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Investigation of MLCT and ML'CT Transitions of $M(CO)_3LL'$ Complexes, (M = Cr, Mo, W; L = diimine; L' = isocyanide) with the Resonance Raman Effect.

Identification of Two Isomers of the *p*-Nitrophenylisocyanide Complex

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The resonance Raman (RR) spectra of the complexes $M(CO)_3LL'$ (M = Cr, Mo, W; L = N,N'-di(i-propyl)-1,4-diazabutadiene, pyridine-2-carbaldehyde-(i-propyl)imine; L' = CN–R with R = t-butyl, p-*CH_3-phenyl,* p-*Cl-phenyl and* p-*NO_2-phenyl) have been investigated by exciting within the metal-to-ligand L and L' transitions. With the use of these RR spectra the CT transitions to these ligands L and L' could be characterized. The properties of the excited electronic states of these complexes are discussed and related to those of the corresponding complexes containing L' = $P(OMe)_3$ and CO. In the case of L' =* p-*nitrophenylisocyanide two (C≡N) stretching modes are observed in the infrared and Raman spectra. Their origin and the change of relative intensity in the RR spectra is discussed. Irradiation within the MLCT as well as the ML'CT band causes photosubstitution of the carbonyl ligand* cis *with respect to the diimine with quantum yields varying from 10^{-3} to 10^{-5}. The relationship between the photoreactivity and RR behaviour is discussed.*

Introduction

Quite recently [1] we investigated the resonance Raman (RR) spectra of a series of $M(CO)_{4-x}L[P(OMe)_3]_x$ complexes (M = Cr, Mo, W; L = diimine; x = 0, 1). Special attention has been paid to the resonance enhancement of Raman bands upon excitation within the first MLCT band. Apart from all symmetric metal–ligand stretching modes and several symmetric stretching modes of the diimine ligand, the (symmetrical) stretching mode of the carbonyl(s) *cis* with respect to the diimine [= $\nu_{(s)}(CO^{cis})$] also appeared to be resonance enhanced. The corresponding vibration of the *trans* carbonyls [= $\nu_s(CO^{trans})$] did however, not show such an RR effect and could not even be observed in the Raman spectra of any of the compounds.

This resonance enhancement of $\nu_{(s)}(CO^{cis})$ was explained by assuming an excited state interaction between molecular orbitals having predominantly $L\pi^*$ and $CO\pi^*$ character, respectively [1, 2]. Furthermore, a qualitative relationship appeared to exist between the resonance enhancement of $\nu_{(s)}(CO^{cis})$ and the photochemical reactivity (release of a *cis* carbonyl ligand) upon irradiation within the MLCT transition.

In this article infrared, electronic absorption and RR data are reported for the related complexes $M(CO)_3L(CN–R)$ (M = Cr, Mo, W; L = N,N'-di(i-propyl)-1,4-diazabutadiene(DAB), pyridine-2-carbaldehyde(i-propyl)imine (PyCa); R = t-butyl (t-bu), *p*-tolyl (*p*-CH_3–Ph), *p*-Cl-phenyl (*p*-Cl–Ph) and *p*-NO_2–phenyl (*p*-NO_2–Ph)). With the use of the RR results the properties of the excited MLCT states of these complexes are discussed and related to those of the $M(CO)_{4-x}L\ [P(OMe)_3]_x$ complexes. Furthermore, RR spectra have been taken by irradiation within the metal-to-isocyanide charge transfer transition ($ML'CT_I$) and the results will be discussed in detail. RR spectra of the mixed (diimine)(cyanide) complexes have been reported by Miller *et al.* who studied the resonance enhancement of Raman bands by excitation within the MLCT transition of $[Fe(L)_x(CN)_{6-2x}]^{2x-4}$ complexes (L = 2,2'-bipyridine; x = 1–3) [3].

Apart from these spectroscopic results, the photochemical behaviour of these complexes upon irradiation within both MLCT and $ML'CT_I$ bands will be discussed in relation to the RR data.

The structure of one of the complexes is show in Fig. 1.

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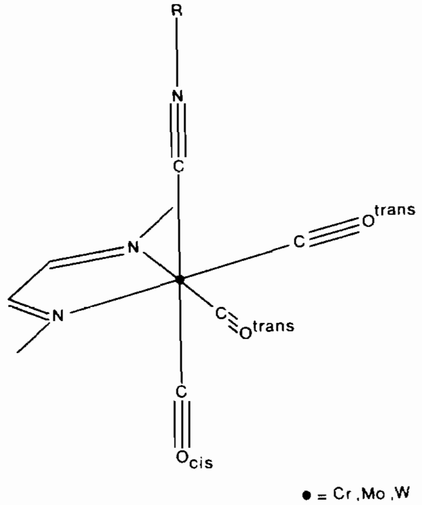

Fig. 1. Structure of $M(CO)_3DAB(CN{-}R)$.

Experimental

Preparations

The isocyanides were prepared by known methods [4, 5], applying slight modifications in the case of the *para*-nitrophenylisocyanide.

The (tricarbonyl)(isocyanide)(diimine) metal complexes were prepared as follows: 0.5 mmol of the (tetracarbonyl)(diimine) was converted to the (acetonitrile)(tricarbonyl) either by refluxing (Cr, Mo) or by irradiating (W) with a medium pressure Hg-source in pure acetonitrile. Reactions were followed by IR spectroscopy. The tricarbonyls were isolated, and after dissolving in benzene stirred with a slight excess of isocyanide. The complexes were isolated, chromatographed over silicagel and recrystallized from THF/hexane mixtures.

The PyCa-complexes of the arylisocyanides contained one or two equivalents of THF in their crystals.

Physical Measurements

The electronic absorption spectra were recorded on a Cary 14 spectrophotometer, the infrared spectra on Beckman IR 4250 and Perkin Elmer model 283 spectrophotometers.

Resonance Raman spectra were recorded on a Jobin-Yvon HG 2S Ramanor, using a SP model 171 Ar^+ laser and model CR 490 and 590 tunable dye-lasers with Rhodamine B, 6 G, Sodium fluoresceine and stilbene-3 in ethyleneglycol as dyes and cyclooctatetraene as photosensitizer. The spectra were recorded with a spinning cell from 2–10 X 10^{-4} *M* solutions in cyclohexane, benzene and chloroform.

Raman intensities were measured with a Hewlett Packard model 10 calculator using a 9864 A Digitizer and by the trace-and-weight technique and corrected for decomposition and the sensitivity of the spectrophotometer. The spectra in the figures are also corrected.

Photosubstitution quantum yields were measured by irradiating 4 ml benzene solutions (~10^{-4} *M*) which were carefully degassed, with either an excess of trimethylphosphite or pyridine (~0.02 *M*) in 40 X 10 X 10 mm quartz cells with a 100 mW laser beam. The photon flux was calculated from the laserpower, which was measured by a Coherent model 201 power meter. Before calculation of the quantum yields, corrections were applied for reflections of the light within the cell, for transmission of the laserbeam and for absorption of the photoproduct. The equipment was tested with ferrioxalate actinometry [6]. The reactions, which only proceeded during excitation, were followed with a Cary 14 UV–Vis spectrophotometer. The dicarbonyls were identified spectroscopically.

Results and Discussion

Infrared Spectra: $\nu(C{\equiv}N)$ and $\nu(C{\equiv}O)$

In Table I the frequencies of $\nu(C{\equiv}N)$ and $\nu(CO)$ of a series of $Mo(CO)_3(DAB)$ (L′) complexes (L′ =

TABLE I. $\nu(C{=}O)$ and $\nu(C{\equiv}N)$ IR Frequencies of a Series of $Mo(CO)_3DAB(L')$ Complexes (in cm^{-1}).[a]

	ν (C≡N)	ν ($C{\equiv}O^{cis}$)	ν ($C{\equiv}O^{trans}$)	
			ν_s	ν_a
$Mo(CO)_3DAB(CO)$		2016 1918	1895	1843
$Mo(CO)_3DAB(C{\equiv}N\text{-}Ph\text{-}p\text{-}NO_2)$	2049* (75)	1922	1880	1827
$Mo(CO)_3DAB(C{\equiv}N\text{-}Ph\text{-}p\text{-}Cl)$	2077 (48)	1929	1868	1821
$Mo(CO)_3DAB(C{\equiv}N\text{-}Ph\text{-}p\text{-}CH_3)$	2090 (38)	1929	1863	1818
$Mo(CO)_3DAB(C{\equiv}N\text{-}t\text{-}bu)$	2120 (20)	1929	1851	1813
$Mo(CO)_3DAB(P(OMe)_3)$		1942	1856	1815

[a] The spectra are recorded in chloroform. In parenthesis the shift of $\nu(C{\equiv}N)$ to lower frequency upon coordination of the isocyanide ligand, with respect to the free ligand frequencies from ref. 4.

*Maximum of the most intensive $\nu(C{\equiv}N)$ band.

isocyanide) are presented. For reasons of comparison the results for the complexes with L′ = CO and $P(OMe)_3$ are also included in the table. The results show that the frequencies of the CO stretching modes are lowered when L′ = CO is replaced by C≡N–R because of an increase of π-backbonding towards the carbonyls. The isocyanides have stronger σ and π electron donating and weaker π electron withdrawing properties than CO. When R becomes more electron-withdrawing, the σ- and π-donating properties of the isocyanide decrease whereas the π-acceptor properties increase. This can be deduced from the larger frequency decrease of ν(C≡N) with respect to the free ligand and from the concomitant frequency increase of the *trans* carbonyl vibrations [7]. The shifts of ν(C≡N) to lower frequency upon complexation are measured with respect to ν(C≡N) of the free isocyanide ligands in the 'infinite dilution' range, as reported by R. W. Stephany. He showed that the frequency of ν(C≡N) of the free ligands is not only dependent on the solvent, but also on their concentration, due to dimer formation [4, 8].

The frequency of the *cis* carbonyl ligand however, hardly changes when R of the isocyanide becomes more electron withdrawing although a distinct frequency increase is expected. This result is most certainly caused by the increase of the coupling between ν(C≡N) and $\nu(CO^{cis})$ when ν(C≡N) is lowered in frequency, which will cause a frequency lowering of $\nu(CO^{cis})$. Apparently, both effects compensate each other in these complexes.

A remarkable feature is found for the *p*-NO_2–Ph–NC complexes, which show more than one (C≡N) stretching mode in the infrared. The main IR band possesses two shoulders at the high and the low frequency side of the band, respectively (see *e.g.* Fig. 6). For complexes with L′ = CN–Ph–*p*-Cl this band is only slightly asymmetric. It will be shown in a later section that the RR spectra can explain the occurrence of these different (C≡N) stretching modes.

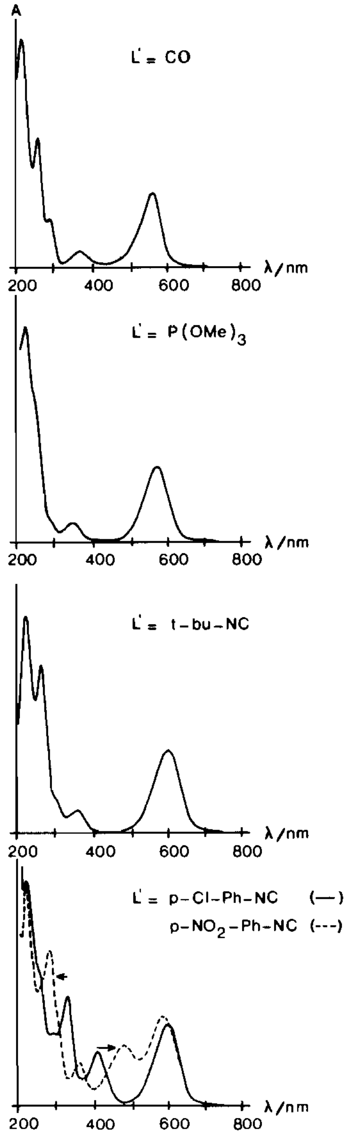

Fig. 2. Electronic absorption spectra of a series of $Mo(CO)_3$-DAB(L′) complexes in cyclohexane.

Electronic Absorption Spectra

Figure 2 presents the spectra of three isocyanide complexes and for comparison those of the complexes $Mo(CO)_{4-x}DAB[P(OMe)_3]_x$ (x = 0, 1). From these spectra it can be deduced that the metal-to-diimine π-backbonding is larger for the tricarbonyls. The MLCT band of the tricarbonyls has a lower energy, its position varying from 550 to 650 nm, whereas the solvatochromism of the band is smaller (see Table II). However, with respect to the $P(OMe)_3$ complex, the energy of the MLCT band is rather low for the isocyanide complex compared with the solvatochromism (0.8 for $Mo(CO)_3DAB[P(OMe)_3]$). This also holds for other PR'_3 complexes [9]. This effect is most likely due to the relatively strong σ- and π-donor and π-acceptor properties of the isocyanide with respect to PR'_3.

The high energy region of the spectra shows some interesting features. The low-intensity band, observed for $Mo(CO)_4DAB$ at about 370 nm and assigned to LF transitions [9], remains essentially unchanged for the tricarbonyl complexes. Only a small shift to higher energy is observed going from CO to C≡N–R and $P(OMe)_3$ as a result of an increase of the LF strength. The shoulder just below 300 nm is observed for all complexes at the same position and is assigned to an intra-ligand transition of the diimine. The band at 280 nm, observed in the spectrum of $Mo(CO)_4DAB$, has disappeared from this

TABLE II. UV–Vis Spectral Results, Photosubstitution Quantum Yields and Relative Raman Intensities for a Series of $M(CO)_3L(CN–R)$ Complexes.

Complexes	$\sigma^{max}_{c\text{-}C_6H_{12}}$ (in 10^3 cm^{-1})				$\epsilon^{max}_{C_6H_6} \times 10^{-3}$ MLCT	$\phi^i_p \times 10^4$ [c]	Relative Raman intensities[d] upon excitation within the MLCT band				
	MLCT[a]	ML'CT$_1$[b]		ML'CT$_2$			ν(C≡N)	ν(CO^{cis})	ν(C=N)	ν(PyII)	ν(PyIII)
$Cr(CO)_3PyCa(CN\text{-}t\text{-}bu)$	14.5 (2.7)		37.0		7.2	2.6 (640)	0.10	0.31	0.35	1.0	0.43
$Cr(CO)_3PyCa(CN\text{-}Ph\text{-}p\text{-}Cl)$	15.1 (2.8)	22.7	(0.4)	27.8	7.6	7.9 (610)	0.15	0.20	0.41	1.0	0.44
$Cr(CO)_3PyCa[P(OMe)_3]$[e]	15.4 (2.2)				7.55	5.0 (617)		0.51	0.35	1.0	0.51
$Mo(CO)_3PyCa(CN\text{-}t\text{-}bu)$	15.5 (3.0)		37.6		9.1		0.03	0.21	0.31	1.0	0.50
$Mo(CO)_3PyCa(CN\text{-}Ph\text{-}p\text{-}Cl)$	15.9 (3.4)	23.6	(0.6)	29.6	9.1		0.09	0.15	0.34	1.0	0.50
$Mo(CO)_3PyCa(CN\text{-}Ph\text{-}p\text{-}NO_2)$[f]	[17.1]	[19.8]		36.0	[14.5]						
$Mo(CO)_3DAB(CN\text{-}t\text{-}bu)$	16.6 (1.1)		38.1		13.6	1.0 (420)	0.01	0.08	1.0		
$Mo(CO)_3DAB(CN\text{-}Ph\text{-}p\text{-}CH_3)$	16.6 (1.4)	25.2	(0.4)	30.8	14.8						
$Mo(CO)_3DAB(CN\text{-}Ph\text{-}p\text{-}Cl)$	16.7 (1.4)	24.4	(0.6)	30.3	12.1	7.7 (420)	0.02	0.05	1.0		
$Mo(CO)_3DAB(CN\text{-}Ph\text{-}p\text{-}NO_2)$	17.1 (1.4)	20.8	(0.0)	36.0	15.8	0.2 (488)					
$W(CO)_3PyCa(CN\text{-}t\text{-}bu)$	15.5 (2.3)		38.0		12.8		0.0	0.07	0.18	1.0	0.43
$W(CO)_3PyCa(CN\text{-}Ph\text{-}p\text{-}Cl)$	15.8 (2.6)	23.8	(0.5)	29.9	11.7		0.03	0.06	0.22	1.0	0.45

[a,b] In parenthesis: the solvatochromism of the band $(\sigma_{CH_3CN} - \sigma_{c\text{-}C_6H_{12}})^{max}$. [c] In parenthesis: the exciting wavelength in nm. [d] Intensities relative to the strongest ligand band. [e] Values from ref. 1. [f] The values in square brackets are not certain due to strongly overlapping MLCT and ML'CT$_1$ bands.

position in the spectrum of the $P(OMe)_3$ complex and is therefore assigned to a Mo → CO^{cis} CT transition. As a result of the stronger π-backbonding to the CO groups in the tricarbonyl complexes the π*CO^{cis} orbitals will be more destabilized than in the tetracarbonyls. The CT transition to the *cis* carbonyl will therefore shift to higher energy going from the tetra- to the tricarbonyls and probably coincide with the band system which peaks at about 210 nm. The band at 280 nm in the spectrum of $Mo(CO)_3DAB$ (C≡N-t-bu) is assigned to a CT transition to a π* level of the isocyanide ligand. The bands, observed at 330 and 410 nm in the spectrum of $Mo(CO)_3DAB$ (C≡N–Ph–*p*-Cl) and at 270 and 480 nm for $Mo(CO)_3DAB$ (C≡N–Ph–*p*-NO_2) also belong to Mo → isocyanide transitions. The blue shifts of these bands going from apolar to polar solvents, confirm their ML'CT character. Molecular orbital calculations of the free isocyanide ligands show the presence of three low-lying π* orbitals for C≡N–Ph–*p*-R″ [10]. Two of these levels are out-of-plane (π^*_v) and delocalized over the phenyl ring, the third one is in plane (π^*_h) and (mainly) localized at the C≡N moiety [11]. One of these π^*_v orbitals (π^*_{v1}) is strongly stabilized by interaction with phenyl orbitals but has a relatively small density at the C atom of the C≡N group (about two times less than the π^*_{v2} level). The calculated splitting between π^*_{v1} and π^*_{v2} corresponds roughly with the energy difference between the two ML'CT transitions. We therefore assign these bands to CT transitions from Mo to these two π^*_v levels. It will be shown that the assignment of the lower energy band can be confirmed by the RR results (*vide infra*).

Resonance Raman Spectra

Excitation within the MLCT band

The complexes under study show strong resonance enhancement of Raman intensity for various metal–ligand stretching and bending modes (in cyclohexane solution, see Table III), which are all partly polarized. Besides, several symmetric diimine ligand modes, ν(C≡N) of the isocyanide ligand and ν(CO^{cis}) of the carbonyl ligand *cis* with respect to the diimine, are enhanced in intensity.

Although we are most likely dealing here with Franck–Condon emission since the intensity of the MLCT band is high and only symmetrical modes are enhanced in intensity, no vibrational progressions are observed. Instead, resonance enhancement is observed for many modes. This means that the potential energy curve of the MLCT excited state is only slightly shifted along their normal coordinates with respect to the ground state potential energy curve [12]. Only for the DAB complexes a very weak first overtone of ν_s(C=N) is observed (in $CHCl_3$ solution, room temperature).

TABLE III. Resonance Enhanced Metal–Ligand Vibrations of $Mo(CO)_3DAB(L')$ Complexes in Cyclohexane Solutions (in cm^{-1}).

	L′ = CO	CN–Ph–*p*-NO_2	CN–Ph–*p*-Cl[a]	CN-t-bu	$P(OMe)_3$
δ(M–C–O)	635 s[b]	632 m 622 w	635 (0.38) s	638 s	635 s
δ(M–C–O)	591 w	592 w	596 (0.20) w	598 w	595 sh(w) 585 vs
$\nu_s(M–C^{trans})$	464 s	462 s	469 (0.30) s	470 s	462 s
$\nu(M–C^{cis})$	407 s	410 sh	425 (0.24) s	420 sh	418 s
	331 vw	332 s	336 (0.26) s	333 m	
ν_s(M–N)	231 s	232 s	237 (0.41) s	240 s	242 s

[a] In parenthesis the depolarization ratio, measured at 600 nm. This ratio is 0.70 for the depolarized 218 cm^{-1} band of CCl_4 at this wavelength. [b] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

The observation of a RR effect for the diimine vibrations confirms the MLCT character of the absorption band. These vibrations are for the DAB complexes: ν_s(C=N), a very weak band at ~1470 cm^{-1} and a band at 1140 cm^{-1} (presumably ν_s(C–C)); for the PyCa complexes: ν(C=N), ν(PyII), ν(PyIII) and a few vibrations at lower frequency (*e.g.* at about 1000 cm^{-1}) [9, 13]. The resonance enhancement of $\nu(CO^{cis})$ is remarkable because no such effect is observed for $\nu_s(CO^{trans})$. This result has been discussed in previous articles [1, 2] and ascribed to a delocalization of the MLCT excited state over the *cis* carbonyl ligands. This delocalization is presumably caused by a 'through-space' or 'through-metal' interaction between virtual molecular orbitals mainly localized at the diimine ligand and the *cis* carbonyl group, respectively.

ν(C≡N) of the isocyanide ligand is also enhanced in intensity and this effect can be caused either by coupling between ν(C≡N) and $\nu(CO^{cis})$ or by charge transfer from the metal to the isocyanide ligand as a result of excited state interactions between isocyanide, metal and diimine orbitals. If the frequency of ν(C≡N) is changed, *e.g.* by substitution of the t-bu-isocyanide by *p*-Cl–Ph–NC, also the intensity of this mode changes with respect to $\nu(CO^{cis})$. This behaviour agrees with the expected intensity changes upon variation of the coupling between ν(C≡N) and $\nu(CO^{cis})$. On the other hand, the relative intensity of ν(C≡N) with respect to $\nu(CO^{cis})$ decreases if Cr is replaced by the larger Mo atom (see Table II), whereas the coupling between these modes is not expected to differ much for similar complexes of these two metals. This behaviour is in accordance with a change of interaction between π^*_L and $\pi^*_{L'}$. The relative intensities of ν(C≡N), $\nu(CO^{cis})$ and several diimine stretching modes which are presented in Table II, demonstrate this influence of the size of the central metal atom. Furthermore, the relative intensities of ν(C≡N) and $\nu(CO^{cis})$ with respect to the diimine modes also decrease when the solvatochromism or CT character of the MLCT band decreases, going from Mo to W. The same behaviour has been observed for the tetracarbonyl complexes [1].

Figure 3 shows a different behaviour for the intensities of $\nu(CO^{cis})$ and ν_s(C=N) (at about 1500 cm^{-1}) on the one hand and the metal–ligand modes (between 700 and 200 cm^{-1}) on the other. Whereas the intensities of $\nu(CO^{cis})$ and ν_s(C=N) both decrease going from $Mo(CO)_4DAB$ to $Mo(CO)_3DAB$(C≡N–Ph–*p*-Cl), the metal–ligand modes hardly change in intensity. In the case of $Mo(CO)_3DAB[P(OMe)_3]$ ν_s(C=N) could even hardly be observed (in cyclohexane solution. The same effect is observed going from a benzene to a cyclohexane solution of the isocyanide complex. The decrease of intensity observed for $\nu(CO^{cis})$ and ν_s(C=N) is in agreement with the decrease of solvatochromism going from $Mo(CO)_4$-DAB to $Mo(CO)_3DAB$(C≡N–Ph–*p*-Cl). Furthermore, if cyclohexane is replaced by the more polarizable solvent benzene, a charge shift will occur along the dipole moment axis. As a result more charge will be transferred from the metal to the diimine (opposite to the direction of the dipole moment) if excitation takes place in benzene. This effect causes an intensity increase for $\nu(CO^{cis})$ and ν_s(C=N), whereas the intensities of the metal– ligand stretching modes are hardly influenced.

Table III presents the frequencies and assignments of bands, observed in the low-frequency region of the RR spectra of a series of $Mo(CO)_3DAB(L')$ complexes. The assignments of ν_s(Mo–N), $\nu(Mo–C^{cis})$ and $\nu_s(Mo–C^{trans})$ are based upon previous assignments [1, 2, 13]. The assignment of the δ modes is tentative and based upon comparison with IR spectra of $Mo(CO)_4DAB$ and other complexes in KBr disks [14–16]. It is very unlikely that the strong band showing up at 585 cm^{-1} in the spectrum of $Mo(CO)_3$-$DAB[P(OMe)_3]$ belongs to a ν(Mo–P) or δ(Mo–P–O) vibration because the frequency is rather high.

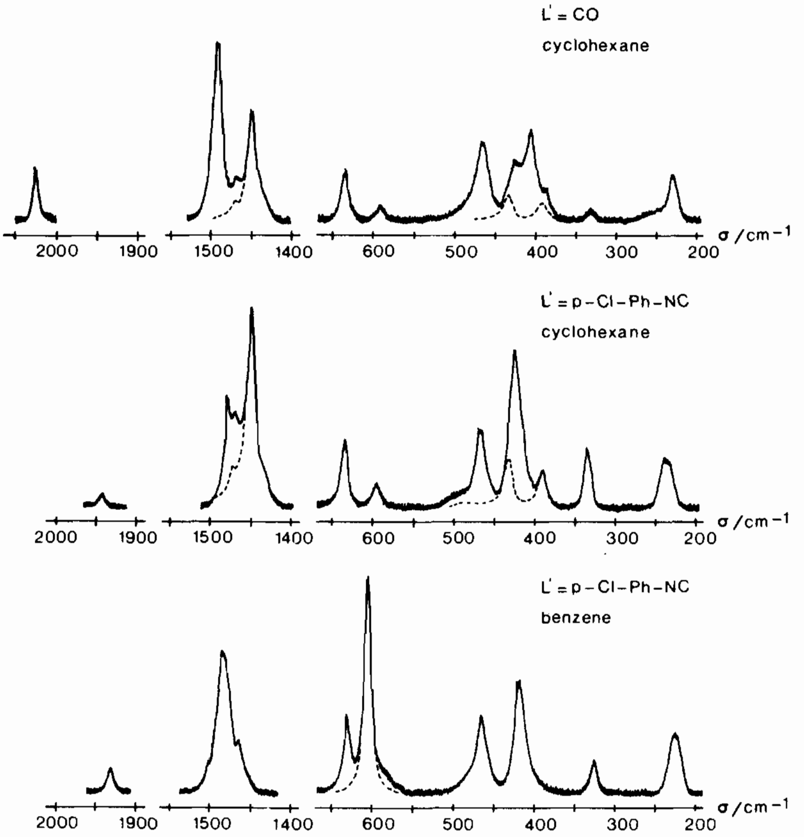

Fig. 3. High- and low-frequency regions of the RR spectra of two Mo(CO)$_3$DAB(L') complexes, excited within the maximum of the MLCT transition. The bands at 390, 440 and 1450 cm^{-1} are cyclohexane bands, while the band at 606 cm^{-1} is a benzene band. The dotted curves represent the shapes of these solvent bands under the resonance enhanced ligand and metal–ligand bands. ν(C≡N) has been omitted from the spectra.

Although little is known about the frequencies of ν(M–P) for phosphine and phosphite carbonyl complexes, they always have, if they are found, a value between 200 and 400 cm^{-1} [17–19]. May be the 585 cm^{-1} band belongs to a ligand mode of the phosphite, because the Raman spectrum of the free ligand shows a strong band at 520 cm^{-1}. The band at 330 cm^{-1}, observed for the isocyanide complexes, is not present in the spectrum of the P(OMe)$_3$ complex and is tentatively assigned to the metal–isocyanide stretching mode [=ν(MO–C^{iso})]. The weak band at about 330 cm^{-1} in the spectrum of the corresponding tetracarbonyl compound is only observed at this position for the DAB complexes and therefore probably due to a diimine ligand mode.

ν_s(Mo–N) shows a regular frequency increase going from left to right in Table III, which reflects the influence of the increase of π-backbonding from molybdenum to the diimine on the strength of the metal–nitrogen bond.

Excitation within the ML'CT$_1$ band of arylisocyanide complexes

RR spectra have also been taken by excitation within the 410 nm band of Mo(CO)$_3$DAB(CN–Ph–*p*-Cl) and the 480 nm band of Mo(CO)$_3$L(CN–Ph–*p*-NO$_2$) (L = DAB, PyCa) (see Fig. 2). These bands belong to the lowest energy molybdenum-to-isocyanide CT transition (ML'CT$_1$). The corresponding band of Mo(CO)$_3$PyCa (CN–Ph–*p*-Cl) has not been studied because it overlaps with a CT transition from the metal to the second excited state of PyCa [9].

First of all, several isocyanide vibrations are enhanced in intensity upon excitation within this band: ν(C≡N) between 2000 and 2100 cm^{-1}, ν(Ph) at about 1580 cm^{-1}, which corresponds to the ν_{e_g} mode of benzene [20, 21], and two bands between 1150 and 1210 cm^{-1}. From these latter bands, the weaker one at higher energy, which is observed in the spectrum of a solution in benzene, is obscured by the 1214 cm^{-1} band of CHCl$_3$ (see Fig. 4). In the case of the CN–Ph–*p*-NO$_2$ complexes also ν_s(NO$_2$) (at about 1330 cm^{-1}, see Fig. 6) shows a very strong RR effect [22, 23]. Apart from these modes, also ν(CO^{cis}) and ν_s(CO^{trans}) show a RR effect (Figs. 4–6). In the low-frequency region only weak RR bands are observed for ν(M–C^{cis}), ν_s(M–C^{trans}), a band at about 490 cm^{-1} and one at 640 cm^{-1} (Table III).

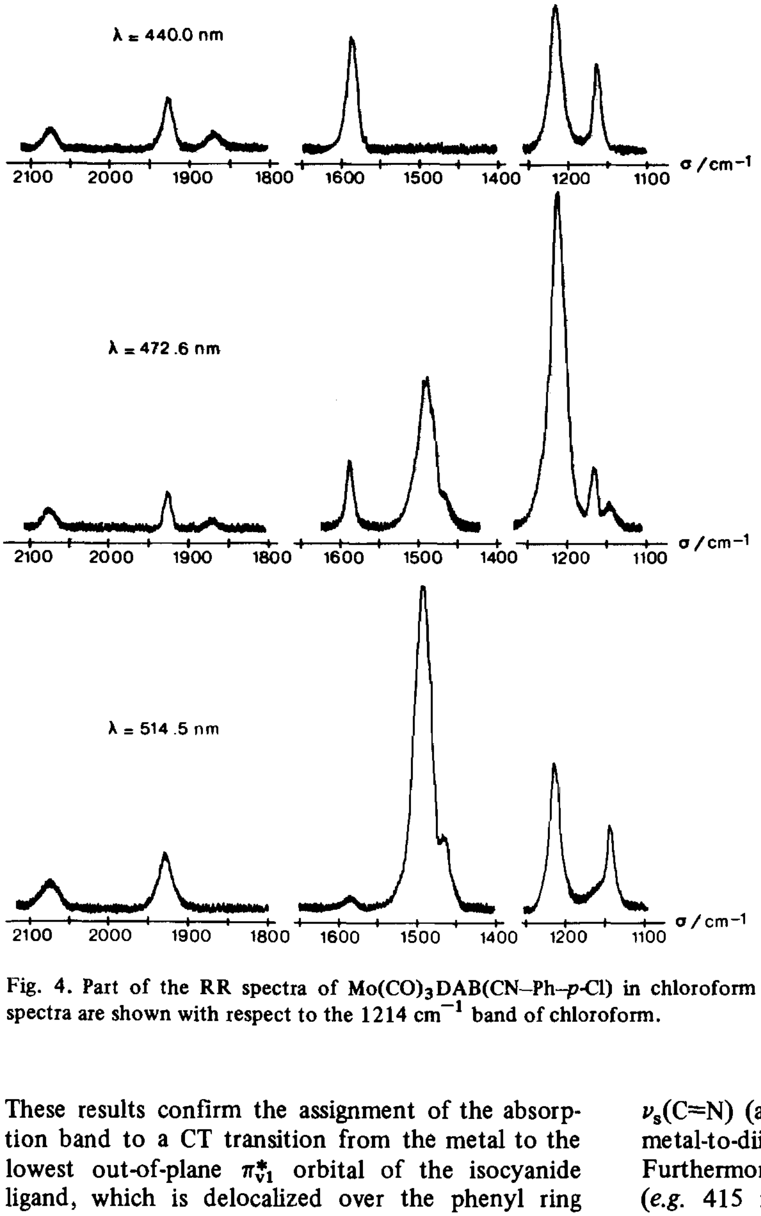

Fig. 4. Part of the RR spectra of Mo(CO)$_3$DAB(CN–Ph–*p*-Cl) in chloroform solution, excited at different wavelengths. The spectra are shown with respect to the 1214 cm^{-1} band of chloroform.

These results confirm the assignment of the absorption band to a CT transition from the metal to the lowest out-of-plane π^*_{v1} orbital of the isocyanide ligand, which is delocalized over the phenyl ring contrary to π^*_h. The low intensity of ν(C≡N) with respect to the phenyl modes shows that π^*_{v1} is hardly localized at the C≡N-moiety but mainly at the phenyl ring which agrees with the m.o. calculations [10]. In the case of the *p*-NO$_2$-isocyanide complex charge is also transferred to the NO$_2$ group which is apparently in plane and fully conjugated with the phenyl ring. Crystal structure determinations performed on several nitro-phenyl compounds confirm this conclusion [24, 25]. Furthermore, the very strong RR effect of ν_s(NO$_2$) (see Fig. 6) agrees with the high (virtual) electron density at and the highly antibonding character of the N–O bonds which has been calculated for the π^*_{v1} level. Figure 4 shows that the RR effect upon excitation within the metal-to-isocyanide transition (excited at 440 nm) is relatively weak with respect to the resonance enhancement of ν_s(C=N) (at 1500 cm^{-1}) upon excitation within the metal-to-diimine CT transition (at 514.5 nm). Furthermore, excitation at still shorter wavelength (*e.g.* 415 nm) hardly changes the intensities with respect to those excited with 440 nm.

This is in contrast with the large increase of intensity observed for ν_s(C=N) if the exciting wavelength approaches the maximum of the metal-to-diimine CT band. This relatively weak RR effect caused by the metal-to-isocyanide transition will partly be due to destructive interference with excited LF states [26]. The lowest LF transition is found just below 400 nm for *e.g.* Mo(CO)$_3$DAB(CN-t-bu).

Such interference effects have also been observed for M(CO)$_4$(bipyridine) and M(CO)$_4$(phenanthroline) complexes [16]. A remarkable feature of the RR spectra is the enhancement of ν_s(CO^{trans}) (at about 1870 cm^{-1} in the spectra of the CN–Ph–*p*-Cl compound) which vibration is not enhanced upon excitation within the MLCT band. We ascribe the resonance effect of this mode to delocalization of the ML'CT$_1$

TABLE IV. Solvent Dependence of Enhanced Ligand Vibrations of Mo(CO)$_3$DAB(CN–Ph-R″) Complexes upon Excitation within the ML′CT$_1$ band.[a]

R″ =	solvent	λ_{laser} (nm)	ν(Ph)	ν(C≡N)	ν_s(CO^{trans})	ν(CO^{cis})
Cl	c-C$_6$H$_{12}$	435.0	1.0	0.15	0.16	0.45
	CHCl$_3$	420.0	1.0	0.20	0.09	0.54
NO$_2$	c-C$_6$H$_{12}$	488.0	1.0	0.78	0.11	0.15
	CHCl$_3$	476.5	1.0	0.91	0.05	0.23

[a] Intensities with respect to ν(Ph).

excited state over the *trans* carbonyls, which are in the *cis* position with respect to the isocyanide. This explanation agrees with the proposed delocalization of the MLCT excited state over the *cis* carbonyls.

The resonance enhancement of ν(CO^{cis}) can be caused either by the vibrational coupling with ν(C≡N) or by the change of interaction between metal d, π^*(CO^{cis}) and π^*(CN–Ph–R″) orbitals which will take place during excitation within the ML′CT$_1$ band. The coupling between ν(C≡N) and ν(CO^{cis}) is expected to increase going from the CN–Ph–*p*-Cl to the CN–Ph–*p*-NO$_2$ complex because of the frequency lowering of ν(C≡N). In contrast with this however, a decrease is observed for the relative intensity of ν(CO^{cis}) with respect to ν(C≡N). This makes an interpretation of the RR effect of ν(CO^{cis}) in terms of vibrational coupling with ν(C≡N) less probable.

Although the ML′CT$_1$ transition of the (CN–Ph–*p*-NO$_2$) complex partially overlaps with the MLCT transition (see Fig. 2) it can be seen from the RR results of this complex shown in Fig. 5 that we have a nearly pure ML′CT$_1$ transition below 500 nm because only a very small resonance enhancement of ν_s(C=N) is observed in that wavelength region.

Table IV shows some interesting properties of the ML′CT$_1$ transitions of Mo(CO)$_3$DAB(CN–Ph–*p*-R″) (R″ = Cl, NO$_2$).

There is a marked difference between the relative intensities of both complexes. The intensity of ν(C≡N) relative to that of ν(Ph) is much larger for the CN–Ph–*p*-NO$_2$ complex than for the corresponding CN–Ph–*p*-Cl compound. M.o. calculations show that the changes in electron density which occur at the CN part of the isocyanide in the lowest π^*_{v1} orbital if Cl is replaced by NO$_2$, are smaller than those found at the phenyl ring of the ligand. Going from the Cl to the NO$_2$ substituted ligand, electron density in π^*_{v1} is shifted from the ring to the substituent, which implies that the RR effect of ν(Ph) will be weaker for the NO$_2$ than for the Cl substituted phenylisocyanide complex. This explains the increase of intensity of ν(C≡N) with respect to ν(Ph). Up to now, attempts to measure these intensity changes quantitatively with respect to a solvent band, have failed.

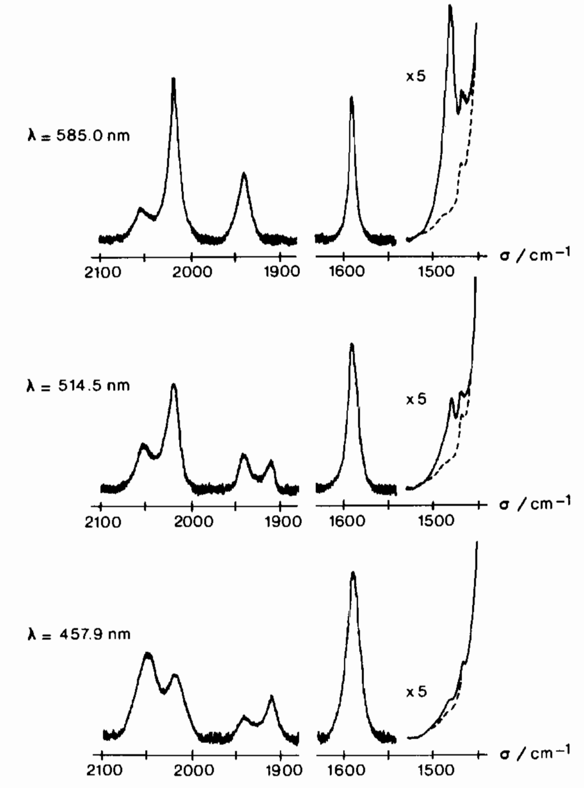

Fig. 5. Part of the RR spectra of Mo(CO)$_3$DAB(CN–Ph–*p*-NO$_2$) in cyclohexane solution, excited at different wavelengths. The dotted line represents the slope of the 1450 cm^{-1} band of cyclohexane under the enhanced ν_s (C=N) diimine mode.

Furthermore, the intensity of ν(CO^{cis}) decreases with respect to both ν(Ph) and ν(C≡N) if Cl is replaced by NO$_2$. This means that the π^* orbital of the *cis* carbonyl ligand is much less involved in the ML′CT$_1$ ground- or excited state of the *p*-NO$_2$-phenylisocyanide complex. This result is not unexpected since the π-backbonding from the metal d to the π^*_{v1} (isocyanide) orbital will increase if Cl is replaced by the more electron withdrawing NO_2 group.

There is a marked difference in the (C≡N) stretching region between the RR spectra of $Mo(CO)_3$-DAB(CN–Ph–*p*-Cl) (Fig. 4) and $Mo(CO)_3$DAB-(CN–Ph–*p*-NO_2) (Fig. 5). In the case of the *p*-NO_2 compound two (C≡N) vibrations are observed at about 2010 and 2050 cm^{-1}, respectively, just as in the IR spectrum. The relative intensities of these two modes change if the exciting laser line is varied from 457.9 to 585.0 nm. Upon excitation within the metal-to-diimine CT transition (at 585.0 nm) the band at 2010 cm^{-1} shows the largest RR effects whereas the relative intensities of these modes do not differ much if excitation takes place within the metal-to-isocyanide CT transition. For the *p*-Cl and also for the corresponding *p*-CH_3 compound only one ν(C≡N) is observed. The strongly electron-withdrawing substituent NO_2 apparently has a particular influence on the behaviour of the isocyanide ligand. We assume that the *p*-NO_2 group by its large electron-withdrawing character causes a charge flow within the isocyanide by which the bond between the (C≡N) group and the phenyl ring (see Fig. 1) acquires partly double bond character. This will cause a hindered rotation around the N–C (phenyl) bond which leads to the presence of the two rotamers of the isocyanide ligand in the complex. These rotamers will have π-backbonding from different metal orbitals which explains the different frequencies of ν(C≡N) for them.

The question remains why the relative intensities of these two modes change if the exciting wavelength is varied from 585.0 to 457.9 nm. Excitation at 457.9 nm occurs within the ML$'$CT$_1$ band, which corresponds to a transition to the π^*_{v1} level of each rotamer. There is no reason why the relative intensities of the two ν(C≡N) vibrations should differ much from those in the IR spectrum and this is in fact not observed. Excitation at 585.0 nm takes place within the MLCT band and we have explained the RR effect of ν(C≡N) and also of $\nu(CO^{cis})$ with a delocalization of the MLCT excited state over the *cis* carbonyl and isocyanide ligands. In order that such a delocalization of the MLCT excited state over the isocyanide ligand can take place there has to be a π^* orbital at the isocyanide which has a relatively large density at the carbon atom of the C≡N group. This will be the orbital π^*_h in the first place, which, contrary to π^*_v, is not delocalized over the phenyl ring but which has a large density at the C≡N group. This level can however not interact strongly with the metal–diimine CT excited state for both rotamers and it is therefore expected that the delocalization of the MLCT excited state over the isocyanide ligand is different for both rotamers. This is in accordance with the large difference in intensity between the ν(C≡N) vibrations of the two isomers observed upon excitation within the MLCT band.

Furthermore, the intensity of ν(C≡N) at 2010 cm^{-1} of the *p*-NO_2 complex (Fig. 5) changes drastically with respect to ν(Ph) at 1580 cm^{-1} going from excitation within the ML$'$CT$_1$ to the MLCT transition. The same effect is observed for the single C≡N stretching mode observed for the *p*-Cl compound. This clearly shows that different excited states of the isocyanide ligand are involved in both transitions. We propose that the rotamer which has the larger intensity and lower frequency of ν(C≡N) has its π^*_h level and therefore also the plane of the phenyl ring directed along the component of the dipole moment of the molecule which is directed from the diimine to the *trans* carbonyls (see Fig. 1).

We have tried to confirm the presence of these rotamers with NMR and IR at different temperatures but up to now these attempts have failed. However, Stone and coworkers also found quite recently two isomeric forms of isocyanide in a complex without being able to detect them separately in the NMR [27].

The situation is more complicated in the case of $Mo(CO)_3$PyCa(CN–Ph–*p*-NO_2) for which compound the RR spectra together with the ν(C≡N) and ν(CO) vibrations in the infrared and with the absorption spectrum are shown in Fig. 6. All spectra are taken from $CHCl_3$ solutions and the strong band at 1214 cm^{-1} in the RR spectra represents a solvent band, whereas its bands at about 1500 and 1970 cm^{-1} are left out.

The RR spectra show that throughout the structured band vibrations of both the isocyanide and the PyCa ligand are enhanced. Only in the case of λ = 457.9 nm the PyCa modes have nearly disappeared. It is clear from the RR effect of $\nu_s(CO^{trans})$ (at about 1860 cm^{-1}) that the transition at the high energy side of the absorption band belongs to the metal-to-isocyanide CT transition. Furthermore, the PyCa modes at about 1600 cm^{-1} (ν(C=N)), 1540 cm^{-1} (ν(PyII)), 1460 cm^{-1} (ν(PyIII)) and 1010 cm^{-1} have their highest intensity with respect to the 1214 cm^{-1} band of $CHCl_3$ at λ = 560.0 nm, which means that the transition at the long-wavelength side of the band has mainly a metal-to-PyCa character.

However, although the RR effect of $\nu_s(CO^{trans})$ strongly indicates that the higher energy transition belongs to the metal-to-isocyanide transition, ν_s-(NO_2) at 1330 cm^{-1}, ν(Ph) at 1580 cm^{-1}, ν(C≡N) at 2040 and 2010 cm^{-1} and an isocyanide mode at 1100 cm^{-1}, have their highest intensity with respect to the 1214 cm^{-1} band of the solvent at λ = 560.0 nm. This result which differs from that of the corresponding DAB compound, is most probably caused by a strong mixing between π^* levels of PyCa and CN–Ph–*p*-NO_2 in the MLCT excited state. Part of the effect may further be due to interference effects.

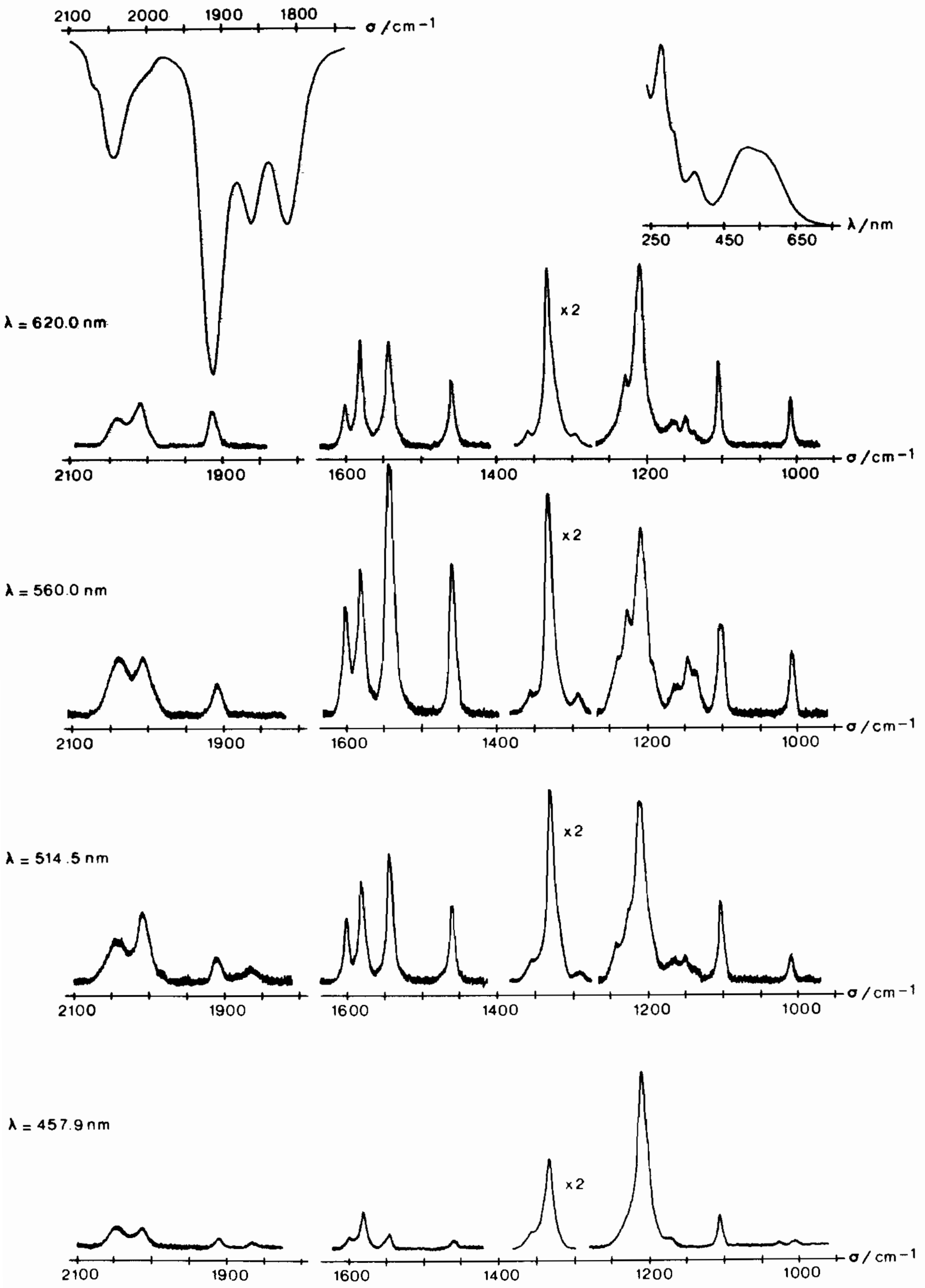

Fig. 6. High-frequency region of the RR spectra of $Mo(CO)_3PyCa(CN{-}Ph{-}p{-}NO_2)$ in chloroform solution, excited at different wavelengths. The spectra are shown with respect to the 1214 cm^{-1} band of the solvent. At the top left: $\nu(C{\equiv}N)$ and $\nu(C{\equiv}O)$ stretching region of the infrared spectrum; top right: the absorption spectrum; both spectra are recorded in chloroform.

Photosubstitution Reactivity

Several of these complexes show photochemical release of the *cis*-CO group and substitution reactions have been performed with $P(OMe)_3$ and pyridine (py).

Upon irradiation within the MLCT band, only the chromium complexes exhibit photoreactivity, their photosubstitution quantum yields varying from 10^{-3} to 10^{-4}.

All complexes show photosubstitution reactivity when irradiation takes place within the ML'CT band. Only the quantum yields of some molybdenum DAB complexes are presented in Table II. With respect to these quantum yields, those of the chromium complexes are a factor ten higher, but these complexes also show decomposition without substitution. $Mo(CO)_3DAB(CN\text{-t-bu})$ does not possess a ML′CT band at 420 nm and the observed photoreactivity at that wavelength will arise from LF excitation [28]. This complex has a very low ϵ value at 420 nm, and after long times of irradiation only very small conversion to $Mo(CO)_2DAB(CN\text{–t-bu})(py)$ is obtained. On the other hand, the substitution quantum yield of the CN–Ph–*p*-Cl complex is higher at 420 nm. This may be due to reactivity of the excited $ML'CT_1$ state [29, 30], but it is also possible that the reactivity of the excited LF state is enhanced by a decrease of the metal–carbon *cis* bond strength going from the CN-t-bu to the CN–Ph–*p*-Cl complex.

In a recent study we described the close relationship between enhancement of Raman intensity of $\nu(CO^{cis})$ upon excitation within the MLCT band of $M(CO)_{4-x}L[P(OMe)_3]_x$ (x = 0, 1) and the photoreactivity of these complexes [1]. Only those complexes appeared to be photoreactive which showed a RR effect for $\nu(CO^{cis})$. This result has been taken as evidence that the RR effect of $\nu(CO^{cis})$ and the photochemical release of a *cis*-carbonyl ligand, are both caused by the delocalization of charge over the *cis* carbonyl(s) in the MLCT excited state.

The same mechanism is proposed for the complexes under study although a direct relationship between the photosubstitution quantum yield and relative intensity of $\nu(CO^{cis})$ does not exist.

Conclusions

The results of the previous section show that the RR effect of these $M(CO)_3LL'$ complexes (M = Cr, Mo, W; L = diimine; L′ = isocyanide) can be used to:

i) characterize the MLCT and ML′CT transitions and excited states

ii) describe the properties of the isomers observed in the case of L′ = *p*-nitrophenylisocyanide

iii) explain the photoreactivity of these complexes.

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