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LETTERS

Infrared Spectra of the Excited States of Coordination Compounds Containing CO Groups: Bandwidths in Polar and Nonpolar Solvents

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Time-resolved infrared spectroscopy has been used to probe the ν(CO) bandwidths of the MLCT excited states of carbonyl-containing metal complexes, in both polar and nonpolar solvents. Considerably broader excited state bands observed in the polar solvents indicate that the broadening of the ν(CO) bands is a consequence of solvent−solute interactions. $\pi\pi^*$ excited states, with no charge-transfer character, exhibit no such broadening of the ν(CO) bands upon excitation.

Introduction

Fast time-resolved infrared (TRIR) spectroscopy has proved to be a valuable tool for probing the short-lived excited states of coordination compounds containing CO or CN groups.[1] Figure 1, for example,[2] shows the TRIR spectrum of ClRe(CO)$_3$(bpy) (bpy = 2,2′-bipyridyl) in CH_2Cl_2. The spectrum shows three negative bands representing parent loss upon excitation and three positive bands of the MLCT excited state. The increase in the frequencies of the ν(CO) bands is due to oxidation of the metal upon metal-to-ligand charge transfer, reducing the amount of back-bonding to the CO π^* orbitals. This applies over a wide range of compounds, and in fact the shift in ν(CO) frequency from ground to excited state is a measure of the degree of charge transfer. A further striking feature of the spectrum in Figure 1 is the increase in bandwidth of the high frequency a′ band in the excited state. Although note quite as noticeable, the other two bands also show an increase in bandwidth. This band broadening occurs often in the excited states of metal carbonyl species. Although several papers have commented on the increase in excited state bandwidths in time-resolved Raman spectroscopy (particularly of the S_1 state of *trans*-stilbene[3]), to the best of our knowledge there have been no explicit studies of excited state bandwidths by infrared spectroscopy. In this paper we present evidence suggesting that the broadening of ν(CO) infrared bands is a consequence of interactions between the charge-separated excited state molecules and a polar solvent. The broadening does not occur for MLCT states in a nonpolar solvent nor for non-charge-transfer states in polar solvents.

Results

An understanding of the excited state behavior of ν(CO) bands requires a compound that is soluble in nonpolar and polar solvents. ClRe(CO)$_3$(bpy) is insoluble in nonpolar solvents; however, W(CO)$_5$(4-AcPyr) is soluble in both types of solvent. The TRIR spectrum of the MLCT excited state in *n*-heptane is already known,[4] except for the high-frequency a_1(l) band. This band is considerably weaker in intensity than the e and lower frequency a_1(2) bands, and the sensitivity of the apparatus used in early TRIR experiments prevented the probing of this ν(CO) band. Improvements in sensitivity[5] now allow us to probe all the ν(CO) bands of W(CO)$_5$(4-AcPyr).

Figure 2 shows the ground state FTIR spectra of W(CO)$_5$(4-AcPyr) in *n*-heptane and in CH_2Cl_2, and Table 1 gives band positions and bandwidths.

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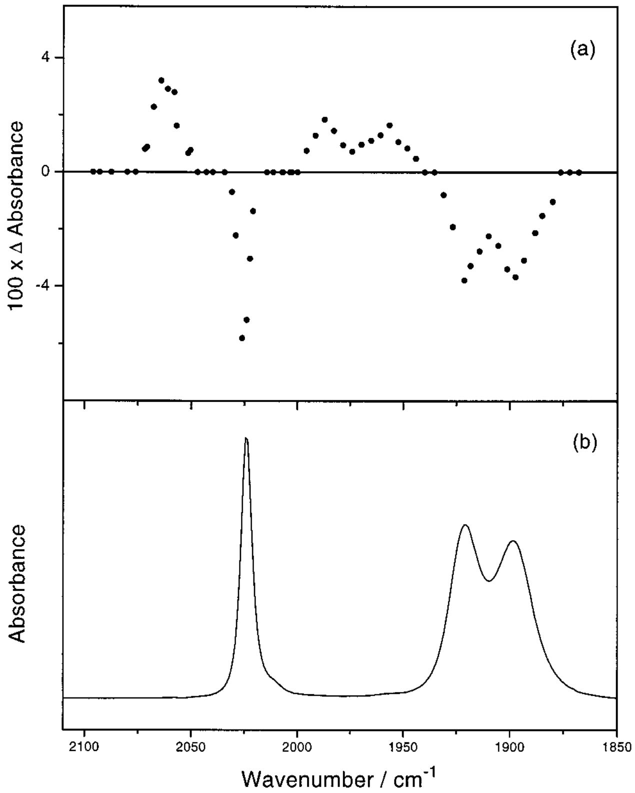

Figure 1. (a) Time-resolved infrared (TRIR) spectrum, recorded ca. 50 ns after 308 nm photolysis, of $ClRe(CO)_3(bpy)$ in CH_2Cl_2. (b) FTIR spectrum of $ClRe(CO)_3(bpy)$ in CH_2Cl_2. The TRIR spectrum shows the loss of parent (negative) and the generation of three (positive) bands of the lowest MLCT state. The shift to high frequency of the excited state bands (ca. 55 cm^{-1}) is due to oxidation of the Re centre [**2**].

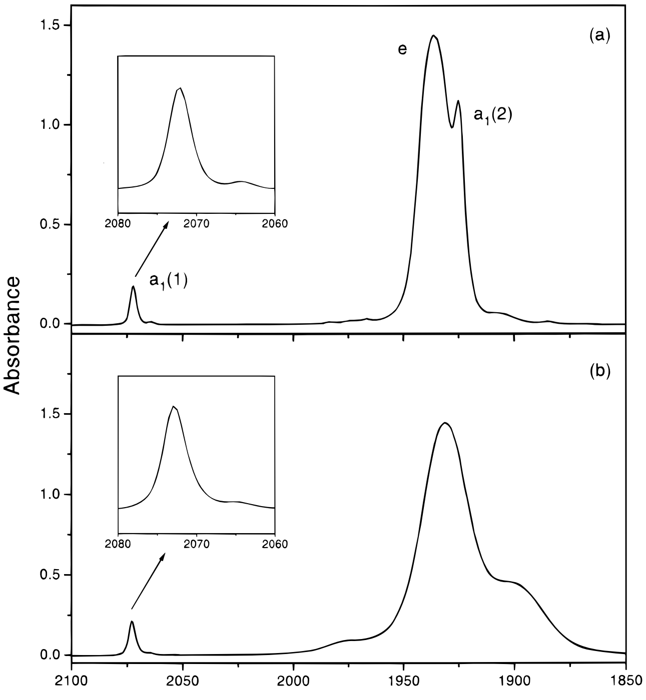

Figure 2. FTIR spectra of $W(CO)_5$(4-AcPyr) in (a) *n*-heptane and (b) CH_2Cl_2. In both (a) and (b) the insets show the high-frequency $a_1(1)$ band on an enlarged scale.

On MLCT excitation, in either *n*-heptane or CH_2Cl_2, the three ν(CO) bands of $W(CO)_5$(4-AcPyr) increase in frequency; the data are in Table 1. This increase is due to decreased back-bonding to the CO groups, as for the MLCT excited state of $ClRe(CO)_3(bpy)$. To illustrate the effect of excitation on the ν(CO) bandwidth, in Figure 3 the excited state spectra in *n*-heptane are plotted on horizontally offset scales. It is apparent that in going from ground to excited state there is only a marginal effect on the bandwidths. However, in CH_2Cl_2 the $a_1(1)$ band of $W(CO)_5$(4-AcPyr) is significantly broadened in the excited state; see Figure 4 and Table 1. The e and $a_1(2)$ bands are also broadened, but because they are broader than the $a_1(1)$ band in the ground state, the effect is not as striking. Clearly the considerable band broadening of ν(CO) bands in the excited state, particularly of the $a_1(1)$ mode, is associated with *polar* solvents. Presumably the cause of this broadening is interaction between the polar solvent molecule and the excited state molecule, which affects the dephasing time of the latter's vibrations. However before considering band broadening in the *excited* state, it is worth commenting on ν(CO) band shapes in the *ground* state.

TABLE 1: Band Positions and Bandwidths of the Ground and MLCT Excited States of $W(CO)_5$(4-AcPyr) in *n*-Heptane and in CH_2Cl_2[e]

solvent	mode	center/ cm^{-1} [a] (GS)	fwhm/ cm^{-1} [a] (GS)	center/ cm^{-1} [b] (ES)	fwhm/ cm^{-1} [b] (ES)	ΔW/ cm^{-1}
n-heptane	$a_1(1)$	2072.1	3.3	2105	5	1.7
	e	1936.1	16	2000	19	3
	$a_1(2)$	1924.5	6	1964	ca. 11[c]	ca. 5
CH_2Cl_2	$a_1(1)$	2072.7	3.6	2114	12	8.4
	e	1931.1	24	ca. 2010[d]	ca. 36[d]	ca. 12
	$a_1(2)$	1899.2	28	ca. 1976[d]	ca. 46[d]	ca. 18

[a] Calculated using the "Curve fit" function contained within Galactic's Grams Research 2000 software. [b] Calculated using a multiple Gaussian fit, a function contained within Microcal's Origin software. [c] Difficult to measure due to overlap with the $W(CO)_5$(*n*-heptane) band. [d] These values taken from Figure 4 are *very* approximate due to the difficulty in fitting the peaks. [e] GS = ground state; ES = excited state; fwhm = full width at half-maximum height; ΔW = fwhm(ES)−fwhm(GS).

Discussion

Metal Carbonyl Infrared Bandwidths—the Ground State. The shape of an infrared band contains detailed information concerning dynamics.[6] The width of the band (fwhm = full width at half-maximum) is governed by the amount of homogeneous and inhomogeneous broadening, which have traditionally been hard to separate. However in recent experiments employing infrared echo measurements, Fayer and colleagues[7] have examined the t_{1u} ν(CO) stretch of $W(CO)_6$ in a variety of solvents. In 3-methylpentane at room temperature, the band (ca. 3 cm^{-1} fwhm) is homogeneously broadened. Direct measurements[8] of excited vibrational state lifetimes show that T_1 relaxation contributes negligibly to the bandwidth of $W(CO)_6$ and many other carbonyls, and thus it has been proved that the t_{1u} bandwidth is determined almost exclusively by pure dephasing. That reorientation makes a small contribution to the ν(CO) bandwidths (e_g in Raman and t_{1u} in IR) is confirmed by NMR ^{17}O relaxation measurements[9] on $W(CO)_6$ in a variety of solvents. Given the narrow width in the ground state of the high-frequency $a_1(1)$ band of $W(CO)_5$(4-AcPyr) in both *n*-heptane and CH_2Cl_2 (Table 1), we suggest that this band is homogeneously broadened by pure dephasing in both solvents, with similar dephasing times and hence similar coupling of the $a_1(1)$ mode to the two solvents. The greater width of the two lower frequency bands (Table 1) makes distinction between dephasing mechanisms more difficult, although it is noticeable that the two bands are considerably broader in CH_2Cl_2 than in *n*-heptane.

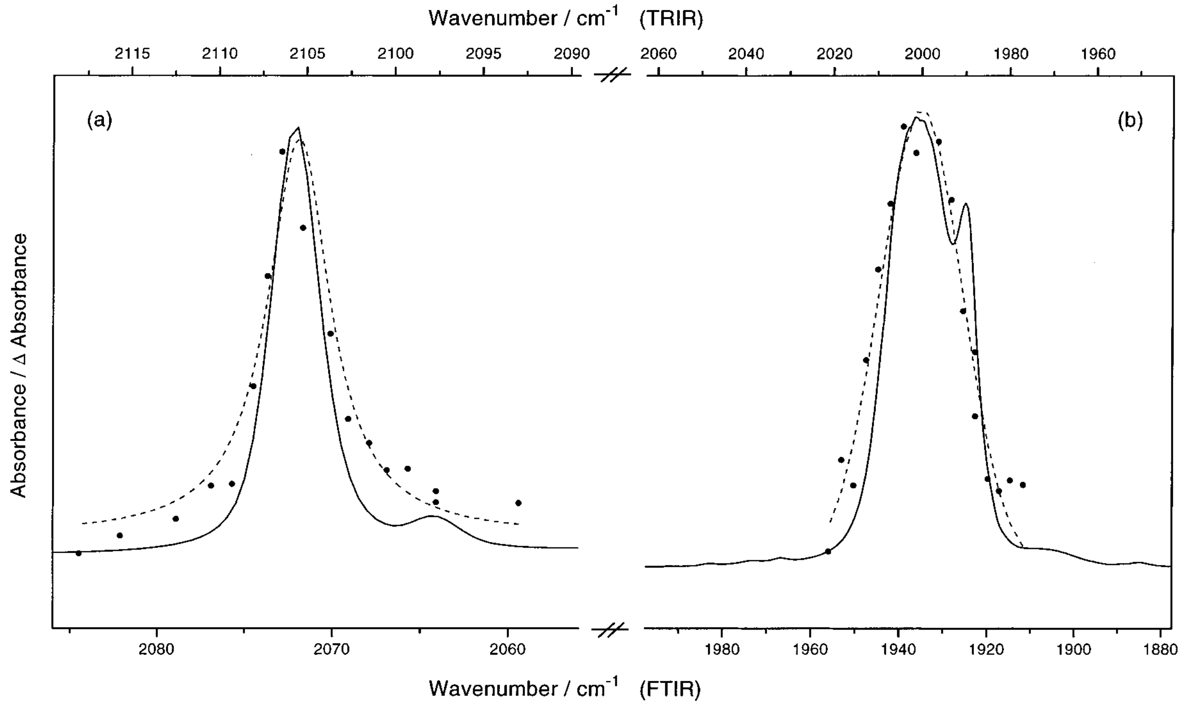

Figure 3. FTIR (—, lower abscissa) and TRIR (●, upper abscissa, recorded 100 ns after 355 nm photolysis) spectra of W(CO)$_5$(4-AcPyr) in *n*-heptane: (a) high-frequency a$_1$(1) band, (b) lower frequency e (FTIR and TRIR) and a$_1$(2) (FTIR only) bands. The dotted lines represent Gaussian fits to the TRIR data. The top and lower abcissa are offset, so that the FTIR and TRIR bands coincide, but are of the same scale. The TRIR spectrum does extend to lower wavenumber to include the excited state a$_1$(2) band (which overlaps the W(CO)$_5$(*n*-heptane) band).

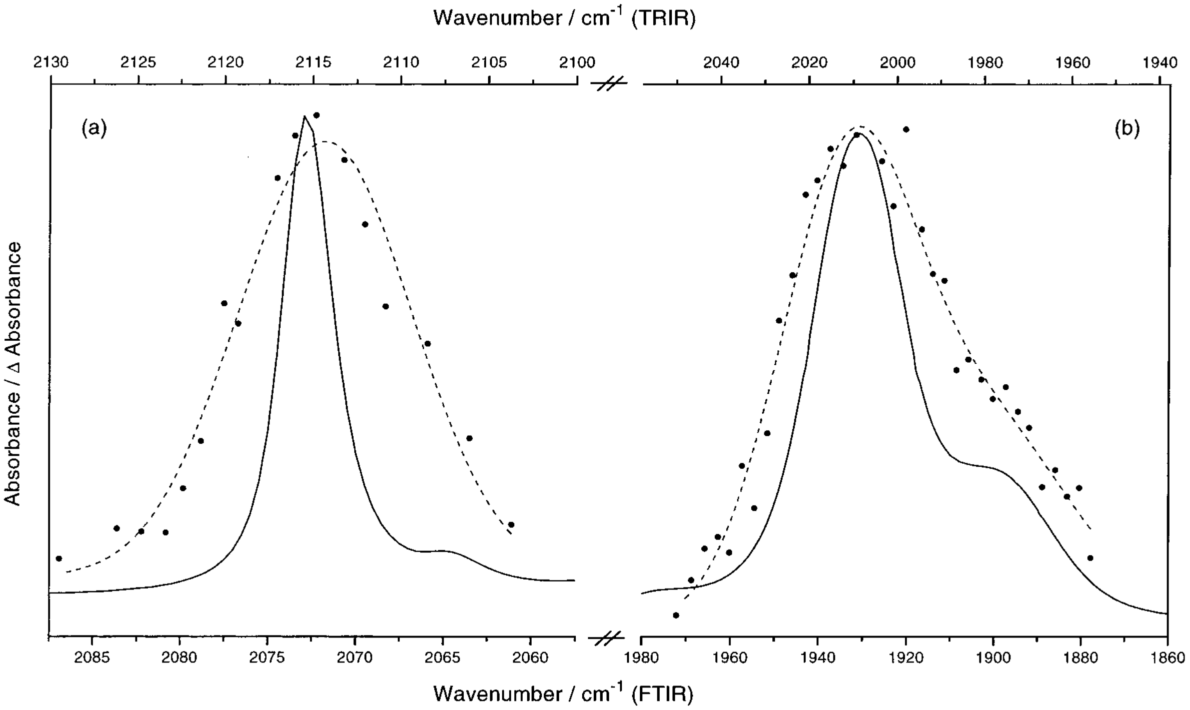

Figure 4. FTIR (—, lower abscissa) and TRIR (●, upper abscissa, recorded 100 ns after 355 nm photolysis) spectra of W(CO)$_5$(4-AcPyr) in CH$_2$Cl$_2$: (a) high-frequency a$_1$(1) band, (b) lower frequency a$_1$(2) and e bands. The dotted lines represent Gaussian fits to the TRIR data. The top and lower abscissa are offset, so that the FTIR and TRIR bands coincide, but are of the same scale (the same scale as in Figure 3).

Metal Carbonyl Infrared Bandwidths—the Excited State. It is worth commenting first on a particularly relevant paper[10] on the picosecond transient Raman spectrum of the excited S$_1$ state of *trans*-stilbene. In the solvents *n*-hexane and acetonitrile, most excited state bands are in similar positions and have similar widths. However the band assigned to the phenyl C=C stretch in *n*-hexane is at 1528 cm^{-1} and has a width of 33 cm^{-1}, whereas in acetonitrile it is at 1544 cm^{-1} with a width of 43 cm^{-1}. The authors note[10] that the two solvents have similar viscosities but very different dielectric constants. Yoshihara et al.[11] described the S$_1$ state as highly delocalized, and on this basis Weaver et al. conclude[10] "A plausible explanation for these observations is that the more polar solvent would tend to localise a greater fraction of the charge density on the phenyl rings. For this reason, the vibrational motions of the rings are anticipated to be more sensitive to the solvent polarity. An increase in the electron density on the rings will tend to increase the phenyl C=C stretching as we observe. The increased band width in acetonitrile is also consistent with this picture, since the stronger coupling to the solvent would result in faster dephasing of the vibrational band. We have observed similar effects for the phenyl C═C band in DMSO".

Since the MLCT state of $W(CO)_5$(4-AcPyr) involves charge delocalization (W to 4-AcPyr), we might expect to observe similar effects. In the more polar solvent CH_2Cl_2, on excitation there is a greater shift to high frequency of the ν(CO) modes, (mean 66 cm^{-1} compared with mean 46 cm^{-1} in *n*-heptane, Table 1), implying greater charge movement from W to 4-AcPyr in this solvent.

Moreover in this solvent, the excited state $a_1(1)$ band is very much broader, even though the bandwidths in the two solvents in the ground state are the same. It is more difficult to interpret the behavior of the lower frequency bands, but certainly the change from ground to excited state is greater in the more polar solvent. We thus conclude that in the MLCT excited state of $W(CO)_5$(4-AcPyr), in the more polar solvent, there is faster dephasing of the ν(CO) bands and hence greater coupling of these modes to the solvent.

If this is the correct explanation, then non-charge-transfer excited states (e.g. $\pi\pi^*$) should not experience broadening of the ν(CO) bands. The lowest excited state of $ClRe(CO)_3$(dppz) (dppz = dipyrido[3,2-*a*:2,2′-*c*]phenazine) is $\pi\pi^*$.[12] On excitation in CH_2Cl_2 the ν(CO) bands of $ClRe(CO)_3$(dppz) show a slight shift to lower frequency, although overlap between the a″ and a′(2) ground and excited state bands makes analysis of these excited state bands impossible; the bandwidth of the high frequency a′(1) excited state band can be determined and is very similar to that of the ground state band. Published spectra of the $\pi\pi^*$ excited state of $[Re(dppz)(CO)_3(PPh_3)]^+$ show similar effects,[13] and the ν(CO) bands broaden by only 2 cm^{-1} in CH_3CN.

Conclusion

Upon excitation of $W(CO)_5$(4-AcPyr) (or $ClRe(CO)_3$(bpy) and other molecules with similar MLCT excited states), the charge separation promotes coupling between the excited molecules and the polar solvent molecules, leading to faster dephasing and broader infrared bands. The much reduced broadening of the excited state bands of $W(CO)_5$(4-AcPyr) in *n*-heptane is due to the fact that the solvent is nonpolar, i.e., reduced solvent−solute coupling. Similarly, the lack of charge separation for $\pi\pi^*$ excited states leads to unbroadened excited ν(CO) bands. Thus the width of the ν(CO) bands in the excited states of CO-containing transition metal species is a direct probe of the nature of the excited states.

Experimental Section

$W(CO)_5$(4-AcPyr) was prepared using conventional literature procedures.[14] All solvents (Aldrich, HPLC grade) were dried over CaH_2, degassed, and purged with argon before use.

FTIR spectra were recorded using a Perkin Elmer System 2000 FTIR spectrometer (0.5 cm^{-1} resolution). The TRIR spectra were recorded using a Nd:YAG laser (Quanta-Ray GCR-11, 355 nm, 7 ns pulse) to excite the molecules, while the infrared absorbance was monitored with a Mütek diode laser (Model MDS 1100, fitted with a MDS 1200 monochromator) using a MCT detector (rise time ca. 50 ns, Laser Monitoring Systems S-100). Signals were digitized using a transient storage oscilloscope (Gould 4084). The TRIR apparatus is described in greater detail elsewhere.[5] Spectra were built up in a "point-by-point" manner and show the change in absorbance upon excitation. It should be noted that photolysis, leading to loss of 4-AcPyr, follows excitation, but this photolysis is on a longer time scale and does not interfere with observations on the excited state.[4]

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