

## LETTER TO THE EDITOR

# A predictive data-based exposition of $nsnp\ ^1,^3P_1$ lifetimes in the Cd and Hg isoelectronic sequences

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**Abstract.** Experimental and theoretical values for the lifetimes of the  $nsnp\ ^1P_1$  and  $^3P_1$  levels in the Cd and Hg isoelectronic sequences are examined in the context of a data-based isoelectronic parameterization. Regularities are used to identify erroneous measurements, to examine to the degree to which theoretical predictions match large scale trends, and to make interpolative and extrapolative predictions.

Several recent studies (Träbert and Curtis 1993, Pinnington and Baylis 1992, Hibbert and Bailie 1992, Träbert and Pinnington 1993) have emphasized the importance of critical evaluations of both experimental measurements and theoretical calculations of the lifetimes of the  $nsnp\ ^1P_1$  and  $^3P_1$  levels in the Zn ( $n = 4$ ), Cd ( $n = 5$ ) and Hg ( $n = 6$ ) isoelectronic sequences. Experimental measurements that were made prior to the widespread use of the method of correlated analysis of decay curves (ANDC) (Curtis *et al* 1971, Curtis 1976) may suffer from errors due to cascade repopulation. Theoretical calculations that do not adequately include the effects of core polarization also may be substantially in error. In some cases, errors in both experiment and theory can produce deceptive agreement for specific ions. A simple data-based exposition has been developed (Curtis 1991) which utilizes isoelectronic regularities to critically evaluate experimental measurements and theoretical calculations. The exposition has already been applied successfully to the Be (Curtis 1991), Mg (Curtis 1991, 1992a) and Zn (Curtis 1992b, Träbert and Curtis 1993) sequences, and its extension to the Cd and Hg sequences is reported herein.

The importance of these considerations is illustrated by recent studies (Träbert and Pinnington 1993, Träbert and Curtis 1993) of the lifetimes of the  $4s4p\ ^3P_1$  levels in the Zn sequence, which revealed that errors in both the calculations and the measurements had produced apparent agreement. It was demonstrated by Hibbert and Bailie (1992) that earlier theoretical calculations had overestimated these lifetimes because of a failure to properly include core polarization. Träbert and co-workers (Träbert and Pinnington 1993, Träbert *et al* 1993) subsequently made new measurements and analyses of these transitions for several ions, which demonstrated that earlier measurements had overestimated lifetimes because of a failure to adequately account for cascade repopulation.

Similarly, Pinnington and Baylis (1992) have recently commented on the calculations by Chou and Huang (1992a) of the lifetimes of the  $6s6p\ ^1P_1$  and  $^3P_1$  levels in the Hg sequence. They have pointed out that these new and comprehensive multiconfiguration relativistic random phase approximation (MCRPRA) calculations did not include core polarization effects and disagree with experiment, whereas earlier work (Migdalek and Baylis 1985) included core polarization and obtained better agreement with experiment. The accuracy of the

available experimental data base was not apparent from the comparisons presented by Chou and Huang (1992a), since the modern ANDC measurements were omitted. Huang and co-workers have also reported MCRRPA calculations for the Zn (Cheng and Huang 1992) and Cd (Chou and Huang 1992b) sequences.

The semiempirical formulation used here parametrizes the effects of intermediate coupling by combining energy level data with lifetime data in an exposition that exhibits a smooth and slowly varying isoelectronic variation. This permits inconsistent data to be identified and discarded, and allows interpolative and extrapolative predictions, as well as smoothing over experimental uncertainties.

For a pure  $nsnp$  configuration in intermediate coupling, the wavefunctions can be written in terms of two normalized singlet-triplet mixing amplitudes that can be expressed as a single mixing angle  $\vartheta$ . This specifies two independent types of experimental data: the splittings among the four  $nsnp$  energy levels; and the lifetimes of the two  $nsnp$   $J = 1$  levels. If the measured excitation energies of the levels are designated by their limiting  $LS$  coupling symbols  ${}^3P_0$ ,  ${}^3P_1$ ,  ${}^3P_2$  and  ${}^1P_1$ , it has been shown (Curtis 1991) that

$$\cot(2\vartheta) = \pm \frac{1}{\sqrt{2}} \left( \frac{3({}^3P_1 + {}^1P_1 - 2{}^3P_0)}{2({}^3P_2 - {}^3P_0)} - 1 \right). \quad (1)$$

Similarly, the line strengths  $S(\text{Res})$  and  $S(\text{Int})$  (obtained from the measured wavelengths and lifetimes using  $S = 3[\lambda(\text{\AA})/1265.38]^3/\tau(\text{ns})$ ) for the resonance and intercombination transitions can be written

$$\begin{aligned} S(\text{Res}) &= 2 \cos^2 \vartheta |ME(\text{Res})|^2 \\ S(\text{Int}) &= 2 \sin^2 \vartheta |ME(\text{Int})|^2 \end{aligned} \quad (2)$$

where  $ME$  denotes the radial dipole transition matrix element. In the non-relativistic limit these are the same and  $S(\text{Int})/S(\text{Res}) \Rightarrow \tan^2 \vartheta$ .

Although these equations are obtained from the single configuration picture, an effective mixing angle  $\vartheta$  can be defined from them irrespective of the validity of this picture. It is possible to utilize the values of  $\vartheta$  obtained from energy level data to characterize the effects of intermediate coupling in the lifetime data. Thus we can use the effective values of  $|ME(\text{Res})|^2$  and  $|ME(\text{Int})|^2$  as *mixing-reduced line strengths*  $S_r$

$$\begin{aligned} S_r(\text{Res}) &\equiv S(\text{Res})/\cos^2 \vartheta \\ S_r(\text{Int}) &\equiv S(\text{Int})/\sin^2 \vartheta. \end{aligned} \quad (3)$$

Empirically, the isoelectronic behaviour of these quantities is often accurately represented by

$$Z^2 S_r \cong a + b/(Z - N_c). \quad (4)$$

where  $N_c$  is the number of closed-shell electrons in the core.

For the Cd sequence, energy level data are available through  $\text{La}^{9+}$  from the measurements of Kaufman and Sugar (1987), which we have earlier extrapolated through  $\text{W}^{26+}$  (Curtis 1986) using a combination of semiempirical and *ab initio* methods. (These energy level data were also omitted by Chou and Huang (1992b) in their comparisons with experiment). These data specify  $\vartheta$  through equation (1), which is used to reduce

Table 1. Cd sequence

Z	Ion	$\lambda$ (Å)	Resonance		Intercombination			sin $\vartheta$
			$\tau$ (ns)		$\lambda$ (Å)	$\tau$ (ns)		
			Pred.	Meas.		Pred.	Meas.	
48	Cd	2288.7	1.554	—	3262.0	2391.0	2390(40) <sup>a</sup>	0.0619
49	In <sup>+</sup>	1586.5	0.760	0.90(8) <sup>b</sup>	2306.9	566.0	125(25) <sup>c</sup>	0.0851
50	Sn <sup>2+</sup>	1251.4	0.490	0.47(3) <sup>d</sup>	1811.7	196.0	—	0.1086
51	Sb <sup>3+</sup>	1042.2	0.349	0.56(6) <sup>b</sup>	1499.3	85.2	—	0.1315
52	Te <sup>4+</sup>	895.2	0.263	0.275(20) <sup>e</sup>	1281.6	42.8	40(10) <sup>f</sup>	0.1536
53	I <sup>5+</sup>	784.8	0.206	0.25(3) <sup>g</sup>	1120.3	23.8	24.4(12) <sup>g</sup>	0.1750
54	Xe <sup>6+</sup>	698.0	0.165	0.15(1) <sup>e</sup>	995.5	14.3	14.0(7) <sup>h</sup>	0.1958
55	Cs <sup>7+</sup>	627.6	0.134	—	895.8	9.11	—	0.2159
56	Ba <sup>8+</sup>	569.1	0.111	—	814.3	6.10	—	0.2353
57	La <sup>9+</sup>	519.5	0.094	—	746.2	4.24	—	0.2541
58	Ce <sup>10+</sup>	476.6	0.079	—	687.6	3.05	—	0.2715
59	Pr <sup>11+</sup>	439.2	0.067	—	637.3	2.26	—	0.2884
60	Nd <sup>12+</sup>	406.1	0.058	—	593.3	1.71	—	0.3044

<sup>a</sup> Byron *et al* (1964), optical double resonance.

<sup>b</sup> Andersen *et al* (1972), curve fit (not used in figure 1).

<sup>c</sup> Andersen and Sørensen (1972), curve fit (not used in figure 1).

<sup>d</sup> Pinnington *et al* (1987b), ANDC.

<sup>e</sup> Pinnington *et al* (1987a), ANDC.

<sup>f</sup> Pinnington *et al* (1985), ANDC.

<sup>g</sup> O'Neill *et al* (1979), ANDC.

<sup>h</sup> Kernahan *et al* (1980), curve fit.

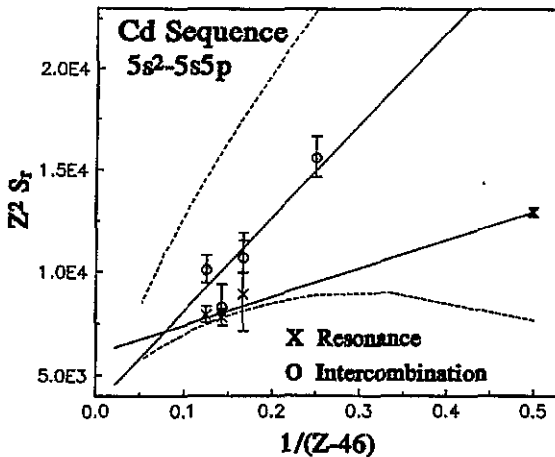


Figure 1. Reduction of the lifetime data for the Cd sequence. Measured values and source references are given in table 1. The full curves are fits to measured data and the broken curves are reductions of MCRPRA calculations.

the experimental lifetime data (listed in table 1) to values for  $S_r(\text{Res})$  and  $S_r(\text{Int})$  using equation (3). These values are scaled by  $Z^2$  and plotted against  $1/(Z - 46)$  in figure 1.

Using the criterion of isoelectronic regularity, three lifetime measurements (Andersen and Sørensen 1972, Andersen *et al* 1972) were discarded from the plotting and fitting

(although they appear in table 1 for comparison). Weighted least-squares adjustments of equation (4) to the remaining measurements were made, which yielded the values for the Cd sequence  $a(\text{Res}) = 3557$ ,  $b(\text{Res}) = 45737$  and  $a(\text{Int}) = 6045$ ,  $b(\text{Int}) = 13798$ . The lifetime values predicted by this linearization are tabulated in table 1 for  $48 \leq Z \leq 60$ , together with the wavelengths, the measured lifetimes and  $\sin \vartheta$ . For  $Z > 60$ , plunging levels from the  $5s4f$  and  $4f^2$  configurations change the ground state (Kaufman and Sugar 1987) and add decay channels, thus altering the unbranched interpretation of the lifetime.

The lifetime predictions given in table 1 provide insights into the difficulties encountered in some of the earlier measurements. The lifetime predicted for the  $\text{In}^+$  intercombination line is 566 ns, which corresponds to a flight path of 40 cm at the lowest energy used by Andersen and Sørensen (1972). Over such distances, the divergence of the beam produced by scattering in the foil can cause downstream escape of particles from the volume viewed by the optical system. Thus the result of  $125 \pm 25$  ns is clearly incorrect and should be discarded from all compilations and comparisons.

A similar plot for the Hg sequence is shown in figure 2. Here, energy level and lifetime measurements are available only for  $80 \leq Z \leq 83$ , since most of the higher members lack stable isotopes. However, the exposition shows that these measurements are well represented by the linear relationship of equation (4). Here the curve fitted value of  $\text{Tl}^+$  (Andersen *et al* 1972) could be retained on the criterion of isoelectronic consistency, indicating that cascade effects were not significant for this case.

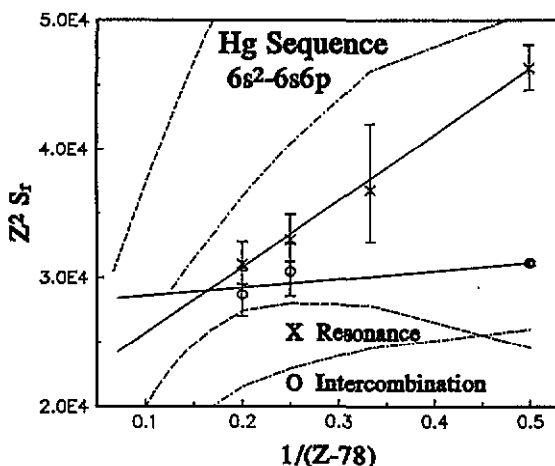


Figure 2. Reduction of the lifetime data for the Hg sequence. Measured values and source references are given in table 2. The full curves are fits to measured data, the broken curves are reductions of MCRPRA calculations and the chain curves are reductions of MCRHF-CP calculations.

A linear fit to equation (4) yielded the values for the Hg sequence  $a(\text{Res}) = 20449$ ,  $b(\text{Res}) = 51509$  and  $a(\text{Int}) = 27912$ ,  $b(\text{Int}) = 6444$ . As before, table 2 lists the wavelengths, the predicted and measured lifetimes and  $\sin \vartheta$ . Predictions up to the actinides were made using the MCRPRA wavelength values of Cheng and Huang (1992a) and an extrapolation of the experimental values of  $\sin^2 \vartheta$  toward the  $jj$  coupling value at infinite  $Z$ .

Both figures 1 and 2 also display reductions of the theoretical calculations of Chou and Huang (1992a,b) which are indicated by broken curves. When presented in this

Table 2. Hg sequence.

Z	Ion	$\lambda$ (Å)	Resonance		Intercombination			$\sin \theta$
			$\tau$ (ns)		$\tau$ (ns)			
			Pred.	Meas.	$\lambda$ (Å)	Pred.	Meas.	
80	Hg	1849.5	1.353	1.35(5) <sup>a</sup>	2537.3	120.7	120.0(7) <sup>b</sup>	0.2030
81	Tl <sup>+</sup>	1321.7	0.6358	0.65(8) <sup>c</sup>	1908.7	36.10	—	0.2495
82	Pb <sup>2+</sup>	1048.9	0.3758	0.380(21) <sup>d</sup>	1553.0	15.27	14.8(10) <sup>d</sup>	0.2876
83	Bi <sup>3+</sup>	872.6	0.2454	0.243(13) <sup>e</sup>	1317.1	7.846	8.0(5) <sup>f</sup>	0.3189
84	Po <sup>4+</sup>	737.4	0.164		1218.9	5.33		0.350
85	At <sup>5+</sup>	641.7	0.119		1072.1	3.21		0.377
86	Rn <sup>6+</sup>	566.5	0.0884		958.0	2.06		0.403
87	Fr <sup>7+</sup>	505.6	0.0677		866.4	1.40		0.427
88	Rn <sup>8+</sup>	455.1	0.0529		791.1	0.98		0.450

<sup>a</sup> Pinnington *et al* (1988a), ANDC.

<sup>b</sup> King and Adams (1974), electron-photon delayed coincidence.

<sup>c</sup> Andersen *et al* (1972), curve fit.

<sup>d</sup> Ansbacher *et al* (1988), ANDC.

<sup>e</sup> Ansbacher *et al* (1989), ANDC.

<sup>f</sup> Pinnington *et al* (1988b), ANDC.

exposition, it is clear that these calculations disagree with experiment both in values and in overall isoelectronic trends in the region where measured data are available. However, the theoretical trends themselves are very similar for the Cd and Hg sequences (a corresponding plot for the Zn sequence using the calculations of Cheng and Huang (1992) also exhibited the same trends). Thus, it seems likely that the inclusion of core polarization effects in this calculation could improve the agreement in all three sequences.

Figure 2 also displays a reduction of the calculations of Migdalek and Baylis (1985) using multiconfiguration relativistic Hartree-Fock methods with a model potential to represent core polarization (MCRHF-CP). Migdalek and Baylis also present an alternative calculation in which the cut-off radius in the CP potential is adjusted to match experimental ionization energies. This brings the curves closer to the data on this plot, but the lack of spectroscopic data limited its application to the first four ions of the sequence. Thus, it might be possible to extend this calculation if accurate semiempirical extrapolations of the energy level data could be made.

It would be interesting to test the persistence at higher  $Z$  of the nearly linear behaviour exhibited by this exposition of the experimental data. This could be done both through new measurements and through the proper inclusion of core polarization in new theoretical calculations.

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