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Excited states of transition metal complexes studied by time-resolved infrared spectroscopy

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Contents

Abstract

This article describes the application of time-resolved infrared spectroscopy (TRIR) to probe structure and reactivity of excited states of transition metal complexes. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

An understanding of the structure and properties of excited states is a prerequisite of photochemistry. In transition metal complexes, absorption into a charge transfer band can result in a structural change if the minimum of the charge transfer state is displaced from the minimum of the ground state. Structural distortions can be monitored by *indirect* techniques such as absorption, emission and excitation spectroscopy. Unfortunately, except in very special circumstances, vibrational fine structure is usually absent, and hence structural information is limited. The analysis of resonance Raman spectra of transition metal complexes in their *ground* states can, in principle, give structural information of *excited* states either via Frank–Condon analysis [1], or time-dependent formulation [2]. These methods also have their limitations, and there has been much effort in obtaining the spectra of excited states *directly* in real time.

The most common *direct* technique for probing excited states in solution is UV–vis transient absorption (TA) spectroscopy, but absorption bands of transient metal complexes are generally broad and featureless, and provide little structural information. However, time-resolved vibrational spectroscopy is a powerful tool for providing structural information of the excited state(s) of transition metal complexes [3]. The most widely used technique is time-resolved resonance Raman spectroscopy (TR^3). In a classical example, Woodruff demonstrated that the lowest ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) was best described as $[Ru^{III}(bpy)_2(bpy^-)]^{2+}$ [4]. However, there are two principal limitations in the application of TR^3 to transition metal excited states: firstly only totally symmetric vibrations are resonance enhanced; secondly, only those vibrations which are coupled the new excited state appear—for example, in the TR^3 of the charge transfer excited state of $[Re(CO)_3Cl(bpy)]$, there was enhancement of the modes of the bpy ligand but not of the ν(CO) modes [5]. The selection rules for IR spectroscopy are less stringent, and there is no requirement for resonance enhancement. Thus IR can provide complementary information to Raman spectroscopy. Time-resolved IR spectroscopy (TRIR), a combination of UV flash photolysis with fast IR detection [6], is particularly useful in studying excited states of transition metals containing moieties such as CO or CN since, as well as having very high IR extinction coefficients, these groups act as probes of the electron distribution in the excited state [7]. For example, the ν(CO) modes of the ^{3}MLCT state of $[Re(CO)_3Cl(bpy)]$ were easily detected by TRIR [8], and the shift of the ν(CO) bands to higher frequency shows the change in electron density on the metal centre following electron transfer from Re to bpy, and the consequent reduction in back bonding to the CO groups. Under appropriate circumstances, TRIR data points can be collected following a *single laser shot* and this has allowed the vibrational spectra of highly photoactive excited states to be determined [9].

There have several recent reviews [3,7,10–14] of the application of time-resolved vibrational spectroscopy to transition metal excited states; in this chapter we draw attention to a number of significant points and illustrate some new developments, mostly from work in our laboratory, employing TRIR.

2. TRIR apparatus

The variety of techniques used to obtain TRIR spectra from ms → fs has been reviewed recently [15]. On the ns → ms time-scale, TRIR spectra are conventionally obtained in a pump–probe approach using a cw IR source, with a fast IR detector to measure changes in IR absorption following irradiation by a short intense UV–vis pulse. Siebert was the first to demonstrate this approach using a black-body globar as the IR source to probe the photodissociation of carboxymyoglobin [16]. Alternative IR sources, such as CO [17] and diode lasers [6], were quickly introduced because of the higher IR photon flux these sources provide, and the early work on transition metal excited states, on the ns timescale, was done in this way. However, recent advances in step-scan FTIR, a technique which benefits from spectral multiplexing, increased IR throughput and fast data acquisition [18], has meant that TRIR spectra of ^{3}MLCT excited states can be obtained on the 50 ns timescale [14]. It is worth pointing out that FTIR techniques rely on the photo-event being highly reversible, or artefacts are introduced into the transformed spectrum [19]; with excited state studies this is not usually a problem. TRIR measurements can be obtained on the ultrafast (pico- and femtosecond) timescale using the pump–probe approach. Two methods are generally used to obtain an ultrafast IR probe, either upconversion of a cw IR signal with a fast visible pulse, or the generation of short IR pulses by difference frequency mixing of two laser pulses [15].

3. TRIR of excited states of coordination compounds containing M–CO or M–CN groups

3.1. ^{3}MLCT excited states

In 1989, we reported the first application of TRIR to the excited states of transition metal complexes, detecting the ^{3}MLCT state of $[Re(CO)_3Cl(4,4'\text{-bpy})_2]$ (4,4′-bpy = 4,4′-bipyridine) [20]. The two low frequency ν(CO) bands of $[Re(CO)_3Cl(4,4'\text{-bpy})_2]$ shifted up in frequency (ca. 55–65 cm^{-1}) on promotion to the ^{3}MLCT excited state (see Table 1). This was expected since in the MLCT excited state, the Re(I) metal centre is formally oxidised to Re(II). There is substantial coupling between the CO groups in this molecule and full interpretation of the significance of the shifts requires analysis of the force field and hence determination of all ν(CO) excited state bands. The initial study [20] used a CO laser as the cw IR source, and the limited range of this laser (ca. 1550–2000 cm^{-1})

meant that the high frequency band of the excited state of $[Re(CO)_3Cl(4,4'\text{-bpy})_2]$ was not detected. Fortunately, with an IR diode laser it was possible to detect this high frequency band (see Table 1) [21].

The energy factored force field (EFFF) has proved to be immensely valuable for the analysis of transition metal carbonyl IR spectra [22]. With this approach it was possible to show that, for $[Re(CO)_3Cl(4,4'\text{-bpy})_2]$ in the ^{3}MLCT state, there was approximately equal increase in the EFFF force constants (k_{CO}) for each bond, compared to the ground state.

In order to attempt an assessment of the distortions in excited states from ν(CO) spectra, we compared the EFFF k_{CO} and crystallographic bond lengths for well characterised compounds, and derived the relationship shown in Eq. (1) [23].

$$r_{CO} = 1.6196 - 0.1736 \ln(k_{CO}) \ (r \text{ is in Å}, \ k_{CO} \text{ is in mdyn Å}^{-1}) \tag{1}$$

Although this equation fits a wide range of data, its most valuable application is in monitoring changes in bond length on excitation. Hence, for $[Re(CO)_3Cl(4,4'\text{-bpy})_2]$, we concluded that the three C–O bonds shorten by equal amounts in the excited state. This has interesting consequences for the interpretation of the resonance Raman spectrum of the ground state [21].

Following the same argument, it is possible to compare the TRIR spectra of the series of compounds, $[Re(CO)_3Cl(L\text{–}L)]$ and $[Re(CO)_3(CH_3CN)(L\text{–}L)]^+$ (L–L = bpy or phen) (see Fig. 1 [24] and Table 1).

Since all complexes show low lying ^{3}MLCT excited states, each shows an upward shift in position of the ν(CO) bands on promotion to this state. Although some differences between the structures of these excited states can be derived from the differences in ν(CO) band position in the ground and excited states, the most striking differences comes from comparing the change in principal force constant (Table 2).

These data, together with Eq. (1), suggest that for the ^{3}MLCT excited states of the chloride complexes, the change in bond lengths (Δr) on excitation are related by $\Delta r_{ax} < \Delta r_{eq}$, while the CH_3CN analogues display a much larger difference in CO bond lengths, $\Delta r_{ax} \ll \Delta r_{eq}$. We interpret this difference as due to the effect of the *trans*-influence of the non-carbonyl ligand (Table 3) [24].

Schoonover, Meyer and Palmer and colleagues have shown that recent advances in step-scan FTIR have made the determination of the IR spectra of ^{3}MLCT a more routine measurement [14], and these advances will allow the TRIR technique to be used by a much wider community. The shift of ν(CO) to higher frequency is now a diagnostic probe for ^{3}MLCT states of transition metal carbonyl compounds (see Table 1).

Schoonover, Meyer and co-workers showed that there was a dramatic difference in the IR spectrum of the $\pi\pi^*$ excited state of $[Re(CO)_3(PPh_3)(dppz)]^+$ (dppz = dipyrido[3,2-a:2′,3′-c]phenazine), which showed the ν(CO) bands shifted slightly to lower frequency upon promotion to the excited state, compared to the shift of ν(CO) to higher frequency in the MLCT spectrum of $[Re(CO)_3(4\text{-Mepy})(phen)]^+$ (4-Mepy = 4-methylpyridine) [25]. In collaboration with Gray, we have used TRIR to examine the nature of the excited state of a related complex, $[Re(CO)_3Cl(dppz)]$ [24].

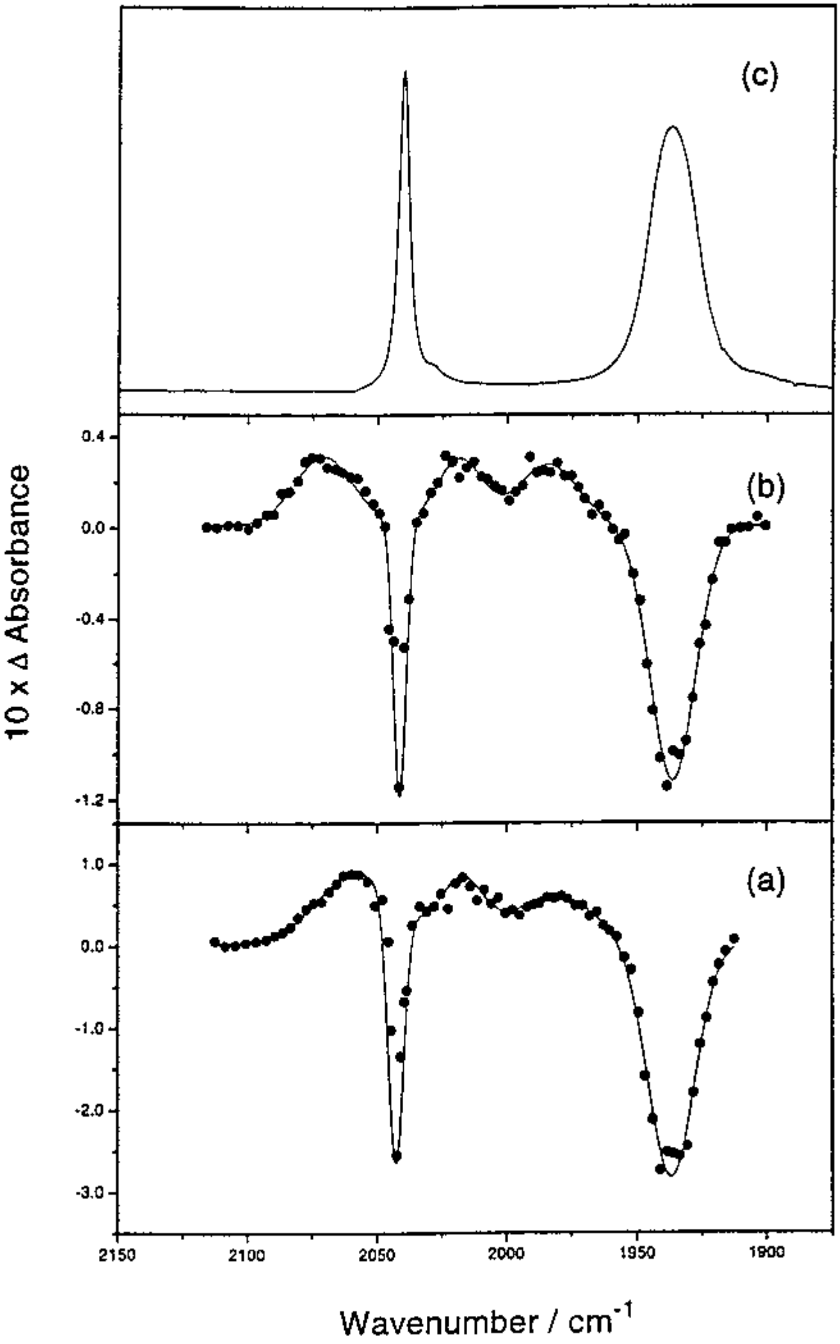


Fig. 1. TRIR spectrum of (a) $[(CH_3CN)Re(CO)_3(phen)]^+$ and (b) $[(CH_3CN)Re(CO)_3(bpy)]^+$ in CH_3CN obtained 100 ns after 355 nm photolysis. (c) FTIR spectrum of $[(CH_3CN)Re(CO)_3(bpy)]^+$ in CH_3CN.

Table 1
Frequencies of the ν(CO) bands (in cm^{-1}) of the ground and excited states of a serious of complexes

Compound	Solvent	λ_{ex} (nm)	ν(CO) bands (cm^{-1})		Excited state	Ref.
			Ground state	Excited state		
$[Re(CO)_3Cl(4,4'\text{-}bpy)_2]$	CH_2Cl_2	308	1891, 1936, 2027	1957, 1992, 2055	^{3}MLCT	[21]
$[Re(CO)_3Cl(bpy)]$	CH_2Cl_2	355	1899, 1921, 2024	1957, 1987, 2064	^{3}MLCT	[8]
$[Re(CO)_3Cl(bpy)]$	CH_3CN	355	1899, 1917, 2023	1957, 1990, 2069	^{3}MLCT	[24]
$[Re(CO)_3Cl(phen)]$	CH_3CN	355	1900, 1917, 2023	1960, 1993, 2062	^{3}MLCT	[24]
$[[Re(CO)_3(CH_3CN)(bpy)]^+$	CH_3CN	355	1937, 2023	1984, 2018, 2071	^{3}MLCT	[24]
$[Re(CO)_3(CH_3CN)(phen)]^+$	CH_3CN	355	1937, 2040	1982, 2017, 2058	^{3}MLCT	[24]
$[Re(CO)_3(4\text{-}Me\text{-}py)(phen)]^+$	CH_3CN	355	1931, 2036	1988, 2015, 2075	^{3}MLCT	[14]
$[Re(CO)_3(4\text{-}Et\text{-}py)(bpy)]^+$	CH_3CN	355	1931, 2036	1988, 2015, 2075	^{3}MLCT	[38]
$[Re(CO)_3(4\text{-}Et\text{-}py)$ $(4,4'\text{-}(NH)_2\text{-}bpy]^+$	CH_3CN	355	1914, 2025	1919, 2002, 2064	^{3}MLCT	[25]
				1881, 2014	$\pi\pi^*$	
$[Re(CO)_2\{P(OEt)_3\}_2(bpy)]^+$	CH_2Cl_2	308	1882, 1956	1927, 2012	^{3}MLCT	[51]
$[Os(CO)(4,4'\text{-}bpy)(bpy)_2]^{2+}$	CH_3CN	355	1969	2035	^{3}MLCT	[52]
$[Os(CO)(py)(bpy)_2]^+$	CH_3CN	355	1967	2041	^{3}MLCT	[53]
$[Os(CO)(tpy)(bpy)]^{2+}$	CH_3CN	355	1974	2044	^{3}MLCT	[14]
$W(CO)_5(4\text{-}CNpy)$	MCH[a]	510	1929, 1936, 2073	1966, 2000,	^{3}MLCT	[27]
$W(CO)_5(4\text{-}Acpy)$	Heptane	510	1925, 1937, 2072	1966, 2000,	^{3}MLCT	[28]

[a] MCH, methyl cyclohexane.

Fig. 2 shows that the ν(CO) bands of the excited state of $[Re(CO)_3Cl(dppz)]$ are shifted *downwards* slightly from the ground state, analogous to the shifts observed

Table 2
Ground and excited state CK force constants for $[Re(CO)_3(R)(L\text{–}L)]$ ($R = Cl$ or CH_3CN; L–L = bpy or phen) in CH_3CN

Compound		k_{co} (N m^{-1})		Δk_{co} (N m^{-1})
		Ground state	Excited state	
$[Re(CO)_3Cl(bpy)]$	k_{ax}	1505	1579	74
	k_{eq}	1544	1649	105
	k_i	60	49	−11
$[Re(CO)_3Cl(phen)]$	k_{ax}	1507	1578	71
	k_{eq}	1544	1647	103
	k_i	60	43	−17
$[Re(CO)_3(CH_3CN)(bpy)]$	k_{ax}	1572	1609	37
	k_{eq}	1572	1679	107
	k_i	56	34	−22
$[Re(CO)_3(CH_3CN)(phen)$	k_{ax}	1571	1600	29
	k_{eq}	1571	1670	99
	k_i	55	27	−28

by Schoonover for $[Re(CO)_3(PPh_3)(dppz)]^+$, and we also interpret this as showing that the lowest excited state of $[Re(CO)_3Cl(dppz)]$ is $\pi\pi^*$ [24].

The shift of ν(CO) to higher frequency for ^{3}MLCT states of transition metal carbonyl compounds can also help elucidate complex reaction mechanisms. For example, the photochemistry of $[Cr(CO)_4(bpy)]$ is interesting because CO dissociation is observed following irradiation into either the LF or MLCT absorption band [26]. Photochemical bond cleavage of $[W(CO)_5L]$ (L = 4-CN-pyridine [27] or 4-actylpyridine [28]), resulting from irradiation into a MLCT absorption, has been monitored by TRIR. We characterised the ^{3}MLCT state and follow its decay to

Table 3
Calculated ground and excited state CO bond lengths for $[Re(CO)_3(R)(L\text{–}L]$ ($R = C1$ or CH_3CN; L–L = bpy or phen)

Compound		r_{co} (Å)		Δr_{co} (Å)
		Ground state	Excited state	
$[Re(CO)_3Cl(bpy)]$	r_{ax}	1.148	1.139	−0.009
	r_{eq}	1.143	1.131	−0.012
$[Re(CO)_3Cl(phen)]$	r_{ax}	1.148	1.139	−0.009
	r_{eq}	1.143	1.132	−0.011
$[Re(CO)_3(CH_3CN)(bpy)]$	r_{ax}	1.140	1.136	−0.004
	r_{eq}	1.140	1.129	−0.011
$[Re(CO)_3(CH_3CN)(phen)]$	r_{ax}	1.140	1.137	−0.003
	r_{eq}	1.140	1.129	−0.011

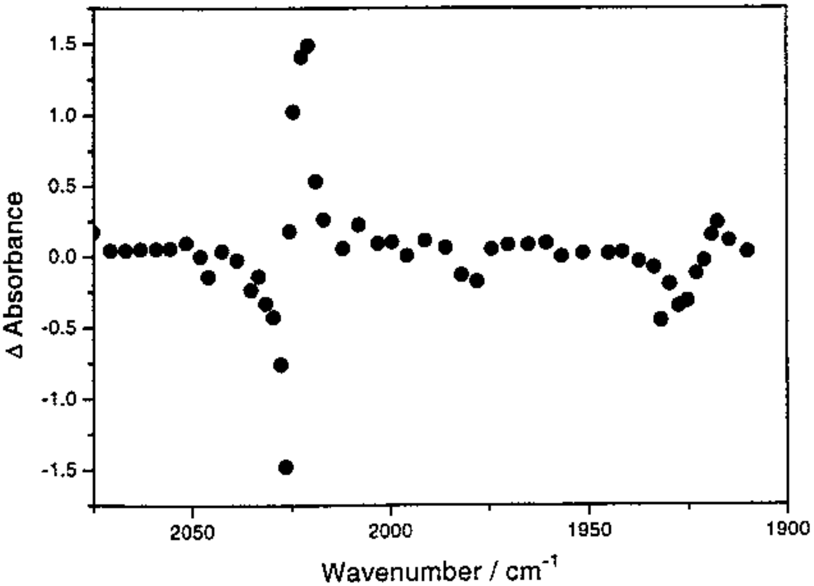


Fig. 2. TRIR spectrum of [ClRe(CO)$_3$(dppz)] in CH$_2$Cl$_2$ obtained 100 ns after 355 nm photolysis.

produce [W(CO)$_5$(solvent)] via equilibrium between the MLCT and LF excited states. Vichova et al found that irradiation into the MLCT absorption band of [Cr(CO)$_4$(bpy)] produced a short lived (50 ps) intermediate which was assigned to the ^{1}MLCT state; irradiation into the LF transition produced an additional longer lived (>10 ns) transient which was assigned to ^{3}MLCT [29]. A recent TRIR study of [Cr(CO)$_4$(bpy)] demonstrated, via the position of the ν(CO) bands of the intermediate, that this longer lived intermediate was not the ^{3}MLCT excited state but rather the solvated intermediate, [Cr(CO)$_3$-(solvent)(bpy)] [30].

Recently, we have used [Re(CO)$_3$Cl(bpy)] as a model to probe two novel aspects of TRIR of excited states: ν(CO) bandwidths and IR rigidochromism.

3.1.1. ν(CO) IR bandwidths

The widths of Raman bands of molecules in electronic excited states are often broader than the corresponding ground state bands [31]. It has been noted by several authors that this behaviour also seems to apply to the ν(CO) bands of coordination compounds in their excited states. This can be seen for the ν(CO) bands of [Re(CO)$_3$Cl(L–L)] (L–L = bpy or phen) shown in Fig. 1. We have investigated this phenomenon by studying the behaviour of the ν(CO) bands of W(CO)$_5$(4-acetylpyridine), in both ground and ^{3}MLCT excited state, and in both polar and non-polar solvents [32]. In non-polar solvents there is only a marginal change in band width, while in polar solvents there is a significant increase in band width (Fig. 3). The most likely explanation of this difference is that there is greater coupling between the charge separated species in the excited state and the polar solvent—compared to the non-polar solvent—leading faster dephasing [32]. If this is true then there should be no ground-to-excited state change on the ν(CO) band widths of non-charge separated excited states, whether in polar or non-polar solvents; this appears to be the case (e.g. [Re(CO)$_3$(PPh$_3$)(dppz)] [25]), and hence in principle, any change in bandwidth on excitation could be used as a probe of charge transfer character [32].

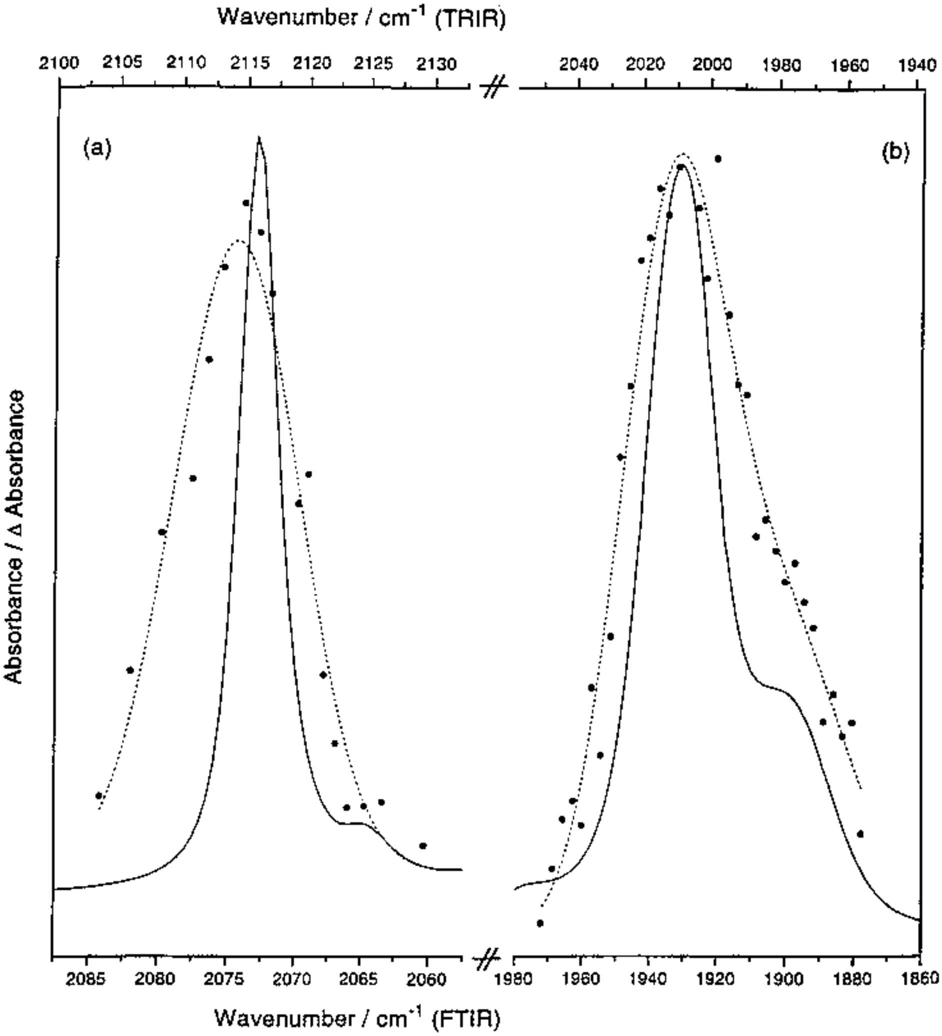


Fig. 3. FTIR (—, lower abcissa) and TRIR (●, upper abcissa, recorded 100 ns after 355 nm photolysis) of W(CO)$_5$(4-Acpy) in CH$_2$Cl$_2$. (a) High frequency a$_1$ band and (b) lower frequency e and a$_1$ bands. The dotted lines represent Gaussian fits to the TRIR data. The two abcissa are offset, so that the FTIR and TRIR bands coincide.

3.1.2. Infrared rigidochromism

The phenomenon of luminescence rigidochromism is well known [33]. It describes the blue-shift in the emission from a charge transfer excited state, when the complex is placed in a rigid matrix. An interesting question is what happens to the IR absorption spectrum? We have investigated the effect on the IR spectrum of $[Re(CO)_3Cl(bpy)]$ in ground and ^{3}MLCT excited state upon freezing a PrCN:EtCN (5:4 v/v) solution [34]. There is only a small shift in ground state bands, but the excited state bands show a big difference between solution and glass (Fig. 4). In the glass the excited state bands shift much less than in room temperature (r.t.) solution. We have called this effect IR rigidochromism [34]. There are two possible explanations for the observations: excited state mixing, or the effect of the environment on the rotational properties of the solvent dipole. Since the emission shifts to the blue on freezing, this implies that the energy of the ^{3}MLCT state is raised. If raising this level increases the mixing with a stable state which is higher in energy—and which is not charge transfer (e.g. $\pi\pi^*$)—then the net effect will be less charge transfer in the excited state, and hence less shift in ν(CO) from ground to excited state on freezing. However recent experiments, in collaboration with Schoonover, showed that the IR spectrum of MLCT excited state of $[Os(CO)(tpy)(bpy)]^{2+}$, showed similar behaviour to $[Re(CO)_3Cl(bpy)]$ and since the excited state of $[Os(CO)(tpy)(bpy)]^{2+}$ is lower in energy, this makes mixing with a $\pi\pi^*$ state an unlikely explanation for the IR rigidochromism phenomenon [24]. Our present interpretation is that at r.t. in a fluid solution, the solvent dipoles can rearrange position very rapidly. On excitation to an MLCT excited state, the solvent molecules can assist the charge transfer. However in a rigid environment, the rearrangement occurs only very slowly and hence charge transfer is inhibited, thus leading to a smaller ν(CO) shift on excitation.

3.2. XLCT and $\sigma\pi^*$ excited states

For many complexes the lowest lying excited state may result from a mixing of two or more excited states. In probing the nature of the lowest excited states of $[Ru(CO)_2(X)(Me)(^i\text{Pr-DAB})]$ (^{i}Pr-DAB = N,N′-diisopropyl-1,4-diaza-1,3-butadiene and X = Cl, Br or I), a combination of TA, TR^3 and TRIR has proved to be very valuable. The lowest excited state of $[Ru(CO)_2(X)(Me)(^i\text{Pr-DAB})]$ is best described as mixture of MLCT and XLCT and the ν(CO) bands increase to higher wavenumber on going from ground to excited state. As the halide is changed from Cl to I, the change in ν(CO) frequency on going from ground to excited state shows a decrease in the order Cl > Br > I, and this is interpreted as a result of the lowest triplet state having increasing XLCT character (Table 4) [35].

Photochemical homolytic dissociation of the metal–alkyl and metal–metal bonds of organometallic compounds containing electron accepting ligands may occur from $\sigma\pi^*$ excited states i.e. excitation of an electron from the dissociating σ-bond to the π^* orbital of the acceptor ligand, usually diimine. It has recently proved possible to detect such a $\sigma\pi^*$ state directly for the first time following flash

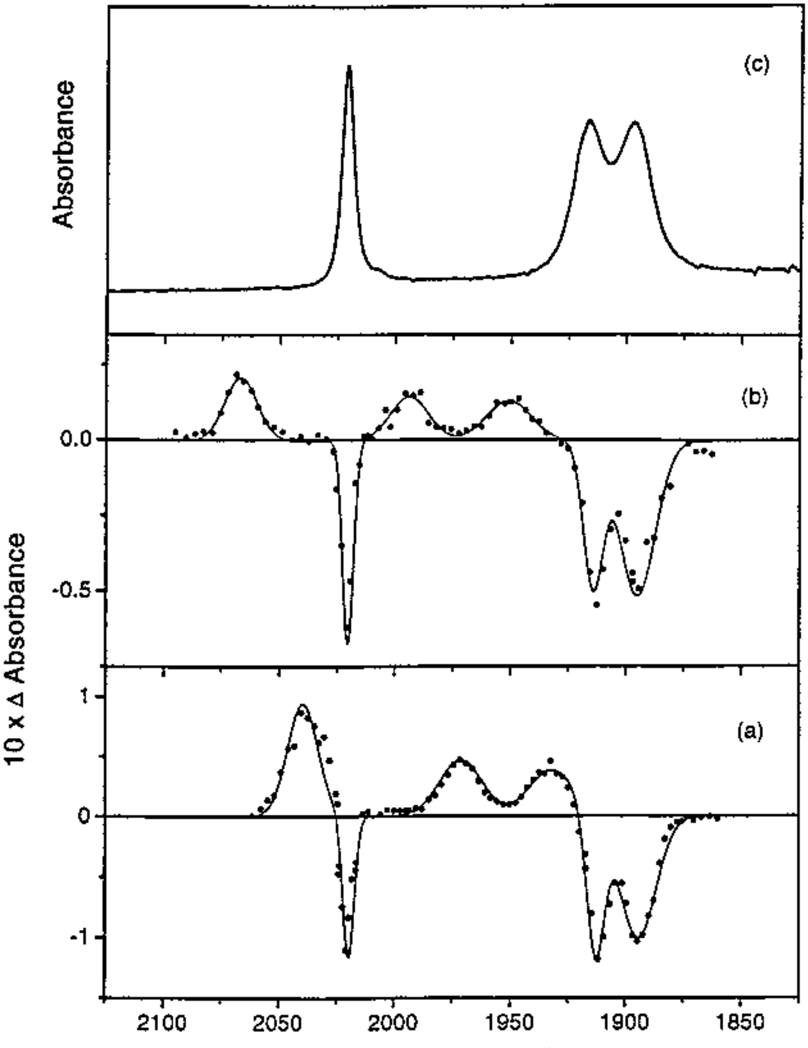


Fig. 4. TRIR spectra of [ClRe(CO)$_3$(bpy)] in *n*-PrCN/*n*-EtCN (5:4 v/v) obtained at (a) 77 K and (b) 135 K following 355 nm photolysis. (c) Room temperature FTIR spectrum of [ClRe(CO)$_3$(bpy)] in *n*-PrCN/*n*-EtCN (5:4 v/v).

photolysis of [Re(CO)$_3$(benzyl)(^{i}Pr-DAB)] in *n*-heptane [9]. The decay of the highly reactive $\sigma\pi^*$ state to form [Re(CO)$_3$(^{i}Pr-DAB)] radicals was monitored by TRIR. The TRIR spectrum of the lowest excited state of [Ru(CO)$_2$Cl(SnPh$_3$)(^{i}Pr-DAB)] confirmed that it is best described as a mixture of MLCT and XLCT, while the lowest excited state of [Ru(CO)$_2$(SnPh$_3$)$_2$(^{i}Pr-DAB)] has $\sigma\pi^*$ character (see Table 4) [36].

3.3. Electron and energy transfer

Time-resolved vibrational spectroscopy has recently been used to probe inorganic complexes, particularly supramolecular systems, that can undergo electron or energy transfer processes in solution [13]. TRIR, particularly on the picosecond timescale, is a powerful tool for elucidating such processes by monitoring ν(CO) and ν(CN) vibrations. Picosecond TRIR has been used to study photo-induced electron transfer in the cyano-bridged mixed valence dimer $[(NC)_5Ru^{II}(CN)Ru^{III}(NH_3)_5]^-$ [37].

$$[(NC)_5Ru^{II}(CN)Ru^{III}(NH_3)_5]^- \underset{k_{et}}{\overset{h\nu}{\leftrightarrows}} [(NC)_5Ru^{III}(CN)Ru^{II}(NH_3)_5]^-$$

Excitation into the MMCT band of $[(NC)_5Ru^{II}(CN)Ru^{III}(NH_3)_5]^-$ showed that the back-electron transfer rate occurs on the femtosecond timescale ($\tau < 0.5$ ps) [38]. Both TR^3 and TRIR have been used to show that irradiation into the Re-based MLCT transition of $[(phen)(CO)_3Re^I(NC)Ru^{II}(bpy)_2(CN)]^+$ results in formation of the Re-MLCT state followed by energy transfer to the Ru-based MLCT state [38].

The lowest excited state of $[(CO)_5W(BL)W(CO)_5]$ (BL, bridging ligand = pyrazine or 4,4′-bipyridine) involves W → BL charge transfer and this has been confirmed by TR^3 which shows that, for example, 4,4-bipyridine becomes negatively charge, i.e. (4,4-bipyridine)$^-$ [39]. We have recently used TRIR to answer the question whether, on the IR timescale, the excited state electron is localised or delocalised (i.e. $W^+(BL)^-W$ or $W^{0.5+}(BL)^-W^{0.5+}$) [40,41]. Fig. 5 shows the high frequency ν(CO) region of $[(CO)_5W(4,4'\text{-bpy})W(CO)_5]$; this demonstrates most clearly that there are *two* W environments, i.e. $(CO)_5W^+(4,4'\text{-bpy})^-$, where the ν(CO) band of the excited state has shifted up in frequency, and $^-(4,4'\text{-bpy})W(CO)_5$, where the ν(CO) band of the excited state has shifted down in frequency. The complete IR

Table 4
Frequencies of the ν(CO) bands (in cm^{-1}) of $Ru(CO)_2(R)(R')$ ^{i}Pr-DAB) complexes (in CH_2Cl_2) in ground and excited state

Compound	Ground state	Excited state
$[Ru(CO)_2(Cl)(Me)(^i\text{Pr-DAB})]$	1963	2014
	2032	2081
$[Ru(CO)_2(Br)(Me)\ (^i\text{Pr-DAB})]$	1965	2010
	2032	2080
$[Ru(CO_2)(I)(Me)(^i\text{Pr-DAB})]$	1967	2010
	2032	2058
$[Ru(CO)(Cl)(SnPh_3)(^i\text{Pr-DAB})]$	1973	2003
	2034	2051
$[Ru(CO)_2(SnPh_3)_2(^i\text{Pr-DAB})]$	1955	1944
	2006	2006

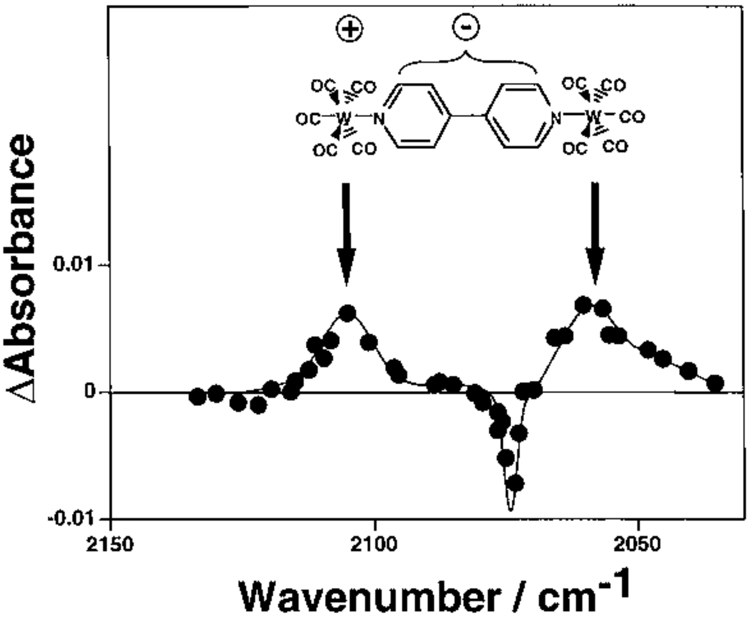


Fig. 5. TRIR spectrum of $[(CO)_5W(4,4'\text{-bpy})W(CO)_5]$ obtained 100 ns following 355 nm photolysis.

spectrum of the ^{3}MLCT of $[(CO)_5W(4,4'\text{-bpy})W(CO)_5]$ confirmed that there are two overlapping sets of ν(CO) bands (see Table 5).

Moore and co-workers have adopted a similar approach, using ps-TRIR, to demonstrate that the short lived ^{3}MLCT excited state of $[(Cl(CO)_3Re(BL)Re(CO)_3Cl]$ (BL = 2,3-di(2-pyridyl)quinoxaline, 2,3-di(2-pyridyl)-6-methylquinoxaline,

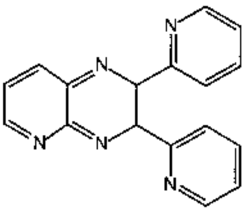
Table 5
Frequencies of the ν(CO) bands (in cm^{-1}) of $[(CO)_5W(4,4'\text{-bpy})W(CO)_5]$, $[(CO)_5W(4,4'\text{-bpy})]$ and $[CO)_5W(pyz)W(CO)_5]$[a] in CH_2Cl_2

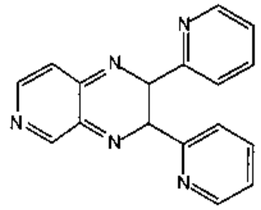
Compound	Ground state	Excited state (i)[b]	Excited state (ii)
$[(CO)_5W(4,4'\text{-Bpy})W(CO)_5]$	1901	1970	1875
	1933	2010	1915
	2072	2105	2059
$[(CO)_5W(4,4'\text{-Bpy})]$	1901	1978	–
	1930	2002	–
	2073	2105	–
$[(CO)_5W(pyz)W(CO)_5]$	1911	1978	1872
	1942	2003	1918
	2069	2105	2046

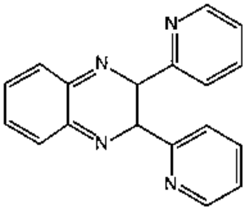
[a] pyz, pyrazine.

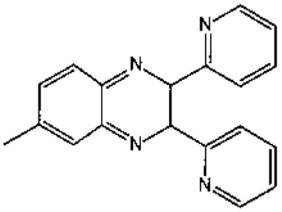
[b] The excited state bands are grouped into those (i) increasing and (ii) decreasing in frequency.

2,3-di(2-pyridyl)pyrido[2,3-b]pyrazine or 2,3-di(2-pyridyl)pyrido[3,4-b]pyrazine) is a Class II mixed valence state, $Re^{+}(BL)^{-}Re$ [42].



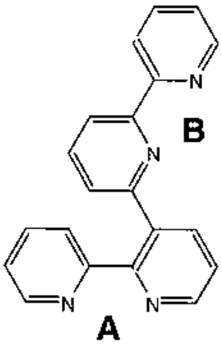






Using a combination of TR^3 and TRIR, Meyer, Schoonover and co-workers have shown that, in the lowest lying MLCT excited state of $[(dmb)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(dmb)]^{2+}$ (dmb $= 4,4\text{-}(CH_3)_2$-bipyridine), the electron is localised on the 4,4′-bpy ligand and in $[(bpy)(CO)_3Re(4,4'\text{-}bpy)Re(CO)_3(bpy)]^{2+}$ there is an equilibrium between 4,4′-bpy and bpy [43]. For both complexes they found that TRIR measurements were consistent with the localised description, $Re^{II}\text{–}Re^{I}$.

Schoonover, Ward and co-workers have examined energy/electron transfer processes of $[(bpy)_2Ru^{II}(AB)Re^{I}(CO)_3Cl]^{2+}$ and $[(bpy)(CO)_3Re^{I}(AB)Ru^{II}(bpy)_2]^{2+}$, where AB is the asymmetric bridging ligand 2,2′:3′,2″:6″,2‴-quaterpyridine:



Irradiation into either the Re or Ru MLCT transition of $[(bpy)_2Ru^{II}(AB)Re^{I}(CO)_3Cl]^{2+}$ resulted in the formation of the Ru-based MLCT state, $[(bpy)_2Ru^{III}(AB)^{-}Re^{I}(CO)_3Cl]^{2+}$, but TRIR data for $[(bpy)(CO)_3Re^{I}(AB)Ru^{II}(bpy)_2]^{2+}$ showed that both Re and Ru MLCT states were formed, i.e. ($[(bpy)(CO)_3Re^{II}(AB)^{-}Ru^{II}(bpy)_2]^{2+}$ and $[(bpy)(CO)_3Re^{I}(AB)^{-}Ru^{III}(bpy)_2]^{2+}$ [44].

3.4. LF excited states

Although most vibrational spectroscopy has focused on charge-transfer excited states, ligand field states are extremely important in photochemistry. One problem in applying either TR^3 or TRIR is that most LF states are very short-lived, at least at r.t. The structure of the LF excited state of $[W(CO)_5(pyr)]$ (pyr = pyridine) was probed by ground-state preresonance Raman spectroscopy and these data led Zink and co-workers to conclude that both the W–N and W–C bonds are longer in the LF excited state than in the ground state [45]. In contrast, TRIR results for $[W(CO)_5(pyr)]$ in a 77K glass suggested that, in the LF excited state, the C–O bonds are longer and hence that the M–C bonds are shorter [46]. Recent ab initio calculations predict that the excited state geometry should show lengthening of the W–N, $W–C_{eq}$, $C–O_{eq}$ bonds and a shortening of the $C–O_{ax}$ [47]. It is suggested that both the TRIR and preresonance Raman spectra are correct, but that an additional band should be observed in the TRIR spectra; this band arises essentially from the shortening of the $C–O_{ax}$ bond [47].

4. TRIR of excited states of coordination compounds not containing M–CO or M–CN groups

One of the major developments in the application of TRIR to the elucidation of excited state structure has been the detection of IR chromophores other than M–CO and M–CN. In solution, organic $\nu(CO)$ bands are ca. 20 times less intense than metal carbonyl bands. Palmer and co-workers used step-scan FTIR to probe the ester $\nu(CO)$ bands of the ^3MLCT excited state of $[Ru(bpy)_2(4,4'\text{-}(COOEt)_2\text{-}bpy)]^{2+}$ and $[Ru(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3\text{-}bpy)]^{2+}$ ($4,4'\text{-}(COOEt)_2$-bpy = 4,4′-(dicarboxyethyl)-2,2′-bipyridine and $4\text{-}COOEt\text{-}4'\text{-}CH_3$-bpy = 4-(carboxyethyl)-4′-methyl-2,2′-bipyridine) [48]. The large negative shift in ^3MLCT $\nu(CO)$ ester bands of $[Ru(bpy)_2(4,4'\text{-}(COOEt)_2\text{-}bpy)]^{2+}$ and $[Ru(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3\text{-}bpy)]^{2+}$ led them to conclude that the excited state electron is localised on the ester-bearing ligand, and the appearance of a single $\nu(CO)$ ester band for the ^3MLCT excited state of the diester demonstrated that the electron is delocalised over both pyridine rings in the diester. This observation complemented the results of Kinkaid and co-workers using TR^3 [49]. Schoonover and co-workers obtained, for $[Ru(bpy)_3]^{2+}$ in solution, the TRIR spectrum in the fingerprint region from 1400–1625 cm^{-1} [50]. The TRIR data complemented the previous TR^3 results [4], showing that the excited state electron is indeed localised on one of the bpy ligands.

5. Future directions

TRIR has been shown to be a powerful technique for the elucidation of inorganic excited states, and use of this technique will increase because the major activity of supramolecular photochemistry is in following electron and energy transfer. Recent improvements in step-scan FTIR will allow this technique to be used by a much wider community. The detection of vibrations other than ν(CO) or ν(CN) will, in principle, allow a more comprehensive structural description of charge transfer excited states.

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References

[1] R.J.H. Clark, T.J. Dines, Angew. Chem. Int. Ed. Engl. 25 (1986) 131.
[2] E.J. Heller, R.L. Sunberg, D. Tannor, J. Phys. Chem. 86 (1982) 1822; J.I. Zink, K.-S.K. Shin, Adv. Photochem. 16 (1991) 119.
[3] C.A. Bignozzi, J.R. Schoonover, R.B. Dyer, Comments Inorg. Chem. 18 (1996) 77.
[4] P.G. Bradley, N. Kess, B.A. Hornberger, R.F. Dallinger, W.H. Woodruff, J. Am. Chem. Soc. 103 (1981) 7441.
[5] W.K. Smothers, M.S. Wrighton, J. Am. Chem. Soc. 105 (1983) 1067.
[6] M.W. George, M. Poliakoff, J.J. Turner, Analyst 119 (1994) 551.
[7] J.J. Turner, M.W. George, F.P.A. Johnson, J.R. Westwell, Coord. Chem. Rev 125 (1993) 101.
[8] M.W. George, F.P.A. Johnson, P.M. Hodges, J.R. Westwell, J.J. Turner, J. Chem. Soc. Dalton Trans. (1993) 2977.
[9] B.D. Rossenaar, M.W. George, F.P.A. Johnson, D.J. Stufkens, J.J. Turner, A. Vlceck, J. Am. Chem. Soc. 117 (1995) 11582.
[10] J.J. Turner, M.W. George, I.P. Clark, I.G. Virrels, Laser Chem. (in press).
[11] J.R. Schoonover, G.F. Strouse, Chem. Rev. 98 (1998) 1335.
[12] J.R. Schoonover, C.A. Bignozzi, T.J. Meyer, Coord. Chem. Rev. 165 (1997) 239.
[13] C.A. Bignozzi, J.R. Schoonover, R.B. Dyer, Comments Inorg. Chem. 18 (1996) 77.
[14] J.R. Schoonover, G.F. Strouse, K.M. Omberg, R.B. Dyer, Comments Inorg. Chem. 18 (1996) 165.
[15] P.C. Ford, J.S. Bridgewater, B. Lee, Photochem. Photobiol. 65 (1997) 57.
[16] F. Siebert, W. Mantele, W. Kreutz, Biophys. Struct. Mech. 6 (1980) 139.
[17] M. Poliakoff, E. Weitz, Adv. Organomet. Chem. 25 (1986) 277.
[18] R.A. Palmer, J.L. Chao, M. Dittmar, V.G. Gregoriou, S.E. Plunkett, Appl. Spectrosc. 47 (1993) 1297.
[19] B.D. Moore, M. Poliakoff, M.B. Simpson, J.J. Turner, J. Phys. Chem. 89 (1985) 850.
[20] P. Glyn, M.W. George, P.M. Hodges, J.J. Turner, J. Chem. Soc. Chem. Commun. (1989) 1655.
[21] D.R. Gamelin, M.W. George, P. Glyn, et al., Inorg. Chem. 33 (1994) 3246.
[22] P.S. Braterman, Metal Carbonyl Species, Academic Press, London, 1975.
[23] S.L. Morrison, J.J. Turner, J. Mol. Struct. 317 (1994) 39.
[24] I.P. Clark, Ph.D. Thesis, University of Nottingham, 1997.
[25] J.R. Schoonover, G.F. Strouse, R.B. Dyer, W.D. Bates, P. Chen, T.J. Meyer, Inorg. Chem. 35 (1996) 273.

[26] D.M. Manuta, A.J. Lees, Inorg. Chem. 28 (1989) 2154.
[27] P. Glyn, F.P.A. Johnson, M.W. George, A.J. Lees, J.J. Turner, Inorg. Chem. 30 (1991) 3543.
[28] F.P.A. Johnson, M.W. George, J.J. Turner, Inorg. Chem. 32 (1993) 4226.
[29] J. Vichová, F. Hartl, A. Vlcek, J. Am. Chem. Soc. 114 (1992) 10903.
[30] I.G. Virrels, M.W. George, J.J. Turner, J. Peters, A. Vlcek, Organometallics 15 (1996) 4089.
[31] H. Hamaguchi, T.L. Gustafson, Annu. Rev. Phys. Chem. 4 (1994) 593.
[32] I.P. Clark, M.W. George, J.J. Turner, J. Phys. Chem. 101 (1997) 8367.
[33] M.S. Wrighton, D.L. Morse, J. Am. Chem. Soc. 96 (1974) 998.
[34] I.P. Clark, M.W. George, F.P.A. Johnson, J.J. Turner, J. Chem. Soc. Chem. Commun. (1996) 1587.
[35] H.A. Nieuwenhuis, D.J. Stufkens, R-A. McNicholl, et al., J. Am. Chem. Soc. 117 (1995) 5579.
[36] M.P. Aarnts, D.J. Stufkens, M.P. Wilms, et al., Chem. Eur. J. 2 (1996) 1556.
[37] S.K. Doorn, P.O. Stoutland, R.B. Dyer, W.H. Woodruff, J. Am. Chem. Soc. 114. (1992) 3133; S.K. Doorn, R.B. Dyer, P.O. Stoutland, W.H. Woodruff, J. Am. Chem. Soc. 115 (1993) 6398.
[38] J.R. Schoonover, K.C. Gordon, R. Argazzi, et al., J. Am. Chem. Soc. 115 (1993) 10996.
[39] R.A. McNicholl, J.J. McGarvey, A.H.R. Al-Obaidi, S.E.J. Bell, P.M. Jayaweera, C.G. Coates, J. Phys. Chem. 99 (1995) 12268.
[40] M.W. George, J.J. Turner, J.R. Westwell, J. Chem. Soc. Dalton Trans. (1994) 2217.
[41] M.W. George, F.P.A. Johnson, J.J. Turner, J.R. Westwell, J. Chem. Soc. Dalton Trans. (1995) 2711.
[42] L.C. Abbott, C.J. Arnold, T-Q. Ye, K.C. Gordon, R.N. Perutz, R.E. Hester, J.N. Moore, J. Phys. Chem. A 102 (1998) 1252.
[43] K.M. Omberg, J.R. Schoonover, T.J. Meyer, J. Phys. Chem. A 101 (1997) 9531.
[44] J.R. Schoonover, A.P. Shreve, R.B. Dyer, R.L. Cleary, M.D. Ward, C.A. Bignozzi, Inorg. Chem. 37 (1998) 2598.
[45] L. Tut, J.I. Zink, J. Am. Chem. Soc. 108, 5830; K.S. Shin, J.I. Zink, Inorg. Chem. 28 (1989) (1986) 4358.
[46] M.W. George, F.P.A. Johnson, S.L. Morrison, J.J. Turner, J. Chem. Soc. Chem. Commun. (1995) 391.
[47] S. Zaric, M. County, M.B. Hall, J. Am. Chem. Soc. 119 (1997) 2885.
[48] P. Chen, K.M. Omberg, D.A. Kavaliunas, J.A. Treadway, R.A. Palmer, T.J. Meyer, Inorg. Chem. 36 (1997) 954.
[49] G.D. Danzer, J.A. Golus, J.R. Kinkaid, J. Am. Chem. Soc. 115 (1993) 8643; S.M. Treffert-Ziemelis, J.A. Golus, D.P. Strommen, J.R. Kinkaid, Inorg. Chem. 32 (1993) 3890.
[50] K.M. Omberg, J.R. Schoonover, J.A. Treadway, R.L. Leasure, R.B. Dyer, T.J. Meyer, J. Am. Chem. Soc. 119 (1997) 7013.
[51] P.S. Braterman, Metal Carbonyl Species, Academic Press, London, 1975.
[52] P. Chen, R.A. Palmer, Appl. Spectrosc. 51 (1997) 580.
[53] R.A. Palmer, P. Chen, S.E. Plunkett, J.L. Chao, Mikrochim. Acta 14 (1997) 595.