Vibrational Effects in the High Resolution Tungsten 4f Core Level Photoelectron Spectra of $[W(CO)_6]$

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The high resolution W 4f photoelectron spectrum of $[W(CO)_6]$ is analogous to the W 5d valence-level spectrum; both spectra show vibrational structure from W–C and C–O vibrations.

For valence-level photoelectron spectra of small molecules, researchers have long used vibrational structure to infer the bonding nature of molecular orbitals.[1] For example, extensive vibrational structure is associated with bonding or antibonding orbitals, while little or no vibrational structure is associated with non-bonding orbitals.[1] Vibrational structure is usually not resolved in large organometallic molecules. However, in a high resolution study, Lichtenberger and coworkers[2] were able to resolve both W–C and C–O vibrational modes in the valence W 5d peaks in $[W(CO)_6]$. Using the above accepted theory, they estimated the importance of the W 5d electrons to the W–CO bond.

Extensive vibrational structure has also been resolved in the photoelectron spectra of non-bonding core orbitals: for example, the C 1s, P 2p and Si 2p orbitals of CH_4, PH_3 and SiH_4 (and other Si molecules) respectively.[3] However, little or no vibrational structure has been observed in the photoelectron spectra of molecules containing heavy elements, such as Xe and I.[4] The core-equivalent model has been useful in rationalizing these vibrational splittings.[5]

In this communication, we report high resolution (total resolution of *ca.* 100 meV)† W 4f photoelectron spectra of $[W(CO)_6]$. Surprisingly, vibrational structure, from both W–C and C–O vibrations, is observed on the W 4f level; this

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† High purity $[W(CO)_6]$ was purchased from Strem Chemicals. The compound was sublimed directly into two different photoelectron spectrometers. The He I spectra of the W 5d levels were recorded with a laboratory McPherson ESCA 36 spectrometer.[6] These spectra were calibrated with the Ar $3p_{3/2}$ line at 15.759 eV, at a resolution of *ca.* 20 meV. The W 4f core-level spectra and valence spectra were obtained at the Canadian Synchrotron Radiation Facility (CSRF) at the 1GeV storage ring Aladdin, using a modified ESCA 36 spectrometer.[3] Many W 4f spectra were recorded between 60 and 120 eV photon energy using both a single channeltron and Quantar model 3395A position-sensitive detector. The spectra were calibrated using the W 5d peaks and the Kr $3d_{5/2}$ peak at 93.798 eV. At 80 eV, the photon and electron resolutions were *ca.* 60 meV and *ca.* 80 meV, respectively, giving a total instrumental linewidth of *ca.* 100 meV. Spectra were deconvoluted with a Gaussian–Lorentzian lineshape using a nonlinear least squares procedure described previously. A single peak shape split by spin–orbit coupling and fixed vibrational splitting was used to fit all spectra.[3b,c]

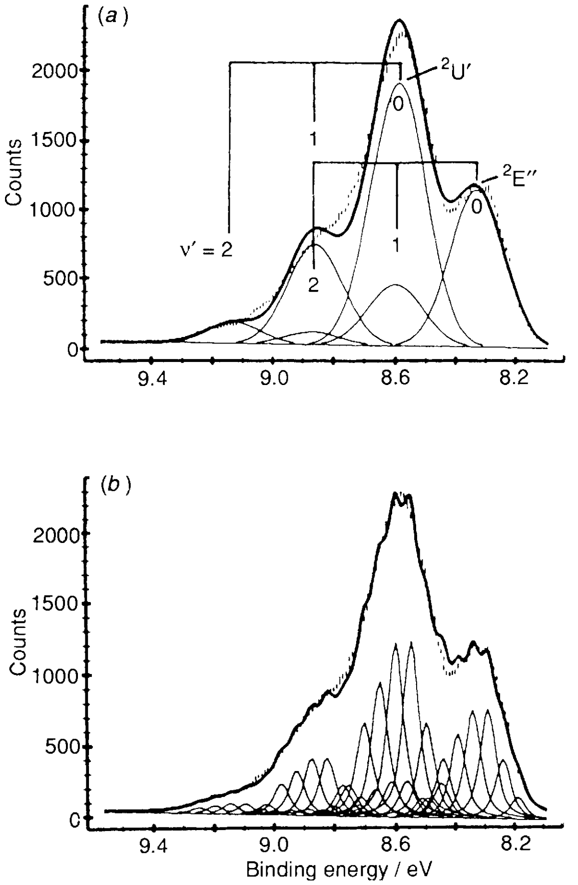

Fig. 1 The high resolution W 5d photoelectron spectra of gas-phase [W(CO)$_6$]. In (*a*), the spectrum is fit considering just spin–orbit splitting, and a ν_1(C–O) vibrational component, (*b*) fits a ν_2(W–C) vibrational envelope as well.

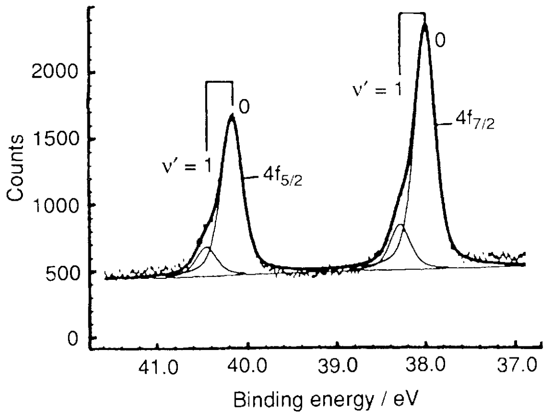

Fig. 2 The high resolution W 4f photoelectron spectrum of [W(CO)$_6$]. The spectrum is fit just considering spin-orbit splitting and a ν_1(C–O) vibrational component, as in Fig. 1(*a*).

structure is very similar to that observed on the valence W 5d orbital. We discuss the importance of these W 4f spectra for the interpretation of both valence-band photoelectron spectra of molecules, and core-level photoelectron spectra of metal core levels on surfaces.

The high resolution W 5d and W 4f spectra are illustrated in Fig. 1(*a*), (*b*) and Fig. 2, respectively, and the spectral parameters for the three fits (plus a multipeak fit to the W 4f spectrum) are given in Table 1. The W 5d spectrum (and the analysis of this spectrum) is almost identical to that published previously.[2] At first sight [Fig. 1(*a*)] the W 5d spin–orbit splitting (0.26 eV), and a C–O vibrational progression (0.27 eV, 2180 cm^{-1}) on each spin–orbit peak, are apparent. On much closer inspection,[2] each of the six peaks in Fig. 1(*a*) is split by the W–C symmetric stretching frequency [Fig. 1(*b*)]. This fit in Fig. 1(*b*) is not, of course, a unique fit, but we believe that the errors (Table 1, from the standard deviation of five spectra) are realistic. The W–C frequency of 410 cm^{-1} is similar to the ground-state frequency of 426 cm^{-1},[7] and a little larger than the 387 cm^{-1} quoted by Hubbard *et al.*[2]

The W 4f spectrum in Fig. 2 is qualitatively similar to the W 5d spectrum; both the W 4f spin–orbit splitting (2.165 eV) and a shoulder due to the C–O vibrational model are evident immediately. For both the W 5d and W 4f spectra, the vibrational spacing is *ca.* 2200 cm^{-1}, definitely indicative of the excitation of the ν_1(C–O) mode which in ground-state [W(CO)$_6$] lies at 2126 cm^{-1}.[7]‡ To confirm this surprising observation of a ligand vibrational splitting on a metal core level, many spectra were recorded between 60 and 120 eV photon energy. All spectra of the W 4f levels, and the Re and Os 4f levels of other carbonyls,[8] are consistent with the fit shown in Fig. 2.

Although there is no further observable vibrational fine structure in the W 4f spectrum, two factors strongly indicate that there is indeed a W–C vibrational progression in the W 4f spectrum, similar to that in the W 5d spectrum. First, the W 4f peak widths in Fig. 2 (0.25 eV) are comparable to the W 5d linewidths (0.21 eV) in Fig. 1(*a*) and much larger than the instrumental linewidth of *ca.* 100 meV. These W 4f linewidths are of course much smaller than the linewidths (1.25 eV) observed with a laboratory X-ray source.[9] Second, and more importantly, the W 4f linewidth of 0.25 eV is much larger than the inherent W 4f linewidths from theory (0.07 eV)[10] and experiment (0.055–0.15 eV).[11]§ To obtain linewidths of $\leq$0.15 eV, we had to fit a similar W–C vibrational progression to the W 4f spectrum (Table 1) as is present in the W 5d spectrum [Fig. 1(*b*)].¶ Because we cannot be confident about the extent of vibrational W–C progression, we cannot at this time derive a W 4f inherent width.

The large vibrational manifold in the W 4f spectrum is expected after considering the core-equivalent model.[5] In this model, the properties of a molecular ion with a core hole are approximated by the molecule with the $Z + 1$ atom. The core-equivalent species for core ionized [W(CO)$_6$] is [Re(CO)$_6$]$^+$. As seen in Table 1 [Re(CO)$_6$]$^+$ has a substantially smaller M–C bond length (2.01 Å) than [W(CO)$_6$] (2.07 Å). This substantial decrease in bond length between neutral and core-ionized [W(CO)$_6$], due to the deshielding effect, should lead to substantial vibrational structure.[3] Also, the ν_1(C–O) frequency of 2260 cm^{-1} is larger than that of ground-state [W(CO)$_6$], and closer to that of [Re(CO)$_6$]$^+$. The ν_2(W–C) frequencies of 410 cm^{-1} are within the error for both [W(CO)$_6$] and [Re(CO)$_6$]$^+$.

We must now reconsider the interpretation of the W 5d vibrational splitting. The vibrational structure on the W 4f level is due to a decrease in W–C bond length in the ion state. Is it possible that the similar vibrational structure in the W 5d spectra is due to a decrease rather than an increase in W–C bond length as was reasonably proposed by Hubbard *et al.*[2] for

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‡ The intensity of the vibrational peak in Fig. 2 (20% of the 'main' peak), is substantially less than in Fig. 1(*a*) (38% of the main peak).

§ The 'experimental' W 4f inherent linewidths were obtained from two different analyses of high resolution W 4f spectra of W metal. These spectra had total experimental linewidths of *ca.* 0.23 eV, and one analysis [11a] gave almost double the widths of the other[11b].

¶ The W–C frequency was fixed at 410 cm^{-1} and the lineshape was fixed at 95% Lorentzian. Fits with 410 ± 30 cm^{-1} and differing lineshapes made little difference to the linewidth (± 0.02 eV). Also, possible anharmonicity is not considered in these fits.

Table 1 Spectral parameters for the W 5d and 4f photoelectron spectra of $[W(CO)_6]^{a,b,c}$

		Binding energy/eV		Spin–orbit splitting/ eV	Spin–orbit intensity ratio/eV	Γ_{expt}/eV	ν_1(C–O)/ cm^{-1}	ν_2(W–C)/ cm^{-1}
		Vertical	Adiabatic					
W 5d	Fig. 1(*a*)	8.33(3), 8.33^d		0.260(5) 0.26^d	1.666(3)	0.210(3)	2180(40) 2090^d	
	Fig. 1(*b*)	8.30(3), 8.19(3)	8.19(3)	0.260(5)	1.600(3)	0.063(3)	2200(40)	410(20) 387^d
W 4f	Fig. 2	37.92(3), 37.84^e		2.165(5)	0.650(3)	0.25(1)	2260(40)	
	Multi-peak fit	38.00(3), 37.88(3)	37.88(3)	2.165(5), 2.16^e	0.650(3)	0.13(1)	2260(40)	410(30)

[a] The vibrational frequencies for the ν_1 and ν_2 modes of $[W(CO)_6]$ are 2126 and 426 cm^{-1} respectively in the neutral molecule.[7] [b] The vibrational frequencies for the ν_1 and ν_2 modes of $[Re(CO)_6]^+$ are from 2197 to 2224 and from 415 to 441 cm^{-1}, respectively in different compounds.[7,12] [c] M–C bond lengths in $[W(CO)_6]$ and core-equivalent $[Re(CO)_6]^+$ species in $[Re(CO)_6][Re_2F_{11}]$ are 2.07 and 2.01 Å, respectively.[12] [d] Ref. 2. [e] Ref. 9.

such a bonding electron? This question cannot be answered with confidence from these data. However, it is apparent that the decrease in W–C bond length from the above deshielding effect must be considered as well as the probable increase in W–C bond length from removal of a bonding electron. Indeed, for a metal carbonyl, it is not even entirely clear whether the W–C bond length will increase substantially when a W 5d electron is removed, because of the synergic nature of the M–CO bond, and the greater importance of σ bonding over π backbonding. Certainly both deshielding and bonding effects should result in an increase in ν_1(C–O) stretching frequency as observed; the error in the ν_2(W–C) frequency is too large to be confident that the W–C bond is weakened. More theoretical calculations need to be performed to distinguish the relative importance of deshielding and bonding effects.

Finally, our observation is important for surface scientists studying small adsorbates on metals with high resolution photoelectron spectroscopy of narrow metal levels such as W 4f or Pd 3d.[13] When deconvoluting complex overlapping spectra of, for example, H, CO, O_2, N_2 *etc.* adsorbed on metals, our result indicates that vibrational contributions to the metal spectra must be considered. Such vibrational contributions on the ligand levels (*e.g.* in the C1s spectra of CO) have already been widely recognized,[14] but no researchers to our knowledge have considered vibrational contributions on the metal levels.

We acknowledge the financial support of the NSERC (Canada), and a helpful discussion with Dr R. J. Puddephatt.

Received, 8th April 1992; Com. 2/01874H

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