3246 *Inorg. Chem.* **1994,** *33,* 3246–3250

Structural Investigation of the Ground and Excited States of $ClRe(CO)_3(4,4'\text{-bipyridyl})_2$ Using Vibrational Spectroscopy

Daniel R. Gamelin,[‡,§] Michael W. George,[†] Paul Glyn,[†] Friedrich-Wilhelm Grevels,[*,‡] Frank P. A. Johnson,[†] Werner Klotzbücher,[‡] Sara L. Morrison,[†] Graham Russell,[‡] Kurt Schaffner,[‡] and James J. Turner[*,†]

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K., and
Max-Planck-Institut für Strahlenchemie, Postfach 101365, D-45413, Mülheim an der Ruhr, Germany

Received July 18, 1993[®]

Fast time-resolved infrared spectroscopy (TRIR) is used to probe the ν(CO) spectrum of $ClRe(CO)_3(4,4'\text{-bipyridyl})_2$ in the lowest MLCT (metal-to-ligand charge transfer) excited state. The three ground-state ν(CO) bands all shift up in frequency, but not by the same amount. The energy-factored force field (EFFF) of the ground state is accurately solved by employing ^{13}CO-enrichment. Approximate methods yield information on the force field of the excited state; the principal EFFF force constants ($k_{CO(axial)}$ and $k_{CO(equatorial)}$) change by the same amount on excitation. This leads to a new interpretation of the resonance Raman spectrum of the compound.

Introduction

An understanding of the photochemistry of transition metal compounds requires a knowledge of the properties of the appropriate excited states.[1] Spectroscopic studies based on a molecule in its ground state, such as low-temperature UV/visible absorption spectroscopy,[2] the excitation profile of resonance Raman spectra,[3] or preresonance Raman intensities employing the Heller formalism,[4,5] can provide very detailed information. However such methods have limitations, particularly in that it is extremely difficult to obtain data for the photoactive state, and there are advantages in obtaining spectroscopic data for the molecule in its appropriate excited state.[6] Apart from straight emission data which, although excellent for lifetime studies, are of limited value for structural studies, the most popular technique has been time-resolved resonance Raman (TR^3) spectroscopy. Classic experiments have probed the structure of the excited states of a range of ruthenium complexes, and have shown, for instance, that in the lowest excited state of $[Ru(bpy)_3]^{2+}$ there is charge transfer from Ru to one of the bpy groups.[7] Detailed isotopic studies[8] have unravelled the details of the excited state structure. There is, however, a limitation of resonance Raman spectroscopy: only certain of the vibrational modes in the excited state will be resonance enhanced, partly because of the nature of the excitation, and partly because of the selection rules which will usually only permit the enhancement of totally symmetric modes. There is thus a persuasive argument for expanding the spectroscopic measurements to the infrared.

Since the first demonstration[9] of the application of time-resolved infrared spectroscopy (TRIR) to the excited states of transition metal species, a few other studies have been reported.[10] These have involved the ν(CO) or ν(CN) vibrations of complexes and have provided information on charge distribution,[11a,b] on rates of electron transfer,[11c] and on the complete course of photochemical processes from ground state to final products.[12]

In the original study[9] of $ClRe(CO)_3(4,4'\text{-bpy})_2$, the IR source was a CO laser, which limited the spectral range to IR bands below about 2010 cm^{-1}. This meant that it was not possible to obtain the complete excited state spectrum, in particular the high-frequency band, and hence it was not possible to evaluate the force field parameters. Because of the importance of this, and related molecules, in approaches to CO_2 reduction,[13] we have carried out more detailed spectroscopic studies and these are reported here.

Experimental Section

Materials. *fac*-$ClRe(CO)_3(4,4'\text{-bipyridyl})_2$, **1**, was synthesized by literature methods,[14] according to the following scheme:

$$ClRe(CO)_5 + \text{excess } 4,4'\text{-bpy} \underset{\text{iso-octane}}{\overset{60\ ^\circ C}{\rightarrow}} \underset{\mathbf{1}}{ClRe(CO)_3(4,4'\text{-bpy})_2}$$

Introduction of ^{13}CO ligands was attempted by irradiation of the parent

---

[†] University of Nottingham.

[‡] Max-Planck-Institut, Mülheim.

[§] Present address: Department of Chemistry, Stanford University, Stanford, CA 94305.

[®] Abstract published in *Advance ACS Abstracts*, June 1, 1994.

(1) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970. Adamson, A. W., Fleischauer, P. D., Eds.; *Concepts of Inorganic Photochemistry*, Wiley: New York, 1975.

(2) E.g. Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

(3) Clark, R. J. H.; Dines, T. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 131.

(4) (a) Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822. (b) Tannor, D.; Heller, E. J. *J. Chem. Phys.* **1982**, *77*, 202. (c) Lee, S. Y.; Heller, E. J. *J. Chem. Phys.* **1977**, *71*, 4777. (d) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368.

(5) Zink, J. I.; Shin, K.-S. K. *Adv. Photochem.* **1991**, *16*, 119.

(6) Turner, J. J. In *Photoprocesses in Transition Metal Complexes, Biosystems and Other Molecules, NATO ASI Series*; Kochanski, E., Ed.; Kluwer: Dordrecht, 1992; p 113.

(7) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.

(8) (a) Strommen, D. P.; Mallick, P. K.; Danzer, G. D.; Lumpkin, R. S., Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 1357. (b) Mallick, P. K.; Strommen, D. P.; Kincaid, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1686. (c) Danzer, G. D.; Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 3976.

(9) Glyn, P.; George, M. W.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1655.

(10) Turner, J. J.; George, M. W.; Johnson, F. P. A.; Westwell, J. R. *Coord. Chem. Rev.* **1993**, *125*, 101.

(11) (a) Doorn, S. K.; Gordon, K. C.; Dyer, R. B.; Woodruff, W. H. *Inorg. Chem.* **1992**, *31*, 2284. (b) Bignozzi, C. A.; Argazzi, R.; Schoonover, R. R.; Gordon, K. C.; Dyer, R. B.; Scandola, F. *Inorg. Chem.* **1992**, *31*, 5260. (c) Doorn, S. K.; Stoutland, P. O.; Dyer, R. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1992**, *114*, 3133.

(12) (a) Glyn, P.; Johnson, F. P. A.; George, M. W.; Lees, A. J.; Turner, J. J. *Inorg. Chem.* **1991**, *30*, 3543. (b) Johnson, F. P. A.; George, M. W.; Turner, J. J. *Inorg. Chem.* **1993**, *32*, 4226.

(13) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. Kutal, C.; Corbin, A. J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553. Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. Pac, C.; Ishii, K.; Yanagida, S. *Chem. Lett.* **1989**, 765.

(14) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.

0020-1669/94/1333-3246$04.50/0

compound under a ^{13}CO atmosphere, but no carbonyl substitution was detectable. This demonstrates the photostability of **1**. More successful was thermally induced ^{13}CO-enrichment of the $ClRe(CO)_5$ starting material at 70 °C (yielding two samples with 35% and 73% ^{13}CO-enrichment, respectively, and statistical distribution as determined by MS analysis), followed by reaction with the bpy ligand as above. The solvent CH_2Cl_2 (Aldrich) was distilled over CaH_2 before use.

Spectroscopic Measurements. FTIR spectra were recorded on either a Nicolet MX-3600, with 32K data points giving ~2-cm^{-1} resolution, or a Perkin-Elmer 1620 with ~0.5-cm^{-1} resolution. The TRIR apparatus at Nottingham[15] uses a pulsed excimer laser (Lumonics HyperEX 440; 308 nm; ~100 mJ per pulse; ~20 ns pulse half-width). The changes in IR absorption are monitored by either a CW CO infrared laser (modified Edinburgh Instruments PL3) which is tunable in steps of ~4 cm^{-1}, or an infrared diode laser (Mütek MDS1100) fitted with a monochromator (Mütek MDS 1200) and custom-built Mütek "Experimental" module. With a photoconductive 77K detector (Infrared Associates MCT-70), used with the diode laser system, the time-resolution is ~300 ns, and with a photovoltaic 77 K detector (Laser Monitoring Systems S-0025), used with the CO laser, the resolution is ~30 ns.

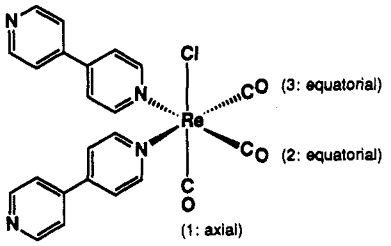
The TRIR apparatus at Mülheim[16] uses a pulsed excimer laser (Lambda Physik EMG 200; 308 nm with XeCl; 15–20 ns pulse half-width; maximum output 400 mJ per pulse, routinely attenuated to 80 mJ per pulse) as the excitation source and a globar or an appropriate infrared diode laser (Spectra Physics) as the monitoring source. In either case photoconductive HgCdTe detectors (77 K) with rise times of 50–70 ns are used for IR detection. The configuration with the globar IR source requires 14000× amplification and has a system response time of 1.5–2 μs, whereas with the IR diode laser in combination with 600× amplification a system response time of 250–400 ns is achieved.

In both the Nottingham and Mülheim systems, IR spectra are built up "point-by-point" by repeating the excimer flash photolysis with the IR source tuned to a different frequency. Note that the spectra are difference spectra; i.e., they compare the intensity of IR bands before and after the flash.

The resonance Raman spectrum was obtained using the 413-nm line of a CW Kr^+ laser. Raman scattering was detected by a photo diode array system (Spectroscopy Instruments) connected to a spectrograph (Spex 1877). Further details of the resonance Raman instrumentation are reported elsewhere.[17]

Results and Discussion

Infrared Spectra of $ClRe(CO)_3(4,4'\text{-bipyridyl})_2$, 1, in Ground and Excited States. Figure 1a shows the ν(CO) IR spectrum of **1** in CH_2Cl_2 solution recorded on a conventional FTIR instrument.



1

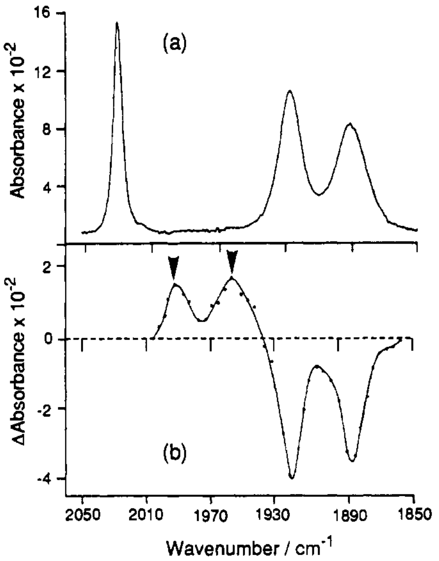


Figure 1. (a) FTIR spectrum (Nicolet instrument), in the ν(CO) region, of $ClRe(CO)_3(4,4'\text{-bpy})_2$, **1**, in CH_2Cl_2 solution (~5×10^{-5} M; pathlength 7 mm). (b) TRIR spectrum of the same solution, degassed under Ar, obtained 240 ns after the excimer laser flash at 308 nm. Each point corresponds to a different line of the CO laser; data points below the dotted horizontal represent depletion of the ground state and those above represent generation of the excited state. The arrows mark the maxima of the bands assigned to the MLCT excited state of **1**. Reproduced with permission from ref 9. Copyright 1989 Royal Society of Chemistry.

Table 1. Observed Frequencies in cm^{-1}, (Fwhm in cm^{-1}; Relative Intensities [Fwhm × peak O.D.]) of the ν(CO) Bands of the Ground and Excited States of $ClRe(CO)_3(4,4'\text{-bipy})_2$ (**1**) in CH_2Cl_2

ground state		excited state
FTIR	TRIR	TRIR
2027.3 (6.5; 1.00)	2025 (8.7; 1.0)	2055 (~25; ~4)
1925.9 (16.2; 1.67)	1927 (14.9; 1.7)	1992 (~26; ~1)
1890.7 (22.3; 1.75)	1891 (22.3; 2.1)	1957 (~25; ~1)

As expected for a tricarbonyl with C_s symmetry there are three ν(CO) IR bands. Figure 1b shows the TRIR spectrum obtained "point-by-point" with a CO laser, 240 ns after the excimer laser flash.[9] It is clear that the ground state is depleted and a new transient is produced with ν(CO) bands at 1957 and 1992 cm^{-1}; i.e., it appears that the low-frequency pair of bands have each moved up in frequency by 66 cm^{-1} (see Table 1). However due to the limited range of the monitoring IR radiation of the CO laser it was not possible to observe the high-frequency band of the ground state, and any excited-state band above ~2010 cm^{-1} (see Figure 1b). Although there is strong evidence for an increase in ν(CO) frequency in the excited state, the absence of the expected third band prevents a complete analysis. Experiments in Nottingham and Mülheim have now resolved this problem.

Figure 2a shows the whole of the ν(CO) range recorded using a globar source rather than a CO laser; parts b and c of Figure 2 show the higher frequency region recorded with diode lasers in both Nottingham and Mülheim. A number of conclusions can be drawn from these and the earlier data. As expected, the high frequency parent band is depleted, and a new band appears at 2055 cm^{-1}. This band has only shifted up ~30 cm^{-1} relative to the ground state; i.e., the three bands do not shift up in frequency by the same amount, and the interpretation of the infrared spectrum of the excited state is not straightforward and requires a force field analysis.

The Energy factored CO force field (EFFF) has proved very successful in providing information on the structure—both geometric and electronic—of transition metal carbonyls.[18] Thus, ideally, having obtained the ν(CO) data in both ground and excited states, for maximum information we should obtain the complete EFFF for **1** in both ground and excited states. However **1** has **four** EFFF force constants, the two principal constants k_{ax} and k_{eq}, and the two interaction constants, k_{axeq} and k_{eqeq}, but exhibits

---

(15) Dixon, A. J.; Healy, M. A.; Hodges, P. M.; Moore, B. D.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; West, M. A. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2083; George, M. W. Ph.D. Thesis, University of Nottingham, 1990. Dixon, A. J.; George, M. W.; Hughes, C.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1992**, *114*, 1719. George, M. W.; Poliakoff, M.; Turner, J. J. *Analyst* **1994**, *119*, 551.

(16) Schaffner, K.; Grevels, F.-W. *J. Mol. Struct.* **1988**, *173*, 51.

(17) Hildenbrandt, P.; Griebenow, K.; Holzwarth, A. R.; Schaffner, K. *Z. Naturforsch. C* **1991**, *46*, 228.

(18) (a) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975. (c) Burdett, J. K.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *Inorg. Chem.* **1978**, *17*, 948.

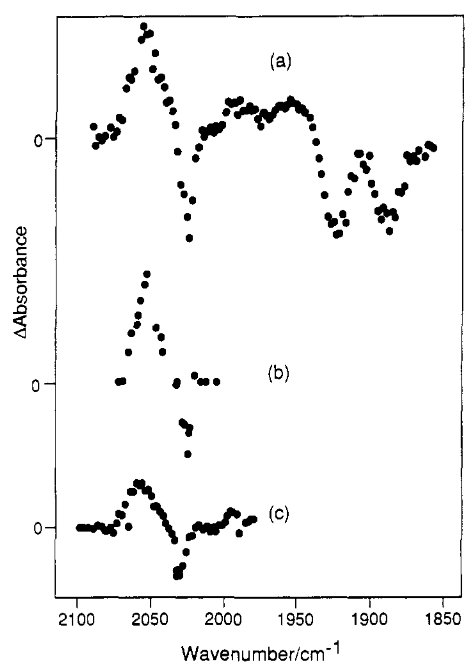


Figure 2. TRIR spectra of **1** in CH_2Cl_2 recorded with (a) the globar source in Mülheim and the diode lasers in (b) Nottingham and (c) Mülheim. Data points below the mean indicate depletion of the ground state and those above indicate generation of the excited state.

only **three** frequencies. Hence isotopic substitution is necessary or approximate methods have to be applied.

The EFFF of ClRe(CO)$_3$(4,4′-bipyridyl)$_2$, 1, in the Ground State. Complex **1** is not soluble in nonpolar solvents and in CH_2Cl_2 the two low-frequency ν(CO) IR bands are unfavorably broad. Fortunately the crucial isotopic information comes from the in-phase vibrational modes of the various isotopomers which derive from the narrower high-frequency band of the unsubstituted parent compound, and these bands are sufficiently well separated to solve the complete force field. Figure 3 shows the ν(CO) spectral region of **1** at natural abundance of ^{13}CO and both low and high ^{13}CO-enrichment. Table 2 lists the observed and calculated frequencies based on an EFFF with the force constants listed; the calculated normal coordinates for the unsubstituted molecule are also listed in Table 2. Particularly important is the observation of the high-frequency bands of all six isotopomeric molecules. The intensity pattern among these bands allows for an unambiguous assignment of the bands associated with the two monolabeled (eq, ax) and the two bislabeled (eqax, eqeq) isotopomers, which in the case of statistical distribution of ^{13}CO groups should be present in 2:1 ratio. Moreover, this information, together with the frequency pattern, immediately demonstrates that k_{eq} is larger than k_{ax}, as is confirmed by the exactly calculated force field data (Table 2). This has two interesting implications. First, the a″ ν(CO) band is in the **middle** (ie a′ > a″ > a′), whereas in most facial C_s tricarbonyl metal complexes it is the band at **lowest** frequency (ie a′ > a′ >a″); there has in fact been previous disagreement about the assignment of the ν(CO) bands in this type of molecule.[19] Second, the normal coordinate of the high-frequency vibration has a larger contribution from the equatorial CO groups than from the axial CO, in contrast to previous deductions from the resonance Raman spectra for closely related molecules.[20]

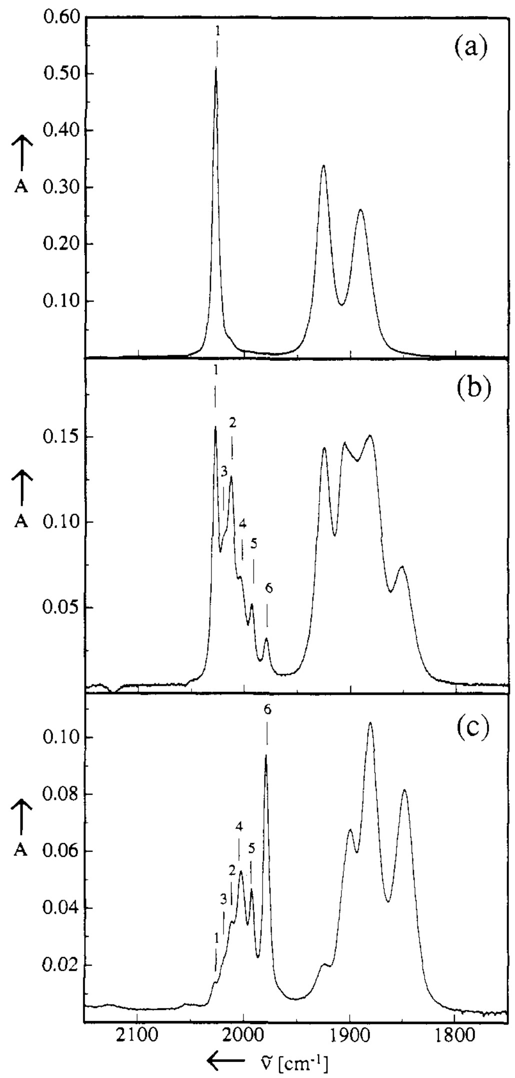


Figure 3. FTIR spectra (Perkin-Elmer instrument) in the ν(CO) region of **1** in CH_2Cl_2: (a) natural abundance of ^{13}CO; (b) low (35%) ^{13}CO enrichment; (c) high (73%) ^{13}CO enrichment. For the numbering of the various isotopomeric molecules see Table 2.

In contrast to the well-resolved isotopic pattern of the ground state molecule (Figure 3) the spectral resolution in the transient spectra of the ^{13}CO-enriched samples is insufficient to allow a reliable positioning and assignment of the excited state bands. In consequence of this we have to introduce appropriate approximations, the reliability of which will be demonstrated in the following for the case of the ground-state spectrum. Since the three CO groups are oriented perpendicular to each other, a simple approximation (originally introduced by Cotton and Kraihanzel[18a]) would be to assume $k_{axeq} = k_{eqeq} = k_i$ (which, judged by comparison with the exact solution, see Table 2, is clearly a good approximation). The remaining set of three force constants can be determined from the three observed frequencies. However the solution depends on the assignment, ie whether a′(1) > a″ > a′(2) (assignment A) or a′(1) > a′(2) > a″ (assignment B). With the two assignments the results (in Nm^{-1}) are as follows:

$$\text{A: } k_{ax} = 1486;\ k_{eq} = 1558;\ k_i = 60$$

$$\text{B: } k_{ax} = 1600;\ k_{eq} = 1500;\ k_i = 56$$

Clearly by comparison with the exact solution assignment B is eliminated, (and assignment A is listed in Table 2).

The EFFF of ClRe(CO)$_3$(4,4′-bipyridyl)$_2$, 1, in the Excited State. As stated above the ^{13}CO isotopic ν(CO) bands in the

---

(19) Wuyts, L. F.; van der Kelen, G. P. *Inorg. Chim. Acta* **1977**, *23*, 19. Brisdon, B. J.; Edwards, D. A.; White, J. *J. Organomet. Chem.* **1978**, *156*, 427. Staal, L. H.; Oskam, A.; Vrieze, K. *J. Organomet. Chem.* **1979**, *170*, 235.

(20) Balk, R. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1124.

Table 2. Experimental and Calculated ^{13}CO Isotopic Spectral Data (cm^{-1}), EFFF Force Constants (N m^{-1}), and Normal Coordinates of ClRe(CO)$_3$(4,4′-bpy)$_2$ (**1**) in CH$_2$Cl$_2$ Solution

molecule[a]	exptl	calcd[b]	
unsubst	2027.3	2027.0	a′(1)
(1)	1925.9	1925.9	a″
	1890.7	1890.7	a′(2)
mono eq	2012.3	2012.6	
(2)		1906.2	
		1878.0	
mono ax	~2019	2018.6	
(3)		1925.9	
		1853.4	
di eq–ax	2002.6	2002.7	
(4)		1900.0	
		1848.4	
di eq–eq	1992.8	1992.8	
(5)		1880.0	
		1877.3	
tri subst	1978.9	1978.7	
(6)		1880.0	
		1845.7	

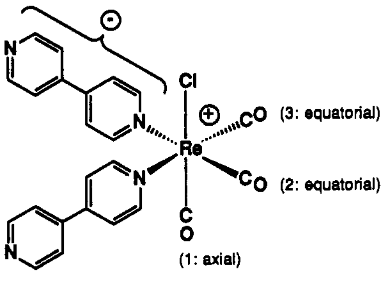
	EFFF based on ^{13}CO bands, producing the calcd spectrum above	EFFF, assuming the two interaction constants equal
k_{ax}	1492.1	1486
k_{eq}	1555.1	1558
k_{axeq}	63.4	60
k_{eqeq}	56.7	60

Normal Coordinates[b] from ^{13}CO-Based EFFF

$$Q_{a'}(1) = 0.4717\ r_1 + 0.6235\ r_2 + 0.6235\ r_3$$
$$Q_{a''} = 0.7071\ r_2 - 0.7071\ r_3$$
$$Q_{a'}(2) = 0.8818\ r_1 - 0.3335\ r_2 - 0.3335\ r_3$$

[a] Refers to degree (un-, mono-, di-, tri-) and position (eq = equatorial, ax = axial: see **1**) of ^{13}CO substitution. [b] r_1, r_2, r_3 refer to CO$_{ax}$ and the two CO$_{eq}$ internal coordinates.

excited state show an unresolved pattern, which thus prevents an exact solution of the force field. We expect that, in the charge-separated excited state of **1**, there will be positive charge on the Re and negative charge on **one** of the 4,4′-bipyridyl ligands, as shown (**1***):



1*

This is also consistent with the early emission studies[14] on this molecule. In principle this lowers the vibrational symmetry of the excited state from the ground state, and the EFFF requires 6 force constants, k_1, k_2, and k_3 plus k_{12}, k_{13}, and k_{23}. At first sight this makes the problem worse. However, very recent experiments[21] on ClRe(CO)$_3$(2,2′-bpy), which must have C_s symmetry in the excited state, show similar ground-to-excited state shifts in the ν(CO) bands. If we assume $k_2 = k_3$ and $k_{12} = k_{13} = k_{23}$, the force field can be solved and the force constants are given in Table 3. The substantial shifts of the ν(CO) bands to higher frequencies in going from the ground to the excited state arise because the CO groups are now seeing a Re atom with an oxidation state increased by approximately one.

Table 3. Summary of ν(CO) Frequencies (cm^{-1}), EFFF Force Constants (N m^{-1}) for Ground and Excited states of **1**, and Change in C–O Bond Lengths (Å)

frequencies			EFFF force constants					
ground	excited	Δ		ground		excited	Δ[d]	Δr_{CO}
2027	2055	+28	k_{ax}	1492[a]	1486[b]	1566[c]	~+80	~–0.010
1926	1992	+66	k_{eq}	1555	1558	1644	~+86	~–0.010
1891	1957	+66	k_{axeq}	63	60	40	~–20	
			k_{eqeq}	57	60	40		

[a] Based on ^{13}CO data (see Table 1). [b] Assuming interaction constants equal (see Table 1). [c] Assuming C_s symmetry and interaction constants equal. [d] Differences for assumption of equal interaction constants in both cases; corresponding principal force constant values[21] for ClRe(CO)$_3$(2,2′-bipyridyl)$_2$ are ~+85 N m^{-1}.

The data presented in Table 3 lead to some rather interesting conclusions. Although the two principal force constants increase by the same amount, there is no uniformity in increase in frequency. The reason is that the interaction force constant decreases; this is expected on the basis of Timney's equations;[22] i.e., as the principal force constants increase, the interaction constant decreases. Having concluded that both k_{ax} and k_{eq} increase by the same amount, we can use these changes to estimate the structural changes in the excited state. There have been many studies relating frequencies or force constants to bond lengths.[8b,11a,23–27] We have examined a wide range of metal carbonyls by comparing C–O bond lengths, determined crystallography, with EFFF C–O force constants. A wide variety of molecules fits the relationship[28]

$$r_{CO} = 1.647 - 0.184\ \ln(k_{CO})\ (r_{CO} \text{ in Å};\ k_{CO} \text{ in N m}^{-1})$$

This relationship will be particularly valuable when used to calculate changes in bond length in the same molecule on electronic excitation. Table 3 includes the estimate of the decrease in r_{CO} from the ground state to the excited state, which, to a good level of approximation, is the same for axial and equatorial CO groups. This conclusion is particularly important in understanding the resonance Raman (RR) spectra of **1** and similar molecules.

The Resonance Raman Spectrum of ClRe(CO)$_3$(4,4′-bpy)$_2$. Diimine complexes of the type ClRe(CO)$_3$(diimine), including ClRe(CO)$_3$(2,2′-bipyridyl), display RR spectra where the only resonance-enhanced ν(CO) band is the high-frequency symmetric mode.[20] A proposed explanation[20] is that this resonance-enhanced band is a stretching mode of the CO ligand *trans* to the halogen (i.e. corresponding to the axial CO in **1**); through-space interaction between this CO and the diimine ligands causes the resonance enhancement. However the infrared spectra of ClRe(CO)$_3$(4,4′-bpy)$_2$ (**1**) and ClRe(CO)$_3$(2,2′-bpy) are almost identical, and we have shown above that the ν(CO) bands of **1** arise from strongly coupled modes and that the normal coordinate of the highest frequency vibration contains a larger contribution from the equatorial CO group than from the axial CO group. To make a more direct comparison, we have recorded the RR spectrum of **1**, a part of which is shown in Figure 4. The only resonance-enhanced ν(CO) mode is again the highest band, i.e. a′(1). We believe that the correct explanation for this is as follows.

---

(21) George, M. W.; Johnson, F. P. A.; Turner, J. J.; Westwell, J. R. *J. Chem. Soc., Dalton Trans.* **1993**, 2977.

(22) Timney, J. A. *Inorg. Chem.* **1979**, *18*, 2502.

(23) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128; *Phys. Rev.* **1935**, *48*, 284.

(24) Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1961**, *35*, 458.

(25) Miskowski, V. M.; Dallinger, R. F.; Christoph, G. C.; Morris, D. E.; Spies, G. H.; Woodruff, W. H. *Inorg. Chem.* **1987**, *26*, 2127.

(26) Conradson, S. D.; Sattelberger, A. P.; Woodruff, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 1309.

(27) Mallick, P. K.; Danzer, G. D.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1988**, *92*, 5628.

(28) Morrison, S. L.; Turner, J. J. *J. Mol. Struct.* **1994**, *317*, 39.

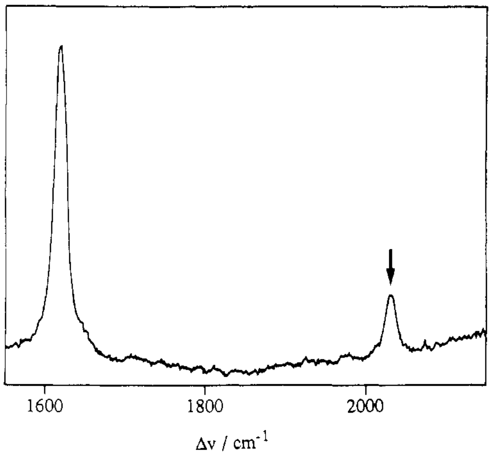


Figure 4. Part of the resonance Raman spectrum of **1**, taken to illustrate the observation of only one band in the ν(CO) region of the spectrum. The ν(CO) band is marked with an arrow. (The strong band near 1620 cm^{-1} is assigned as a C=C stretching vibration of the 4,4′-bpy ligand.)

The ratio of the intensities of two RR bands (strictly speaking this applies to spectra obtained under **pre**resonance conditions), is given by[4,29]

$$I_1/I_2 = (\omega_{1e}{}^3\Delta_1{}^2\omega_{2g})/(\omega_{2e}{}^3\Delta_2{}^2\omega_{1g}),$$

where ω_{1g}, ω_{2g}, ω_{1e}, and ω_{2e}, are the radial frequencies of modes 1 and 2 in the ground and excited states, and Δ_1 and Δ_2 are the distortions in going from ground to excited state along normal coordinates 1 and 2. [In most applications[5] this equation is simplified to $I_1/I_2 = (\omega_{1g}\Delta_1/\omega_{2g}\Delta_2)^2$, since the excited state frequencies are not known; usually, as in the present case, this makes only a small difference.] Strictly speaking, this refers to the state initially excited, which will be the **singlet** MLCT state, whereas the TRIR experiments refer to the **triplet** state. However the differences are unlikely to be significant. We have shown above that, on promotion to the excited state, each of the r_{CO} internal coordinates is distorted by nearly the same value, e.g. "d", so that on the basis of the normal coordinates given in Table 2, the distortions occurring upon promotion in the MLCT excited state are estimated as follows:

$$\Delta[a'(1)] = +0.4717d + 0.6235d + 0.6235d = 1.7187d$$

$$\Delta[a''] = +0.7071d - 0.7071d = 0$$

$$\Delta[a'(2)] = +0.8818d - 0.3335d - 0.3335d = 0.2148d$$

Therefore, as expected, the RR intensity of the out-of-phase a″ mode is zero, and the ratio of the intensities of the two a′ modes is

$$I[a'(1)]/I[a'(2)] = (2055^3 \times 1.719^2 \times 1891)/(1957^3 \times 0.215^2 \times 2027) \sim 66/1$$

Thus, under conditions where the high-frequency band is observed in the RR, the intensity of the lowest frequency band will usually be too weak for detection. It is likely that the same argument applies to the closely related molecule $ClRe(CO)_3(2,2'\text{-bpy})$. Moreover it also seems likely that a similar explanation applies to complexes of general formula $M(CO)_4$(diimine) (M = Cr, Mo, W), which also show resonance-enhancement of only the highest frequency, symmetric ν(CO) mode.[30] A complete explanation will require the solution of the ground-state EFFF, and, via TRIR, the measurement of the distortions of the C–O groups on excitation.

Conclusions

We have shown that time-resolved infrared spectroscopy can probe the MLCT excited state of a transition metal complex, and from the energy factored force field of both the ground state and the excited state, a new interpretation of the resonance Raman enhancement of only one CO stretching vibration of this and related species is proposed.

Acknowledgment. We thank the Science and Engineering Research Council, the Paul Instrument Fund of the Royal Society, Edinburgh Instruments, Mütek GmbH, the DAAD, and the EEC Science Programme (SCIENCE Contract ST 007) for financial support. We thank Dr. P. Hildebrandt for this support in recording the RR spectrum and Miss D. Pagirnus for skilled technical assistance and acknowledge useful discussions with Dr. J. A. Timney, Dr. K. Smit, and Dr. F. Mark.

---

(29) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 4704.

(30) Stufkens, D. J. *Coord. Chem. Rev.* **1990**, *104*, 39, and references therein.