Infrared rigidochromism: a new effect in the IR spectra of the excited states of coordination compounds

Ian P. Clark, Michael W. George,* Frank P. A. Johnson and James J. Turner*

Department of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD

The magnitude of the shift in the ν(CO) IR spectrum of the MLCT excited state of [Re(CO)$_3$Cl(bipy)] (bipy = 2,2′-bipyridyl) in PrCN–EtCN solution, compared with the ground-state spectrum, *decreases* on cooling from fluid to glass; this 'infrared rigidochromic' effect is explained by the change in character of the MLCT state on glass formation.

On lowering the temperature of solutions of coordination compounds in glass-forming materials through the glass transition temperature, there is a sharp variation in some photophysical properties, explained by the change in viscosity.[1] In particular the emission from long-lived charge-transfer states shifts to the blue ('luminescence rigidochromism'[2]) and the emission lifetime lengthens. These changes are superimposed on much slower variations in properties caused by the decrease in temperature. There have however been no corresponding direct measurements of changes in vibrational properties.

Here we report the first example of such a measurement, on the fast time-resolved IR (TRIR) ν(CO) spectrum of [Re(CO)$_3$Cl(bipy)] **1** in the glass-forming solution, butyronitrile–propionitrile (PrCN–EtCN; 5 : 4, *v*/*v*).

Employing TRIR, we[3] and others[4] have described the ν(CO) IR spectra of a number of coordination compounds in their lowest excited states. For **1** in CH$_2$Cl$_2$ solution, the ν(CO) bands shift upwards in frequency compared with the ground state;[3c] this is because in the lowest MLCT excited state there is electron transfer from metal to bipy[5] and the effective oxidation of the metal leads to less back-bonding to the CO groups. Fig. 1 shows the TRIR spectra of **1** in PrCN–EtCN at two different temperatures, in fluid [Fig. 1(*b*)] and in solid [Fig. 1(*c*)]. An FTIR spectrum at room temperature is shown for comparison. It is clear that on excitation there is loss of the three ground-state parent **1** ν(CO) bands and generation of three MLCT excited-state ν(CO) bands, shifted upwards in frequency compared with the ground-state bands. It is also very striking that, although the parent bands are almost unaffected by the change from liquid to glass, the excited-state bands shift by different amounts; data are given in Table 1.

It is important to distinguish between the effects of changes in temperature and in viscosity. To do this we have first employed TRIR to measure the lifetime of the excited state; the results are shown in Fig. 2. This plot corresponds to similar lifetime studies based on fluorescence,[7] and demonstrates that the lifetime changes sharply with change in viscosity.† Secondly, TRIR spectra (not shown) are measured at two other temperatures, one in the fluid and one in the glass region. The temperatures of all four complete spectral measurements are indicated in Fig. 2, and the data are given in Table 1. The data show that in the fluid region, between room temperature and 135 K, there is almost no change in the shift in ν(CO) bands from ground to excited state, and that this shift is similar to that of **1** in CH$_2$Cl$_2$ at room temperature. In addition there is very little change in shift in the glass region from 110 to 77 K. Thus the *change* in the mean shift of approximately 20 cm^{-1} between fluid and glass is due to the change in properties, presumably viscosity, between the two media. We call this effect 'infrared rigidochromism'.

The phenomenon of *luminescence* rigidochromism has been observed several times[1] and it is usually explained by supposing that in the fluid, provided the excited state is sufficiently long lived, the dipoles of the solvent are free to rotate and hence accommodate the change in electron distribution on charge transfer excitation, whereas such accommodation is not possible in the rigid glass. Thus the energy of the MLCT level is raised on glass formation resulting in a blue shift in the emission. We have confirmed that this happens with **1** in PrCN (620 nm at 180 K to 565 nm at 77 K). What effect on the ν(CO) bands might be expected? One possibility is that in the glass the vibrational potential functions are steeper than in the fluid; however this should also apply to the ground-state vibrational spectra, and as we have seen the ground-state ν(CO) bands of **1** are almost constant over the whole temperature range. Moreover any effect on the potential function is likely, if anything, to be greater in the excited state, resulting in an *increased* ν(CO) shift on glass formation.

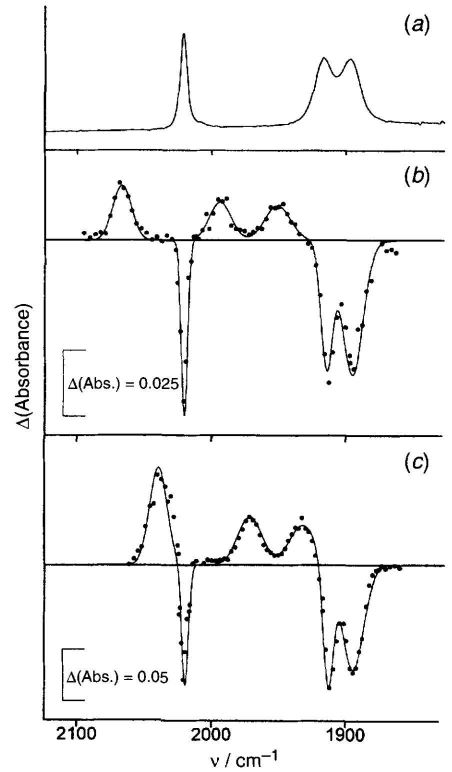

Fig. 1 FTIR (Perkin Elmer System 2000 FTIR; resolution ≈ 2 cm^{-1}) ν(CO) spectrum of [Re(CO)$_3$Cl(bipy)] (≈ 10^{-3} mol dm^{-3}) in PrCN–EtCN solution (5 : 4, *v*/*v*) at room temp.; (*b*) TRIR spectra of similar solution, 100 ns after laser excitation, at (*b*) ≈ 135 and (*c*) ≈ 77 K. The time-resolved spectra in (*b*) and (*c*) were obtained, following excitation with a Nd/YAG laser (355 nm; energy 10 mJ/pulse), using a diode IR laser instrument (Mütek Model MDS 1100, fitted with MDS 1200). The IR detector is ac coupled such that data points going downwards represent parent loss and upwards represent product gain. Full details of the experimental setup are given in ref. 7. The lines represent multiple-Gaussian fits to the spectra.

For charge-transfer excited states the greater the degree of charge transfer the greater the shift in ν(CO) from ground to excited state.[3,4] However the greater the separation of ground state and MLCT state the greater is the degree of charge transfer;[8] this would predict that the shift in ν(CO) bands should *increase* on going from fluid to glass.

Table 1 Wavenumbers (cm^{-1}) of ν(CO) bands of [$Re(CO)_3Cl(bipy)$] in PrCN–EtCN (5:4, *v*/*v*) at various temperatures, and in CH_2Cl_2 at room temperature

	Ground state	Excited state	Difference	Mean difference
Room temp. (FTIR)	2021.5			
	1917.0			
	1896.0			
Room temp. (TRIR)	2022	2065	43	
	1915	1991	76	58
	1895	1951	56	
135 K	2020	2066	46	
	1914	1993	79	60
	1895	1950	55	
110 K	2018	2039	21	
	1913	1976	63	41
	1896	1936	40	
77 K	2020	2040	20	
	1913	1971	58	38
	1894	1932	36	
Room temp. in CH_2Cl_2[3c]	2024	2064	40	
	1921	1987	66	55
	1899	1957	58	

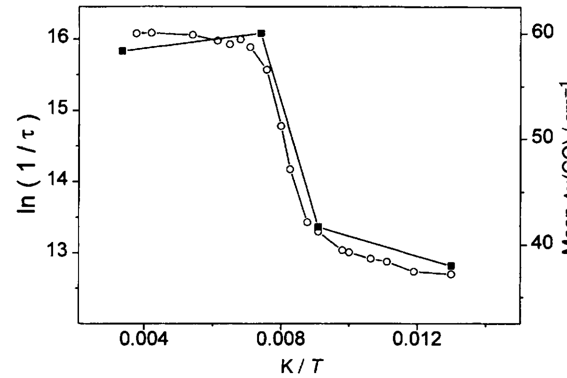

Fig. 2 Plot (○) of ln(1/τ) (τ = lifetime) *vs.* T^{-1} (T = temperature) for the excited state of **1** in PrCN–EtCN (5:4, *v*/*v*). The four points (◆) are the values of the mean shift in ν(CO) from ground to excited state (Table 1) as a function of $1/T$. The τ values above ≈ 150 K are not particularly accurate as the lifetime becomes of the same order as the instrument time resolution.

Arguments based on UV–VIS spectral band fitting[9] would suggest a greater distortion in normal coordinates in glass than fluid, again leading to an *increase* in shift on glass formation.

Thus the direction of the shift change is surprising. It is known that ligand-field and intraligand transition energies are not sensitive to changes in viscosity. It is also known that there is an accessible ππ* state above the MLCT state. It is therefore possible that the raising in energy of the MLCT on glass formation causes increased mixing with the ππ* level. This means that in the glass the excited state involves *less* electron transfer than in the fluid.‡ Experiments which eliminate the possible interference of the ππ* state by examining a range of molecules with different energy level structures are in progress. In any case it is clear that probing the IR spectra of excited states through the fluid to glass transition offers a new way of probing the subtleties of the excited-state structure.

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Footnotes

† The experimental data can be fitted by one of the usual equations;[7] full details will be published elsewhere.

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