

THE INFLUENCE OF COORDINATION ON MANY PARTICLE EFFECTS IN PHOTO-EMISSION SPECTRA

G. HOHLNEICHER, H.-J. FREUND, D. SADDEI and B. DICK

Lehrstuhl f. Theoretische Chemie der Universität zu Köln, W. Germany

Usually the first few ionizations observed in the photoemission spectrum of a small or medium size molecule are closely related to the detachment of a single electron from a specific molecular orbital. This one to one correspondence between photoionization bands and one particle levels, mostly does not hold, however, if we go to higher binding energies. In this "inner valence shell region" many particle effects become increasingly important.^{/1/} A situation of specific interest turns up if a small molecule like CO or N₂ is adsorbed on a metal surface or bound to a metal atom in a complex. In such systems the electrons associated with the metal are usually bound more loosely than those associated with the ligand. It is therefore, questionable whether the uppermost occupied orbitals of such ligands, can still be regarded as outer valence shell orbitals in the adsorbate or complex or not. In the latter case we may find much more pronounced many body effects in the "ligand range" of the coordinated system than we would expect from the free ligand.

For the core spectra such an enhancement of many body effects due to coordination is well known. For a great variety of adsorbates and transition metal complexes extended satellite structure is observed in the core spectra of the ligand which is absent in the free ligand.^{/2/} The appearance of these satellites has been mainly connected with the transition of an electron from occupied metal into unoccupied ligand orbitals.

To study this whole problem in more detail we applied many body perturbation theory to model systems like NiCO, NiN₂ etc. and to carbonyles like Ni(CO)₄ and Cr(CO)₆.^{/3/} The calculations are based on wavefunctions obtained from a modified version of the CNDO-for-

alism which we have developed especially for transition metal containing systems^{/4/}. To include many particle effects we used a type of diagonal 2-particle-1-hole Tam-Dancoff approximation (d2ph-TDA) introduced by Cederbaum et al.^{/5/}. The details of the calculations are given in ref.^{/3/}.

The results obtained for all the studied systems can be summarized as follows:

For the coordinated systems, the valence ionizations associated with ligand orbitals are indeed influenced more strongly by many body effects than the corresponding ionizations in the free ligand. This is true in spite of the fact that most of these orbitals are not altered very much by coordination. For the uppermost ligand orbitals the many particle effects lead to an increased relaxation, thus overcompensating the bond shift. This results in a decrease of ionization potentials instead of the expected increase. For carbonyles this is in accordance with the experimental observation^{/3a/}. Corresponding to the extended relaxation, satellite structure turns up in the ligand range which has also been found experimentally in the case of the carbonyles^{/2/}. In some cases we found a situation where an orbital of the ligand range contributes about equally to different final states. In most cases, however, the first few bands in the ligand range can at least be approximately connected with a specific orbital. Due to non uniform relaxation, the spacing and sometimes also the ordering is, however, not directly related to the one particle levels. It is therefore, difficult to use this data for the experimental determination of bond shifts.

The main reason for the increased importance of many body effects is the appearance of low lying valence excitations associated with a charge transfer from the metal d-orbitals into unoccupied ligand orbitals. Due to the existence of a hole in the usually occupied ligand levels these CT-configurations are stabilized considerably, so that they lie at about the same energies - or even sometimes lower - than the Koopmans configurations which describe the direct removal of electron from the ligand orbitals. Thus the main source of the enhancement of many body effects in the ligand range of the valence spectrum is the same as the one usually believed to be responsible for the appearance of the the extended satellite structure found in the

core spectra of the coordinated systems^{/2/}.

For the core spectra our calculations confirm the above given explanation. The extended satellite structure is mainly connected with low lying valence excitations with metal to ligand CT-character. To some extent, however, local metal excitations also contribute to the newly appearing satellites. In addition, the weak satellites found in the free ligand should show up in the coordinated systems, too, but at somewhat larger distances from the main peak than in the free ligand. Some hints to these satellites, which result from the local ligand excitations, are found in the core spectra of carbonyles^{/2/} but not in the adsorbates up to now.

To one respect our results are, however, not in accordance with the recently published analysis of the core spectra of model system NiCO by Bagus and Hermann^{/6/}. These authors came to the conclusion that the first peak in the C and O core spectra is related to the screened state in which considerable charge is transferred from the Ni-atom to the ligand. The satellite newly appearing in the bonded system is then attributed to the unscreened state. An analysis of the intensity distribution, given in the same paper, shows, however, that the so called "screened" state contains about eight times more of the Koopmans configuration than the "unscreened" one. Together they contain about 80% of this configuration. We cannot understand why one should term a final state which contains about 70% of the Koopmans configuration - in full agreement with our calculation - "screened" state and another one containing only about 10% "unscreened". To our opinion the most prominent of the newly appearing satellites in the coordinated systems are related to valence excitations with pronounced CT-character.

/1/ I. Schirmer, L.S. Cederbaum, J. Phys. B11, 1889 (1978)

/2/ E.W. Plummer, W.R. Salaneck, I.S. Miller, Phys. Rev. B18, 1973 (1978)

/3/a) D. Saddei, H.-J. Freund, G. Hohlneicher, Chem. Phys. submitted

b) D. Saddei, H.-J. Freund, G. Hohlneicher, Surf. Science, in press

c) D. Saddei, H.-J. Freund, G. Hohlneicher, Surf. Science, submitted

/4/a) H.-J. Freund, G. Hohlneicher, Theoret. Chimica Acta 25, 289 (1979)

b) H.-J. Freund, B. Dick, G. Hohlneicher, Theoret. Chimica Acta in press

/5/ L.S. Cederbaum, W. Domcke, in Advances in Chemical Physics

Vol 36, Ed. I. Prigogine and S.A. Rice (Wiley, New York, 1977)

/6/ P.S. Bagus, K. Hermann, Surf. Science 89, 586 (1979)