

Summary Abstract: An XPS study of "intensity borrowing" in core ionizations of CO upon coordination to transition metal atoms

H.-J. Freund and E. W. Plummer

Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

W. R. Salaneck

Xerox Webster Research Center, Webster, New York 14580

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The pronounced satellite structure accompanying the core ionizations of transition metal complexes has gained increasing interest since it has been shown that these molecules can serve as model systems for surface studies.¹ We show in this paper, experimentally, that the pronounced satellite structure is due to intensity borrowing by excited particle hole ion states caused by the screening of the core hole.²

The concept of intensity borrowing is based on the sudden approximation.³ In this limit, the ionization process does not lead to an ionic state, which is in a pure eigenstate of the $(N-1)$ -system but is rather a superposition of all possible ion-eigen states. The intensity of each ion state is proportional to⁴:

$$|\langle \psi_i^{\text{Ion}} | \psi_o^R \rangle|^2,$$

where ψ_i^{Ion} are the individual ion states and ψ_o^R is the unrelaxed hole state. These intensities fulfill the sum rule:

$$\sum_i |\langle \psi_i^{\text{Ion}} | \psi_o^R \rangle|^2 = 1.$$

If the ionization were adiabatic,⁵ the system would be left in one pure eigenstate and the sum contains only one term. The more ion states are necessary to describe the final state of the ionization, the more terms contribute to the sum. In other words, these additional states "borrow" intensity from the one adiabatic ionization peak.⁶

We have measured the total ionization intensity for the O1s-lines of free CO and Fe(CO)₅ using a capacitance manometer to monitor the pressure. The result is shown in Fig. 1. The figure allows us to compare the intensities of the main ionization lines. Since the relative core ionization intensities are proportional to the number of chemically equivalent atoms in the molecule we expect for Fe(CO)₅ a quintupled CO-intensity. We find that this is however not the case if we only compare the main lines: relative to CO about 30% intensity is missing. If we integrate over the complete spectrum we can account for the missing intensity. It is remarkable however, that the big shake-up-satellite at 5.3/6.6 eV only makes up for about half of the missing intensity. The rest is redistributed over a variety of states. Note, especially the broad low intensive peak at energies higher than 30 eV. A comparison with KKL Auger data¹ for transition metal complexes which provide the minimal energy for the creation

of a double ion shows that this peak is already in the continuum. This peak therefore has to be classified as shake off⁷ rather than shake up. It demonstrates that the continuum has to be taken into account when shake processes in transition metal carbonyls and also surfaces are discussed.^{2,8} This fact becomes even more obvious when relaxation energies are compared. We show elsewhere⁹ that the shake-processes into the continuum determine about 70% of the relaxation energy.

In order to assign the shake up peaks² in transition metal complexes we proceed again through a comparison with the

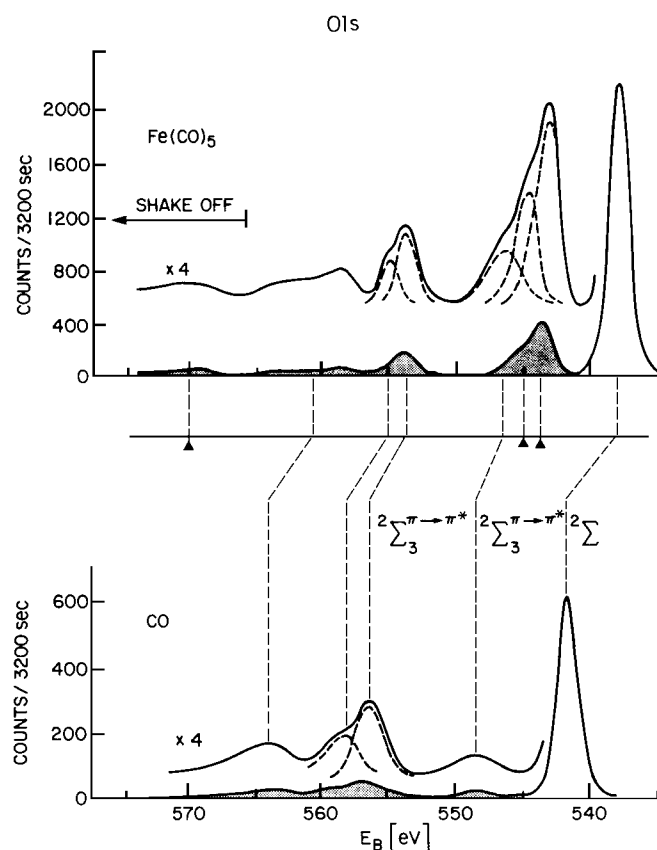


FIG. 1. Comparison of the O1s-core-ionization spectrum of CO and Fe(CO)₅. The two shake-up peaks at lowest energy in free CO are assigned according to Refs. 9 and 12.

uncoordinated molecule. According to hole state calculations¹² and comparisons to the excitation spectra of the neutral molecule⁹ the two lowest lying shake up peaks in CO must be assigned to the singlet and triplet coupled doublet states resulting from a $1\pi \rightarrow 2\pi$ excitation. The higher lying states are either $\sigma \rightarrow \sigma^*$ or Rydberg excitations. Upon coordination the main line shifts by about 3.3 eV. This energy contribution is due to the additional screening provided by the metal atoms if a hole is created on the ligand.² It is not a chemical shift in the initial neutral system resulting from alterations in the charge density on the ligand.¹³ It is not necessary to assume that the relaxed main line is a shake up peak (two-particle-hole) itself but rather a normal hole state.¹⁰ The $1\pi \rightarrow 2\pi$ derived shake up peaks are basically shifted by a similar energy as the main line, namely 2.5/2.0 eV. The difference in the shift is equivalent to an increase in excitation energy due to the expected increase in energy of the 2π levels upon coordination.¹¹ The higher excited states can as well be assigned with reference to the uncoordinated molecule as $\sigma \rightarrow \sigma^*$ and Rydberg states. The assignment is only tentative for the free molecule as well as for the complex. The most intense shake up peak has no analog in the uncoordinated molecule. It is assigned to a metal to CO charge transfer excitation. This excitation has no direct corresponding transition in the neutral

molecule. The basic mechanisms and the theoretical background is discussed in detail elsewhere by the authors.^{2,9} It is shown in Ref. 2, that the assignment presented in this paper can be successfully applied to CO-adsorbates as well.

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⁷Information on shake off-excitations in general can be found for example in: T. A. Carlson, *Photoelectron and Auger-Spectroscopy* (Plenum, New York, 1975), and references therein.

⁸A detailed discussion on shake off excitations in connection with free and coordinated CO will be published elsewhere (Ref. 9).

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¹⁰The theoretical basis for our conclusions is discussed in depth in Ref. (2).

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