Is a Shake up Process Responsible for the Multi-peak Structure of the X-ray Photoelectron Spectra of Metal Hexacarbonyls?

S. Pignataro

Istituto Chimico "G. Ciamician", Università di Bologna, Italia

(Z. Naturforsch. **27 a**, 816—818 [1972]; received 2 November 1971)

The X-ray photoelectron energy spectra of chromium, molybdenum and tungsten hexacarbonyls are found to show a multi-peak structure. This is particularly remarkable in the C_{1s} and O_{1s} binding energy region. This peculiarity is tentatively interpreted on the basis of a double excitation process involving the ionization and simultaneous excitation of a valence electron.

There is no doubt that ESCA studies will be very helpful in understanding the structure of organometallic compounds. This is for example demonstrated by the recent study of Jørgensen [1].

We feel, however, that before we can make much progress in photoelectron spectral studies of many compounds, we must first get a clear idea of the basic phenomena which occur during photoelectron ejection in some very simple compounds. This is to avoid basically wrong interpretations of early results, a danger in the infancy of any new technique, which could hinder the proper development of photoelectron spectroscopy for a long time.

This paper will present some preliminary results on one of the simplest classes of organometallic compounds. It will be shown that the spectra of even such simple compounds show some pecularities which are rather difficult to interpret.

In Figs. 1 and 2, the photoelectron energy spectra (AlKα excitation source) of Mo and W hexacarbonyls are reported. Similar spectra were also obtained for Cr hexacarbonyl. The spectra were obtained on an AEI ES 100 electron spectrometer by subliming the commercial samples directly into the ionization chamber of the spectrometer onto a cooled copper surface.

At the time these spectra were first taken (more than one year ago), we thought that the low intensity peaks on the high energy side of the C_{1s} and O_{1s} bands were due to hydrocarbon and water contaminations, respectively.

This explanation of the nature of these peaks is, however, in conflict with the fact that similar spectra were obtained by using a Varian IEE machine and then a second AEI machine having a MgKα excitation source. Again, the same pecularities were found by A. Melera in the photoelectron spectra of metal hexacarbonyl by using a Hewlett-Packard electron spectrometer [2].

The intensity ratios and the energy differences between the two peaks are invariant to the change of the machine type. In addition, it also seems that the metal peaks show very small soulders, always on the high binding energy side.

This obviously means that the background is not responsible for the observed effect which must be connected with the nature of the hexacarbonyls.

Very recently, some pecularities of the photoelectron spectra of He, N_2 and O_2 were interpreted on the base of a "shake up" process [3]. This is an ionisation process which involves a simultaneous excitation of a valence electron. A similar phenomenon was also proposed [4] to interpret the competition phenomena observed [5] in the multiple ionization of the rare gases and in the ionization-fragmentation of several kinds of molecules. According to this last proposal, the ionization processes would occur through an intermediate system which would decay into the final ions following the phase space statistical law. In particular, "from a very naive viewpoint", some ionization processes "could be regarded as internal electron impact, where one of the incipiently ionized electrons may have enough energy to excite the ion still further, during the short time it remains within the atom" [4]. On the other hand, the "shake up" process is based on a different model. "The removal of one electron to infinity by photon impact from a N particle state is considered as a sudden process. The resulting state of $N-1$ particles is not an eigenstate of the new Hamiltonian but a mixture of such eigen-

---

Reprint requests to S. Pignataro, Istituto Chimico "G. Ciamician", Università di Bologna, Via Selmi 2, *I-40126 Bologna.*

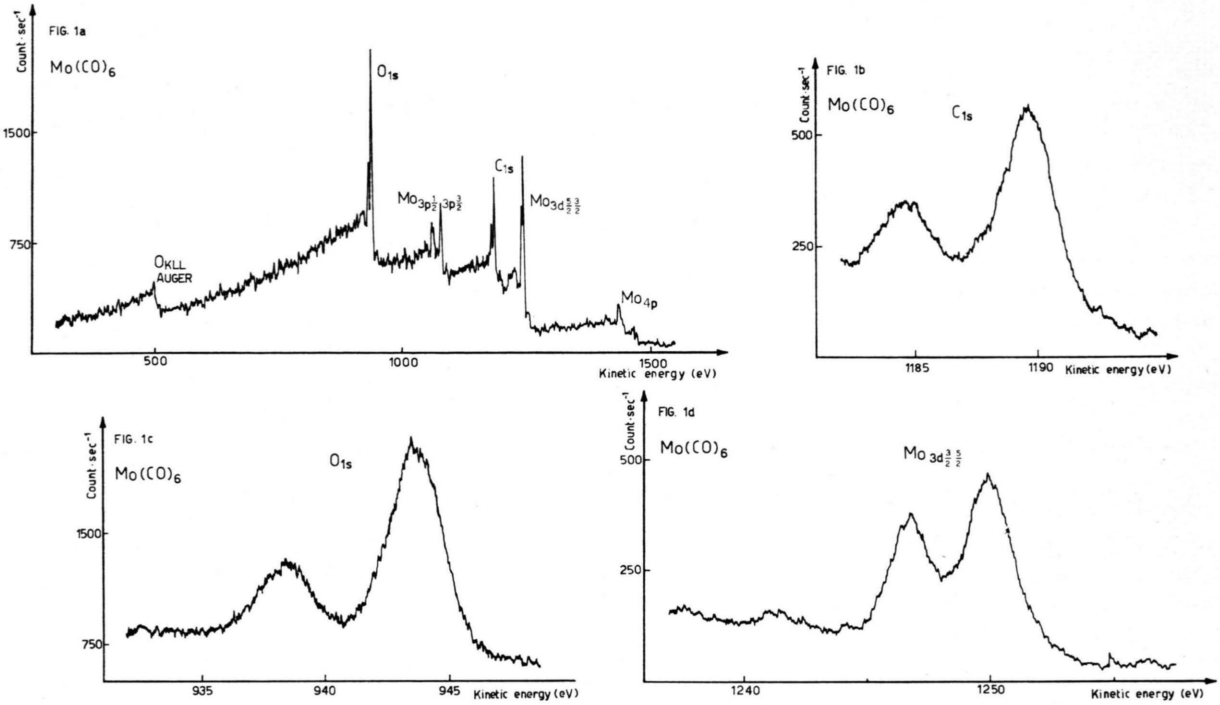

Fig. 1. Photoelectron energy spectrum (AlKα) of Mo(CO)$_6$. The kinetic energy scale is uncorrected: a) full spectrum; b) C$_{1s}$ energy region; c) O$_{1s}$ energy region; d) Mo$_{3d}$ energy region.

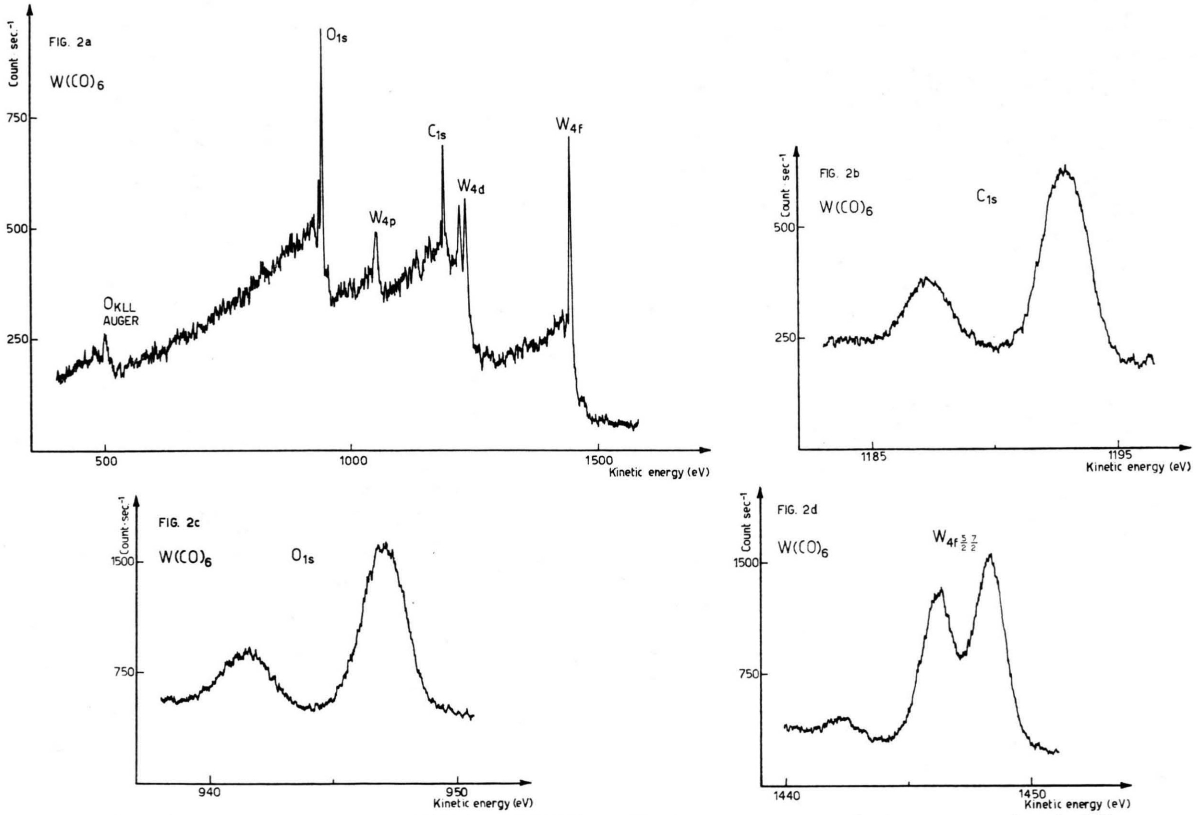

Fig. 2. Photoelectron energy spectrum (AlKα) of W(CO)$_6$. The kinetic energy scale is uncorrected: a) full spectrum; b) C$_{1s}$ energy region; c) O$_{1s}$ energy region; d) W$_{4f}$ energy region.

states"[3, 6]. In other words, the ionization process will produce, obviously with different yields, several molecular ions differing from each other in their electronic configurations.

In any case, whatever model is used, it seems that the ionization processes should be considered as multi-body processes and, that to explain some experimental observations, we need to invoke a double excitation process.

On this basis, it is, therefore, proposed that the doubling effect of the C_{1s} and O_{1s} photoelectron bands in the metal hexacarbonyls is caused by a double excitation phenomenon similar to the above one.

The UV absorption spectrum of all the $M(CO)_6$ compounds in the gas phase or in solution is dominated by a band one order of magnitude stronger than all the others. This band was recently assigned to a $^1A_{1g} \rightarrow d^1T_{1u}$ transition[7] and falls into the $43{,}000 - 45{,}000\ cm^{-1}$ range (~ 5.5 eV). It is, therefore, possible that the "shake up" process proposed involves this kind of transition. There are a number of factors[8] which make the above agreement betheen the UV band energies and the energy differences of the two C_{1s} and O_{1s} electron bands rather puzzling. However, since similar correspondence has also been found for other kinds of metal compounds[8, 9], we feel that the UV abs. – XPS comparison is meaningful.

The $^1A_{1g} \rightarrow d^1T_{1u}$ has been interpreted[7] as a Metal → Ligand charge transfer transition. So that, the "shake up" process should involve an excitation from one orbital mainly localized on the central metal to one mainly localized on the ligand. If this is true, by using arguments similar to those developed[10] by GELIUS for the shake up of the C_3O_2, we should expect very strong "shake up" satellites for the metal lines and weak "shape up" satellites for the C_{1s} and O_{1s} lines. Thus, the observed satellite intensities would suggest that the $M(CO)_6$ "shake up" is different from the C_3O_2 one, being probably inter-atomic in character.

On the other hand, it is interesting to notice that the UV photoelectron energy spectra[11] of all the metal hexacarbonyls show the first two bands separated again by about 5 eV. On the basis of the recently proposed molecular structure of the hexacarbonyls[7], this is perhaps only a fortuitous coincidence.

In any case, whether the above explanation of the double peaks in the C_{1s} and O_{1s} regions of the metal hexacarbonyls is correct or not *, it is evident that our knowledge on the photoelectron ejection process is still rather naive and further discussion on the above point is needed. There are two interesting points to consider: a) four papers[12–15] dealing with binding energies of core electrons in $M(CO)_x$ [M = Cr, W, Ni and Fe] complexes appeared recently in the literature, but only one of those[15] mentioned the multi-peak structure of the C_{1s} and O_{1s} bands (the interpretation of the phenomenon given in this last paper was however based on a poor description "of the ground state of these molecules by a single determinantal function in the Hartree-Fock limit"); b) the above effect is probably widespread and other shoulders found in the X PS of other samples might have the same nature as those reported here.

Acknowledgements

The author gratefully acknowledges the AEI manufacturer for the availability of the instrument, Prof. C. K. JØRGENSEN for his valuable comments and Dr. A. MELERA for the private communication. The author also wishes to thank Dr. W. BREMSER for having taken some spectra at the Varian Lab. in Darmstadt and for his helpful discussions. The work was supported in part by a research grant from the Consiglio Nazionale delle Ricerche.

---

* A discrete energy loss[8, 9] is another possible explanation of the observed effect, but a gas phase photoelectron spectrum at low pressure is needed to rule out or confirm this possibility.

[1] C. K. JØRGENSEN, Chimia **25**, 213 [1971].

[2] A. MELERA, private communication.

[3] K. SIEGBAHN, C. NORDLING, G. JOHANSON, J. HEDMAN, P. F. HEDEN, K. HAMRIN, U. GELIUS, T. BERGMARK, L. O. WERME, R. MANNE, and Y. BAER, ESCA Applied to Free Molecules, p. 32, North-Holland, Amsterdam 1969.

[4] J. D. MORRISON and J. C. TRAEGER, J. Chem. Phys. **53**, 4053 [1970].

[5] B. CANTONE, F. GRASSO, and S. PIGNATARO, J. Chem. Phys. **44**, 3115 [1966].

[6] R. MANNE and T. ÅBERG, Chem. Phys. Letters **7**, 282 [1970].

[7] N. A. BEACH and H. B. GRAY, J. Amer. Chem. Soc. **90**, 7513 [1968].

[8] T. NOVAKOV and R. PRINS, Proceedings of the International Conference on Electron Spectroscopy, Asilomar 1971, in press. — G. K. WERTHEIM and A. ROSENCWAIG, Phys. Rev. Letters **26**, 1179 [1971].

[9] C. J. ALLAN and K. SIEGBAHN, Institute of Physics, Uppsala University, Report UUIP 754 (November 1971), and references.

[10] U. GELIUS, Proceedings of the International Conference on Electron Spectroscopy, Asilomar 1971, North-Holland, Amsterdam, in press.

[11] D. W. TURNER, C. BAKER, A. D. BAKER, and C. R. BRUNDLE, Molecular Photoelectron Spectroscopy, p. 370, Interscience, New York 1970.

[12] M. BARBER, J. A. CONNOR, I. H. HILLIER, and V. R. SAUNDERS, Chem. Comm. **1971**, 682.

[13] D. T. CLARK and D. B. ADAMS, Chem. Phys. Letters **10**, 121 [1971].

[14] D. T. CLARK and D. B. ADAMS, Chem. Comm. **1971**, 740.

[15] M. BARBER, J. A. CONNOR, and I. H. HILLIER, Chem. Phys. Letters **9**, 570 [1971].