# The High Energy Photoelectron Spectra of and Bonding in Transition Metal Carbonyls

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*Summary* The bonding in transition metal carbonyls is discussed with the aid of high energy photoelectron spectra, reported here, and the measurements are correlated with the results of SCF–MO calculations.

DESPITE many semi-empirical molecular orbital studies,[1] and indirect experimental evidence, from *e.g.*, force-constant measurements, the nature of the bonding and charge distribution in transition metal carbonyls is still unresolved. Core binding energies as measured by high energy photoelectron spectroscopy are sensitive to the distribution of the valence electrons. Thus, measured changes in the binding energies of the carbon and oxygen 1*s* electrons in CO on complex formation may be used to obtain information on the associated change in ligand charge distribution.

TABLE 1†

| | Binding energies relative to internal standards* | | Binding energies relative to CO | |
|---|---|---|---|---|
| | 1*s* (C) | 1*s* (O) | 1*s* (C) | 1*s* (O) |
| $Ni(CO)_4$ .. .. | 3·4 | 1·0 | −2·2 | −1·4 |
| $Fe(CO)_5$ .. .. | 3·2 | 0·8 | −2·4 | −1·6 |
| $Cr(CO)_6$ .. .. | 3·1 | 0·7 | −2·5 | −1·7 |
| $W(CO)_6$ .. .. | 3·1 | 1·0 | −2·5 | −1·4 |

†All binding energies are in eV.
* Carbon 1*s* in hexane; oxygen 1*s* in water.

We here report such measurements on a series of transition metal carbonyls and use them to discuss the bonding in these molecules. The measurements were performed on solids condensed from the vapour phase at liquid nitrogen temperature and were obtained on an A.E.I. ES 100 photoelectron spectrometer using both Al- and Mg-$K_\alpha$ radiation. To obtain absolute binding energies close internal standards were condensed at the same time as the carbonyls. The carbon 1*s* level in hexane[2] and the oxygen 1*s* level in water[3] were used in this way to remove any error due to sample charging effects and energy scale calibration. The measured shifts from these standards are given in Table 1. The change in carbon and oxygen 1*s* binding energies on complex formation are also given in Table 1 with the aid of the reported gas-phase values for free CO.[3] A generous error of approximately ±0·4 eV is suggested for the chemical shifts relative to gaseous CO given in Table 1, due to uncertainties in the extrapolation from solid to gas. In all four carbonyls, both the carbon and oxygen 1*s* electrons are less tightly bound than in free CO by *ca.* 2·5 and 1·5 eV respectively, the differences between the carbonyls being of dubious significance. These results indicate that there is an increase in electron density on the ligands of the complexes compared with free CO. This is at variance with the results of a number of semi-empirical MO calculations,[1] particularly on $Ni(CO)_4$ where an appreciable negative charge on the nickel atom is predicted. The experimental results suggest that there is more $\pi$-back bonding into the first virtual orbital of CO ($2\pi$) having a large carbon 2*p* component than $\sigma$-donation from the highest filled "lone pair" orbital of CO($5\sigma$). We have performed *ab initio* SCF MO calculations of the electronic structure of $Ni(CO)_4$ and CO, the results relevant to a discussion of the experimental measurements reported here being shown in Table 2. Assuming Koopmans' theorem we predict that both the carbon and oxygen 1*s* electrons are less tightly bound in the carbonyl than in CO, in agreement with experiment, although the calculated chemical shifts (0·3 eV for the carbon, and 0·4 eV for the oxygen 1*s* electrons) are rather smaller than the measured values. The calculated decrease in binding energy correlates with the calculated increase in electron density on the ligands, the increase in the population of the 2*p* carbon orbitals being greater than the decrease in 2*s* population on formation of the Ni–C bonds.

TABLE 2

| | | | Orbital populations | | | |
|---|---|---|---|---|---|---|
| | | | Carbon | | Oxygen | |
| | Orbital | Energy (a.u.) | 2*s* | 2*p* | 2*s* | 2*p* |
| $Ni(CO)_4$ | $3a_1$ | −20·4668 | 1·557 | 2·212 | 1·835 | 4·519 |
| | $4a_1$ | −11·3892 | | | | |
| CO | $1\sigma$ | −20·4813 | 1·631 | 1·999 | 1·839 | 4·534 |
| | $2\sigma$ | −11·4011 | | | | |

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[1] K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, 1968, **7**, 1273; W. C. Nieuwpoort, Philips Res. Rept. Suppl., 1965, No. 6, 1; A. F. Schreiner and T. L. Brown, *J. Amer. Chem. Soc.*, 1968, **90**, 3366; I. H. Hillier, *J. Chem. Phys.*, 1970, **52**, 1948.
[2] T. D. Thomas, *J. Chem. Phys.*, 1970, **52**, 1373.
[3] ESCA Applied to Free Molecules, K. Siegbahn *et al.*, North-Holland, 1969.