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Photoionization cross section of lead near the $6s^2\,6p\ ^2P_{3/2}$ threshold

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Measurements of the total photoionization cross section of lead in the energy range between the $6s^2\,6p\,(^2P_{1/2})$ ionization threshold at 59 819 cm^{-1} and the $6s^2\,6p\,(^2P_{3/2})$ threshold at 73 900 cm^{-1} are reported. Just above the ionization threshold the cross section is dominated by broad window resonances, members of the $6p\,nd$ and $6p\,ns$ Rydberg series converging to the $6s^2\,6p\,(^2P_{3/2})$ threshold. The Rydberg series are perturbed by a very broad and intense autoionizing resonance near the threshold. The resonance energy, width, and shape parameter of this resonance are determined. Close to the $6s^2\,6p\,(^2P_{3/2})$ series limit the data indicate the presence of a further broad-window-type resonance.

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The total photoionization cross section of the ground state $6s^2\,6p^2\,^3P_0$ of lead in the energy range between 59 000 and 64 000 cm^{-1} was first determined by Heppinstall and Marr [1] using spectrophotometry. These authors measured a total photoabsorption cross section of 10±1 Mb at the ionization threshold. This value was later confirmed by an extrapolation of the oscillator strength density to the ionization limit by Kozlov, Mileshina, and Startsev [2]. The window resonances above the ionization threshold belong to *ns* and *nd* Rydberg series which had first been observed and assigned by Garton and Wilson [3] . Later, the photoabsorption spectrum between the photoionization threshold and the $6s^2\,6p\,(^2P_{3/2})$ threshold was reinvestigated by Brown, Tilford, and Ginter [4] using a high-resolution spectrograph. In this experiment a great number of new levels belonging to the 6*pns* and 6*pnd* configurations were discovered.

All these photoabsorption experiments failed to observe any of the levels belonging to the $6s\,6p^3$ configuration although it was predicted from Hartree-Fock intermediate coupling calculations by Connerade *et al.* [5] that some of the levels should lie within the investigated energy range. Similar calculations of energy positions of $6s\,6p^3$ levels were performed by Pejcev *et al.* [6] in an attempt to identify transitions to the $6s\,6p^3$ levels in their ejected electron spectra. These calculations also predicted a number of levels arising from the $6s\,6p^3$ configuration in the energy range investigated by the experiments mentioned above. The origin of the minimum in the background cross section observed by Heppinstall and Marr [1] remained equally unclear.

First evidence for $6s\,6p^3$ levels came from a photoionization experiment by Krause, Gerard, and Fahlmann [7], who discovered a strong resonance in the partial cross section of the photoionization with a $^2P_{1/2}$ ionic state close to the $^2P_{3/2}$ limit at a photon energy of about 9 eV. It was suggested that this resonance was caused by $6s \longrightarrow 6p$ transitions located near the threshold. This was subsequently confirmed in a paper by Radojevič [8] who performed multiconfiguration Dirac-Fock (MCDF) calculations for some of the $6s\,6p^3$ bound states. One of the levels with a dominant $(6s\,6p_{1/2}^2\,6p_{3/2})_1$ configuration was found at 8.91 eV, close to the energy of the resonance observed by Krause, Gerard, and Fahlmann [7].

Our previous investigations of the photoionization spectra of calcium and ytterbium (Griesmann and coworkers [9,10]) have shown that thermionic diode detectors are sensitive ion detectors suitable to measure relative photoionization cross sections at a resolution often exceeding the resolution achievable in comparable photoionization experiments and a very good signal-to-noise ratio . (A detailed account of the thermionic diode techniqe was given by Niemax [11].) The photoionization cross section of lead was therefore remeasured with the aim to determine energy position, width, and shape parameter of the resonance at the $^2P_{3/2}$ threshold.

The spectrum was recorded using synchrotron radiation from the DORIS II storage ring at the Deutsches Elektronen-Synchrotron (DESY). The experiment was installed at a 1-m normal-incidence monochromator (HIGITI) which was set to a bandpass of 1 Å . For some of the spectra a bandpass of 3 Å was used. A lithium fluoride (LiF_2) window separated the thermionic diode detector from the ultrahigh vacuum of the monochromator and also absorbed any radiation from the second order of the grating. Lead vapor was produced by heating a piece of lead in the anode tube of the thermionic diode to a temperature of about 1100 °C. Argon gas at a pressure of 2 Torr was admitted to the thermionic diode to confine the lead vapor in the heated zone of the detector. A unique property of thermionic diodes is that the sample effectively becomes part of the detector as vapor from the sample is deposited on the cathode and thus determines its efficiency as an electron emitter. Lead is not as well suited for thermionic diode detection as, e.g., the alkaline-earth elements because it has a high work function and does not emit electrons easily, which makes it difficult to establish the necessary space charge in the detector. To sustain a sufficient anode current a wire of thoriated tungsten, heated to a temperature of about 1900 °C, served as the cathode. The data were sampled by a PDP-11 computer which also controlled the monochromator. Subsequently the spectra were corrected for the light intensity transmitted by the LiF_2 window. The decrease in the signal to noise ratio noticeable at higher photon energies (see Fig. 2 in particular) is due to the low intensity near the LiF_2 transmission cutoff. Absolute cross sections were obtained by normalizing the data to the cross section at the ionization limit measured by Heppinstall and Marr [1]. The energy scale of our spectra was calibrated on the basis of high-resolution data (Brown, Tilford, and Ginter [4]) to correct for wavelength shifts caused by the buffer gas in the thermionic diode and inaccuracies in the wavelength calibration of the monochromator.

Figure 1 shows the total photoionization cross section recorded in our experiment. Just above the ionization threshold the cross section is dominated by the three window resonances belonging to the Rydberg series

$$\begin{aligned} 6s^2\,6p^2\,{}^1P_0 &\longrightarrow 6p\,ns\,(\tfrac{3}{2},\tfrac{1}{2})^o_1, \quad n \geq 7 \\ &\longrightarrow 6p\,nd\,(\tfrac{3}{2},\tfrac{5}{2})^o_1, \quad n \geq 6 \\ &\longrightarrow 6p\,nd\,(\tfrac{3}{2},\tfrac{3}{2})^o_1, \quad n \geq 6 \end{aligned} \tag{1}$$

converging to the $6s^2\,6p^2\,(^2P_{3/2})$ threshold, the ground state of Pb II. The group of resonances at about 67 000 cm^{-1} are the next members of these Rydberg series. We assume that the dip at 64 800 cm^{-1} is caused by an impurity since the line does not show the transmission window associated with resonances coupled to a single open channel. The background cross section above the $^2P_{1/2}$ limit decreases with increasing photon energy and passes through a minimum at about 68 000 cm^{-1}. Towards the $^2P_{3/2}$ threshold the background is strongly enhanced due to the broad resonance which was first observed by Krause, Gerard, and Fahlmann [7]. For brevity this broad resonance will simply be dubbed B in this paper. To determine the parameters of this perturber state and the parameters of the well-resolved resonances above the ionization threshold the following parametrization of the total photoionization cross section derived by Mies [12] was fitted to the part of the spectrum between 60 000 and 68 000 cm^{-1} where the shape of the lines is not completely blurred by the low resolution of the monochromator :

$$\sigma(E) = \sigma_0 \frac{\left(1 + \sum_n q_n \varepsilon_n^{-1}\right)^2}{1 + \left(\sum_n \varepsilon_n^{-1}\right)^2}\,, \tag{2}$$

where

$$\varepsilon_n = \frac{E - E_n}{\Gamma_n/2} \tag{3}$$

are the reduced energies. The fit included the first six resonances above the ionization threshold and the broad resonance B which shapes the background cross section between the $^2P_{1/2}$ and $^2P_{3/2}$ thresholds. It was not attempted to deconvolve the monochromator transmission function out of the measured data. Although this could improve the parameters obtained for the lowest-lying resonances it would have little bearing on the parameters of the resonance B. The dashed curve in Fig. 1 shows the resulting cross section as emerging from the fit. The fit parameters are summarized in Table I.

The observed cross section is very well described by Eq. (2) in the vicinity of the window resonances above the ionization threshold. It is worth noting that the shape parameters q of the $6p\,6d\,(\frac{3}{2},\frac{5}{2})$ and $6p\,8s\,(\frac{3}{2},\frac{1}{2})$ resonances are *not* zero as reported by Heinzmann [13]. Although they appear to be nearly symmetric window resonances their q values are different from zero due to the interaction with the resonance B which causes the sloping background cross section. The group of resonances at 67 000 cm^{-1} is not well resolved and in consequence it is not possible to describe them by Eq. (2)

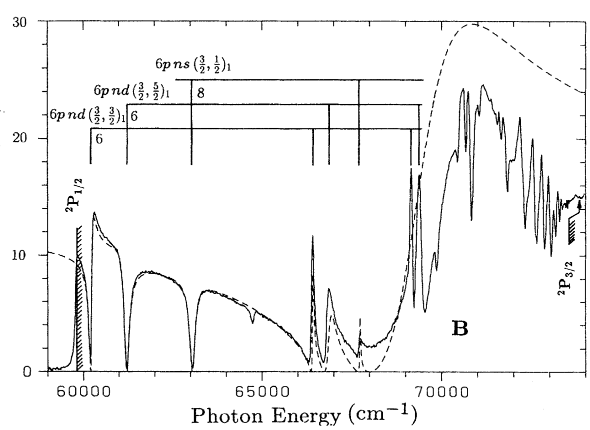

FIG. 1. The total photoionization cross section of Pb between the $^2P_{1/2}$ ionization threshold and the $^2P_{3/2}$ threshold at an exerimental resolution of 1 Å (solid curve). The dashed curve shows the fitted cross section according to a formula by Mies [12].

TABLE I. Summary of resonance parameters. E_r is the resonance energy, Γ the resonance width, q the shape parameter. An asterisk indicates that the respective parameters are to be regarded as estimates. The level B has the dominant configuration $(6s\,6p^2_{1/2}\,6p_{3/2})_{J=1}$ according to Radojevič [8].

Level	E_r (cm^{-1})	Γ (cm^{-1})	q
$6p\,6d\,(\frac{3}{2},\frac{3}{2})_1$	60 210	87	0.19
$6p\,6d\,(\frac{3}{2},\frac{5}{2})_1$	61 176	178	−0.34
$6p\,8s\,(\frac{3}{2},\frac{1}{2})_1$	63 027	204	−0.15
$6p\,7d\,(\frac{3}{2},\frac{3}{2})_1$	66 392	76	0.36
$6p\,7d\,(\frac{3}{2},\frac{5}{2})_1$	66 810	228*	0.31*
$6p\,9s\,(\frac{3}{2},\frac{1}{2})_1$	67 778*		
B	69 430	2892	1.06

as well as the resonances at lower energies. However, the shape of these resonances contains a hint to the resonance energy of the broad resonance B. When line shapes of the three resonances at 67 000 cm^{-1} are compared to the line shapes of the higher members at 72 487 cm^{-1} of the same Rydberg series recorded by Brown, Tilford, and Ginter [4] (see Fig. 2 of the paper by Brown, Tilford, and Ginter [4]) a clear q-reversal effect is noticed. According to Connerade and Lane [14] this means that the Rydberg series are disturbed by a broad intruder state. Since q reversals happen at the *maximum* of the intruding state we can infer that the resonance energy of the state B must lie between 68 000 and about 72 000 cm^{-1}, the maximum of the resonance B. The shape of this resonance is well reproduced by the fit although the observed cross section is smaller than the fitted cross section above 69 000 cm^{-1} because it was averaged over many resonances belonging to the Rydberg series which converge to the $^2P_{3/2}$ threshold in our measurement. From the fit we get a resonance energy of 69 430 cm^{-1} and a resonance width of 2892 cm^{-1} which corresponds to a lifetime of 1.84×10^{-15} s.

It is difficult to give meaningful errors for the fitted parameters since the parameters calculated in the fit are affected by the low experimental resolution which distorts the recorded resonance shape. We estimate that the error in the parameters of the resonance B is of the order of 1%.

Another interesting observation is the minimum in the cross section at about 73 000 cm^{-1}. It can be seen more clearly in the low-resolution spectrum Fig. 2. This minimum could be caused by a broad window resonance just below the $6s^2\,6p\,(^2P_{3/2})$ series limit "filled in" with the oscillator strength of the unresolved Rydberg lines.

In conclusion, we have determined the resonance energy and the width of the broad resonance B near the $^2P_{3/2}$ threshold from new measurements of the total photoionization cross section. The resonance energy derived from our data is lower than the energies calculated by Radojevič [8] for the levels with a $(6s\,6p^2_{1/2}\,6p_{3/2})_{J=1}$ dominant configuration. The result from the self-consistent MCDF calculation of 8.91 eV

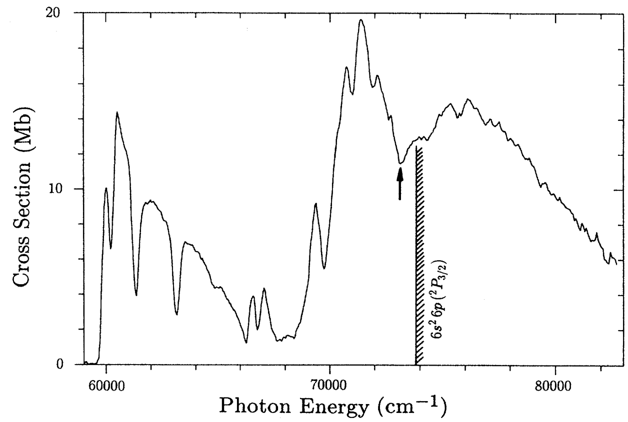

FIG. 2. Total photoionization at a lower resolution (3 Å). The arrow indicates a minimum in the cross section which could be due to a further resonance just below the $^2P_{3/2}$ threshold overlapping with the resonance B.

(71 866 cm^{-1}) agrees with the value found in our experiment within the error margins of 5% given by Radojevič [8]. To elucidate the level structure near the $^2P_{3/2}$ threshold the origin of the minimum in the cross section at 73 000 cm^{-1} needs to be clarified. We presume that it is due to another resonance overlapping with the broad resonance B but a further experiment with higher resolution and linear detection is necessary to determine its parameters. More accurate calculations would then be needed before a conclusive level designation for the broad resonances near the $^2P_{3/2}$ threshold can be given.

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