

The Structure of $W(CO)_5L$ ($L = \text{pyridine, piperidine}$) in the Lowest Ligand Field Excited State determined by Fast Time-resolved IR Spectroscopy; Unexpected C–O Bond Length Changes

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The frequencies of the $\nu(CO)$ bands of $W(CO)_5L$ ($L = \text{pyridine and piperidine}$) in the lowest ligand field (LF) excited states have been obtained by fast time-resolved IR spectroscopy of the species dissolved in low-temperature glasses, and the shifts from the ground state indicate that the C–O bonds lengthen on excitation, contrary to the interpretation of the pre-resonance Raman spectroscopy on the ground state.

There has been extensive study of the excited state and photochemical properties of the complexes of general formula $M(CO)_5L$, where $M = \text{Cr, Mo or W}$, and L is a nitrogen donor ligand.^{1–6} It is generally agreed that for $W(CO)_5L$, if L is pyridine **1** or piperidine **2**, then the lowest excited state is ligand field (LF) in character ($^1A_1 \rightarrow ^3E$; weak absorption *ca.* 442 nm for both **1** and **2**), too short-lived to be measured at room temperature but with a lifetime, based on emission studies, quoted as: 2.5 **1** and 3.1 **2** μs in MCH (methyl cyclohexane) at 77 K;¹ 0.86 **1** and 0.82 **2** μs in EPA at 77 K;² 3.4 **1** μs in argon at 12 K.³ In LF terms this 3E state is best described by eqn. (1),⁴

$$\Phi_E = \frac{1}{(1 + \lambda^2)^{1/2}} \left\{ \left(\frac{\sqrt{3} + \lambda}{2} \right) [d_{xy}^2 d_{xz}^2 d_{yz}^1 d_{z^2}^1] + \left(\frac{1 - \sqrt{3}\lambda}{2} \right) [d_{xy}^2 d_{xz}^2 d_{yz}^1 d_{x^2-y^2}^1] \right\} \quad (1)$$

where λ is the mixing coefficient. With d_{z^2} lower in energy than $d_{x^2-y^2}$, the state is dominated by the d_{z^2} term. Since both d_{z^2} and $d_{x^2-y^2}$ are antibonding, on this approximation, population of this state should result in lengthening of the W–N and W–C bonds with the greatest distortions occurring in the z direction. Zink and colleagues⁷ have obtained the ground state pre-resonance Raman (PRR) spectra of **1** and **2**, by pumping at 476.5 and 488 nm respectively; at these wavelengths the involvement of the 1E states ($^1A_1 \rightarrow ^1E$, 382 nm for **1**; 404 nm for **2**) is avoided. Employing the time-dependent formalism,⁸ they concluded that, in the lowest excited state (3E), **1** and **2** are distorted from the ground state by lengthening of the W–N, W–C_{ax} and W–C_{eq} bonds by 1.018, 0.12 and 0.04 Å, and **2** < 0.3, 0.25 and 0.05 Å, respectively, *i.e.* entirely consistent with the above bonding scheme; there is also a change in the C_{ax}–W–C_{eq} bond angle but in the absence of a complete force field this cannot be even approximately calculated. The PRR spectra also showed effects due to changes in the C–O normal coordinates, but these were not converted into bond length changes. However, as stated by Zink,⁷ it is a reasonable assumption that if the W–C bonds lengthen then the corresponding C–O bonds will shorten. In this communication we show that the C–O bonds in fact are longer in the excited state than in the ground state; this observation has implications for the W–C distortions and for the photochemistry of **1** and **2**.

We, and others,⁹ have shown that changes in $\nu(CO)$ frequencies, monitored by fast time-resolved infrared (TRIR) spectroscopy, provide information on changes in C–O bond lengths on promotion to an excited state. Most studies have involved compounds where the lowest excited state is MLCT in character. For example¹⁰ in the MLCT excited state of $\text{ClRe(CO)}_3(\text{bpy})$, the $\nu(CO)$ bands shift up in frequency from the ground state by an average of *ca.* 55 cm^{-1} . This is because the charge transfer effectively oxidises the Re centre, and the CO groups experience less back-bonding in the excited state, thus shortening the bond length and increasing the $\nu(CO)$ frequency. Exactly the same effect is expected if in the LF

excited state of **1** and **2** there is lengthening of the W–C bonds and corresponding shortening of the C–O bonds.

As stated above, the 3E LF excited states of **1** and **2** are very short-lived at room temperature and, moreover, the quantum yields for loss of pyridine and piperidine from this state are very high.^{2,4a,11,12} Both these problems make room temperature measurement of the excited state spectra difficult. Hence we have studied the excited state IR of **1** and **2** in a methylcyclohexane/isopentane (MCH/Pⁱ) glass at *ca.* 90 K. The $\nu(CO)$ FTIR spectrum of **1** (except for the weak high frequency a_1 band) is

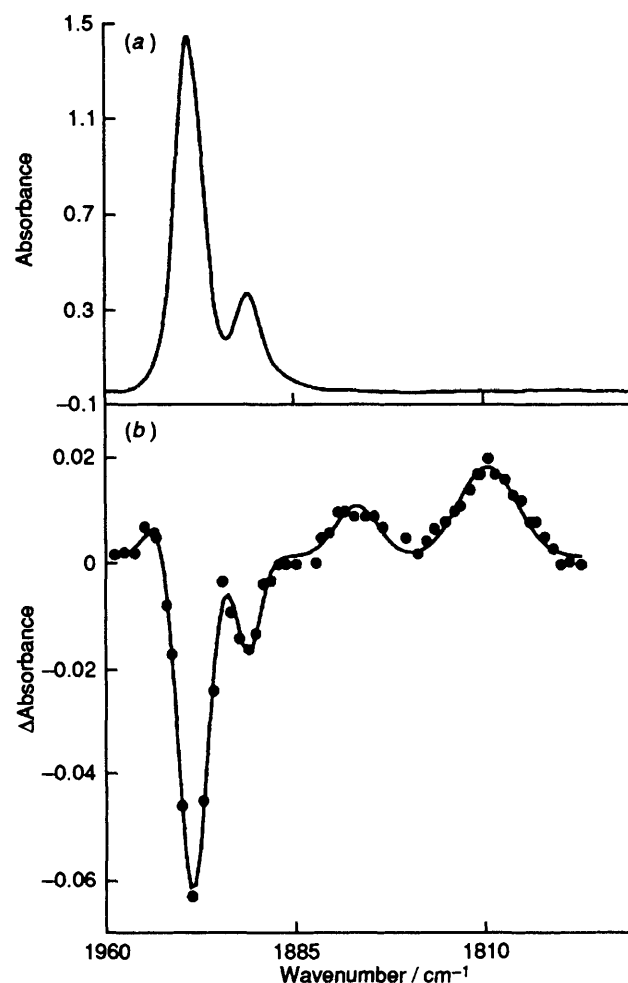


Fig. 1 (a) FTIR spectrum (Perkin Elmer 2000) in $\nu(CO)$ region of $W(CO)_5(\text{pyr})$ **1** in (MCH/Pⁱ) (5:1) glass at *ca.* 90 K; (b) TRIR spectrum of **1** in the glass recorded *ca.* 100 ns after the laser flash. Data points plotted downwards represent loss of parent; data points plotted upwards represent generation of excited state (1^*). The solid line is a multiple Gaussian fit to the data points. The flash was generated with a Quanta-Ray GCR-12S Nd-YAG laser (355 nm); the emission spectrum ($^3E \rightarrow ^1A_1$) at 77 K is independent of pump wavelength > 300 nm. TRIR data points were obtained using a MDS diode laser. Full details of the time resolved apparatus and cold cell are given elsewhere.¹⁹

shown in Fig. 1(a), and the data are given in Table 1. The assignment is based on the local C_{4v} symmetry of the CO groups. With this symmetry, in the energy factored force field there are five C–O force constants (k_{ax} , k_{eq} , k_{trans} , k_{cis} and k_{cis}'), which, with only three frequencies, is not soluble without isotopic data; thus the force field is approximated following Cotton and Kraihanzel¹³ (i.e. $k_{trans} = 2k_{cis} = 2k_{cis}' = 2k_i$). On flash photolysis, the TRIR spectrum shown in Fig. 1(b) was obtained. It is clear that there is loss of the parent $\nu(\text{CO})$ bands and the generation of three $\nu(\text{CO})$ bands (Table 1). No new $\nu(\text{CO})$ bands were observed at higher frequency up to a maximum of 2170 cm^{-1} , the present upper limit of the IR range of the diode laser in the Nottingham TRIR apparatus; simple calculations¹⁴ based on the $\nu(\text{CO})$ PRR data suggest that any excited state $\nu(\text{CO})$ IR bands will fall well within this range. The time dependencies of one band of the new species and one band of the parent are illustrated in Fig. 2. This shows that the new species is generated from the parent within the lifetime of the photolytic flash (ca. 10 ns), and its first order decay rate equals the rate of recovery of parent. We have illustrated the decay of the excited state from its weakest $\nu(\text{CO})$ feature; less noisy decay curves, which display very similar kinetic behaviour, are obtained from the other two $\nu(\text{CO})$ bands. Hence the three new $\nu(\text{CO})$ bands can be assigned to the same species. The lifetime of this new species (τ ca. $0.8\ \mu\text{s}$ at ca. 90 K) corresponds reasonably well with the quoted lifetimes of the excited ^3E state of **1**. It is extremely likely therefore that this excited state is the new species.†

The assignment of the bands in Table 1 is based on the intensity pattern, i.e. that the most intense band is associated with the e mode. The C–K force constants are also given on this assumption; the obvious alternative, with the assignments of the 1809 and 1860 bands reversed, leads to unreal force constants. Using the recently derived relationship¹⁵ between C–O bond length and C–O force constant,

$$r_{\text{CO}} = 1.674 - 0.184 \ln k_{\text{CO}} \quad (\text{with } r_{\text{CO}} \text{ in } \text{\AA} \text{ and } k_{\text{CO}} \text{ in } \text{mdynes } \text{\AA}^{-1})$$

we can obtain very approximate values for the changes in C–O bond lengths in going from ground to excited state. These are also given in Table 1, together with data from the experiments with **2**.

The approximate relationship,

$$[\ln(e)]/[\ln(a_1^{\text{high}}) + \ln(a_1^{\text{low}})] = [4 \sin^2\theta]/[5 - 4 \sin^2\theta],$$

allows an estimate of the $C_{ax}\text{--W--}C_{eq}$ bond angle θ from the intensities of the three $\nu(\text{CO})$ modes. Unfortunately the integrated IR intensities in the excited state are subject to considerable error. Nevertheless there is the implication that this bond angle is considerably increased in the excited state.‡

Compared with what might have been expected, there are two striking features of these data:

- (i) The $\nu(\text{CO})$ vibrational frequencies, and the corresponding C–O force constants, all decrease on promotion into the

lowest excited state; correspondingly the C–O bond lengths all increase.

- (ii) The difference between the ground and excited state force constants, Δk , is considerably larger for the equatorial than for the axial CO groups; correspondingly the changes in bond length are greater for the equatorial than for the axial CO groups.

The implication is that the W–C bond lengths all decrease on excitation rather than increase. However, as pointed out by

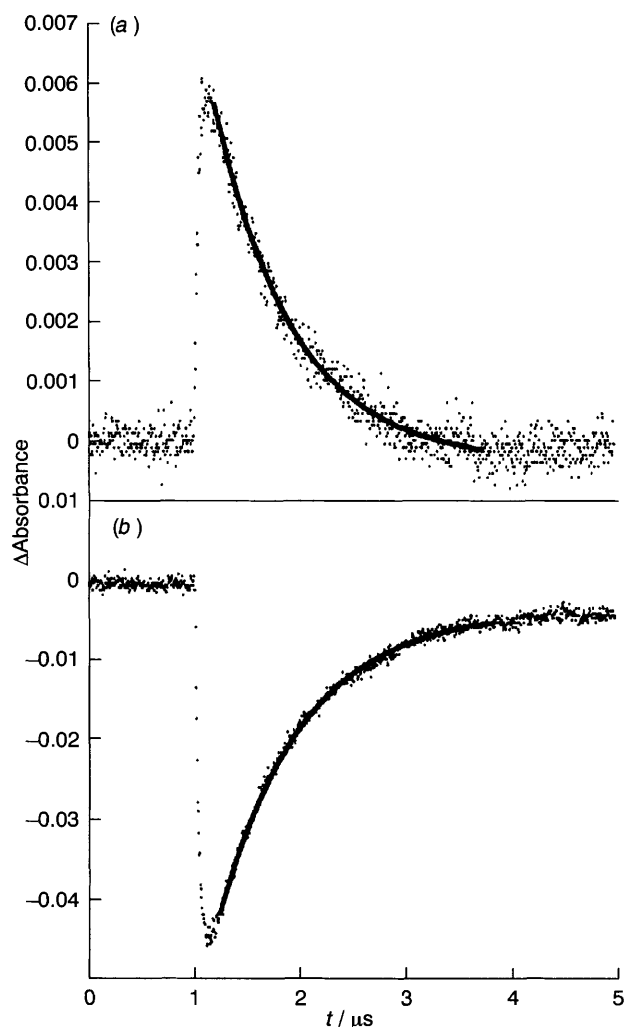


Fig. 2 Time dependence of data points at (a) 1940.8 cm^{-1} , associated with the highest frequency band of **1*** and (b) 1921.7 cm^{-1} , associated with the e mode of the ground state **1**. The thick lines represent exponential fits to the curves with (a) $\tau = 0.75\ \mu\text{s}$ and (b) $\tau = 0.81\ \mu\text{s}$.

Table 1 The frequencies (cm^{-1}), and assignments, of the $\nu(\text{CO})$ bands, and the energy factored force constants, k , (N m^{-1}), of (a) **1**, and (b) **2**, in the ground and ^3E excited states in MCH/Pi glass at ca. 90 K; and the calculated changes in C–O bond lengths, Δr (\AA)

Ground state	Excited state	$\Delta\nu$	$k(\text{gs})$	$k(\text{es})$	Δk	Δr
(a) $\text{W}(\text{CO})_5(\text{pyr})$ 1 (excited state lifetime $\tau \sim 0.8\ \mu\text{s}$)						
2071 (vs, a_1)	1942 (w, a_1)	-129	$k_{ax} = 1482$	$k_{ax} = 1433$	-49	ax: +0.006
1927 (vs, e)	1809 (s, e)	-118	$k_{eq} = 1571$	$k_{eq} = 1377$	-194	eq: +0.024
1903 (s, a_1)	1860 (s, a_1)	-43	$k_i = 35.5$	$k_i = 28$	-7.5	
(b) $\text{W}(\text{CO})_5(\text{piperidine})$ 2 (τ ca. $1.2\ \mu\text{s}$)						
2069 (vs, a_1)	1942 (w, a_1)	-127	$k_{ax} = 1472$	$k_{ax} = 1431$	-41	ax: +0.005
1920 (vs, e)	1788 (s, e)	-132	$k_{eq} = 1563$	$k_{eq} = 1354$	-209	eq: +0.026
1898 (s, a_1)	1855 (s, a_1)	-43	$k_i = 36.5$	$k_i = 31.5$	-5	

Zink,¹⁶ it is an important limitation of the application of the time-dependent PRR method that only the magnitude of bond length changes can be obtained since the relationship between normal coordinate distortions and PRR intensities is given, in the simplest formulation, by:

$$I_k/I_j = (\Delta_k\omega_k)^2/(\Delta_j\omega_j)^2$$

where I_k and I_j are the intensities of two PRR bands at frequencies ω_k and ω_j , and Δ_k and Δ_j are the distortions along normal coordinates k and j . It is thus consistent with the PRR data if the W–C bonds do in fact shorten rather than lengthen. Is this feasible? There are two naive arguments which support this idea. The quantum yield for loss of pyridine or piperidine from **1** or **2** is very high^{2,4a,11,12} (~ 0.5), but for loss of CO is almost zero. This is a little surprising if the excitation results in increase in W–C bond length, particularly in the W–C_{ax} bond. The second argument relies on a molecular orbital picture of the excited state. Zink¹⁷ originally introduced a simplified extended Hückel (EHMO) model to examine the photochemical behaviour of some transition metal species. We have performed preliminary EHMO calculations^{14,18} on the model compound W(CO)₅(NH₃); the π orbitals on pyridine cannot play a significant role since the results for **1** and **2** are so similar. These calculations indicate that the LUMO has the Mulliken overlap populations: W–N (–0.063); W–C_{ax} (0.05); W–C_{eq} (0.003); C–O_{ax} (–0.0013); C–O_{eq} (–0.33). These data are striking in several respects: although the LUMO is antibonding with respect to W–N, it is bonding with respect to W–C; the LUMO is antibonding with respect to C–O, with by far the greatest effect being observed for the C–O_{eq} bond. § Population of this orbital will lead to the distortion changes predicted on the basis of the excited state IR data. Of course this ignores what is happening to the HOMO, but the results are at least indicative.

It is thus clear that the IR spectra of excited states can provide additional valuable information for structural change and photochemical behaviour.

We are very grateful to Professor J. I. Zink and Dr A. Vlcek Jr. for valuable discussions, to Professor O. Eisenstein and Dr P. Mountford for help with EHMO calculations, to Mr K. Stanley, Mr A. Buckland and Mr R. K. Cartwright for technical assistance, and to the SERC (Studentship to F. P. A. J. and GR/H63296), the Paul Instrument Fund of the Royal Society, EC Human Capital and Mobility, Müttek GmbH, Perkin Elmer and the Government of the Isle of Man (Studentship to S. L. M.) for financial support.

Received, 30th September 1994; Com. 4/06007E

Footnotes

† Obvious other possibilities such as W(CO)₅ (C_{4v}) or W(CO)₄L (C_s) can be eliminated since these species are well known and their $\nu(\text{CO})$ frequencies^{20,21} are very different from those observed in the present experiments. One, rather unlikely possibility, is the D_{3h} structure of W(CO)₅; however this would produce frequencies which are identical on photolysis of both **1** and **2**, and Table 1 shows that this does not occur. This argument also applies to, for instance, any excited state of W(CO)₅.

‡ Since the excited state is ³E, there may also be Jahn–Teller distortion.

§ This is because in the LUMO there is considerable interaction between the p_z metal orbital and the four equatorial π^* orbitals on the CO groups.

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