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Reassignment of the Valence Photoelectron Spectra of $Ni(\eta^3\text{-}C_3H_5)_2$ Using Variable Energy Photoelectron Spectroscopy

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Photoelectron spectra, combined with molecular orbital calculations, have been widely used to assign the molecular orbital (MO) ordering in molecules but, even for some small molecules, the assignments have often been controversial. In particular, for the simple "sandwich" molecule $Ni(\eta^3\text{-}C_3H_5)_2$, there have been many different assignments since the first theoretical calculation[1] and photoelectron spectrum.[2a] Most of the controversy has centered on the assignment of the low ionization energy peak (peak 1) at 7.8 and 7.6 eV in the Ni and Pd analogues respectively. Some early theoretical[3] and experimental He I studies[2] (along with a He II spectra of $Ni(\eta^3\text{-}CH_3C_3H_4)_2)$[2b] support the assignment of peak 1 to the ionization of a metal d electron, whereas the earliest[1] and later[4,5] theoretical papers have agreed that the lowest ionization energy is due to the nonbonding $7a_u$ molecular orbital.

In 1980, Böhm et al.[4] obtained the He I and He II spectra of $Pd(\eta^3\text{-}C_3H_5)_2$, $Pd(\eta^3\text{-}CH_3C_3H_4)_2$, and $Pt(\eta^3\text{-}CH_3C_3H_4)_2$. Using a detailed experimental and theortical analysis, they assigned peak 1 in all $M(\eta^3\text{-}C_3H_5)_2$ (M = Ni, Pd and Pt) compounds to the ligand $7a_u$ orbital. A wide variety of theoretical calculations[5] have agreed with this assignment.[6] Indeed, the latest theoretical papers in 1989 by Decleva et al.[5j] use Böhm's assignment[4] as a benchmark for their theoretical calculations.

Despite this apparent broad agreement on the assignment, there are discrepancies. The most important one involves the different intensity variations of peak 1 from He I to He II photon energies between the Ni and Pd, Pt analogues.[5f,g] For Ni (i.e. $Ni(\eta^3\text{-}CH_3C_3H_4)_2$),[2] peak 1 increases in relative intensity from He I to He II spectra, whereas peak 1 decreases sharply for Pd and Pt compounds. Since the metal d orbital cross sections increase dramatically from He I to He II energies (while the C2p cross section decreases dramatically),[7] it seems highly unlikely that peak 1 should be assigned to $7a_u$ for $Ni(\eta^3\text{-}C_3H_5)_2$. However, the theoreticians continue to argue that the MO ordering is the same in all the Ni, Pd, and Pt compounds and that the apparent odd intensity behavior for peak 1 in Ni was due to some type of resonance effect (e.g. shape resonances, multielectron resonances) which have been seen in other compounds using variable-energy photoelectron spectra.[8]

We have undertaken a detailed He I, He II, and variable energy photoelectron study of $Ni(\eta^3\text{-}C_3H_5)_2$ and its Pd and Pt analogs.[9] Representative spectra for the Ni and Pd compounds at 32 and 70 eV photon energies are shown in Figure 1. These spectra show, more clearly than the He I and He II spectra, that the relative intensities for peak 1 in the two compounds change very differently with photon energy: peaks 1 (and 2) in $Ni(\eta^3\text{-}C_3H_5)_2$ increase in relative intensity from 32 to 70 eV, while, for the Pd analogue, peak 1 decreases dramatically.

Of even greater importance, the relative intensities vary smoothly in both compounds from 20 to 80 eV. These smooth variations in intensity are best shown by the branching ratios ($A_i/\Sigma A$) in Figure 2a. This plot shows that there are no strong resonance effects for the $Ni(\eta^3\text{-}C_3H_5)_2$ MO's from 20 to 80 eV. Two conclusions are evident. First, the assignments of peak 1 in the Ni and Pd analogues *must* be different. Second, peak 1 in $Ni(\eta^3\text{-}C_3H_5)_2$ must be due to 3d ionization(s) while peak 1 in the Pd analogue is due to the ligand $7a_u$ orbital.

A Gelius model treatment[13] of the intensities further confirms the above assignment and leads to a complete assignment of the Ni spectrum. At low photon energy, this atomic treatment of cross sections is usually not valid, but by the use of ~50 eV photon energies, the Gelius treatment gives good semiquantitative agreement with experiment.[8] We use the atomic cross sections from Yeh and Lindau,[7] and the orbital characters from the INDO calculations of Böhm[4] assigning the peaks as in Figure 2b (similar with the assignment in 1976 by Batich),[3b] which yields semiquantitative agreement with experiment for five of the six peaks. Peak 1 thus contains two Ni 3d ionizations, while peak 2 contains one Ni 3d ionization plus the ligand $7a_u$ orbital. Obviously, the exact position of this latter orbital cannot be ascertained and it

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(6) Many of these calculations have focused on the large reorganization energies (=relaxation plus correlation energies) of the metal d orbitals which make it difficult to use Koopmans' theorem for assignment. However, even after considering the large Ni 3d reorganization energies, all theoretical calculations in the recent decade[5] agree with the assignment of peak 1 in $Ni(\eta^3\text{-}C_3H_5)_2$ to the ligand $7a_u$ orbital.

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(9) The compounds were synthesized by methods in the literature.[10] The He I and He II spectra were obtained using an ESCA 36 spectrometer with a resolution of ~20 meV. The variable energy spectra were obtained at the Canadian Synchrotron Radiation Facility (CSRF) at the 1-GeV storage ring of Aladdin, using a modified ESCA 36 spectrometer.[11] The spectra were recorded between 20 eV and 80 eV photon energy using a Quantar No. 3395A position sensitive detector. Over 20 spectra at different photon energies were recorded for the Ni and Pd compounds; but only enough Pt compound was available for six spectra. The spectra were calibrated with the Ar $3p_{3/2}$ line at 15.759 eV, at a resolution of ~100 meV. Band areas were obtained by fitting the spectra with Gaussian/Lorentzian lineshapes using an iterative procedure.[12]

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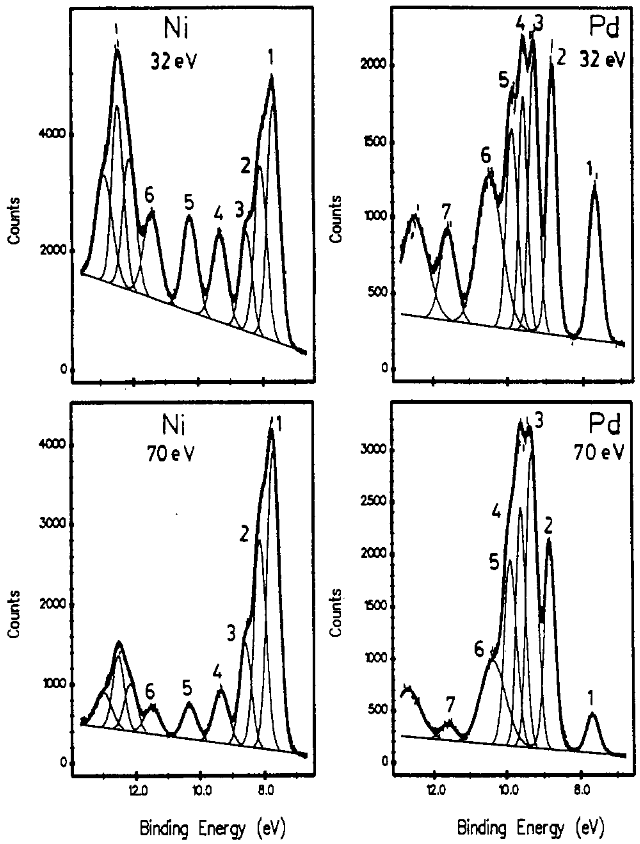

Figure 1. Photoelectron spectra at 32 and 70 eV for Ni(η^3-C_3H_5)$_2$ and Pd(η^3-C_3H_5)$_2$. Eight molecular orbitals are expected to result from the 2p$_\pi$ orbitals of allyl and the 3d or 4d orbitals of Ni or Pd respectively, of which six are resolved for Ni and seven for Pd. Assignments for the Ni compound are given in Figure 2.

could have an IP between peaks 1 and 3. A more detailed analysis of these branching ratios using MS–Xα cross sections[8] is underway.

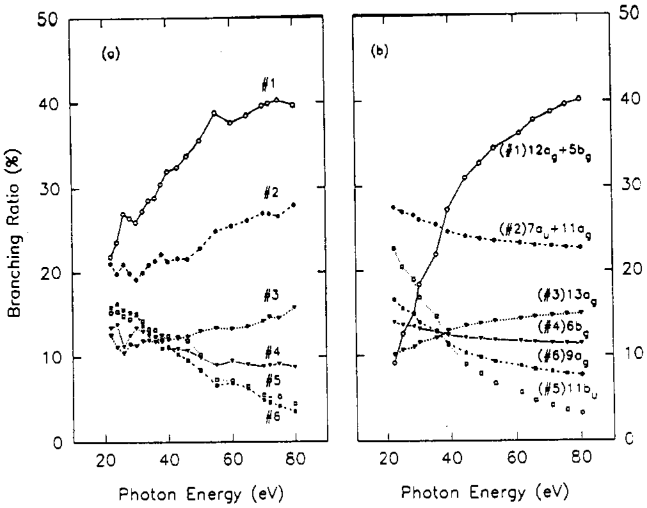

Figure 2. (a) Experimental and (b) calculated branching ratios with the Gelius model and MO characters from the INDO calculations[4] for Ni(η^3-C_3H_5)$_2$. MO assignments: band 1, Ni 3d$_{z^2}$ + Ni 3d$_{xy}$; band 2, diallyl π a$_u$ + Ni 3d$_{x^2-y^2}$; band 3, Ni 3d$_{yz}$; band 4, Ni 3d$_{xz}$ bound with diallyl π b$_g$; band 5, diallyl π b$_u$; band 6, diallyl π a$_g$. This assignment gives by far the best agreement between experimental and theoretical branching ratios.

Because of the large Ni 3d orbital reorganization energy, the Ni 3d orbitals in the ground state will most likely lie below the ligand 7a$_u$ orbital. Böhm has pointed out[4] that the reorganization energies are similar for Ni 3d, Pd 4d, and Pt 5d orbitals, although Lichtenberger has emphasized that the 3d reorganization energy is generally considerably larger than the 4d.[14] The trend in d IP's from our photoelectron spectra is consistent with the d reorganization trend and also with the trend in IP's for the d^{10} atoms (Ni 3d = 5.9 eV; Pd 4d = 8.6 eV; Pt 5d = 8.7 eV),[15] as well as the recent analyses of the metal d MO energies in metal carbonyls by Ziegler.[16]

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