The Palladium 4d Cooper Minimum: its Application in Assignment of the Gas-phase Photoelectron Spectra of $[Pd(\eta^3\text{-}C_3H_5)_2]$

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The valence band intensities in the gas-phase photoelectron spectra of $[Pd(\eta^3\text{-}C_3H_5)_2]$ have been determined as a function of photon energy (range 20–170 eV): the band intensities for the non-bonding Pd 4d orbitals are in good agreement with the trend predicted by the atomic model and show a very well-defined Cooper minimum, thus allowing a definitive assignment of the spectra.

Since Cooper showed that a minimum is expected in the atomic photoelectron (PE) cross section for a subshell having radial node(s) in its initial wave function,[1] the Cooper minimum effect has been thoroughly studied for atoms[2] and, more recently, for a variety of small molecules containing atoms (sulfur, chlorine, bromine, iodine or phosphorus) with *n*p ($n \geq 3$) lone-pair orbitals.[3] These results showed that the lone-pair orbitals of molecules behave like their atomic counterparts.[3,4] It has also been recognized that a Cooper minimum is expected for molecules containing *n*d ($n \geq 4$) orbitals. However, while the transition metal *n*d Cooper minimum effect has been observed by using solid-state photoemission techniques for pure or adsorbed metals,[5] studies of the Cooper minimum in gaseous organometallic compounds using synchrotron radiation have been carried out only on metal hexacarbonyls,[6] $[M(CO)_6]$, (M = Mo and W) and metallocenes,[7] $[M(\eta^5\text{-}C_5H_5)_2]$, (M = Ru and Os). For these molecules, the intensities of bands with mainly *n*d character decrease at higher photon energies, consistent with the approach to the Cooper minimum, but the experiments were not carried out to high enough energy to observe the complete effect. This prompts us to report a study of the PE spectra for $[Pd(\eta^3\text{-}C_3H_5)_2]$ from 20 eV to 170 eV,† a range that is expected to cover both the cross-section maximum and Cooper minimum (around 35 and 115 eV in theory,[8] respectively) region in the atomic Pd 4d photoionization cross-section. The He^I and He^{II} PE spectra of $[Pd(\eta^3\text{-}C_3H_5)_2]$ have been assigned previously,[9] and the assignment of the PE spectrum of its analogue, $[Ni(\eta^3\text{-}C_3H_5)_2]$, has been the subject of a prolonged controversy.[10] The measurement of the variable PE spectra for $[Pd(\eta^3\text{-}C_3H_5)_2]$, particularly the observation of the Cooper minimum, is important in making definitive assignments for these two compounds.

The He^I PE spectrum of $[Pd(\eta^3\text{-}C_3H_5)_2]$, is shown in Fig. 1. Bands 1, 6, 7 and 8 were assigned to molecular orbitals (MO) with mainly allyl ligand C 2p character, and band 2, 3, 4 and 5 were attributed to MOs with mainly Pd 4d character.[9] The new experimental results described below, especially the intensity variations for these bands as a function of energy, are fully consistent with this assignment and with theoretical predictions of atomic cross-sections.

† $[Pd(\eta^3\text{-}C_3H_5)_2]$ was synthesized by the literature method and purified by vacuum sublimation.[15] The He^I (Fig. 1) and He^{II} spectra were obtained using an ESCA 36 spectrometer with a resolution of *ca.* 20 meV. The variable photon 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[16] fitted with a Quantar No. 36 position sensitive detector. The spectra were recorded between 20 and 170 eV photon energy at a resolution of *ca.* 100 meV between 20 and 80 eV, and *ca.* 500 meV between 80 and 170 eV. The He^I spectrum was calibrated with the Ar $3p_{3/2}$ line at 15.759 eV. The sample was introduced into the ionization region by allowing it to sublime from a side-arm tube into the gas cell at 5 °C. The spectra were fitted with Lorentzian–Gaussian peak shapes using an iterative procedure,[17] and peak areas were used to determine intensities.

The experimental spectra (Fig. 1) show immediately that band 1 (mainly of C 2p character) drops greatly in intensity relative to bands 2, 3, 4 and 5 (Pd 4d character) from 21.2 to 90 eV, and then increases greatly to *ca.* 130 eV before decreasing again. This trend is shown more quantitatively by the theoretical ratio of atomic cross sections,[8] σ(Pd 4d)/σ(C 2p) (the dashed line in Fig. 2), along with the experimental Pd 4d/C 2p band intensity ratio ($A_{2+3+4+5}/A_1$, closed

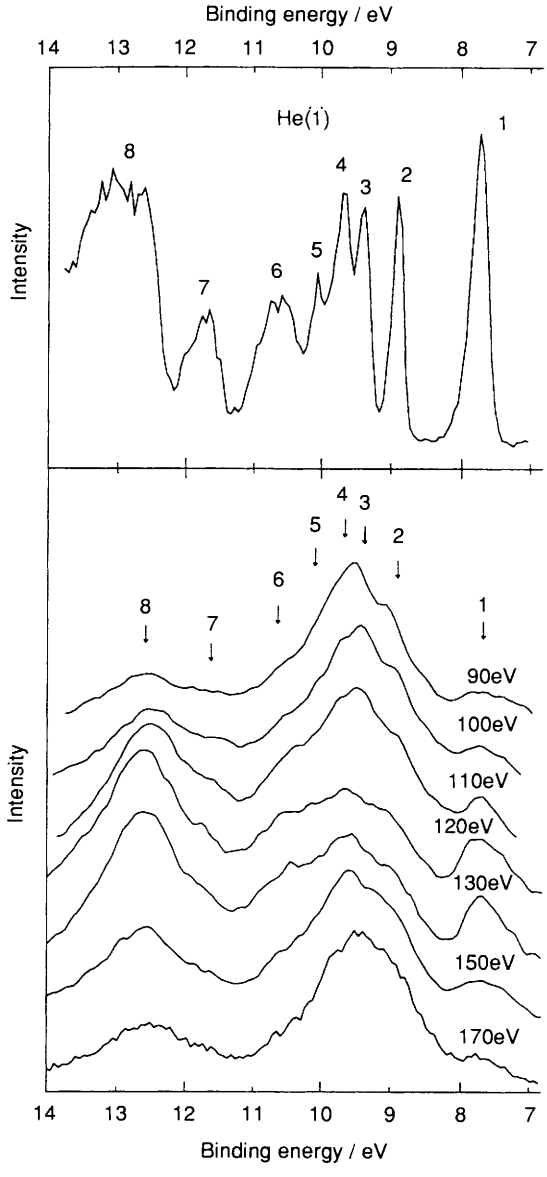

Fig. 1 The He^I PE spectrum (20.1 eV, above) and a selection of variable energy PE spectra (90–170 eV, below) of $Pd(\eta^3\text{-}C_3H_5)_2$, showing the trends in intensity as a function of photon energy. The band labelling is defined above the spectra.

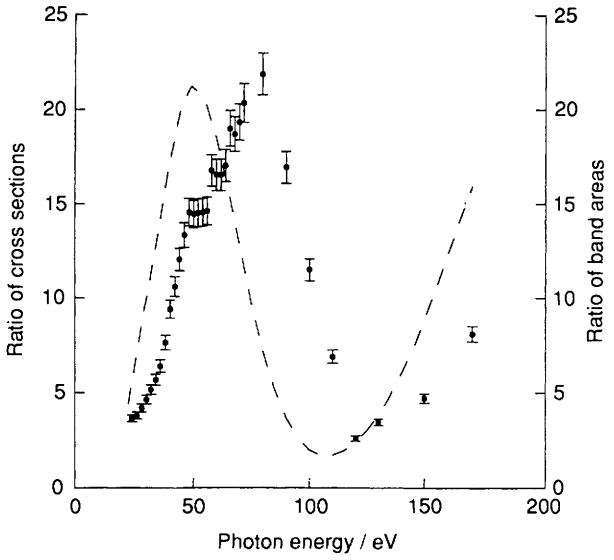

Fig.2 Dashed line—the theoretical ratio of atomic cross-sections σ(Pd 4d)/σ(C 2p) as a function of photon energy.[8] Closed circles—experimental values of the band intensity ratio $A_{2+3+4+5}/A_1$ (A_n is the intensity of band n in the PE spectrum) as a function of photon energy. The ratio of cross-sections, rather than σ(Pd 4d) alone, is used because absolute cross-sections are difficult to determine accurately.

circles in Fig. 2, A_n is the observed intensity of band n). Both experimental and theoretical ratios reflect the dramatic but smooth decrease in C 2p cross section from 20 to 170 eV, the increase in Pd 4d cross-section from 20 to *ca.* 50 eV, and the great decrease in Pd 4d cross-section to a Cooper minimum at *ca.* 110 eV. Note that the theoretical ratio Pd 4d/C 2p fluctuates dramatically from *ca.* 5 at 20 eV to *ca.* 20 at *ca.* 50 eV, to *ca.* 2 at *ca.* 110 eV, and back to *ca.* 18 at 180 eV and that the experimental Pd 4d/C 2p ratio of band intensity is in excellent qualitative agreement. The position of the experimental maximum and minimum are shifted to higher energies (Fig. 2), but this is not surprising considering the known sensitivity of the outfoing f wave potential for heavy atoms[11,12] and the approximations made in the calculations.[8] The potential effect due to the Pd 4p resonance[13] (the binding energy of Pd $4p_{3/2}$ is *ca.* 51 eV and Pd $4p_{1/2}$ *ca.* 56 eV)[14] is not large in this molecule, although there are distinct shoulders on the experimental ratios at about these energies (Fig. 2). This is probably because all 4d orbitals in $[Pd(\eta^3\text{-}C_3H_5)_2]$ are filled or involved in bonding while the resonance effect requires a vacant orbital.

Why is the Cooper minimum so clear for this molecule? According to the molecular orbital energy diagram for $[Pd(\eta^3\text{-}C_3H_5)_2]$,[9] among the eight outer-valence molecular orbitals (corresponding to bands 1–7 in Fig. 1, with one degeneracy) only one is bonding, while all others are essentially non-bonding (four MOs with mainly Pd 4d character and three with mainly allyl C 2p π character). Band 1 is assigned to a non-bonding C 2p π combination (a_u symmetry) and bands 2–5 to non-bonding Pd 4d orbitals and, since mixing is not symmetry allowed, these orbitals should largely retain their atomic character. This may account for the particularly good agreement between theory and experiment shown in Fig. 2. Of the other bands, band 6 is assigned to a combination of the degenerate metal–ligand bonding [Pd $4d_{xz}$ with the $(allyl)_2$ b_g orbital] and ligand C 2p non-bonding (symmetry b_u) orbitals, band 7 to a ligand C 2p non-bonding orbital (symmetry a_g), and band 8 to one or more ligand σ bonding orbitals. Band 6 shows a much smaller Pd 4d Cooper minimum effect than bands 2–5, as expected for a bonding orbital with much lower Pd 4d character.

From the above observations, the following conclusions can be made: (*i*) The non-bonding *n*d ($n \geq 4$) molecular orbitals, like the non-bonding *n*p ($n \geq 3$) lone-pair orbitals,[3] behave according to the atomic model and exhibit a strong Cooper minimum effect in molecules. (*ii*) Mixing of *n*d with C 2p orbitals through chemical bonding in organometallic compounds greatly reduces the Cooper minimum effect. It follows that mesurement of the Cooper minimum in the PE spectra should give information on the degree of covalency in organometallic compounds. (*iii*) Clearly, the intensity variations observed in the present work allow an unambiguous assignment of the photoelectron spectra of $[Pd(\eta^3\text{-}C_3H_5)_2]$.

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References

1 (*a*) J. W. Cooper, *Phys. Rev.*, 1962, **128**, 681; (*b*) S. T. Manson and J. W. Cooper, *Phys. Rev.*, 1968, **165**, 126.
2 (*a*) Ar: R. G. Houlgate, J. B. West, K. Codling and G. V. Marr, *J. Phys. B*, 1974, **7**, L470; *J. Electron Spectrosc. Relat. Phenom.*, 1976, **9**, 205; (*b*) Kr: D. L. Miller, J. D. Dow, R. G. Houlgate, G. V. Marr and J. B. West, *J. Phys. B*, 1977, **10**, 3205; (*c*) Xe: L. Torop, J. Morton and J. B. West, *J. Phys. B*, 1976, **9**, 2035.
3 (*a*) CS_2 and COS: T. A. Carlson, M. O. Krause and F. A. Grimm, *J. Chem. Phys.*, 1982, **77**, 1701; (*b*) CCl_4: T. A. Carlson, M. O. Krause, F. A. Grimm, P. Keller and J. W. Taylor, *J. Chem. Phys.*, 1982, **77**, 5340; (*c*) Cl_2: T. A. Carlson, M. O. Krause, F. A. Grimm and T. A. Whitley, *J. Chem. Phys.*, 1983, **78**, 638; (*d*) HX (X = Cl, Br and I): T. A. Carlson, A. Fahlman, M. O. Krause, T. A. Whitley and F. A. Grimm, *J. Chem. Phys.*, 1984, **81**, 5389 and references cited therein; (*e*) $SiCl_4$: T. A. Carlson, A. Fahlman, M. O. Krause, T. A. Whitley, F. A. Grimm, M. N. Piancastelli and J. W. Taylor, *J. Chem. Phys.*, 1986, **84**, 641; (*f*) PF_3: J. C. Green, N. Kaltsoyannis, K. H. Sze and M. A. MacDonald, *J. Chem. Soc., Dalton Trans.*, 1991, 2371.
4 V. McKoy, T. A. Carlson and R. R. Lucchese, *J. Phys. Chem.*, 1984, **88**, 3188.
5 (*a*) I. Abbati, L. Braicovich, G. Rossi, I. Lindau, U. del Pennino and S. Nannarone, *Phys. Rev. Lett.*, 1983, **50**, 1799; (*b*) P. S. Wehner, S. D. Kevan, R. S. Williams, R. F. Davis and D. A. Shirley, *Chem. Phys. Lett.*, 1978, **57**, 334; (*c*) G. Rossi, I. Lindau, L. Braicovich and I. Abbati, *Phys. Rev. B*, 1983, **28**, 3031; (*d*) I. Abbati, L. Braicovich, C. Carbone, J. Nogami, J. J. Yeh, I. Lindau and U. del Pennino, *Phys. Rev. B*, 1985, **32**, 5459.
6 G. Cooper, J. C. Green, M. P. Payne, B. R. Dobson and I. H. Hillier, *J. Am. Chem. Soc.*, 1987, **109**, 3836.
7 G. Cooper, J. C. Green and M. P. Payne, *Mol. Phys.*, 1988, **63**, 1031.
8 J. J. Yeh and I. Landau, *At. Nucl. Data Tables*, 1985, **32**, 1.
9 M. C. Böhm, R. Gleiter and C. D. Batich, *Helv. Chim. Acta*, 1980, **63**, 990.
10 (*a*) M. C. Böhm and R. Gleiter, *Chem. Phys. Lett.*, 1986, **87**, 123; (*b*) D. Moncrieff, I. H. Hillier, V. R. Saunders and W. von Niessen, *Chem. Phys. Lett.*, 1986, **131**, 545.
11 B. R. Tambe and S. T. Manson, *Phys. Rev. A*, 1984, **30**, 256.
12 K. Gürtler, K. H. Tan, G. M. Bancroft and P. R. Norton, *Phys. Rev. B*, 1987, **35**, 6024.
13 C. Guillot, Y. Ballu, J. Paigné, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Pétroff and L. M. Falicov, *Phys. Rev. Lett.*, 1977, **39**, 1632.
14 J. C. Fuggle and N. Mårtensson, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **21**, 275.
15 J. K. Becconsall, B. E. Job and S. O'Brien, *J. Chem. Soc. (A)*, 1967, 423.
16 G. M. Bancroft, D. J. Bristow and L. L. Coatsworth, *Chem. Phys. Lett.*, 1981, **82**, 344.
17 G. M. Bancroft, J. Adams, L. L. Coatsworth, C. D. Bennewitx, J. D. Brown and W. D. Westwood, *Anal. Chem.*, 1975, **47**, 586.