

Chemical Effect on the ${}^2D_{5/2}$: ${}^2D_{3/2}$ Branching Ratio of the $5d$ Photoionization of Pb

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(Received 12 August 1985)

Significant intershell interaction effects are observed in the $5d$ branching ratio of the heavy non-transition metal Pb. Atomic calculations reveal their atomic character, but a distinct influence of the chemical environment on the branching-ratio's energy dependence is reported for the compounds PbI_2 and PbO_2 .

PACS numbers: 32.80.Fb, 32.80.Hd, 79.60.Cn, 79.60.Eq

Atomic photoionization cross sections and branching ratios have attracted much attention over recent years because they are very sensitive to atomic many-body interactions.¹ This is also generally true for photoionization processes in solids. Some experiments have been reported recently in which partial subshell cross sections of solids² and branching ratios of a solid compound³ show deviations from atomic behavior. This raises the important question of how, and to what extent, atomic exchange and correlation effects are modified in solids.

In this paper we study this question by an investigation of the $5d$ branching ratios in metallic Pb and in the solid compounds PbI_2 and PbO_2 which we compare with atomic calculations. We demonstrate for the first time that the structure in the branching ratio of solids arises from coupling to other core excitations, in the present case from $5d$ - $4f$ coupling. In addition, we observe a pronounced chemical effect on the $5d$ branching ratio in Pb compounds which we attribute to a chemical effect on the $5d$ - $4f$ intershell interaction. We argue that the intershell interaction is extremely sensitive to the small change in the $5d$ electronic wave function introduced by the chemical environment of a Pb atom in a solid. Note that the $5d$ electron binding energies of Pb are 18 eV ($J = \frac{5}{2}$) and 21 eV ($J = \frac{3}{2}$), and the $5d$ level is usually considered an atomiclike core level, hardly affected by chemical bonding in compounds. Such small changes do not influence the partial subshell cross sections notably, but are clearly detectable in the $5d$ photoionization branching ratio.

Experiments have been performed with the angle-integrated photoemission setup at the FLIPPER monochromator^{4,5} at the Hamburger Synchrotron-

strahlungslabor HASYLAB. The base pressure of the system was 1×10^{-10} Torr. Metallic Pb samples were evaporated from Ta baskets onto stainless-steel substrates. PbI_2 was prepared by cleaving a single crystalline sample *in situ*; Fig. 1 shows a valence-band energy-distribution curve (EDC) of this compound.⁶ PbO_2 could not be prepared *in situ*; we introduced a

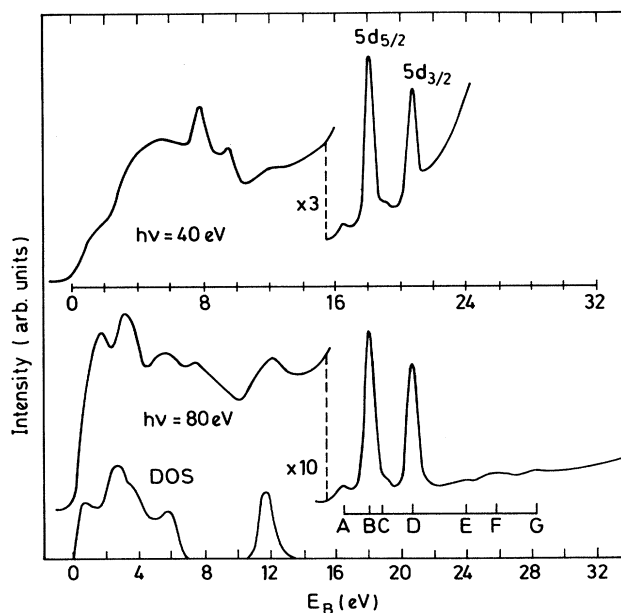


FIG. 1. Energy-distribution curve of PbI_2 , excited by s -polarized light. For comparison, the calculated density of states by Schlüter and Cohen (Ref. 7) is also shown. The $5d$ photoemission is accompanied by satellite structure labeled A-G.

powder sample, pressed into an In substrate, into the spectrometer chamber. While this preparation procedure does not yield a sample of high purity, the $5d$ branching ratio so obtained may still be regarded as a reference measurement of Pb in its highest oxidation stage.

The $5d$ branching ratio is obtained from EDC's taken at stepwise-varied photon energies and after subtraction of a linear background. The ionized $5d_{5/2}$ and $5d_{3/2}$ electrons have different kinetic energies as a result of the spin-orbit interaction. The measured photoemission intensities depend on the atomic cross sections, but also on photoelectron mean free path, surface refraction, and analyzer transmission, which are all dependent on the kinetic energy.⁸ The latter factors describe the probability of the photoelectrons leaving the solid without being scattered inelastically and the experimental detection probability for the photoelectron (analyzer transmission) which can be determined experimentally.⁵ The escape probability of photoelectrons from a solid sample has recently been investigated for Au.⁵ Here we shall use these results to evaluate branching ratios and cross sections for Pb metal and its compounds using measured photoemission intensities which can then be compared with atomic cross-section calculations. Note that this evaluation procedure is not very critical for branching ratios because only the differences of escape and detection probabilities are needed for photoelectrons having little relative energy difference.

The $5d$ photoemission spectrum of PbI_2 shows satellite structure (see Fig. 1) concerning which some comments are necessary. Two main $5d$ emission lines, labeled B and D in Fig. 1, are clearly dominant, and we relate these two peaks to the atomic $^2D_{5/2}$ and $^2D_{3/2}$ core hole states of Pb. Structures A and C, which have the same energy separation as B and D (2.6 eV), are probably due to crystal-field splitting. Because B and C partly overlap and cannot be deconvoluted reliably for all spectra as a result of limited experimental resolution, we have neglected the satellite structure in our study. The possible error can be estimated from the energy dependence of the intensity ratio between peaks A and B which was found to be constant at a value of 0.1 for photon energies above 70 eV. Thus the energy dependence of the main $5d$ spin-orbit components is not disturbed by underlying unresolved satellite structure.

Figure 2 shows the $5d$ branching ratio of Pb. Included are results of a previous measurement for metallic Pb by Johansson *et al.*⁹ which covers the energy range below 200 eV. Our data for the metal at 160- and 180-eV photon energies agree reasonably well with the earlier results, but the pronounced rise in the branching ratio between 180 and 250 eV shown by our data escaped the previous authors' attention.

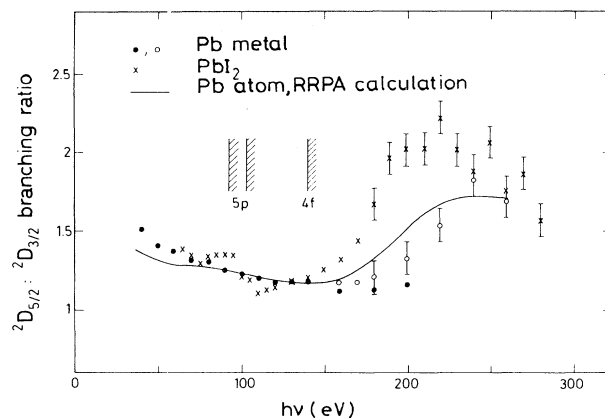


FIG. 2. Comparison of the $5d$ branching ratio of Pb for the metal, solid PbI_2 , and the atom. Experimental errors for our data are ± 0.02 below, and ± 0.1 above, 180 eV. Data of Johansson *et al.* (solid circles) are taken from Ref. 9.

The result of calculations in the relativistic random-phase approximation (RRPA)¹⁰ for a free Pb atom is also shown in Fig. 2. These calculations were performed by including all twelve channels allowed by relativistic dipole excitations of the $5d$ and $4f$ shells. It has been found in similar calculations¹¹ for Hg that the inclusion of other channels which might contribute, namely the channels arising from excitations of $5s$ and $5p$ shells, does not change the results substantially.

By comparing theoretical results for the atom and experimental data for the metal we find a satisfactory agreement over the entire energy range. The differences do not exceed those previously found for the photoionization parameters of Hg where the results of the atomic RRPA calculation¹¹ were compared to metal-vapor experiments.¹² At this level of accuracy we can conclude that the behavior of the $5d$ branching ratio in the metal is essentially atomlike. Note in particular that this includes the pronounced rise of the branching ratio at around 200 eV as a result of coupling of the $5d$ excitations to the $4f$ excitations which reach their maximum oscillator strength above 200 eV. This atomic intershell interaction is clearly reflected in the metal data contrary to the conclusion of the earlier work on Pb metal.⁹

Further included in Fig. 2 are our experimental results for the branching ratio of the solid compound PbI_2 . Previously determined branching-ratio data for PbI_2 are available for photon energies below 55 eV¹³; at selected photon energies these data were reproduced. Figure 2 contains our results above 65 eV. Up to 150 eV they agree quite well with the metal with some slightly more pronounced structure around 100 eV. For higher photon energies, however, the branching ratios for PbI_2 and Pb metal are distinctly different: for the compound the rise of the branching ratio is

shifted by some 40 eV towards lower photon energies, and a maximum value of 2.0 is reached while the maximum measured value for the metal is 1.8, and the calculated value is 1.7. Essentially the same behavior is found for PbO_2 . Since the branching ratios of the two compounds agree within the margin of error we have not included the PbO_2 values in Fig. 2.

We conclude that the difference in branching ratios between the metal and the compound is related to the $5d$ - $4f$ coupling because it is this interaction which shapes the $5d$ branching ratio in the energy region studied. The effect of this intershell coupling on the photoionization parameters is sensitive to the detailed form of the electronic wave function, and it appears possible that a change in the $5d$ wave function in the compound induced by the chemical environment accounts for the observed difference. Note that this change is only small because the Pb $5d$ electrons form a shallow core state rather than dispersive valence band states.⁶

Chemical effects on core absorption spectra in the presence of intershell interactions have been reported for a number of compounds^{14,15} demonstrating sensitivity of the absorption process to the detailed form of the potential in the absorbing atom. Very dramatic effects have been observed in the series of successively valence-ionized atoms¹⁶ Ba , Ba^+ , and Ba^{++} ; these were induced by distortions of the atomic potential on a much larger scale. In these instances, however, the final-state wave functions show severe deviations from the single-particle approximation due to exchange and correlation interactions with the core hole.¹⁷⁻¹⁹ The resonance character of the inner-core excitations is clearly recognized from the absorption spectra.

Such effects are much less significant for Pb where the final states in the region of interest really correspond to continuum wave functions. Figure 3 displays the $5d$ and $4f$ photoionization cross sections, both experimentally determined for PbI_2 and calculated within the atomic RRP A framework. In the energy region around 200 eV the $5d$ cross section is dominated by the $5d \rightarrow \epsilon f$ transitions with a clearly discernible Cooper minimum, and the $4f$ cross section reflects the decreasing $4f \rightarrow \epsilon d$ oscillator strength close to threshold and the delayed onset of $4f \rightarrow \epsilon g$ transitions some 30 eV above. Compared on a relative scale (no attempt was made experimentally for an absolute cross-section determination), the measured values for the compound are in excellent agreement with the calculated atomic results. We note, however, that the experiment yields a ratio between $4f$ and $5d$ cross sections which is about a factor of 2 smaller than calculated. A similar finding was already reported for Hg .¹²

Two observations must be emphasized which are evident from Fig. 3. First, the $5d$ cross section exhibits no obvious indication of a coupling to inner-core

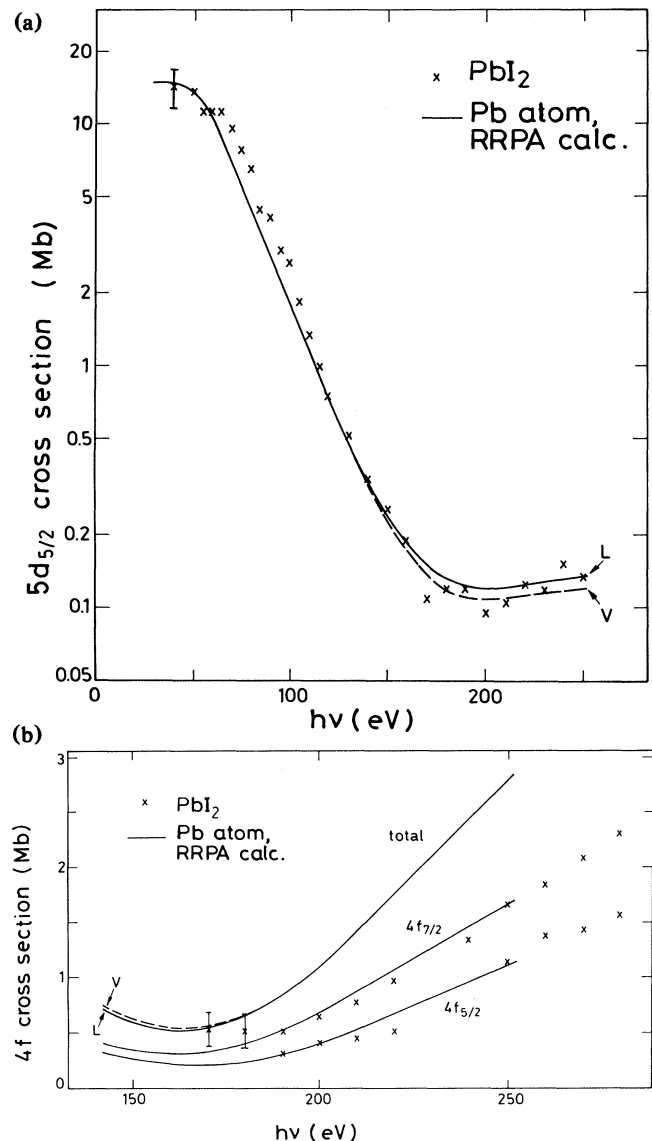


FIG. 3. Comparison of (a) $5d_{5/2}$ and (b) $4f$ photoionization cross section as obtained by the atomic RRP A calculation (solid and dashed curves), and as measured on solid PbI_2 . L and V stand for length and velocity form (Ref. 10). Experimental data are measured in relative units only, with an estimated uncertainty of $\pm 30\%$. Below 190 eV the $4f_{5/2}$ component is not evaluated.

excitations in contrast to the $^2D_{5/2}$ - $^2D_{3/2}$ branching ratio. Second, the good agreement between experiment and theory precludes a significant direct influence of the chemical environment on the partial subshell cross sections. Observe in particular that the $4f$ partial subshell cross section of PbI_2 does not show a shift in oscillator strength towards lower energies compared with the atomic calculation as might be conjectured on the basis of the behavior of the $5d$ branching ratio.

In summarizing the above, we find significant inter-shell interactions for Pb which is a heavy nontransition metal. These interactions are readily identified in the outer-core-shell branching ratio. Being essentially of atomic character these interactions are also found in the solid and solid compounds but distinct changes in the photon energy dependence of the branching ratio could be observed for the compounds studied here. We attribute these changes to the influence of the chemical environment on the intershell interaction by slight modifications of the Pb $5d$ wave function. Contrary to intershell interactions in the presence of strong absorption resonances, however, no effect of comparable significance is found in the partial subshell cross sections of the interacting subshells themselves. We conclude that outer-core-shell branching ratios which are very easily and accurately obtainable by experiments appear to be a very sensitive tool to study inter-shell interactions in heavy nontransition metals.

This work was supported in part by the Bundesministerium für Forschung und Technologie from funds for synchrotron radiation research, and by the National Science Foundation through Grant No. PHY-83-08136.

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