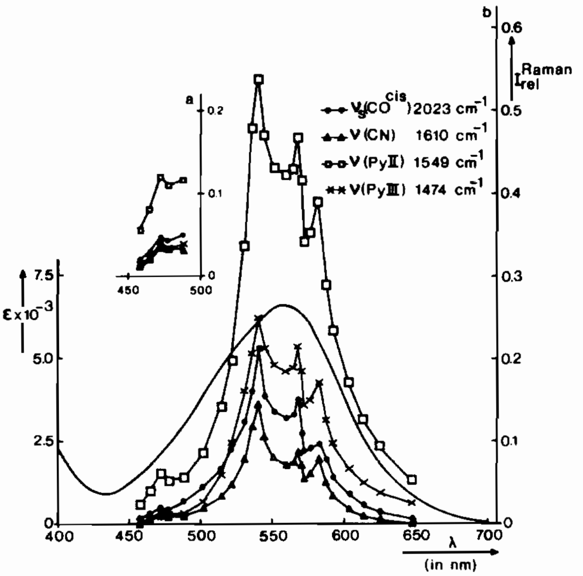

Fig. 5. Excitation profiles of $Mo(CO)_4PyCa\text{-}Ph$ in $CHCl_3$, relative to the 758 $cm^{-1}$ band of this solvent.

field and $f_1$ and $f_2$ are frequency functions describing the shape of the absorption bands [12, 13]. For $Mo(CO)_4PyCa\text{-}Ph$ which has no degenerate orbitals only B-terms are expected which arise from the mixing of levels by the magnetic field. The MCD spectra, shown in Fig. 4, have been recorded in solvents with different polarity. The spectra in n-hexane and $CHCl_3$ show between 450–600 nm one distinct negative and two positive B-terms which are all solvatochromic. Besides a weak shoulder is observed in the n-hexane spectrum between the negative and positive B-terms, at the position of the strongest electronic transition within the CT band.

These MCD results show the presence of at least four different electronic transitions within the CT band from which only two are observed in the low temperature absorption spectra. The corresponding positions of these four transitions in both the MCD and electronic absorption spectra have been used for a Gaussian analysis which gave a good fit for both spectra.

The negative B-term at 400 nm, which belongs to a ligand-field transition, shows a remarkable increase of intensity, when we go from n-hexane to acetonitrile. At this moment a sound explanation for this effect cannot be given.

## Resonance Raman Spectra

New evidence for different electronic transitions within the CT band appeared from the resonance Raman (RR) spectra which are taken under conditions in which the frequency of the exciting laser line (nearly) coincides with the maximum of an allowed electronic transition.

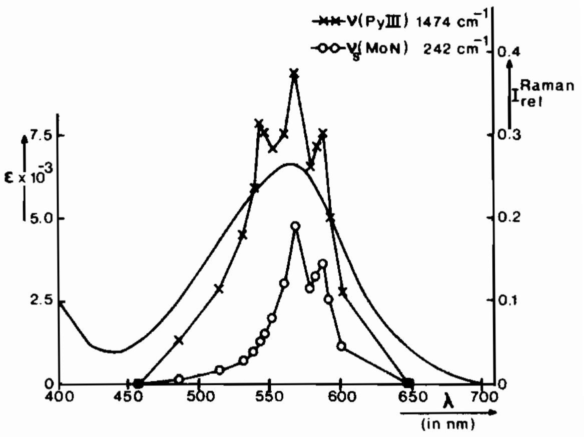

Fig. 6. Excitation profiles of $Mo(CO)_4PyCa\text{-}Ph$ in $C_6H_6$, relative to the 606 $cm^{-1}$ band of this solvent.

Normally a large increase of Raman intensity is found for symmetric vibrations which interact with a single electronic excited state [14]. Also B-term enhancement might be present here [15], but this effect can not be distinguished from A-term enhancement for these low-symmetry complexes. However, for the closely related diazabutadiene complexes with symmetry $C_{2v}$ no enhancement of intensity has ever been found for any asymmetric mode [2].

### *Excitation Profiles*

Strong resonance enhancement of Raman intensity was found for three ligand modes, $\nu(PyIII)$, $\nu(PyII)$ and $\nu(CN)$, for the symmetric stretching mode of the *cis*-carbonyls, $\nu_s(CO^{cis})$ and for $\nu_s(Mo\text{–}N)$. The intensities of the first four vibrations were measured in $CHCl_3$ with respect to the 758 $cm^{-1}$ band of this solvent (Fig. 5). $\nu_s(Mo\text{–}N)$ which could not be observed in $CHCl_3$ because of coincidence with a solvent band, was measured together with $\nu(PyIII)$ in $C_6H_6$ with respect to the 606 $cm^{-1}$ band of this solvent (Fig. 6).

The excitation profiles show the presence of four distinct maxima which coincide for all four vibrations. This points to the presence of four different electronic transitions within the CT band in close agreement with our MCD results.

The enhancement of vibrations of both the diimine ligand and the *cis*-carbonyls show that orbitals of both these ligands are involved in the first excited state of this complex. This effect which has been observed by us before [1–3, 5] will be discussed in more detail.

The relative intensities of $\nu(PyIII)$, $\nu(PyII)$ and $\nu(CN)$ hardly differ from each other at the maxima lying at 582.5, 568.2 and 545.0 nm, which indicates that these three maxima correspond to the electronic transitions to the same (first) virtual orbital of the complex.

TABLE I. Relation between Solvatochromism and Relative Raman Intensities.

| Complexes | $\sigma_{C_6H_{12}}$ [a] (kK) | $\Delta$ [b] (kK) | $\sigma_{CHCl_3}$ (kK) | $\lambda_{laser}$ (nm) | Relative Raman Intensities [c] | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $\nu_s(CO^{cis})$ | $\nu$(CN) | $\nu$(PyII) | $\nu$(PyIII) |
| $Cr(CO)_4$PyCa-i-prop | 16.55 | 3.5 | 18.1 | | | | | |
| $Cr(CO)_4$PyCa-Ph | 15.6 | 2.9 | 16.8 | | | | | |
| $Cr(CO)_4$DAB-i-prop | 17.1 | 2.0 | 17.8 | | | | | |
| $Mo(CO)_4$PyCa-i-prop[d] | 17.4 | 3.9 | 19.2 | 501.7 | 0.59 | 0.47 | 1.0 | 0.58 |
| $Mo(CO)_4$PyCa-Ph | 16.4 | 3.5 | 17.9 | 542.0 | 0.39 | 0.27 | 1.0 | 0.46 |
| $Mo(CO)_3(PBu_3)$PyCa-i-prop[d] | 15.0 | 2.4 | 15.3[e] | 615.0 | 0.30 | 0.37 | 1.0 | 0.61 |
| $Mo(CO)_4$DAB-t-Bu | 17.7 | 3.1 | 18.9 | 514.5 | 0.16 | 1.0 | | |
| $Mo(CO)_4$DAB-i-prop | 17.8 | 2.2 | 18.7 | 514.5 | 0.10 | 1.0 | | |
| $Mo(CO)_4$DAB-Ph-p-$OCH_3$ | 16.3[f] | 1.3 | 16.5 | 590.0 | 0.11 | 1.0 | | |
| $Mo(CO)_3(PPh_3)$DAB-i-prop | 17.0 | 0.9 | 17.2 | 568.2 | 0.0 | 1.0 | | |
| $W(CO)_4$PyCa-i-prop | 17.3 | 3.4 | 18.8 | 514.5 | 0.30 | 0.24 | 1.0 | 0.49 |
| $W(CO)_4$PyCa-Ph | 16.4 | 2.8 | 17.5 | 550.0 | 0.17 | 0.11 | 1.0 | 0.35 |
| $W(CO)_4$DAB-i-prop | 18.3 | 1.5 | 18.7 | 514.5 | 0.06 | 1.0 | | |

[a] $\sigma \equiv$ maximum of the CT band. [b] $\Delta \equiv \sigma_{CH_3CN} - \sigma_{C_6H_{12}}$. [c] The intensity of the strongest ligand vibration has been put equal to 1. [d] Data from ref. 3. [e] Measured in carbon disulphide. [f] Measured in carbon tetrachloride.

The excitation profile of $\nu_s$(Mo–N) in $C_6H_6$ (Fig. 6) only shows two maxima which coincide with two of the maxima for $\nu$(PyIII). Although the spectra of these vibrations were measured for $C_6H_6$ solutions, they are not expected to deviate much from those in $CHCl_3$ because the CT band only shifts about 3 nm going from $CHCl_3$ to $C_6H_6$.

The two maxima for $\nu_s$(Mo–N) are very important for the assignment of the electronic transitions, because resonance enhancement of this vibration is only expected for electronic transitions in the xz-plane of the molecule (see Fig. 1). The maximum at 568.2 nm has already been assigned to the second, mainly z-polarized $a''^* \leftarrow a''$ transition. Accordingly, the first maximum at 585.0 nm will correspond to the (mainly) x-polarized transition, while the third maximum at 542.0 nm in $CHCl_3$ corresponds to the (out-of plane) y-polarized transition for which no enhancement of $\nu_s$(Mo–N) is expected. This assignment agrees well with the observation that the enhancement of $\nu_s(CO^{cis})$ is larger at the 542.0 nm maximum than at the maxima at longer wavelengths.

This new evidence is in accordance with the tentative M.O.-diagram shown in Fig. 2, in which the sequence of metal d-orbitals has been reversed with respect to the corresponding diagram used in previous articles [2, 3].

The fourth, weak maximum observed in Fig. 5 is also present as a positive B-term in the MCD spectra at about 470 nm in $CHCl_3$ and 480 nm in n-hexane. Assignment of this maximum to a transition from the metal d-orbitals to the second excited state of the ligand is not very likely, because transitions to this level are expected at higher energy. In fact, for the corresponding compounds in which one or two carbonyls are replaced by phosphines, transi-

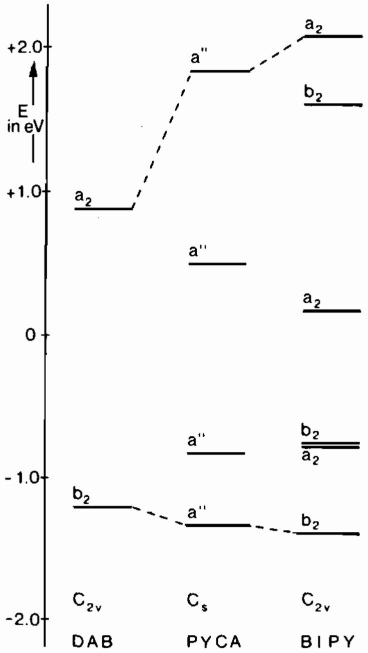

Fig. 7. Energy diagram of the excited states of three types of α-diimine ligands.

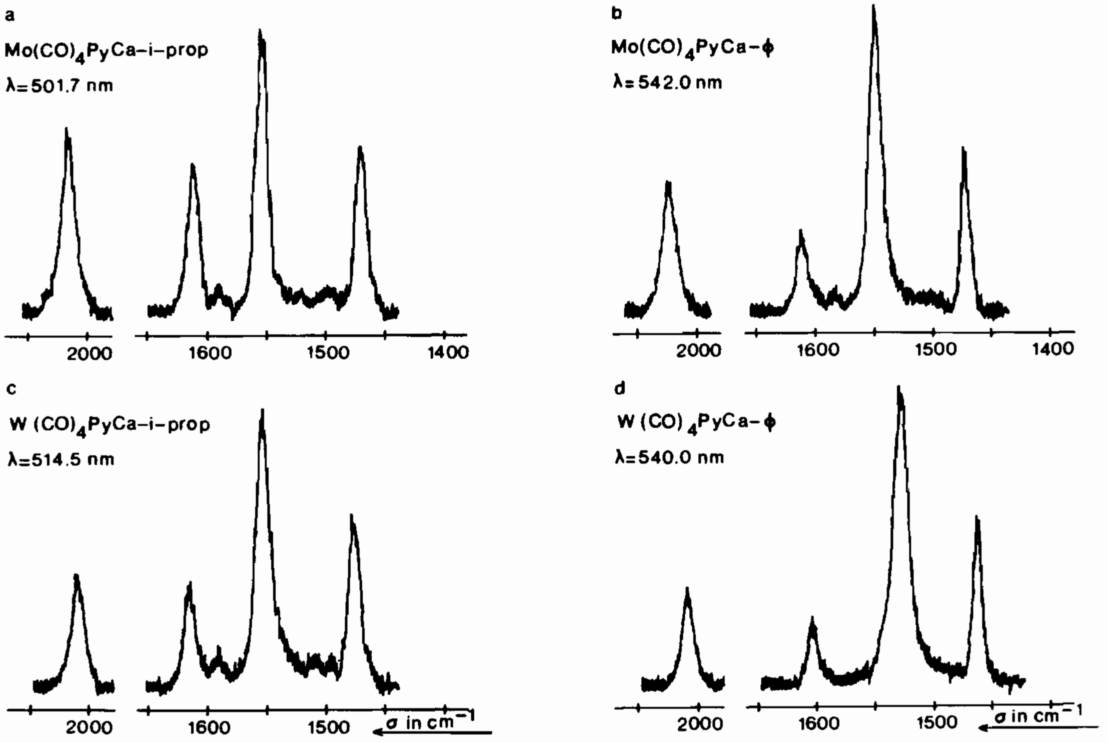

Fig. 8. Resonance Raman spectra of some $M(CO)_4PyCa\text{-}R_1$ complexes.

tions to the second excited state have been observed about 6–8 kK higher in energy than transitions to the first level [3]. Furthermore, although CNDO/S calculations show that the separation between the two excited states of the free bipy(2,2′-bipyridine) and PyCa ligands is much smaller than for DAB (Fig. 7), the complexes of these three ligands all show the presence of this electronic transition [2, 3].

### *Raman Activity of $\nu_s(CO^{cis})$*

From Table I and Fig. 8 it can be seen that a relation exists between the Raman intensity of $\nu_s(CO^{cis})$ and the solvatochromism of the CT band. When the solvatochromism is small, no resonance enhancement is found for $\nu_s(CO^{cis})$ as is the case for *e.g.* $Mo(CO)_3$-DAB-i-prop($PPh_3$). This behaviour was also found by R. Meij *et al.* for $M(CO)_4(R–N=S=N–R)$ complexes [5]. These latter compounds showed resonance enhancement for $\nu_s(CO^{cis})$ in the case of Cr and Mo for which the solvatochromism of the CT band is about 1.0 kK, while this vibration could even not be observed for the W-complexes which showed no solvatochromism.

This activity of $\nu_s(CO^{cis})$ was then attributed to the mixing of sulfurdiimine ligand and *cis* carbonyl excited orbitals of the same symmetry. In view of our results we prefer to explain this effect with a (second order) mixing of excited molecular orbitals as demonstrated in Fig. 9.

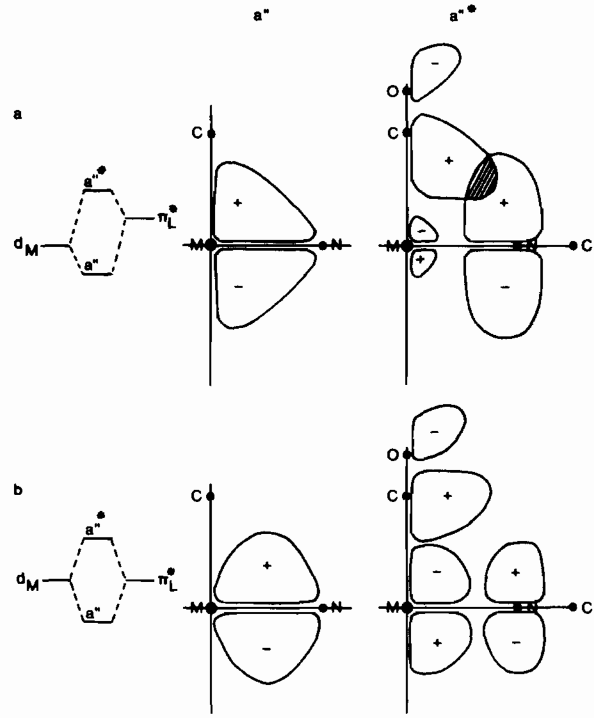

Fig. 9. Interaction of excited metal–ligand and metal–carbonyl states in dependence of the solvatochromism.

When there is a large solvatochromism of the CT band the mixing of $d_M$ and $\pi_L^*$ orbitals will be small

TABLE II. Energies and Atomic $p_y$ Orbital Coefficients for Excited State Orbitals of PyCa in the *syn* Conformation (see Fig. 11).

| Energy (eV) | Atomic $p_y$ Orbital Coefficients | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| −1.325 | −0.450 | 0.369 | 0.453 | −0.408 | 0.021 | 0.380 | −0.332 | −0.165 |
| −0.825 | −0.140 | 0.134 | 0.100 | 0.332 | −0.564 | 0.132 | 0.460 | −0.542 |
| 0.508 | 0.427 | −0.582 | 0.342 | −0.015 | −0.310 | 0.420 | −0.288 | −0.024 |
| 1.844 | −0.136 | 0.257 | −0.465 | 0.350 | −0.374 | 0.379 | −0.374 | 0.392 |

(Fig. 9a). The excited state will have its largest density at the N-atoms of the ligand and (attractive) interaction can occur with a molecular orbital concentrated at the C-atoms of the *cis*-carbonyls. Excitation of an electron into the first excited level will at the same time cause an increase of charge density at the *cis*-carbonyls and a resonance enhancement of $\nu_s(CO^{cis})$.

When the mixing of $d_M$ and $\pi_L^*$ orbitals is strong, *i.e.* in the case of small or zero solvatochromism (Fig. 9b), interaction with excited states concentrated at $CO^{cis}$ will be repulsive and excitation into the a″* level will cause no increase of charge density at the *cis* carbonyls. As a result no resonance enhancement is observed for $\nu_s(CO^{cis})$.

When a small metal atom is used, such as chromium, the excited state mixing will be particularly strong and as a result a large enhancement of intensity is expected for $\nu_s(CO^{cis})$. Although this appears to be the case, no quantitative results could be obtained so far for these Cr complexes because of their high photochemical lability. In fact, such a high photochemical lability, which is caused by a substitution of *cis* carbonyls [16], is always observed by us for complexes with a strong enhancement of $\nu_s(CO^{cis})$. These preliminary results are the subject of further investigation.

### *Relative Intensities of ν(C=N), ν(PyII) and ν(PyIII)*

Table I and Fig. 8 also show that the intensity of ν(C=N) decreases with respect to those of the pyridine modes when an alkyl group in the PyCa ligand is replaced by an aryl group (Fig. 8 a, b) and also when the solvatochromism of the complex decreases (Fig. 8 c, d).

The first effect may be due to conjugation of the diimine moiety with the aryl group and to coupling of ν(C=N) with the aryl–nitrogen and aryl stretching modes which is normally found for this type of ligands [2, 17].

The decrease of intensity of ν(C=N) with respect to those of the pyridine modes which accompanies the decrease of solvatochromism going from molybdenum to tungsten or from tetracarbonyl to tricarbonyl [3] represents a change of the difference between the electron density distributions of the ground and excited state. This can be caused by several effects.

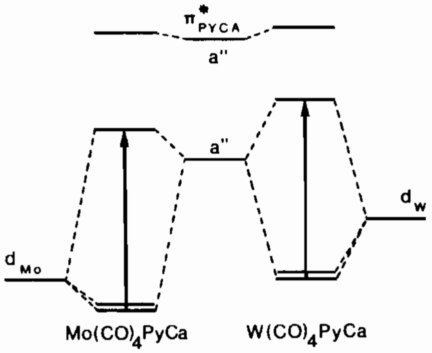

Fig. 10. The strongest a″* ← a″ transition of corresponding molybdenum and tungsten PyCa complexes.

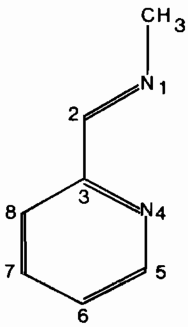

Fig. 11. Labelling of N and C atoms of PyCa for Table II.

First of all, the bonding interaction between metal and ligand increases. As a result the electron density in the ligand increases in the ground state, while the net charge transfer to the ligand decreases during excitation.

Secondly, a decrease of solvatochromism is accompanied by a decrease of excited state interaction with a M.O. localized at the *cis* carbonyls as shown before.

Finally, the relative intensities can also be influenced by excited state interactions between ligand orbitals *via* the metal d-orbitals. These interactions will be different for molybdenum and tungsten and also for tetracarbonyls and tricarbonyls. *E.g.* in the latter case the d-orbitals are raised with respect to the $\pi^*$ ligand orbitals [3], and as a result mixing of the second excited ligand orbital into the metal–ligand orbitals will increase. The same holds going from molybdenum to tungsten (see Fig. 10).

This second excited orbital has been shown to be more localized at the pyridine ring of the PyCa ligand then the first one (see ref. 3 and Table II).

Mixing of this state into the lowest lying $a''^*$ state will cause a decrease of excited state density in the C=N part of the ligand and as a result the activity of $\nu$(C=N) will decrease with respect to those of $\nu$(PyII) and $\nu$(PyIII) in the resonance Raman spectra.

## Conclusions

It is shown that the combination of MCD and resonance Raman spectra can be a new and powerful tool for the detection and assignment of different electronic transitions within a CT band. Furthermore, the resonance Raman spectra gave detailed information about the differences in mixing of orbitals in the excited states between the various complexes.

## Acknowledgements

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