Electron Distribution in the Excited State of $[(OC)_5W(4,4'\text{-bipy})W(CO)_5]$ (4,4'-bipy = 4,4'-bipyridyl) determined by Time-resolved Infrared Spectroscopy

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Employing fast time-resolved infrared (TRIR) spectroscopy, the pattern of the ν(CO) IR bands in the lowest excited state of $[(OC)_5W(4,4'\text{-bipy})W(CO)_5]$ (4,4'-bipy = 4,4'-bipyridyl) shows that the electron distribution in this state is localised on the IR time-scale.

Complexes of formula $[\{M(CO)_5\}_2L]$, where M is Cr, Mo or W, and L is a bridging ligand containing two nitrogen donors such as pyrazine (pyz) or 4,4'-bipyridyl (4,4'-bipy), have been the object of considerable interest,[1–7] particularly because of the opportunity to probe the effects on the photophysical and redox properties of changing from the monomer, $[M(CO)_5L]$, to the dimer, $[(OC)_5M(L)M(CO)_5]$, and because the electron-transfer properties of the excited states of the dimers are of fundamental importance. The lowest excited states of the majority of the dimers involve charge transfer from metal to bridging ligand. That the bridging ligand in $[(OC)_5W(4,4'\text{-bipy})W(CO)_5]$ **1** becomes negatively charged (*i.e.*, $4,4'\text{-bipy}^-$) in the lowest excited state has been confirmed *via* time-resolved resonance-Raman (TR^3) spectroscopy in recent work by McGarvey and co-workers.[8] Dodsworth and Lever[7] noted that the excited state of $[(OC)_5W(pyz)W(CO)_5]$, formally $W^+(pyz^-)W^0$, is related to the ground state of the Creutz-Taube ion, $[(H_3N)_5Ru(pyz)Ru(NH_3)_5]^{5+}$; the former can be written as $W(d^5)(pyz^-)W(d^6)$, and the latter as $Ru(d^5)(pyz)Ru(d^6)$. A similar analogy exists between **1** and $[(H_3N)_5Ru(4,4'\text{-bipy})Ru(NH_3)_5]^{5+}$. The Creutz-Taube ion is believed to be delocalized, mixed-valence Class III,[9] whereas $[(H_3N)_5Ru(4,4'\text{-bipy})Ru(NH_3)_5]^{5+}$ is Class II, with an estimated[10] rate constant for electron transfer (k_{el}) > 10^8 s^{-1}. For the metal carbonyl species, there is thus an interesting question as to the effect of the electron, localised in the bridging ligand in the excited state, on the electronic properties of the excited state. Fast time-resolved infrared (TRIR) spectroscopy has been shown to be a powerful tool for examining electron distribution in excited states.[11,12] By using TRIR spectroscopy we have now measured the ν(CO) bands of both $[(OC)_5W(4,4'\text{-bipy})W(CO)_5]$ **1** and $[(OC)_5W(4,4'\text{-bipy})]$ **2** in their lowest metal-to-ligand charge-transfer (m.l.c.t.) excited states; as described below, these data clearly help to distinguish between localised and delocalised behaviour for **1**.

In their ground states, both **1** and **2** show very similar ν(CO) IR spectra (Table 1) reflecting the local C_{4v} symmetry of the $W(CO)_5$ group; there is very weak activity in the formally forbidden b_2 mode because the 4,4'-bipy ligand lowers the symmetry from strict C_{4v}. The ν(CO) IR spectra in the excited states of **1** and **2** were obtained by monitoring the spectra with either CO or diode IR laser, following flash photolysis of **1** or **2** in CH_2Cl_2 solution, using an excimer pumped dye laser (460 nm for **1**; 420 nm for **2**), or a Nd/YAG laser (355 nm).† Because of band overlap, the spectral region in the vicinity of the e and low-frequency a_1 modes is rather crowded and full details will be published elsewhere,[13] together with details of the photochemistry, and related electrochemical studies, of these compounds. However, the high-frequency ν(CO) region provides a direct and simple interpretation of the behaviour of the excited states; Fig. 1 shows this spectral region.

Table 1 Infrared vibrational data, in the ν(CO) region (in cm^{-1}), for the ground and excited states of $[(OC)_5W(4,4'\text{-bipy})W(CO)_5]$ **1** and $[(OC)_5W(4,4'\text{-bipy})]$ **2** in CH_2Cl_2 solution

1

Ground state		Excited state[a]			
FTIR[b]	TRIR[c]	(i) TRIR	Shift[d]	(ii) TRIR	Shift[d]
2072 (a_1, w)	2073	2105	+33	2059	−13
1933 (e, vs)	1936	≈2010	+77	≈1915	−18
1901 (a_1, s)	1900	≈1970	+69	≈1875	−26

2

Ground state		Excited state[a]	
FTIR[b]	TRIR[c]	(i) TRIR	Shift[d]
2073 (a_1, w)	2074	2104	+31
1930 (e, vs)	1933	2005	+75
1901 (a_1, s)	1890	1965	+64

[a] The excited bands are grouped into: (i) those increasing in frequency, (ii) those decreasing in frequency. [b] Fourier-transform (FT) IR spectrum measured in CH_2Cl_2 (5×10^{-4} mol dm^{-3}); very weak shoulders appear at ≈1973 (**1**) and ≈1974 (**2**) cm^{-1} due to the b_2 bands, which are formally forbidden under C_{4v} symmetry; w = weak, s = strong, v = very. [c] The positions of the ground-state bands can also be determined from TRIR spectroscopy, less accurately, from the loss on excitation. [d] The shift is measured from ground-state FTIR to excited-state TRIR.

In Fig. 1(*a*) it is clear that there is loss of the parent band of **1** at 2073 cm^{-1}, and generation of *two* new bands at 2105 and 2059

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† The excimer laser is a Lumonics HyperEx 440 operating at 308 nm, with a pulse of ≈30 ns and a pulse energy of ≈100 mJ, pumping an Oxford Lasers EDL1 dye laser (≈10 mJ per pulse using Stilbene 420 or Coumarin 460). The Nd/YAG laser is a Quanta-Ray GCR-12S operating at 355 nm (≈7 ns; ≈50 mJ)). There are two IR lasers, a continuous-wave CO laser (Edinburgh Instruments PL3, ≈100 mW per line, line-tunable in steps of ≈4 cm^{-1}) and a diode laser (Mütek MDS 1100, ≈1 mW).

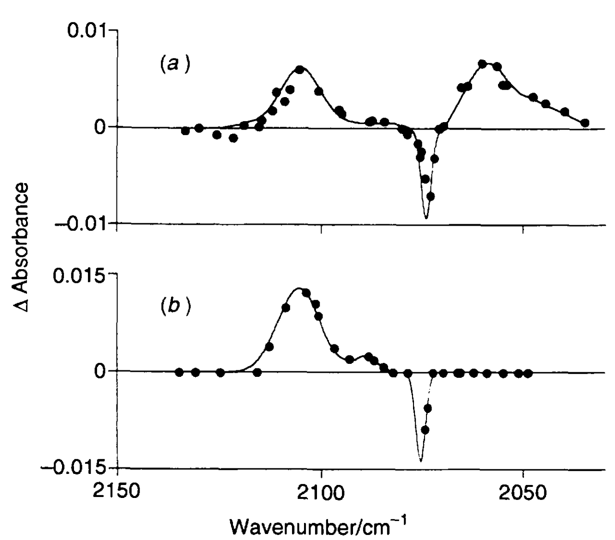

Fig. 1 (*a*) TRIR spectrum at ≈85 ns after flash (355 nm, 40 mJ) of **1** in CH_2Cl_2 (≈3.5 × 10^{-3} mol dm^{-3}; path length 1 mm); (*b*) TRIR spectrum at ≈65 ns after flash (355 nm, 30 mJ) of **2** plus excess 4,4′-bipy in CH_2Cl_2 (≈2 × 10^{-3} and 2 × 10^{-2} mol dm^{-3} respectively; path length 1 mm). (In the absence of excess 4,4′-bipy, the monomer decomposed to produce both dimer and free 4,4′-bipy.). In both (*a*) and (*b*), data points plotted downwards signify loss of ground state of parent, points plotted upwards signify generation of excited state. A brief description of the apparatus is given in footnote † on the previous page, and further details in ref. 14

cm^{-1}; Fig. 1(*b*) shows loss of the parent band of **2** at 2074 cm^{-1} and generation of *one*† new band at 2104 cm^{-1} (see Table 1 for complete data). Figs. 2(*a*) and (*b*) show that these excited state bands of **1** and **2** decay with lifetimes of, respectively, ≈160 and ≈220 ns; the second band of **1** decays with a lifetime of ≈170 ns and hence, within experimental error, the two ν(CO) IR bands of **1*** belong to the same excited state. The lifetimes of **1** and **2** are shorter than the published data,[5] measured by emission for **1** and **2** in benzene (394 and 415 ns, respectively), the difference being accounted for, as in $[ReCl(CO)_3(4,4'\text{-bipy})_2]$,[15,16] by the change in solvent. Consider the behaviour of **2**. In the lowest excited state, there is electron transfer from tungsten to 4,4′-bipy; this effectively oxidises the metal atom and hence the carbonyl groups experience reduced back-bonding and the ν(CO) frequencies will increase. The pattern of shifts (Table 1) is consistent[11] with a charge migration of approximately one unit and hence the charge distribution of the excited state of **2** can be described as $(OC)_5W^{(\approx+1)}(4,4'\text{-bipy}^{(\approx-1)})$. In the excited state of **1**, there are two extreme possibilities, with the charge distribution described as either $(OC)_5W^{(\approx+\frac{1}{2})}(4,4'\text{-bipy}^{(\approx-1)})W^{(\approx+\frac{1}{2})}(CO)_5$ (*i.e.*, delocalised) or $(OC)_5W^{(\approx+1)}(4,4'\text{-bipy}^{(\approx-1)})W^{(\approx0)}(CO)_5$ (*i.e.*, localised). In the former case, we expect the ν(CO) pattern to be similar to that of the excited state of **2**, but with shifts from the ground state of approximately half that of **2**. In the latter we expect there to be *two* overlapping patterns, one derived from the $(OC)_5W^{(\approx+1)}$ group and one from the $W^{(\approx0)}(CO)_5$ group; the first group pattern should be similar to that of the excited state of **2**, and with similar shifts from the ground state, whereas the second pattern should resemble the ground-state pattern but with the bands displaced somewhat to *lower* frequency because, in the excited state, there will be interaction between 4,4′-bipy^{-1} and W^0 and hence a lowering of its ν(CO) frequencies. It is important to note that the distinction between 'localised' and 'delocalised' in such an experiment refers to electron transfer at rates slower than, or faster than, the IR time-scale.‡ It is clear from Fig. 1(*a*), that the excited-state spectra demonstrate a localised electron distribution. The complete data in Table 1 support this interpretation, and in particular the similarity of the upwards shifts in monomer and dimer indicate that the degree of W–W coupling in the excited state of **1** must be very small. Preliminary TRIR experiments[18] show that the electron distribution in the excited state of $[(OC)_5W(pyz)W(CO)_5]$ is also localised. It may be that this strong localisation is caused by the extra bridging electron in the excited state which blocks communication between the tungsten atoms; note that *trans,mer*-$[(PPr^i_3)_2(OC)_3M(pyz)M(CO)_3(PPr^i_3)_2]^+$ (M = Mo or W), formally $M^{(+1)}(pyz^{(0)})M^{(0)}$ is *delocalized* on the IR time-scale.[17a,b] On the other hand, in the complex $[(NC)(2,2'\text{-bipy})_2Ru(CN)Ru(2,2'\text{-bipy})_2(CN)]^+$ (2,2′-bipy = 2,2′-bipyridyl), TRIR spectroscopy indicates[12] that, in the lowest excited state, the charge migration is from ruthenium to the terminal ligand, but the electron distribution is again localised and the structure can be represented as $[(NC)(2,2'\text{-bipy})_2Ru^{II}(CN)Ru^{III}(2,2'\text{-bipy}^{-1})(2,2'\text{-bipy})(CN)]^+$.

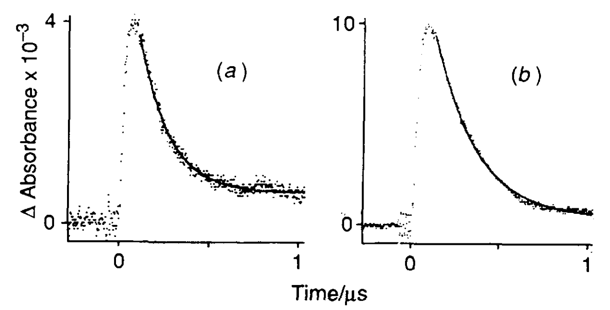

Fig. 2 (*a*) A trace showing the change in intensity of one of the excited-state bands of **1**, recorded at 2108 cm^{-1}; (*b*) a similar trace for an excited-state band of **2**, recorded at 2108 cm^{-1}. The continuous lines represent exponential fits to the decay data with lifetimes of ≈160 and ≈220 ns respectively; the second band of **1** at 2059 cm^{-1} decays exponentially (not shown) with a lifetime of ≈170 ns. A small residual absorbance is seen in (*a*) due to a small acoustic 'shock' wave which occurs at all frequencies during this experiment

There is clearly still much to learn about the electronic structure of the excited states of species such as $[(OC)_5M(L)M(CO)_5]$, and it is likely that TRIR spectroscopy will be particularly helpful.

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† There is a small absorption at 2088 cm^{-1}, which is assigned as the a_1 ν(CO) band of solvated $[W(CO)_5]$. This is produced instantaneously because of overlap between the excitation source at 355 nm and the ligand field (LF) absorption band of **2**; the LF state is dissociative. Moreover as the m.l.c.t. excited state of **2** decays, there is further production of $[W(CO)_5]$ because the m.l.c.t. state is in thermal equilibrium with the LF state.[13]

‡ There are excellent recent examples of the application of this argument to ground-state molecules.[9,17]

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