Fast Time-resolved IR Studies of the Excited States of Co-ordination Compounds: Direct Observation of Intramolecular Charge Transfer

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Fast time-resolved IR (TRIR) spectroscopy is used to record ν(C–O) bands of the lowest lying excited state of [$ClRe(CO)_3(4,4'\text{-bipyridyl})_2$] (half-life of approximately 1 μs in CH_2Cl_2 solution); there is a shift of the ν(C–O) bands to higher frequency relative to the ground state, which is consistent with oxidation of the metal centre *via* electron transfer to the bipyridyl ligands.

The direct observation of excited states is of importance in unravelling the photochemical mechanisms of co-ordination compounds.[1] Most such studies have involved either UV/VIS absorption or luminescence.[2] However, although these experiments provide information on lifetimes, they are not usually relevant to structure. For this, vibrational data would be particularly valuable, and time-resolved resonance Raman spectroscopy has supplied important data on time scales as fast as picoseconds, for a range of transition metal compounds,[3] including biological species.[4]

A series of elegant studies[5—7] have provided spectra of excited states of 2,2′-bipyridyl (bpy) complexes of Ru and Re, generated by UV radiation. The resonance enhanced vibrations of the bpy moiety demonstrate that, in these species, there is charge transfer from the metal to the bpy ligand. However, resonance enhancement only occurs for those vibrations directly coupled to the chromophore; hence important vibrational data may be unobtainable, a point emphasized by Adamson.[8]

For *fac*-[$ClRe(CO)_3(2,2'\text{-bpy})$],[9] for instance, there is no enhancement of the ν(C–O) modes in the excited state and hence no information on these groups. However, electron transfer from Re to bpy involves oxidation of the Re and this should result in a shift in the ν(C–O) modes to higher frequency.

We have now applied time-resolved IR spectroscopy (TRIR) to the closely related species [$XRe(CO)_3L_2$] (X = Cl, Br; L = 4,4′-bpy). There is considerable information on their

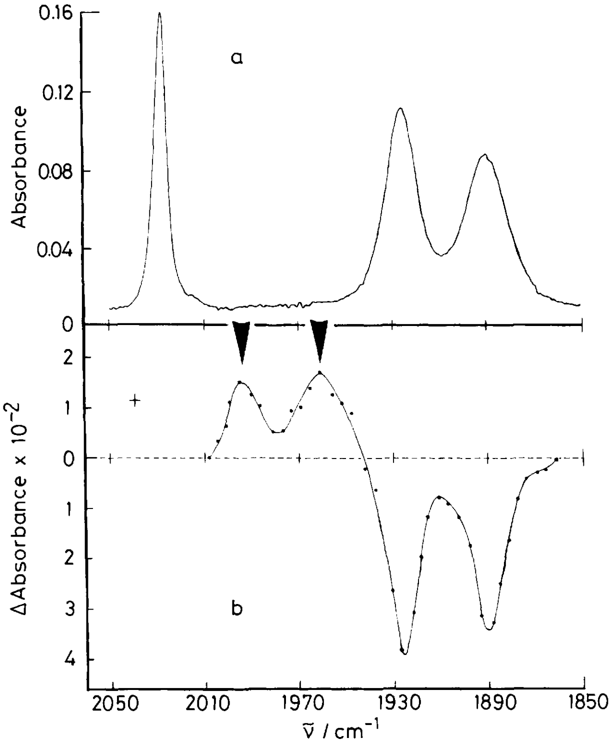

Figure 1. (a) FTIR spectrum (Nicolet MX-3600; 32K data points, 2 cm^{-1} resolution), in the ν(C–O) region, of a solution of [ClRe(CO)$_3$(4,4′-bpy)$_2$] in CH_2Cl_2 (approximately 5 × 10^{-5} M) in a 7 mm path length cell. (b) TRIR spectrum of the same solution as in (a), degassed under Ar, in the same cell, obtained 240 ns after the excimer laser flash. Each data point corresponds to a different line of the CO laser; data points below the dotted horizontal represent depletion and those above represent generation. The arrows mark the maxima of the bands assigned to the excited state of [ClRe(CO)$_3$(4,4′-bpy)$_2$].

excited states.[10] The lowest lying excited state involves metal to bpy charge transfer; the emission efficiency is independent of excitation wavelength but the decay rates of the excited state are very sensitive to solvent. These are properties which are important in the TRIR studies, described below, which show that the ν(C–O) bands shift exactly as expected.

Several laboratories have developed fast TRIR apparatus for the detection, structural determination, and kinetic measurements of organometallic photo-intermediates.[11] Our apparatus[12]† operates in a 'point-by-point' mode. Following an excimer laser flash, the change in intensity at a particular wavelength is monitored as a function of time, hence providing kinetic data; the flash is repeated and a different wavelength monitored. From these several decay curves it is possible to construct IR spectra, with a nominal resolution of 8 cm^{-1}, corresponding to different time delays after the flash.

Figure 1(a) shows the FTIR spectrum in the ν(C–O) region of a solution of [ClRe(CO)$_3$(4,4′-bpy)$_2$] in CH_2Cl_2. Figure 1(b) shows a TRIR spectrum of the same solution obtained by the method outlined above over the wavenumber range accessible to our apparatus. The TRIR spectrum corresponds to 240 ns after the flash. The spectral data are given in Table 1. It is clear that the flash destroys the parent compound and generates a species with two observable ν(C—O) bands at higher frequency than that of the parent. No transient IR bands were seen at lower wavenumbers down to 1650 cm^{-1}. We are confident in assigning these two new absorption bands to an electronic excited state for the following reasons.

Table 1. Frequencies (cm^{-1}) of the ν(C–O) bands of ground and excited states of [ClRe(CO)$_3$(4,4′-bpy)$_2$].

Excited state[a]	Ground state		Difference (excited − ground)
	TRIR[b]	FTIR[c]	
1957	1891	1891	+66
1992	1927	1926	+65
—	—	2027	

[a] Figure 1(b); it is assumed that the expected high frequency band is outside the range. [b] From depletion of the ground state measured in the TRIR spectrum, Figure 1(b); the high frequency band of the ground state is outside the spectral range of the equipment. [c] Figure 1(a).

Table 2. Lifetime data ($t_{1/2}$/μs) for the electronically excited state of [ClRe(CO)$_3$ (4,4′-bpy)$_2$] in CH_2Cl_2 and benzene solutions at 25 °C.

CH_2Cl_2[a]				Benzene[a]	
Ar	CO	O_2	—[b]	Ar[c]	—[b]
1.01 ± 0.10	0.96 ± 0.10	*ca.* 0.08	0.9	2.1 ± 0.1	3.3

[a] Degassed *via* several freeze–thaw cycles, then saturated with the gas indicated. [b] Emission data from ref. 10, all other data from TRIR. [c] In 4 mm cell; too much solvent absorption in 7 mm cell.

(a) The rate of loss of transient absorption is equal, within experimental error, to the rate of recovery of the ground state absorption (see Figure 2). It is known that, following excitation with a UV laser pulse, non-radiative decay occurs rapidly to the lowest excited state.[10] This state reverts to the ground state *via* both emission and non-radiative decay. Thus in the absence of any intervening states the rates of decay of excited state and recovery of ground state should be the same, as is observed.

(b) Under similar conditions, the lifetimes measured by TRIR and emission are identical‡ (see Table 2). Table 2 also illustrates the importance of degassing the solution rigorously since dissolved oxygen considerably shortens the lifetime.

(c) The half-life of the excited state is unchanged when CO is added to the solution (see Table 2). Most metal carbonyl compounds lose CO on photolysis[13] but there is no evidence of a significant quantum yield for this process in [ClRe(CO)$_3$(4,4′-bpy)$_2$] and related species.[10] However, it is still necessary to show that the new bands do not correspond to a CO-loss intermediate, and that the observed decay in signal is not due to the back reaction of such an intermediate with CO to re-form the parent. Such a reaction would be sensitive to CO concentration.

(d) The IR spectrum is consistent with the limited data available for related species. The only useful comparison is

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† The apparatus consists of three parts: i, an excimer laser (Lumonics HyperEx HE-440, operating on XeCl at 308 nm) with a pulse length of approximately 10 ns for excitation; ii, a continuous wave CO laser (Edinburgh Instruments PL3) which is line-tunable in steps of approximately 4 cm^{-1} over the range 2010—1550 cm^{-1}, for IR spectroscopic monitoring of transients; iii, fast detection, amplification and data handling.

‡ Our first TRIR experiments with this system were carried out in our standard 1 mm path length IR cell. This necessitated the use of higher concentrations than were used for previous emission studies, because TRIR is a less sensitive technique than UV/VIS emission spectroscopy. Using this cell, the life-time of the excited state was consistently shorter than that measured previously by emission spectroscopy. Good agreement was obtained, however, by switching to a special IR cell with a 7 mm path length where more dilute solutions could be used. This dilution effect implies some self-quenching and we are investigating this effect in collaboration with colleagues at Loughborough University.

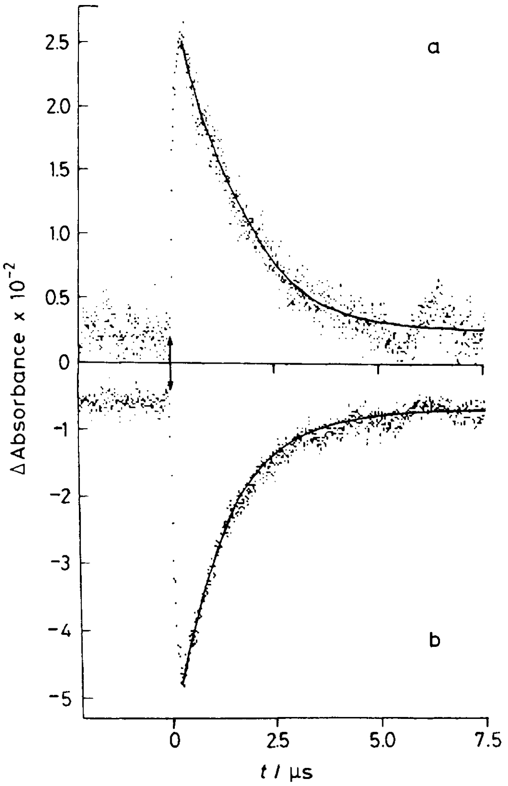

Figure 2. TRIR data showing that the decay in the excited state of $[ClRe(CO)_3(4,4'\text{-}bpy)_2]$ and the recovery of the ground state occur at the same rate. The change in intensity of ν(C–O) bands of (a) the excited state at 1992 cm^{-1} and (b) the ground state at 1893 cm^{-1} are shown. The arrows depict the time of the excimer flash. The thicker continuous lines represent exponential fits to the decay curves with first order rate constants for (a) of $6.9 \times 10^5\ s^{-1}$ and for (b) of $7.2 \times 10^5\ s^{-1}$.

with charged and uncharged metal carbonyl species. From matrix isolation IR studies on neutral and charged carbonyl fragments[14] and from IR data on electrochemically generated species,[15] we might expect a shift to a higher wavenumber of between 50 and 100 cm^{-1}. If we assume that the high frequency band of the excited state is shifted to a region outside the CO laser range, the shifts observed for the two other bands are approximately 65 and 66 cm^{-1} (Table 1). We are now measuring the shifts for a series of related molecules and believe this will provide information about the electron transfer process as a function of the metal and the ligands.

We conclude that on excitation of $[ClRe(CO)_3(4,4'\text{-}bpy)_2]$ with light of wavelength 308 nm, an excited state is produced and in this excited state the ν(C–O) bands are to higher frequency than those of the parent. This is the first time that TRIR has been used for detecting intramolecular electron transfer. We believe that these experiments represent a significant addition to the methods available for probing electron transfer processes. Such TRIR experiments have considerable potential for studying biological systems.

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