

Determination of Theoretical Transition Probabilities for the Pb III Spectrum

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Abstract

Theoretical values of absolute transition probabilities for 54 lines arising from the $6s\ np$ configuration of Pb III have been obtained. These values were obtained in intermediate coupling (IC) and using *ab initio* relativistic Hartree–Fock calculations. We used for the IC calculations the standard method of least square fitting of experimental energy levels by means of computer codes from Cowan. These values, although in general agreement with the rare experimental data, do present some noticeable discrepancies. Analysis of the interaction between 1D_2 levels of $6p^2$ and $6s6d$ configurations shows a 40% contribution from the $6s6p^2$ configuration for the lowest one, and a 27% contribution from $6s6d$ for $6s6p^2$.

1. Introduction

Data on atomic properties are relevant not only to spectroscopy, but these values are also of interest in a variety of other fields in physics and technology. In this work we present transition probabilities for the $6s^2-6snp$, $6sns-6snp$ and $6snd-6snp$ lines of Pb III. For these lines there are few published theoretical and experimental results. This has been the motivation for two studies. One is by Colón *et al.* [1] and presented experimental transition probabilities for 10 lines corresponding to the $6s\ 7p$ level of Pb III using the emission of a plasma generated by focusing a laser beam on a Pb target. The second is this theoretical study that was carried out using the relativistic Hartree–Fock calculations with configuration interaction in an intermediate coupling scheme. The Cowan [2] code (1981) was selected for this purpose.

Relativistic Hartree–Fock calculations for Pb III, including a potential model to represent core polarisation, have been reported by Migdalek and Baylis [3,4]. In 1972 Andersen [5] presented a beam foil study of atomic lifetimes showing two strong spectral lines at 1 049 Å and 1 028 Å of Pb III. In 1988 new beam-foil lifetime analyses of the low lying levels in Pb III were reported (Ansbacher *et al.* [6] and Pinnington *et al.* [7]). Recently transition analyses from the autoionizing states $5d^9\ 6s^2\ nf$ and $5d^9\ 6s^2\ np$ to the ground state $5d^{10}\ 6s^2\ ^1S_0$ in Pb III have been reported by Raassen *et al.* [8].

We shall first describe in Section 2 the theoretical considerations and then in Section 3 the results and discussion.

2. Theoretical calculations

In most cases the single configuration and Russell-Saunders scheme is insufficient to describe adequately the Pb III ion (Desclaux and [9]). A more detailed description is neces-

ary to take into account some experimental results for the $6s6d$ and $6s6p^2$ configurations. We have obtained theoretical values of transition probabilities in intermediate coupling (IC) and using *ab initio* relativistic Hartree–Fock (HFR) calculations.

For the IC calculations we used the standard method of least-square fitting of experimental energy levels by means of computer codes from Cowan [2]. In this way we obtained the *LS* composition of each level and the degree of configuration mixing, when we considered their interaction. For the HFR calculations the Cowan computer code provided us with the radial parts for determination of transition probabilities and initial estimates of the parameters for the IC fittings. The radial integrals for calculations of transition probabilities were obtained from the HFR wavefunctions.

The system considered is complex, since at high Z both relativistic and correlation effects are important. Least-square fitting of experimental energy levels partially accounts for correlation effects not explicitly calculated in our work.

3. Results and discussion

3.1. $6p^2-6s6d$ configuration interaction

Levels from the Pb III $6s6d$ configurations present some anomalies. The most obvious effect is the relative energy position of the $6s6d\ ^1D_2$ level. Experimentally this level is found below the 3D levels of this configuration. Corresponding to Hund's rule, in such a configuration the minimum energy would correspond to the triplet levels. A similar situation has already been found in the homologous $4s4d$ levels in Zn I (Ansbacher *et al.* [10]) and in the $5s5d$ state in In II (Martínez *et al.* [11]). Thus interactions between the $6s^2$, $6s6d$ and $6p^2$ configurations were introduced in our study.

The energy level positions expected for $6s6d$ and $6p^2$ configurations in the absence of interactions can be observed in the left-hand section of Fig. 1. The values of this first diagram come from a theoretical HFR calculation of separated $6s6p^2$ and $6s6d$ configurations with no consideration of their interaction. A comparison between these results and the experimental values (Moore [12]) (the right section of Fig. 1.) shows a large discrepancy.

The second diagram in Fig. 1 shows the effect of allowing for configuration interaction in the HFR calculation. The effect of “energy level repulsion” is clearly significant between $6p^2\ ^1D$ levels and $6s6d\ ^1D$ and the $6s6d\ ^1D_2$ level is found correctly below the $6s6d\ ^3D$ levels.

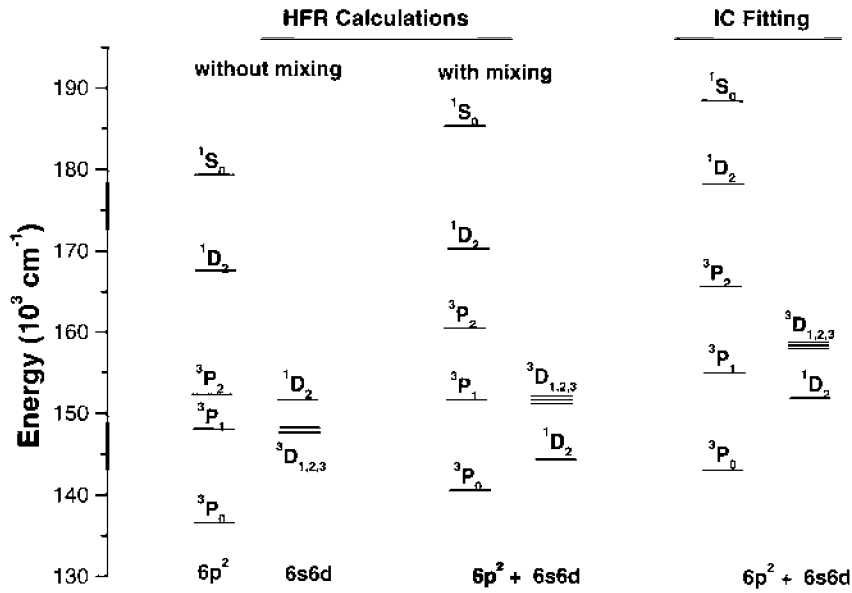


Fig. 1. Effects of $6p^2$ - $6s6d$ configuration interaction. (Experimental situation of energy levels is not shown as they are close to the IC ones).

Table I. *Energy levels and configuration mixing effects in Pb III.*

Levels (Moore)	Energy (cm ⁻¹)		Lande Factor			Composition		
	Exp	Cal	Exp	Cal	<i>J</i>	%1 st comp	%2 nd comp	%3 rd comp
6s6p								
³ P ₀	60 397	60 625			0	100 6s 6p ³ P		
³ P ₁	64 391	64 125		1.46	1	92 6s 6p ³ P	8 6s 6p ¹ P	
¹ P ₁	95 340	95 357		1.04	1	92 6s 6p ¹ P	8 6s 6p ³ P	
³ P ₂	78 984	78 888		1.05	2	99 6s 6p ³ P	1 6s ² 6p ³ P	
6s7p								
³ P ₀	170 917	170 917			0	100 6s 7p ³ P		
³ P ₁	171 081	171 081	1.38	1.39	1	78 6s 7p ³ P	22 6s 7p ¹ P	
¹ P ₁	177 181	177 142	1.15	1.11	1	77 6s 7p ¹ P	23 6s 7p ³ P	
³ P ₂	176 022	176 053	1.34	1.50	2	100 6s 7p ³ P		
6s8p								
³ P ₀	206 809	206 816			0	100 6s 8p ³ P		
³ P ₁	206 979	206 972	1.38	1.38	1	77 6s 8p ³ P	23 6s 8p ¹ P	
¹ P ₁	209 318	209 321	1.12	1.12	1	77 6s 8p ¹ P	23 6s 8p ³ P	
³ P ₂	208 922	208 920	1.50	1.50	2	100 6s 8p ³ P		
6s7s								
¹ S ₀	153 783	153 784			0	100 6s 7s ¹ S		
³ S ₁	150 083	150 083	1.98	2.00	1	100 6s 7s ³ S		
6s8s								
¹ S ₀	199 400	199 392			0	100 6s 8s ¹ S		
³ S ₁	197 892	197 867	2.00	2.00	1	100 6s 8s ³ S		
6s7d								
³ D ₁	201 398	201 399	0.50	0.50	1	100 6s 7d ³ D		
³ D ₂	201 597	201 597	1.16	1.16	2	97 6s 7d ³ D	3 6s 7d ¹ D	
³ D ₃	202 046	202 046	1.33	1.33	3	100 6s 7d ³ D		
¹ D ₂	203 301	203 301	1.00	0.98	2	96 6s 7d ¹ D	4 6s 7d ³ D	
6s ² +6p ² + +6s6d								
³ P ₀	142 551	142 552			0	85 6p ² ³ P	15 6p ² ¹ S	
¹ S ₀	188 615	188 615			0	85 6p ² ¹ S	15 6p ² ³ P	
³ P ₁	155 431	155 431		1.50	1	100 6p ² ³ P		
³ D ₁	157 444	157 395	0.50	0.50	1	100 6s 6d ³ D		
¹ D ₂	151 884	151 884	1.07	1.06	2	47 6s 6d ¹ D	40 6p ² ¹ D	13 6p ² ³ P
³ D ₂	157 925	158 013	1.16	1.16	2	98 6s 6d ³ D	1 6p ² ¹ D	1 6p ² ³ P
³ P ₂	164 817	164 819	1.40	1.31	2	62 6p ² ³ P	34 6s 6d ¹ D	4 6p ² ¹ D
¹ D ₂	178 432	178 432		1.14	2	54 6p ² ¹ D	29 6p ² ³ P	27 6s 6d ¹ D
³ D ₃	158 956	158 922	1.33	1.33	3	100 6s 6d ³ D		

Finally, the fitting of experimental energy levels in the IC calculations confirms this situation providing the results than can be seen at the right-hand side of Fig. 1 and in Table I.

The values found for the different parameters involved in the IC calculations are shown in Table II. These calculations can be considered successful and some conclusions must be made at this point. In the first place, the values quoted in Table I show the strong mixing of 1D_2 levels of both configurations.

Secondly, no configuration mixing can be found in the $J = 1$ family. Although relevant amounts of $6s6d\ ^1D_2$ and $6p^2\ ^1D_2$ are found, in the $6p^2\ ^3P_2$ level IC mixing, there is no appreciable amount of 3D_2 in this composition.

3.2. $6s6p$ and $6s7p$ configurations

A discrepancy of about 200 cm^{-1} remains between experimental and theoretical energy levels values in the case of the $6s6p$ configuration. In comparison, theoretical values of $6s7p$ energy levels, shown in Table I, present a lesser discrepancy with the experimental ones. In both cases, we think that it must have its origin in an interaction with other configurations. Clear evidence for configuration mixing is the existence of the observed $6s7p-6p^2$ dipole forbidden

transitions. The $6s6p$ and $6s7sp$ IC set can not remove these discrepancies, and there is not an appreciable amount of $6s6p\ ^3P_2$ in the IC composition of $6s7p\ ^3P_2$. We have analysed other set candidates but we have found very small perturbations not accounting for the discrepancy. A good example is the $5d^96s^26p$ configuration for which a decrease in the $6s7p$ discrepancies was found when treated together with the $6s6p+6s7p$ ones. Nevertheless this set only accounts for about 2% IC mixing of 3P_2 levels corresponding to $6s6p$ and $6s7p$ configurations and cannot explain the $6s7p-6p^2$ transitions. Considerations of other candidates with experimentally observed energy levels which might be able to explain this transition, such as $6p7s$ and $6p7d$, were also analysed. The *ab initio* HFR calculations showed only small mixing. The IC fitting was unfruitful, due to the increase in the number of parameters above the number of experimental energy levels. More detailed calculations are necessary to answer this open question.

3.3. Transition probabilities

Transition probabilities, displayed in Fig. 2, obtained for 54 lines of Pb III with wavelengths in the range 1000 and $30\,000\ \text{\AA}$ are displayed in column three of Table III, while columns one and two give the transitions and corresponding

Table II. Parameters resulting from the least square fitting of the intermediate coupling calculations.

Configuration	Parameters (cm^{-1})		
$6s6p$	$E_{av}=77729.6$	$G^1(6s,6p)=29954\ (48762)$	$\zeta_{6p}=12174\ (11181)$
$6s7p$	$E_{av}=174675.2$	$G^1(6s,7p)=2255\ (3064)$	$\zeta_{7p}=3508\ (3064)$
$6s8p$	$E_{av}=208358.0$	$G^1(6s,8p)=833\ (2138)$	$\zeta_{8p}=1403\ (1356)$
$6s7s$	$E_{av}=151008.3$	$G^0(6s,7s)=1850\ (2978)$	
$6s8s$	$E_{av}=198248.0$	$G^0(6s,8s)=762\ (967)$	
$6s7d$	$E_{av}=202150.4$	$G^2(6s,7d)=3632\ (3164)$	$\zeta_{7d}=258\ (189)$
$6s6d+6p^2$	$E_{av}=159046.2$	$G^2(6s,6d)=7347\ (9778)$	$\zeta_{6d}=611\ (443)$
	$E_{av}=164460.6$	$F^2(6p,6p)=31998\ (39207)$	$\zeta_{6p}=11709\ (11132)$
		$R^1(6s,6d,6p,6p)=18995\ (30526)$	

Values in parenthesis are *ab initio* HFR results.

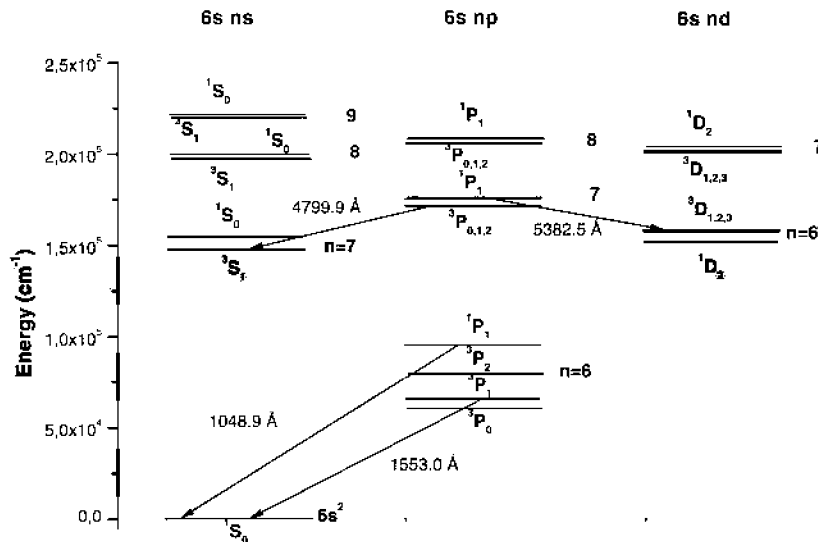


Fig. 2. Partial energy level diagram for Pb III showing some transitions studied in this work.

Table III. *Transition Probabilities of some Pb III lines.*

Transition			Transition Probabilities (10^8 s^{-1})				
Upper	Levels Lower	Wavelength $\lambda(\text{\AA})$	This work	Other authors			
				(a)	(b)	(c)	(d)
6p 3P_1	6s ² 1S_0	1553.0	1.51	0.75			
6p 1P_1	6s ² 1S_0	1048.9	55.00	59.33	53.55	26.3±1.5	
7p 3P_0	7s 3S_1	4799.9	1.39				1.72±0.16
	6d 3D_1	7422.1	0.42				
7p 3P_1	6s ² 1S_0	584.5	0.14				
	7s 3S_1	4762.4	1.15				1.19±0.12
	7s 1S_0	5781.0	0.18				1.18±0.12
	6d 1D_2	5209.2	0.18				0.036±0.004
	6d 3D_1	7332.8	0.09				
	6d 3D_2	7600.9	0.23				
7p 3P_2	7s 3S_1	3855.2	2.75				2.11±0.21
	6d 1D_2	4142.8	0.0026				0.015±0.002
	6d 3D_1	5382.5	0.019				0.022±0.002
	6d 3D_2	5525.5	0.15				0.63±0.07
	6d 3D_3	5859.7	0.74				0.66±0.06
7p 1P_1	6s ² 1S_0	564.4	0.56				
	7s 3S_1	3690.3	0.70				
	7s 1S_0	4273.9	1.55				
8p 3P_0	7s 3S_1	1762.9	0.033				
	6d 3D_1	2025.7	0.37				
	8s 3S_1	11215.5	0.32				
	7d 3D_1	18483.3	0.12				
8p 3P_1	6s ² 1S_0	483.1	0.55				
	7s 3S_1	1757.6	0.022				
	7s 1S_0	1879.8	0.23				
	6d 1D_2	1815.1	0.16				
	6d 3D_1	2018.8	0.071				
	6d 3D_2	2038.6	0.17				
	8s 3S_1	11005.7	0.26				
	8s 1S_0	13195.4	0.041				
	7d 3D_1	17920.2	0.025				
	7d 3D_2	18581.5	0.078				
	7d 1D_2	27193.1	0.0030				
	8p 3P_2	7s 3S_1	1699.6	0.035			
6d 1D_2		1753.2	0.0009				
6d 3D_1		1942.6	0.0042				
6d 3D_2		1960.9	0.060				
6d 3D_3		2001.4	0.33				
8s 3S_1		9066.8	0.61				
7d 3D_1		13292.0	0.0031				
7d 3D_2		13652.4	0.042				
7d 3D_3		14545.0	0.20				
7d 1D_2	17792.3	0.0005					
8p 1P_1	6s ² 1S_0	477.7	1.04				
	7s 3S_1	1688.2	0.011				
	7s 1S_0	1800.7	0.57				
	6d 1D_2	1741.1	0.69				
	6d 3D_1	1927.7	0.026				
	6d 3D_2	1945.8	0.12				
	8s 3S_1	8752.6	0.15				
	8s 1S_0	10083.3	0.31				
	7d 3D_1	12627.4	0.021				
	7d 3D_2	12952.2	0.024				
7d 1D_2	16621.2	0.11					

^aMigdalek and Baylis (1985).^bWarner (1968).^cPinnington *et al.* (1988).^dColón *et al.* (1999).

wavelengths, respectively. The remaining columns give the theoretical (Migdalek and Baylis [4] and Warner [13]) and experimental (Pinnington *et al.* [7] and Colón *et al.* [1]) transition probability values to be found in the bibliography.

These values, although in agreement with the rare experimental data, present some noticeable discrepancies: The resonant transition $6p^1P_1$ to $6s^2^1S_0$ is twice the experimental value. This discrepancy can be reduced using a set of calculations including a potential model to represent core polarisation by Migdalek and Baylis [4]. The $7p^3P_1$ to $7s^1S_0$ transition probability is an order of magnitude smaller than in the experiment. In this case there is a forbidden dipole transition. The existence of this transition is a further clear evidence of configurations mixing detected in our work. However, small contributions of other excited configurations not included in our work, due to the increase in the number of parameters above the number of experimental energy levels, can induce a large effect in the calculation of transition probabilities.

4. Conclusions

This work provides theoretical transition probabilities for transitions arising from $6s6p$, $6s7p$ and $6s8p$ configurations, for which no previous values were known. We have also studied the interaction of 1D_2 levels from $6s6d+6p^2$ configurations.