VARIABLE PHOTON ENERGY PHOTOELECTRON SPECTROSCOPY OF TRANSITION METAL COMPLEXES

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Variable photon energy PhotoElectron Spectroscopy (PES) is now well established as a powerful tool in electronic structure determination.

We have already investigated a wide range of chemical systems, with examples drawn from both classical coordination and organometallic chemistry and have found the technique to be a sensitive probe of the localization properties of valence electrons [1,2]. In particular, the very different behaviour of the photoionization cross sections of d and f electrons with respect to s and p ones through the appearance of features due to the atomic dynamic effects of the photoelectrons (Cooper minima, delayed maxima, autoionizations) provides extensive information on metal-ligand covalency [3]. Obviously synchrotron radiation is a unique tool to observe such phenomena, allowing the access to an extensive range of photon energies in VUV-PE experiments.
Here we present some results from variable photon energy investigations of gas-phase transition metal compounds, in particular those on $TiMeCl_3$ and on $Ni(acac)_2$. (acac=acatylacetonate) [2].
The photoelectron spectrum of $TiMeCl_3$ has been measured with photon energies varying between 20 and 50 eV. Obtained results enable unambiguous assignment of the PE bands and indicate a significant contribution of Ti *3d* character to the metal-carbon bond. Indeed we can observe that at low energies the spectrum is dominated by halogen ionizations, between 28 and 40 eV carbon based ionization

increase in relative intensity, and above 40 eV the metal based ionizations dominate the spectrum.

The photoelectron spectra of Ni(acac)$_2$ have been measured in the 30÷80 eV photon energy range. An analysis of the branching ratio of the first band as a function of photon energy confirms our (previous) [4] description of the HOMO (Highest Occupied Molecular Orbital) as the b3$_g$ component of the ligand _3 orbitals, with modest admixture of Ni d_{yz} orbital. Moreover the whole PE spectrum has been reassigned on the ground of the observed variations in relative band intensity ratios. The enhancement shown by the bands in the IE region between 7.6 and 8.8 eV in the spectra taken at photon energies near the Ni 3p threshold, most likely due to resonant processes following Ni 3pØ3d excitations, confirms the nature of almost pure *d* orbitals of these bands.

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