PHYSICAL REVIEW A VOLUME 34, NUMBER 5 NOVEMBER 1986

Effects of the admixed state on the photoionization in the 6p subshell of Pb

Manfred O. Krause, Patrick Gerard, and Anders Fahlman*
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
(Received 7 July 1986)

Photoelectrons that leave the residual Pb ion in the $6s^2 6p(^2P_{1/2})$ and $6s^2 6p(^2P_{3/2})$ states were observed from the ionization threshold (7.42 eV) to 12 eV. Partial and total cross sections were obtained, the latter also from ion measurements. The $6p_{1/2}$ cross section was found to be unexpectedly small near threshold ($^2P_{1/2}$), but strongly enhanced near the $^2P_{3/2}$ threshold associated with the admixed $6p_{3/2}$ configuration. The $6p_{3/2}$ cross section is unusually large at threshold.

Admixture of additional states to the ground-state orbital of the one-electron model has been known for some time to be important to account for observed level energies,[1-4] transition rates,[1-7] photoelectron lines,[8-11] and photoabsorption spectra.[12-15] However, in the formulation of the multiconfiguration ground state it is seldom very clear how many states must be admixed to obtain the desired result. This holds especially true for the calculation of photoionization dynamical properties, such as cross sections and the angular distribution and spin parameters for the photoelectrons in the outer region of the atom. The presence of admixed states, or electron correlation in the outermost atomic level, leads to autoionization resonances and photoelectron lines, which would not occur in a single-configuration description and can, in turn, be used as a sensitive probe for the correct description of the multiconfiguration state. In this paper, we report on strong manifestations of the multiconfiguration state in the photoionization of the 6p subshell of lead at energies less than the 6s ionization energy. We feel that these results may serve as a testing ground for advanced theoretical developments that have been initiated in recent years.[14,15]

In the simplest form, the multiconfiguration state of Pb is given by $\psi = c_1(6p^2_{1/2}) + c_2(6p^2_{3/2}), J=0$. The lowest ionic state $6p\,^2P_{1/2}$ is reached from the $6p^2_{1/2}$ configuration, but the upper ionic state $6p\,^2P_{3/2}$ can be reached only from the admixed $6p^2_{3/2}$ configuration in a dipole transition. Although the probability for the $6p^2_{3/2}$ state is small, namely $c_2^2/c_1^2 = 0.075$ according to theory[16] and 0.05 to 0.07 according to experiment,[17-19] we will show in this Rapid Communication that transitions from this state have a strong effect on photoionization and, in particular, influence the transitions from the main $6p^2_{1/2}$ state by strong channel interactions. We measured the partial cross sections for the available channels which leave the ion in the $6p\,^2P_{1/2}$ and $6p\,^2P_{3/2}$ states by using photoelectron spectrometry and the total cross section by measuring the photoions. Previously, absorption measurements showed the autoionization features up to the $^2P_{3/2}$ threshold;[20,21] and photoelectrons associated with the $^2P_{3/2}$ ionic state were observed at higher energies.[9,17,22]

In this work, synchrotron radiation from the Tantalus storage ring was used and dispersed by a Seya Monochromator. Photoelectons were analyzed at an angle of 55° in respect to the major polarization vector of the 96%-polarized radiation. Although the osmium grating used was not ideal at low energies, the photon flux was sufficient to allow a continuous scanning of the photoelectron peaks in the constant-ionic-state (CIS) mode of operation from the ionization threshold to about 12 eV. As shown in Fig. 1, the photoelectron spectrum (PES) has two photolines, corresponding to the channels that leave $Pb(6s^2 6p^2)$ either in the $6p\,^2P_{1/2}$ (threshold at 7.42 eV) or $6p\,^2P_{3/2}$ (threshold at 9.16 eV) ionic state. These channels, the only ones accessible below the 6s threshold, are distinguishable in the electron spectrometric measurement, but not in the ion spectrometric measurement. However, the ion signal complements the electron signal because it cor-

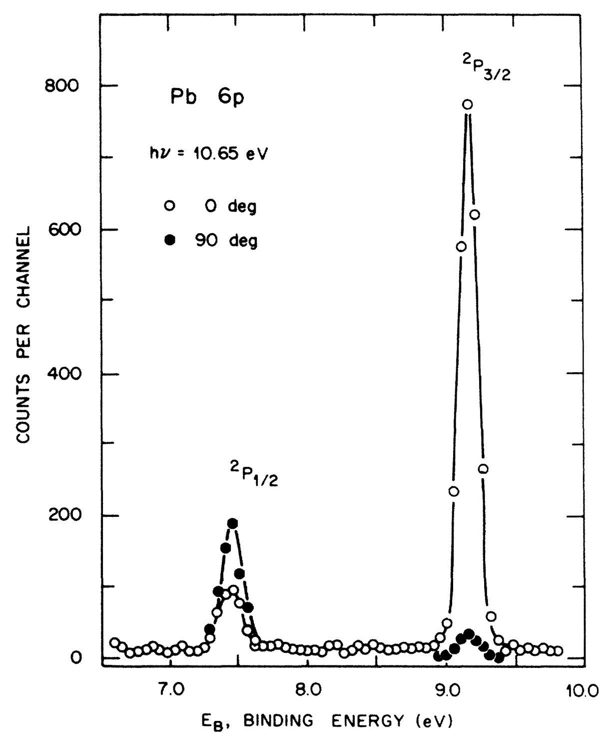

FIG. 1. Photoelectron spectrum of the Pb atom recorded in the resonance at $h\nu = 10.65$ eV. $\Delta E/E = 1\%$, 5 eV preacceleration. This spectrum identifies the available channels and illustrates the angular distribution of the corresponding electrons; ordinarily, data were taken at 55° in order to obtain partial strengths or cross sections.

responds to the sum of the (relative) partial strengths deduced from the CIS electron spectra obtained at the magic angle $\phi_m = 55°$. Details of the apparatus and procedure for the electron spectrometry study can be found elsewhere.[23] For the ion study, the same apparatus was employed: Ions were expelled from the source volume by a weak electric field, about 10 V/cm, and detected by a channeltron multiplier following passage through an electrostatic analyzer and acceleration to 1.8 keV. Mass analysis was not employed, nor needed, because at energies below about 12 eV ordinarily present residual gas molecules could not be ionized and the only ions generated were the desired Pb^+ ions. The Pb vapor was produced in a Ta oven resistively heated to 1150 K. The vapor pressure in the source was estimated to be $(0.5-2)\times 10^{-2}$ Pa, while the background pressure amounted to $\leqq 2\times 10^{-5}$ Pa.

Continuous CIS scans of the photolines shown in Fig. 1 yield the two partial-strength spectra plotted in the lower part of Fig. 2. These spectra were recorded simultaneously by using two electron energy analyzers set to ϕ_m and $\phi_m + 180°$. The spectra are corrected for background, grating efficiency, analyzer response, and vapor density and their relative strengths were established with the aid of photoelectron spectra (PES) measured between 9.2 and 12.3 eV. The low-energy response of the analyzers was determined with the aid of rare-gas spectra. In addition, to minimize differences in the low-energy response of the analyzers, measurements were repeated with the two analyzer settings interchanged. Also shown in Fig. 2 is the sum of the partial strengths together with the photoion spectrum matched at 9.2 eV to the sum spectrum. The ion and the electron sum spectra, which both represent the total strength, agree satisfactorily over the entire range, and a comparison between the two allows one to infer the accuracy of the data (except for the grating efficiency which affects both sets of data and adds a 30% uncertainty toward 7 eV and 15% toward 12 eV relative to the 9-eV value). We believe that the ion spectrum is more reliable because it is subject to fewer corrections. However, the ion spectrum was not corrected for contributions from second-order radiation, which was estimated from extrapolation of measurements above 12.2 eV to amount to less than 10% of the first-order radiation.

A major point that emerges from the spectra of Fig. 2 is the extremely low cross section for the ionization of a $6p_{1/2}$ electron ($^2P_{1/2}$ ionic state) near threshold which is in contrast to the usual behavior of p cross sections as for example seen in the single-particle Dirac-Slater calculation[24] of the Pb $6p_{1/2}$ cross section or the R-matrix result[25] for Al $3p_{1/2}$. However, ionization from $6p_{3/2}$ ($^2P_{3/2}$ state) proceeds in a regular fashion with an appropriate jump at threshold.

The existence of the upper $^2P_{3/2}$ ionic state leads to a series of autoionization features[20] as shown in more detail in Fig. 3 for both the $6p_{1/2} \to \varepsilon l$ channel and the corresponding ion spectrum. At the same time, the "background" or continuous cross section for $6p_{1/2}$ increases and, together with the averaged autoionization contribution, leads to a high value at and beyond the $^2P_{3/2}$ threshold. The slope of the continuous part is of course affected by the instrumental resolution; but it remains steep even in the high-resolution absorption spectrum[20] in which discrete features are clearly resolved. The strength of the $6p_{1/2} \to \varepsilon l$ channel just above the $^2P_{3/2}$ threshold is found to be 15 to 30 times greater than at its own $^2P_{1/2}$ threshold. On the other hand, the strength of the $6p_{3/2} \to \varepsilon l$ channel just above its $^2P_{3/2}$ threshold is roughly 15% of the strength of the $6p_{1/2} \to \varepsilon l$ channel at the same photon energy and, hence, 3 to 6 times the $^2P_{1/2}$ threshold value in spite of the small "occupation" probability of the $6p_{3/2}^2$ level (about 7%).

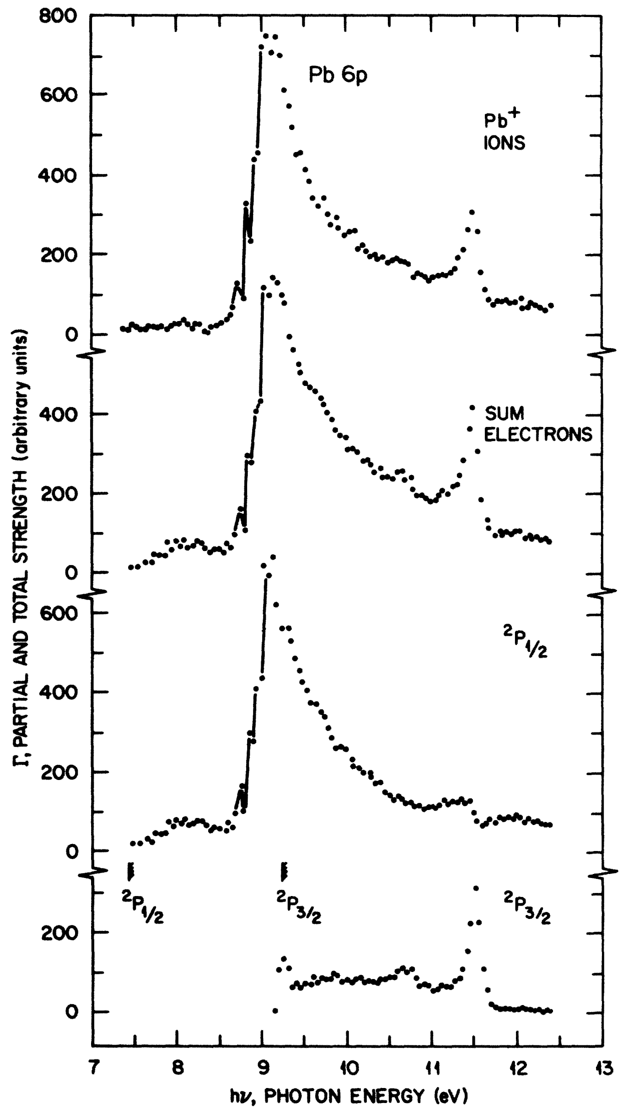

FIG. 2. Photoionization of atomic Pb from the ionization threshold to 12.3 eV. The two lower spectra show the partial strengths of the two channels that leave the ion in the $^2P_{3/2}$ and $^2P_{1/2}$ states, respectively, as obtained from photoelectron CIS spectra. Also shown are the sum of these two partial strengths and the intensity of ions measured as a function of photon energy. The electron sum spectrum and the ion spectrum are both proportional to the total photoionization cross section. All spectra are fully corrected and displayed in the proper proportions.

Two autoionization resonances previously unreported

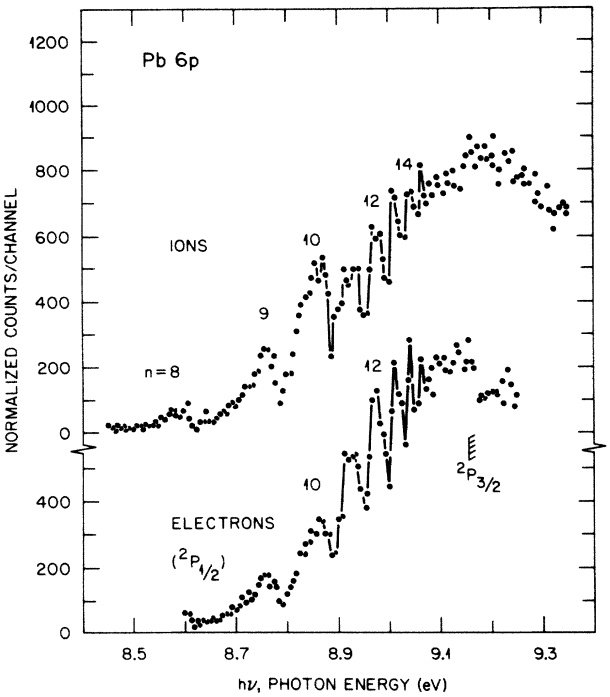

FIG. 3. Detailed recording of the autoionization resonances converging onto the $^2P_{3/2}$ ionic state with the principal quantum number n indicated. Up to threshold, ion and electron spectra of the only accessible ionization channel are in principle identical. Photon bandpass was 0.16 nm.

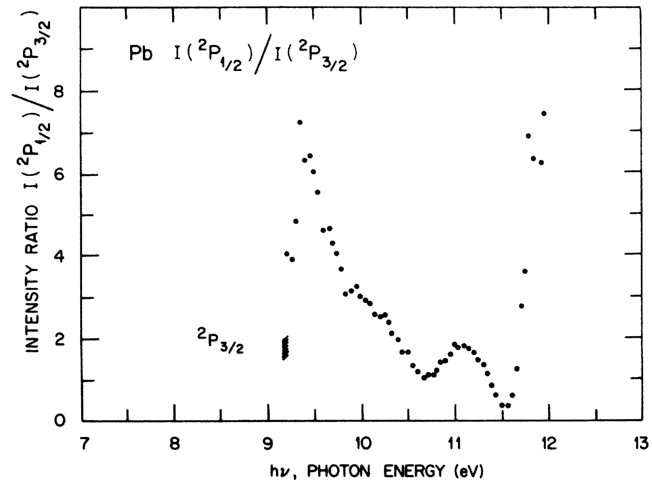

FIG. 4. Strength of the $6p\,^2P_{1/2}$, εl channel relative to the $6p\,^2P_{3/2}$, εl channel above the $^2P_{3/2}$ threshold and through two resonances still to be identified. Each point has an accuracy of about 12%.

were found at $h\nu = 10.65$ and 11.50 eV. They make a positive contribution to the strength of the $6p_{3/2} \rightarrow \varepsilon l$ channel, and a negative one to that of the $6p_{1/2} \rightarrow \varepsilon l$ channel. This behavior can be seen especially clearly in the intensity ratio for the two channels shown in Fig. 4. A similar behavior was observed earlier[22] for the $n=7$ member of the $6s^{-1}[^4P_{1/2}]np_{3/2}$ series; we suspect that these resonances, not reported before, belong to the $n=6$ manifold.

In conclusion, this work in which the possible ionization channels were distinguished revealed an unusually low threshold strength for the $6p_{1/2} \rightarrow \varepsilon l$ transition, but a more regularly behaved and surprisingly large strength for the transition from the admixed $6p_{3/2}$ configuration. The small cross section for $6p_{1/2}$ electrons can be qualitatively attributed to two effects. First, relativistically the $p_{1/2} = \bar{p}$ electrons have a rather spherically symmetric charge distribution and, hence, behave like s electrons, which often display a quite small cross section near threshold. This s-like behavior of the $6\bar{p}$ electrons in Pb also seems to be reflected in the data on the photoelectron angular distribution parameter β outside the resonance regions at $h\nu \geqq 24$ eV.[17] Values of $\beta = 1.7$ to 2.0 were obtained, values quite similar to those for the $6s$ electrons. Second, the presence of the admixed $6p^2_{3/2}$ configuration, which gives rise to several autoionization resonance series converging onto the $^2P_{3/2}$ state, produces some window resonances near threshold[20,21] and, generally, might shift the strength of the $6p_{1/2} \rightarrow \varepsilon l$ channel away from threshold. In contrast to the depression of the $6p_{1/2}$ strength by channel interactions, an enhancement of the $6p_{3/2}$ strength could occur if some $6s \rightarrow 6p$ resonance states were located in the threshold region and were to contribute to this channel. A quantitative theoretical treatment of these effects is still to be done and will require a relativistic multiconfiguration calculation within a multichannel-quantum-defect model. Such a calculation would have to reproduce the partial strength for the $6p_{3/2} \rightarrow \varepsilon l$ channel and for the $6p_{1/2} \rightarrow \varepsilon l$ channel in the discrete and the adjacent continuum portions of the spectrum. It should also reveal whether more states, e.g., $6d^2$, need be admixed to reproduce the experimental data.

This work was sponsored by The Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc. The National Science Foundation supported the Synchrotron Radiation Center, Stoughton, Wisconsin, under Grant No. DMR-83-13523. One of us (A.F.) acknowledges support from the Swedish National Science Research Council.

*Permanent address: Department of Physics and Measurement Technology, Linköping Institute of Technology, S-581 83 Linköping, Sweden.

[1]P. S. Bagus and C. M. Moser, Phys. Rev. **167**, 13 (1968).
[2]V. McKoy and O. Sinanoglu, J. Chem. Phys. **41**, 2689 (1964).
[3]J. P. Desclaux and Y.-K. Kim, J. Phys. B **8**, 1177 (1975).
[4]I. P. Grant, Comput. Phys. Commun. **5**, 263 (1973).
[5]H. P. Kelly, Phys. Rev. **136**, 896 (1964).
[6]B. Edlén, Phys. Scr. **31**, 345 (1985).
[7]N. A. Kulagin and I. I. Zaljubovsky, J. Phys. B **14**, 1537 (1981).
[8]V. L. Jacobs and P. G. Burke, J. Phys. B **4**, L67 (1972).

[9]S. Suzer, M. S. Banna, and D. A. Shirley, J. Chem. Phys. **63**, 3473 (1975).

[10]W. R. Fielder and L. Armstrong, Phys. Rev. A **28**, 218 (1983).

[11]S. T. Manson, Adv. Electron. Electron Phys. **41**, 73 (1976).

[12]U. Fano and J. W. Cooper, Rev. Mod. Phys. **41**, 724 (1969).

[13]A. F. Starace, in *Handbuch der Physik,* edited by W. Mehlhorn (Springer, New York, 1982), Vol. XXXI, p. 1.

[14]M. Cavagnero, Phys. Rev. A **30**, 1169 (1984).

[15]V. Radojević and W. R. Johnson, Phys. Rev. A **31**, 2991 (1985).

[16]J. P. Desclaux, Int. J. Quantum Chem. **6**, 25 (1972).

[17]M. O. Krause, P. Gerard, A. Fahlman, T. A. Carlson, and A. Svensson, Phys. Rev. A **33**, 3146 (1986).

[18]L. Frost, J. Mitroy, and E. Weigold, Aust. J. Phys. (to be published).

[19]H. Derenbach, H. Kossmann, R. Malutzki, and V. Schmidt, J. Phys. B **17**, 2781 (1984).

[20]C. M. Brown, S. G. Tilford, and M. L. Ginter, J. Opt. Soc. Am. **67**, 1240 (1977).

[21]N. Karamatskos, M. Müller, M. Schmidt, and P. Zimmermann, 1983 BESSY Annual Report, Berlin, West Germany (unpublished), p. 38.

[22]M. O. Krause, F. Cerrina, A. Fahlman, and T. A. Carlson, Phys. Rev. Lett. **23**, 1093 (1983).

[23]M. O. Krause, T. A. Carlson, and P. Woodruff, Phys. Rev. A **24**, 1374 (1981); M. O. Krause, T. A. Carlson, and A. Fahlman, *ibid.* **30**, 1316 (1984).

[24]S. T. Manson, C. J. Lee, R. H. Pratt, I. B. Goldberg, B. R. Tambe, and A. Ron, Phys. Rev. A **28**, 2885 (1983).

[25]M. Le Dourneuf, Vo Ky Lan, P. G. Burke, and K. T. Taylor, J. Phys. B **8**, 2640 (1975).