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Time-resolved Infrared Spectroscopy of Excited States of Transition Metal Species

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Abstract

This article describes examples of the application of time-resolved infrared spectroscopy (TRIR) to the probing of the excited states of transition metal species. Other "direct" methods for excited states include time-resolved absorption spectroscopy, and, more importantly, time-resolved resonance Raman spectroscopy (TR^3). Both of these techniques have limitations and hence TRIR is of value in complementing them. The common "indirect" methods are absorption, emission, and excitation spectroscopies, to which has been more recently added, resonance Raman, particularly in the time-dependent formulation. The relevance of these methods is also discussed.

1. INTRODUCTION

In the photochemistry of transition metal species it is important to understand the nature of the excited state(s) [1]. Figure 1 shows a schematic representation of a simple system involving just two states, the ground state and one excited state. The diagram illustrates the well-known features of the various spectroscopies. Thus, the *absorption* and *excitation* spectra, in principle, provide information about the vibrational levels of the excited state, and the *emission* spectrum - in addition to lifetime data on the excited state - provides vibrational data about the ground state. Via Franck-Condon analysis, the intensities of the vibrational components of these spectra can give details of the structure of the excited state with respect to the ground state, ie along the distortion coordinate Q_k. Unfortunately, it is only in a few cases , and then at low temperatures or in free jet expansion experiments, that sufficient fine structure is observed to give such structural information. However, Figure 1 also illustrates a Resonance Raman (RR) transition in which the excited state is involved as a "virtual" state. In principle, RR spectra should provide similar structural information to electronic spectra [2]. However, such analysis for large molecules can be extremely complex, but another way of unravelling the RR spectra has been introduced by Heller, the so-called

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"time-dependent" model [3]. The application of this technique to transition metal species has been very successfully exploited by Zink [4].

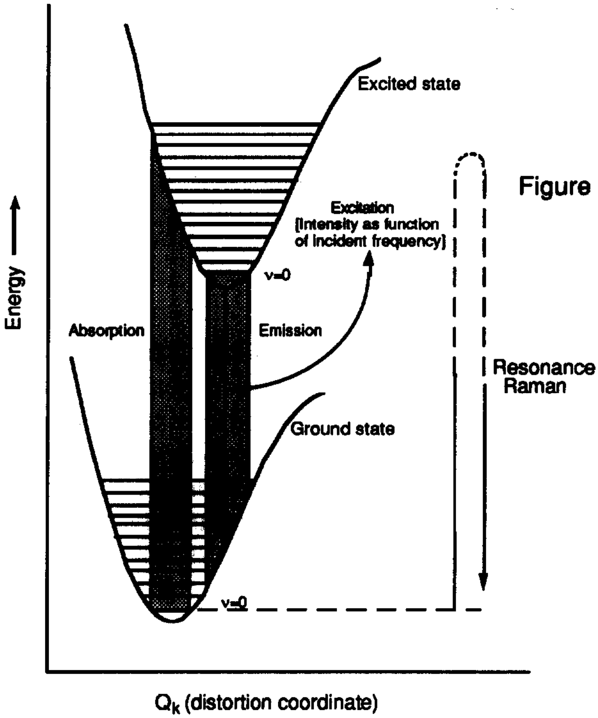


Figure 1. Schematic representation of Potential Energy Curves

None of these methods involve the probing of the excited state in real time. For structure determination it would clearly be an advantage to obtain vibrational data directly while the species remains in the excited state. The most widely used technique for this has been time-resolved resonance Raman spectroscopy (TR^3), first exploited for transition metal species by Woodruff. In a classic experiment on **[Ru(bpy)$_3$]$^{2+}$**, the TR^3 of the lowest ^{3}MLCT excited state showed that the structure in this state was best described as [Ru^{3+}(bpy)$_2$(bpy$^-$)]$^{2+}$ [5]. A detailed study of the isotopically enriched compound permitted a sophisticated normal coordinate analysis and, based on Badger's rule and its subsequent variations, a determination of the ground-to-excited state distortions [6]. There have been very few TR^3 studies on organometallic species, two exceptions being **ClRe(CO)$_3$(bpy)** [7] and **W(CO)$_4$(diimine)** [8]. In the former case, TR^3 clearly showed charge transfer from Re to bpy, although there was no evidence for enhancement of the ν(CO) modes; in the second case, in the MLCT state, enhancement of only *one* of the ν(CO) modes was observed and this showed an upward shift from the ground state of about 50 cm^{-1}. Thus, there are some limitations in the application of TR^3 to excited states and it is clear that time-resolved infrared spectra (TRIR) will be important in elucidating their structures.

2. INFRARED SPECTRA OF EXCITED STATES

2.1. Introductory examples

Until recently no IR data on the excited states of transition metal complexes had been published. There have, however, been many reports of the application of TRIR to the detection and characterisation of organometallic *intermediates*, mostly via the very intense ν(CO) bands [9]. The apparatus in use at Nottingham is shown schematically in Figure 2.

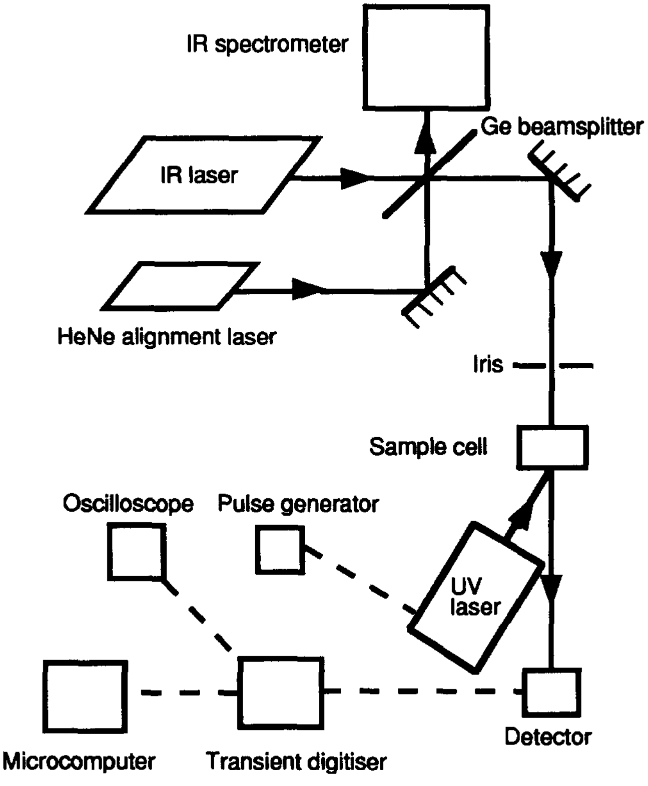
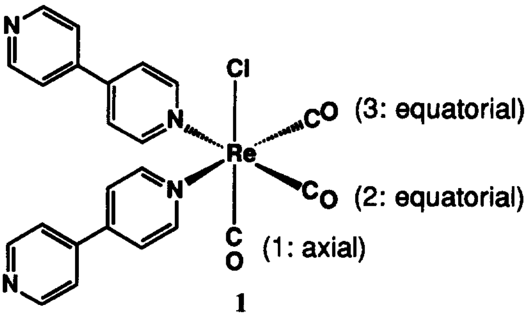


Figure 2. A schematic representation of the TRIR apparatus at Nottingham. The UV pulsed laser generates transients (excited states and/or intermediates). The continuous IR laser monitors the change in transmission at a particular IR wavelength (determined by the IR spectrometer), producing a trace showing change of IR intensity with time. The experiment is repeated at different IR wavelengths and hence a complete IR spectrum of the transient can be built up.

The first report of the application of TRIR to the excited states of transition metal complexes was on **$ClRe(CO)_3(4,4'\text{-bpy})_2$** [10].



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This species was chosen for several reasons. The lowest MLCT state is known to be stable and long lived (~1μs [11]), whereas, in $ClRe(CO)_3(2,2'\text{-bpy})$, the corresponding excited state is much shorter-lived; on charge transfer from Re to bpy, the metal centre is oxidised and this should result in a clear shift to high frequency of the ν(CO) bands; similar species have been shown to be capable of reducing CO_2 [12]:

$$R_3N + CO_2 \xrightarrow[\text{DMF/ClRe(CO)}_3\text{(2,2'-bpy)}]{h\nu} CO$$

the mechanism of such reactions is open to debate [13], but must certainly involve the MLCT state of the Re complex.

Figure 3 shows the IR spectrum of $ClRe(CO)_3(4,4'\text{-bpy})_2$ at 240 ns after the laser flash [10]. The obvious interpretation of Figure 3 is that, on promotion to the excited state, the two low frequency ν(CO) bands move up in frequency to the positions marked by arrows. However, the range of the CO laser is limited to about 2000 cm^{-1} at the high frequency end; thus, if the high frequency ν(CO) band is shifted up by about the same as the low frequency pair, both the ground and excited state bands will be outside the range of the CO laser. Fortunately, with an IR diode laser it has proved possible to find this third band and the results are given in Table 1 [14]. Each ν(CO) band shifts to high frequency. However, there is substantial coupling between the CO modes and an interpretation of the significance of the shifts requires an analysis of the force field. The energy factored force field (EFFF) has proved to be immensely valuable for transition metal carbonyls; Table 1 also lists approximate values for the CO EFFF constants. In the ground state the bands are sufficiently sharp to permit an exact solution to the EFFF using ^{13}CO substitution; unfortunately, in the excited state, the bands are broader, the ^{13}CO

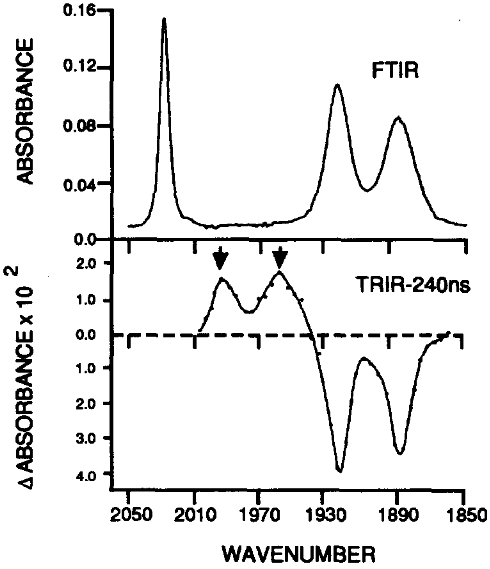


Figure 3. The upper curve shows a conventional FTIR spectrum in the ν(CO) region of 1 in CH_2Cl_2. The lower curve shows the TRIR spectrum of the same solution at 240 ns after the laser flash. Each point corresponds to a different line of the CO IR laser; points below the zero line depict loss of parent, while points above the line depict generation of species.

Table 1

Frequencies of the ν(CO) IR bands, EFFF force constants (k's), and estimated changes in CO bond lengths of $ClRe(CO)_3(4,4'\text{-}bpy)_2$ in ground and ^{3}MLCT excited states.

	ν(CO) (cm^{-1})			EFFF (Nm^{-1})			
Ground state	1891	1936	2027	k_{ax}	1492	k_{eq}	1555 (a)
Excited state	1957	1992	~2055	k_{ax}	1566	k_{eq}	1644 (b)
Difference	66	56	38		74		89
CO bond change (Å)					-0.008		-0.010 (c)

(a)From ^{13}CO analysis [14]; (b) Based on Timney method [15,14]; (c)Applying equation (1)

bands are not resolved, and a more approximate method had to be used [15]. The question then is whether the EFFF can be used to estimate the change in structure from ground to excited state. There have been many attempts to relate force constants and/or frequencies to bond length [6, 16]. The most extensive studies were carried out by Herschbach and Lawrie; however, they used harmonic force constants for diatomics. EFFF constants are not harmonic and of course there is considerable coupling. We have recently completed a study of EFFF k(CO)s and bond length which is very encouraging [17]. An equation of the form,

$$r_{CO} = 1.6196 - 0.1736\ln(k_{CO}) \qquad [r_{CO} \text{ in Å; } k_{CO} \text{ in Nm}^{-1}], \tag{1}$$

fits a wide range of data, particularly when used to calculate differences in bond length rather than absolute values. On this basis, Table 1 includes the changes in CO bond lengths calculated for promotion from ground to excited state.

Thus, TRIR is capable of providing information about the subtle changes in structure from ground to excited state. In this example, the excited state is an MLCT state ; in principle, TRIR should also be able to provide information about the *rates* of such electron transfers. The apparatus described above has a time resolution of about 50 ns; this time scale is limited by the response time of IR detectors and is far too slow to monitor fast electron transfer. However, there have been novel technical advances applied to transition metal species, and these permit very much faster (<1ps) timescales to be monitored [18]. In an elegant application of these techniques to electron transfer, Woodruff and colleagues [19] have probed the photobehaviour of a mixed valence compound, **$[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^-$**:

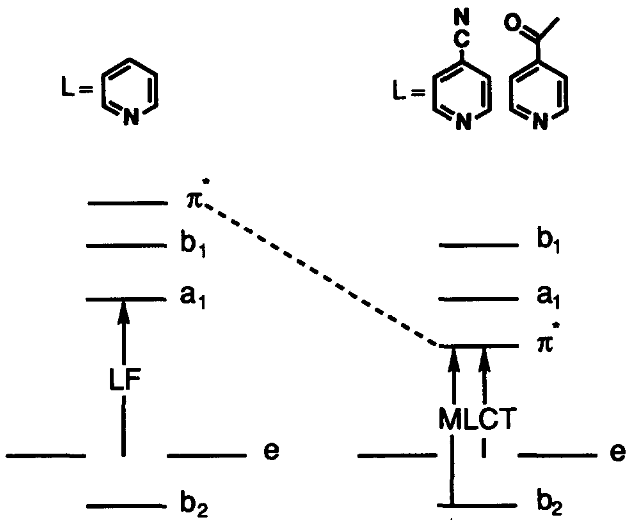
$$[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^- \xrightarrow{h\nu} [(NC)_5Ru^{III}CNRu^{II}(NH_3)_5]^-$$

Excitation into the MMCT band centred at 683 nm promotes ultrafast electron transfer, which reverses on a time scale of a few picoseconds. The elecron transfer process is monitored by following the TRIR of the terminal ν(CN) stretching vibration, which in the ground state is at 2053 cm^{-1} and in the excited state at 2110 cm^{-1}. In what follows, we give some further examples of the application of TRIR to excited states.

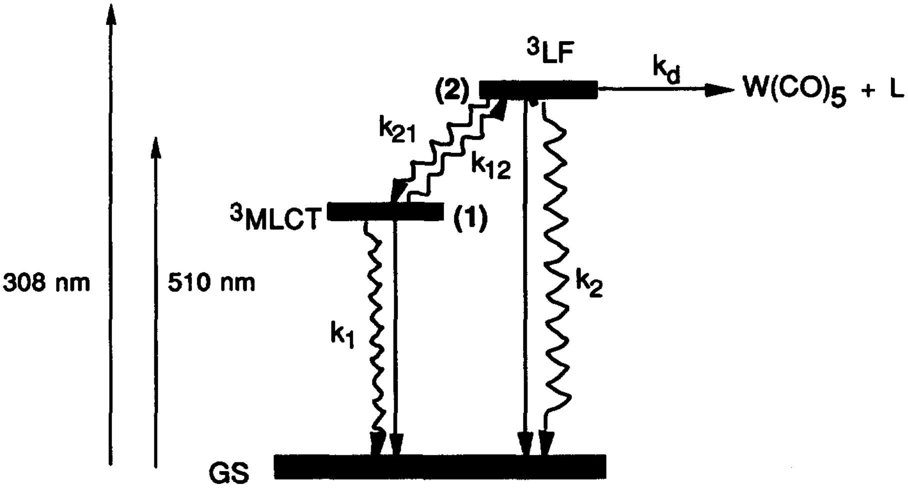
2.2. Monitoring the photochemistry

In the two examples given above, there was no overall photochemistry since, following excitation, there is virtually complete recovery to the ground state. We now consider an example where it has proved possible to monitor a complete photochemical process.

Complexes of the type **$W(CO)_5L$** have energy level schemes which depend on the nature of L [20], thus:



In these complexes, the lowest state is ligand field if L is pyridine, but if the pyridine is substituted with an electron withdrawing group, the charge transfer state(s) is the lowest. Anticipating what follows later, the photochemistry of such a species can be summarised:[21]:



Here we have represented only the lowest of two MLCT states. The photochemistry depends on the relative values of the appropriate rate constants, but, in addition, depends on the wavelength of excitation; at 510 nm, in contrast to 308 nm, there is no direct population of the reactive LF state. Figures 4 and 5 show an experiment [22] in which the photochemistry of **$W(CO)_5$(4CN-pyridine)** was probed by TRIR.

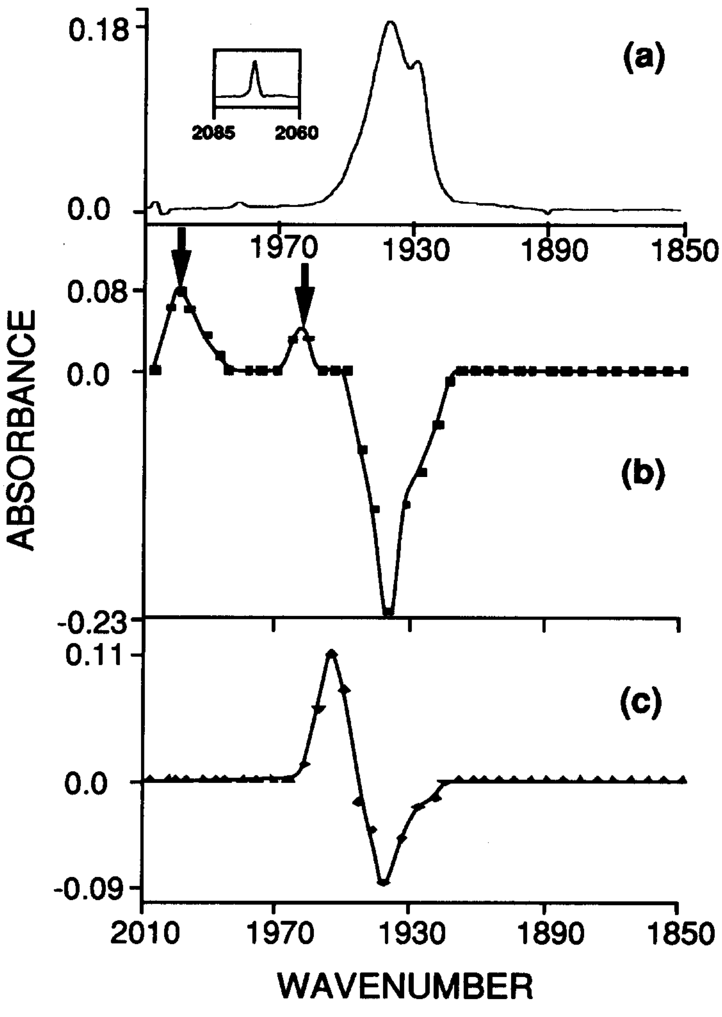


Figure 4 (a) FTIR spectrum of $W(CO)_5$(4-CNpyr) in methyl cyclohexane (ca. 4 x 10^{-5} M, pathlength 4 mm); the insert shows the high wavenumber band. TRIR spectra at (b) 150 ns and (c) 5 μs, after the dye laser flash (510 nm, 10 ns) of solutions of $W(CO)_5$(4-CNpyr) in methyl cyclohexane (ca. 4 x 10^{-5} M, pathlength 5 mm). (Reproduced, with permission, from reference [22]).

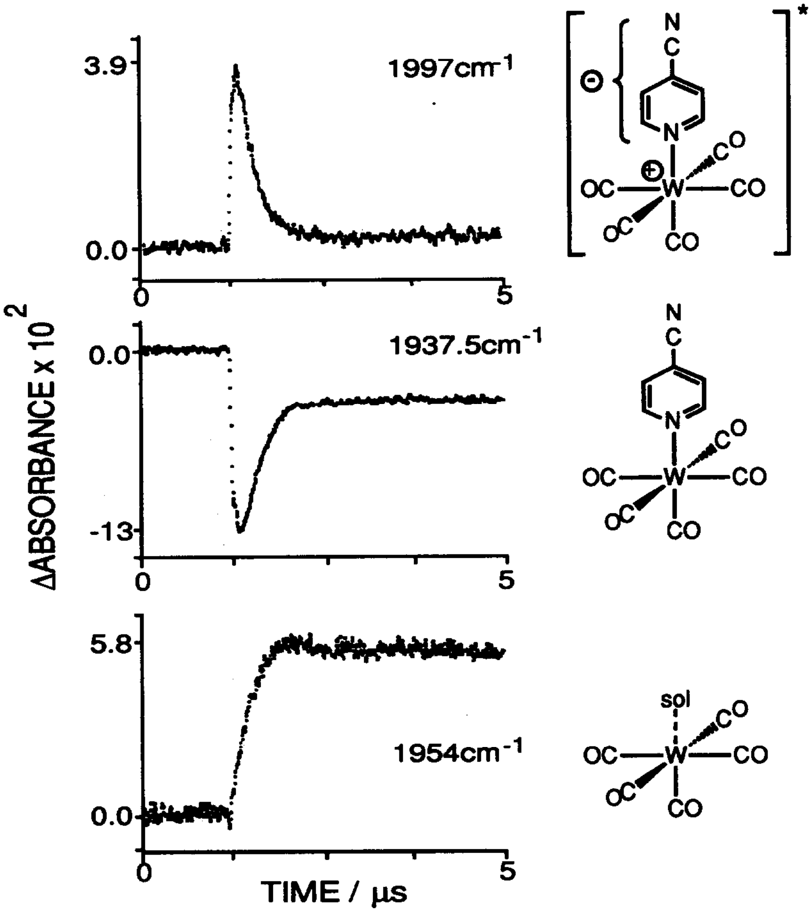
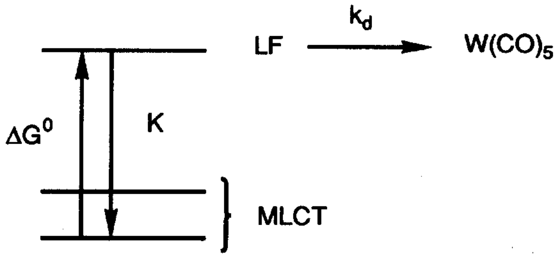


Figure 5. Curves of Absorbance versus time taken at the ν(CO) frequencies shown.

Thus, TRIR can monitor, firstly, the formation of the MLCT excited state - in which, as expected, the ν(CO) bands are higher in frequency - and, secondly, its consequent decay as it is partly converted back to the ground state and partly converted to solvated $W(CO)_5$. Proof that $W(CO)_5$ is formed comes from experiments with CO-doped solutions, when the generation of $W(CO)_6$ can be followed.

Two further points are of interest:

(1) If the formation of $W(CO)_5$, following 510 nm irradiation, depends on establishing a rapid equilibrium between MLCT and LF state, then the yield of $W(CO)_5$ should depend on temperature:



This has been demonstrated in quantum yield measurements [21], but it is more strikingly shown in TRIR experiments [23], where the production of W(CO)$_5$ can be monitored directly. The yield of W(CO)$_5$ versus temperature provides an estimate of the energy difference between the lowest MLCT and LF states of ~4000 cm^{-1}.

(2) If the photolysis is carried out at 308 nm, then the generation of W(CO)$_5$ should proceed directly, rather than via the MLCT/LF equilibrium. TRIR shows that W(CO)$_5$ is produced instantaneously, rather than after generation of the MLCT excited state [23].

2.3. Charge distribution and structure

It is clear from what has been described so far that the change in force field from ground to excited state will be a sensitive probe of charge distribution and structure. The simplest compounds will be those with only one CO or CN group, or where there is no vibrational coupling between the groups. Woodruff [24] has looked at a series of compounds of the type **[Os(bpy)$_2$(CO)Cl]$^+$**; these species have low-lying MLCT states and, on excitation, the ν(CO) bands shift upwards by about 70 cm^{-1}.

A further splendid example is **[Rh(CNCH$_2$CH$_2$CH$_2$NC)Rh]$^{2+}$**; TR^3 had shown [25] that in going from ground state ($^1A_{1g}$) to excited state ($^3A_{2u}$, τ~6μs), the ν(Rh-Rh) and ν(Rh-C) modes increased in frequency from 79 to 144 and 467 to 484 cm^{-1}, respectively. This was consistent with the change in character of the Rh-Rh bond (dσ^* antibonding to pσ bonding), and increased backbonding from metal to isocyanide. Further confirmation of this comes from TRIR [26]. The ν(CN) streching vibration shifts from 2193 to 2177 cm^{-1}. Assuming that the Rh-Rh, Rh-C and C-N modes can be approximately treated as those of diatomic species, Woodruff and colleagues applied a set of empirical relationships to calculate the changes in the appropriate bond lengths:

	Rh-Rh	Rh-C	C-N
Δr (Å)	-0.210	-0.022	+0.002

There has been considerable debate as to whether the lowest CT excited state of **$[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{II}(bpy)_2\text{-}CN]^+$** is best described as localised on one Ru [27] or delocalised [28]. Recent TRIR measurements [29] show that, in the excited state, there are *two* clearly resolved IR bands assigned to two terminal ν(CN) modes and hence the structure is localised, ie the structure is $[NC\text{-}Ru^{II}(bpy)_2\text{-}CN\text{-}Ru^{III}(bpy^-)(bpy)\text{-}CN]^+$.

In **$(OC)_5W(4,4'\text{-}bpy)W(CO)_5$**, preliminary ν(CO) TRIR results imply that the MLCT state is not delocalised [30].

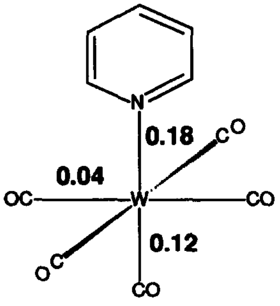
2.4. Rates of electron transfer

On 300 nm excitation of **$[(phen)(CO)_3Re^{I}(NC)Ru^{II}(CN)(bpy)_2]^+$**, the TRIR spectrum at 1 ps clearly shows an increase in ν(CO) frequencies consistent with the process Re^{I} -> phen. However, within 10 ps the spectrum changes dramatically with large ν(CN) shifts, but with only minor shifts from the ν(CO) ground state spectrum. Thus, the initial excited state very rapidly changes to Ru^{II} -> bpy, and this lasts for hundreds of nanoseconds [31].

3. SOME FUTURE DIRECTIONS

Clearly TRIR will prove increasingly valuable in its applications to the CT excited states of transition metal species. One major area of activity is going to be supramolecular photochemistry [32], where the ability to monitor ν(CN) and ν(CO) vibrations will provide a very powerful probe. We now consider some other potential applications.

As mentioned above, with L = pyridine (and many other ligands), the lowest-lying excited states of $W(CO)_5L$ compounds have LF character. In elegant RR experiments on **$W(CO)_5(pyridine)$**, employing the time-dependent method [3], Tutt and Zink [33] have concluded that the lowest LF excited state is distorted from the ground state by the changes in the W-C and W-N bond lengths (in Angstrom units) as shown:



Preliminary experiments [34] on this compound in a low-temperature glass suggest that, as expected, the v(CO) bands are substantially shifted in the excited state.

As in the $W(CO)_5$(4-CNpyr) example described above, TRIR will be very useful in interpretation of reaction mechanisms. Of relevance to the CO_2 reduction cycle, preliminary experiments with the CO_2 reducing species **$[Re(CO)_2\{P(OEt)_3\}_2(bpy)]^+$ ($[Q]^+$)** show that TRIR can monitor the formation of the excited state $([Q]^+)^*$, and its conversion to the neutral species (Q), as it reacts by electron transfer with an electron donor such as DABCO [35].

In principle, ps and sub-ps TRIR should be able to monitor the very early stages of photochemical processes. Two examples have been given above. The classic *organometallic* compound for photochemical study has been $Cr(CO)_6$. Recent very fast UV/vis spectroscopy [36] has been interpreted largely by reference to early matrix isolation studies [37], which suggested that the fragment $Cr(CO)_5$ is produced first in an excited electronic state with C_{4v} structure, and that this then relaxes via a D_{3h} structure to the C_{4v} ground state. One of the problems has been the generation of species with substantial vibrational excitation, ie "hot" molecules. This is particularly noticeable in fast TRIR [36]; the v=0 to v=1 transitions of all the species are complicated by the v=1 to v=2, v=2 to v=3, etc., transitions, and it is proving very difficult to positively identify the various initial intermediates. This problem is likely to prove a complicating factor in many very short time-scale experiments.

4. ACKNOWLEDGMENTS

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