



HIGH ENERGY C1s AND 01s PHOTOELECTRON SPECTRA OF CO

J. Schirmer, G. Angonoa, S. Svensson, D. Nordfors, U. Gelius

► To cite this version:

J. Schirmer, G. Angonoa, S. Svensson, D. Nordfors, U. Gelius. HIGH ENERGY C1s AND 01s PHOTOELECTRON SPECTRA OF CO. Journal de Physique Colloques, 1987, 48 (C9), pp.C8-711-C8-714. 10.1051/jphyscol:19879120 . jpa-00227229

HAL Id: jpa-00227229

<https://hal.science/jpa-00227229>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

HIGH ENERGY C1s AND O1s PHOTOELECTRON SPECTRA OF CO

J. SCHIRMER, G. ANGONOA, S. SVENSSON*, D. NORDFORS* and
U. GELIUS*

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faraday-Weg
4-6, D-1000 Berlin 33, F.R.G.*

**Department of Physics, Uppsala University, PO Box 530,
S-751 21 Uppsala, Sweden*

Abstract:

An experimental and theoretical study of the K-shell photoionization in CO molecules is reported. The O1s and C1s satellite structures are found to be strikingly different already at low shake-up energy. As an explanation the intramolecular charge transfer associated with $\pi-\pi^*$ and $5\sigma-n\sigma$ valence excitation is discussed.

The C1s photoelectron spectrum of CO was recorded at high resolution over a decade ago using monochromatized X-ray line sources [1]. A thorough theoretical study of the C1s shake-up states by means of a large scale configuration interaction (CI) calculation was given by Guest et al [2]. For the case of the O1s shake-up spectrum, however, neither experimental nor theoretical investigations of comparable quality were available. Here we report briefly on recent experimental and theoretical work on both C1s and O1s photoelectron spectra of CO. A more comprehensive account can be found elsewhere [3].

The experimental spectrum was run on an electrostatic electron spectrometer which is equipped with a monochromator for AlK α X-rays. The O1s shake-up spectrum (Fig. 1) shows at least 14 resolved peaks and structures. The first three peaks a-c are inelastic loss peaks. The C1s spectrum shown in Fig. 2 is similar to the previous spectrum [1] but extends up to 85 eV shake-up energy. The weak structures a-c are due to inelastic scattering.

Calculations of (vertical) ionization energies E_n and relative intensities P_n (in the sudden limit) were performed within the many-body Green's function approach employing a new fourth-order approximation scheme (ADC(4)). A detailed report on the calculations is to appear elsewhere [4]. The ADC(4) is based on the zeroth-order representation in terms of Hartree-Fock (HF) orbitals of the neutral molecule ("frozen" orbitals). The electronic relaxation is accounted for on the respective level of approximation in the ADC(4) scheme: very accurate results are expected for the single hole (1s) main states, whereas the results for the shake-up satellites, in particular, for the three-hole-two-particle (3h-2p) satellites will be affected by incomplete consideration of relaxation contributions. A basis set of 5s, 4p and 1d contracted Cartesian Gaussian functions was used to generate the HF input data.

C1s

In Table 1 the ADC(4) results for the lowest $^2\Sigma^+$ C1s-hole states are listed and compared with the experimental values. The first two shake-up features correspond to two distinct $^2\Sigma^+$ states arising from the electron configuration $(2\sigma)^{-1}(1\pi)^{-1}(2\pi)^1$. As has been found previously by Guest et al [2], the first state has about 80% $\pi-\pi^*$ character and is characterized by triplet-coupled ($S'=1$) π -electrons; the second state represents the corresponding singlet ($S'=0$) coupled state, its $\pi-\pi^*$ character, however, is only 50%. For the latter state the calculated shake-up energy is 2.2 eV above the experimental value, a consequence of the admixture of 3h-2p states not properly described on the ADC(4) level.

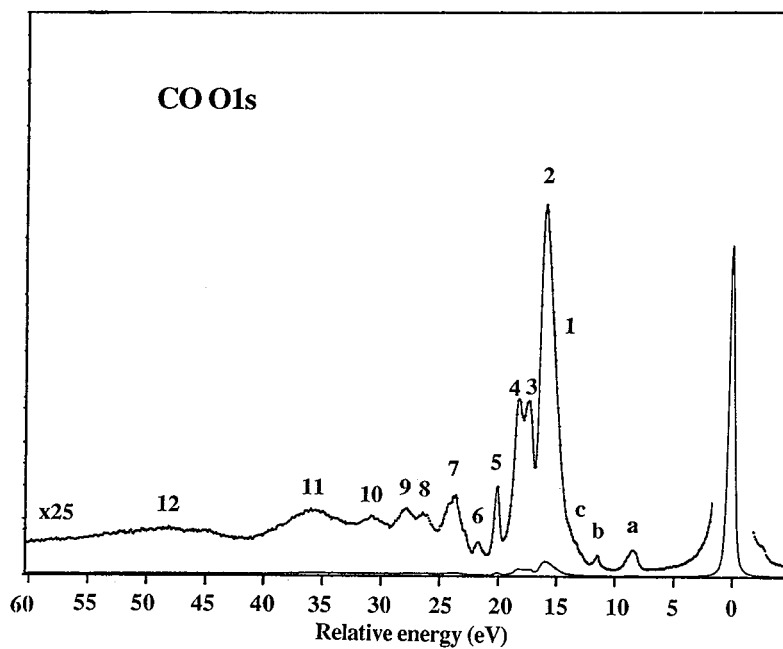


Fig. 1: The O1s shake-up spectrum of CO

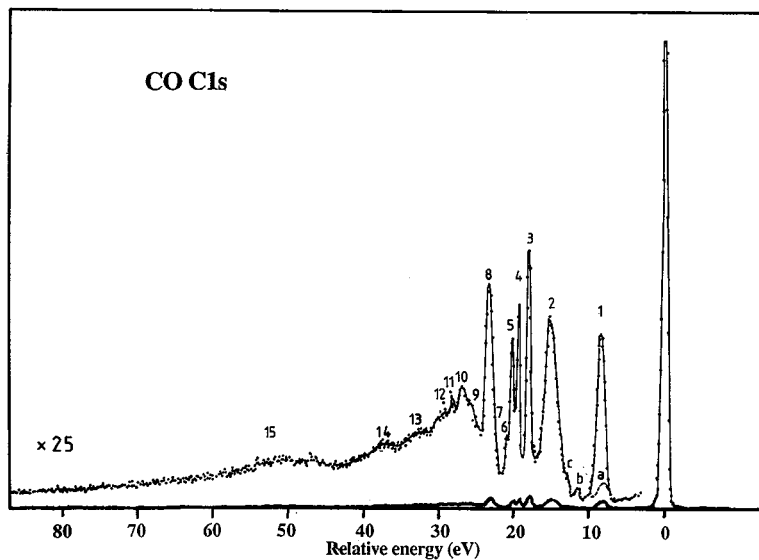


Fig. 2: The C1s shake-up spectrum of CO

At higher energy the lines 3-4 can be identified with 5σ - $n\sigma$ valence-Rydberg excitations. The calculation shows the occurrence of low lying double excitations of the type $(1\pi)^{-2} (2\pi)^2$ and $(5\sigma)^{-2} (2\pi)^2$. Although these states may not be directly visible in the photoelectron spectrum as a consequence of considerable

Table 1: Calculated C1s ionization spectrum of CO. Vertical ionization energies E_n and relative intensities P_n for the lowest six states of ${}^2\Sigma^+$ symmetry.

Assignment (Fig. 2)	Main configuration	E_n		P_n	
		ADC(4)	Expt.	ADC(4)	Expt.
Main	$2\sigma^{-1}$	296.08	296.2	100	100
1	$2\sigma^{-1} 1\pi^{-1} 2\pi^1$ ($S'=1$)	+ 9.11	+ 8.3	2.2	2.3
2	$1\pi^{-1} 2\pi^1$ ($S'=0$)	17.12	14.9	5.0	4.8
3	$5\sigma^{-1} 6\sigma^1$	19.89	17.9	1.3	1.9
-	$1\pi^{-2} 2\pi^2$	20.79	-	0.4	-
4	$5\sigma^{-1} 6\sigma^1$	21.18	19.2	0.2	1.1
-	$4\sigma^{-1} 5\sigma^{-1} 2\pi^2$	21.35	-	0.2	-
-	$1\pi^{-2} 2\pi^2$	21.49	-	0.1	-
5	$5\sigma^{-1} 7\sigma^1$	21.64	20.1	1.3	1.6

Table 2: Calculated O1s spectrum of CO. Ionization energies E_n and relative intensities P_n of the lowest 12 states of ${}^2\Sigma^+$ symmetry.

No.	Main configuration	E_n	P_n
1	$1\sigma^{-1}$	541.56	100
2	$1\sigma^{-1} 1\pi^{-1} 2\pi^{-1}$ ($S'=1$)	+ 14.88	0.02
3	$5\sigma^{-1} 6\sigma^1$	15.80	0.001
4	$5\sigma^{-1} 6\sigma^1$	17.00	0.4
5	$5\sigma^{-1} 7\sigma^1$	17.47	0.2
6	$5\sigma^{-1} 7\sigma^1$	18.37	0.9
7	$5\sigma^{-1} 8\sigma^1$	20.32	1.5
8	$5\sigma^{-1} 8\sigma^1$	20.54	1.5
9	$5\sigma^{-1} n\sigma^1 + 1\pi^{-1} 2\pi^1$	21.67	5.9
10	$5\sigma^{-1} n\sigma^1$	22.11	0.6
11	$5\sigma^{-1} n\sigma^1 + 1\pi^{-1} 2\pi^1$	22.50	4.3
12	$5\sigma^{-1} n\sigma^1$	24.19	0.01

vibrational broadening they may nevertheless influence the spectral profile by perturbing the valence-Rydberg single excitations.

O1s

The theoretical ionization energy of the O1s main state, is 1.0 eV below the experimental value. The lesser agreement here may be due to a basis set effect or due to the considerably larger relaxation energy (21 eV) that has to be accounted for in the case of O1s hole generation.

A completely different picture is drawn by the present results (Table 2) for the O1s shake-up spectrum. The triplet-coupled ($S'=1$) $\pi-\pi^*$ shake-up satellite is predicted 14.9 eV above the O1s main state, however, with the extremely small intensity of 0.02% relative to the O1s main state: such a state is hardly to be seen in the photoelectron spectrum (if the sudden limit conditions apply). The next shake-up peak in the O1s spectrum is no longer due to the singlet ($S'=0$) $\pi-\pi^*$ state, but states of the $(5\sigma)^{-1}(n\sigma)^1$ Rydberg-type series are pulled down right above the triplet-coupled $\pi-\pi^*$ satellite. As a result of strong configuration interaction between the higher lying second $\pi-\pi^*$ state ($S'=0$) and $(5\sigma)^{-1}(n\sigma)^1$ states, there is no longer a state with dominating $\pi-\pi^*$ character. Although the details of the calculated spectral distribution may be not taken literally at the present stage, the major qualitative features seem to be reproduced correctly, that is the missing triplet $\pi-\pi^*$ shake-up peak and the mixing of the singlet $\pi-\pi^*$ state with close lying $5\sigma-n\sigma$ valence-Rydberg states.

The different photoelectron spectra for C1s and O1s ionization can be rationalized by considering the localization properties of the orbitals 1π and 5σ involved in the low energy part of the shake-up spectrum. The 1π orbital in CO is localized on the side of the O atom while the centroid of the 5σ orbital is near the C atom. Thus a $\pi-\pi^*$ excitation introduces a charge transfer from O to C, a $5\sigma-n\sigma$ excitation an opposite charge transfer, assuming here that the unoccupied orbitals π^* and $n\sigma$ are only little biased to one or another side. Depending on the presence of a hole in the C1s or O1s level, such a charge transfer means either a screening of the core hole and is reflected by a low shake-up energy, or an antiscreening and a corresponding high shake-up energy. In the case of the C1s hole the $\pi-\pi^*$ satellites are pulled down and the $5\sigma-n\sigma$ satellites are pushed up. Reversed conditions apply to the case of an O1s hole: here the $\pi-\pi^*$ satellites are pushed up, while the $5\sigma-n\sigma$ state are pulled down, resulting in a mixing of the second (singlet) $\pi-\pi^*$ state with $5\sigma-n\sigma$ states.

References:

- 1) U. Gelius, J. Electr. Spectr. Rel. Phenom. 5, 985 (1974)
- 2) M.F. Guest, W.R. Rodwell, T. Darko, I.H. Hillier, and J. Kendrick, J. Chem. Phys. 60, 5447 (1977)
- 3) J. Schirmer, G. Angonoa, S. Svensson, D. Nordfors, and U. Gelius, J. Phys. B, in press
- 4) G. Angonoa, O. Walter, and J. Schirmer, J. Chem. Phys., in press