# THE MODIFIED BEER–LAMBERT LAW AND THE CURVE OF GROWTH FOR THE ATOMIC RESONANCE TRANSITION Sn(6s($^3$P$^o_1$) ← 5p$^2$($^3$P$_0$))

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## Summary

We present a detailed study of the curve of growth for the resonance transition of ground state atomic tin Sn(6s($^3$P$^o_1$) ← 5p$^2$($^3$P$_0$)) at $\lambda$ = 286.3 nm. An experimental curve of growth is reported from resonance absorption measurements for the $\lambda$ = 286.3 nm transition on atomic tin vapour in equilibrium with solid tin in the temperature range $T$ = 943 - 1238 K obtained using the method of phase sensitive detection. Expressing the extent of resonance absorption by the modified Beer–Lambert law

$$I_{tr} = I_0 \exp\{-\epsilon(cl)^\gamma\}$$

or

$$I_{tr} = I_0 \exp(-\epsilon cl)^\gamma$$

the logarithmic form of the experimental curve of growth yields $\gamma$ = 0.65 ± 0.02. This is found to be in good agreement with previously determined empirical calibrations for this transition derived from time-resolved resonance absorption measurements ($\gamma$ = 0.64 ± 0.09 and $\gamma$ = 0.66 ± 0.03). Curve of growth calculations, including the effects of nuclear hyperfine interaction, using the three-layer model are found to be unable to generate departures of this magnitude from the standard Beer–Lambert law employing sensible parameters in the model. This is entirely in accord with previous results of similar measurements on the resonance transition Pb(7s($^3$P$^o_1$) ← 6p$^2$($^3$P$_0$)) at $\lambda$ = 283.3 nm.

## 1. Introduction

The relation between the extent of atomic resonance absorption and particle density is both of fundamental interest and of practical concern in kinetic measurements employing time-resolved attenuation of atomic

resonance radiation. Departures from the Beer–Lambert law are generally expressed in one of two forms [1], namely

$$I_{tr} = I_0 \exp\{-\epsilon(cl)^\gamma\}$$

or

$$I_{tr} = I_0 \exp\{-(\epsilon cl)^\gamma\}$$

to take account of effects such as differing line shapes in the spectroscopic source and in the reaction system being investigated. From the kinetic viewpoint, a knowledge of $\gamma$ is required for analysis of first order rate measurements where the slope of a plot of $\ln\{\ln(I_0/I_{tr})\}_t$ against time is given by $-\gamma k'$, where $k'$ is the appropriate first order decay coefficient for atomic decay. $\gamma$ can be seen to be the instantaneous value of the slope of $\ln\{\ln(I_0/I_{tr})\}$ *versus* $\ln c$, where $c$ is the atomic concentration, whether derived from an experimental calibration or from a calculated curve of growth [2]. In the absence of convenient absolute calibrations of atomic particle densities, such as in the N + NO titration [3], a constant value of $\gamma$, which is determined by empirical calibration [1], is employed in time-resolved measurements. This is derived from a plot of $\ln\{\ln(I_0/I_{tr})\}(t = 0)$ for the particular resonance transition against the logarithm of the initial particle density of the photochemical precursor [4 - 7]. We have recently described [8] such empirical measurements for the resonance transition of atomic lead at $\lambda = 283.3$ nm $(Pb(7s(^3P_1^o) \leftarrow 6p^2(^3P_0)))$ [9, 10]. The empirical procedure [1] yielded $\gamma = 0.41 \pm 0.04$ [8]. Phase sensitive detection measurements of $I_0/I_{tr}$ at $\lambda = 283.3$ nm as a function of the absolute atomic concentration of lead in equilibrium with solid lead [11] yielded $\gamma = 0.54 \pm 0.01$ [8], clearly substantiating the conclusion that $\gamma$ is considerably less than unity. In this report we extend the investigations to measurements on resonance absorption by atomic tin at $\lambda = 286.3$ nm $(Sn(6s(^3P_1^o) \leftarrow 5p^2(^3P_0)))$, $gA = 5.3 \times 10^8$ $s^{-1}$ [9, 10]). Empirical and absolute calibrations of $\gamma$ for the transition are compared with the results of curve of growth calculations which include the effects of nuclear hyperfine interaction.

## 2. Experimental

A detailed description of the experimental arrangement for measurement of the curve of growth for a resonance transition by an atomic vapour in equilibrium with the solid at high temperatures using the method of phase sensitive detection has been given for the measurements on atomic lead [8]. Two minor modifications should be noted. Obviously, a tin hollow cathode lamp was employed as the spectroscopic source (Pye Unicam Sn lamp No. 61150, current 8 mA, voltage, 1100 V). In view of the lower vapour pressures of atomic tin in equilibrium with solid tin relative to those for lead [11] at a given temperature, the furnace windings around the absorption cell [8] were reconstructed for operation across the range $T =$

943 - 1238 K. Mass spectrometric measurements [12] clearly show that the concentrations of $Sn_2$ can be neglected in the present investigation.

## 3. Results and discussion

### 3.1. Experimental measurement of $\gamma$

The empirical measurement of $\gamma$ [1] from time-resolved resonance absorption experiments on $Sn(5^3P_0)$ following the pulsed irradiation of a molecule such as tin tetramethyl ($SnMe_4$) requires the assumption of a linear relation between $[Sn(5^3P_0)]$ ($t = 0$) and an experimentally variable parameter. Two independent measurements of $\gamma$ in different laboratories, involving different assumptions, have been described for the region of optical densities typically encountered in single-shot time-resolved measurements and have yielded $\gamma$ values for the $\lambda = 286.3$ nm transition which are in good agreement. Foo *et al.* [13] (Cornell University, Ithaca, U.S.A.) employed the assumption of a linear relation between $[Sn(5^3P_0)]$ ($t = 0$) and $[SnMe_4]$ (initial) for a given pulse energy and obtained $\gamma = 0.64 \pm 0.09$ [13]. Chowdhury and Husain [14] (Cambridge University, England) assumed a linear relation between $[Sn(5^3P_0)]$ ($t = 0$) and pulse energy $E$ for a fixed concentration of $SnMe_4$ and obtained $\gamma = 0.66 \pm 0.03$ [14]. Both sets of measurements employed microwave-powered spectroscopic lamps as sources of the resonance radiation.

The detailed procedure for measuring $\gamma$ by resonance absorption measurements on an atomic vapour in equilibrium with the solid has been given elsewhere [8]. We must emphasize that these measurements were carried out with considerable care. Special attention was paid to thermal equilibration and temperature measurement at various points in the heated absorption cell, especially to ensure that the temperature in the main body of the cell on which the absorption measurements are carried out was about 40 K *higher* than in the region of the solid in a side arm so that there was no deposition on the end windows. The vapour pressure employed was, of course, that commensurate with the lower temperature. The constancy of $I_0$ at $\lambda = 286.3$ nm from the hollow cathode source for the period of the experiment was carefully checked. As with the experiments on lead [8], the resonance absorption measurements on tin were carried out by making observations when the cell was both heated and subsequently cooled, and by taking measurements on different days. Hence, a plot of $\ln\{\ln(I_0/I_{tr})\}$ ($\lambda = 286.3$ nm) against $\ln[Sn(5^3P_0)]$ was constructed as shown in Fig. 1. This yields $\gamma = 0.65 \pm 0.02$, demonstrating, by absolute calibration, that $\gamma$ is *not* unity and substantiating the empirically measured values of $\gamma$ [13, 14]. The agreement between the present measurement and the empirical measurements using microwave-powered lamps [13, 14] indicates the relative independence of the result on the detailed nature of the resonance source.
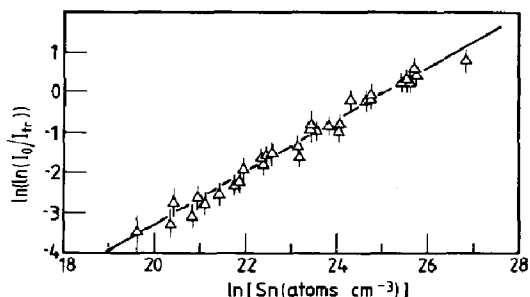
Fig. 1. Experimental curve of growth for the absorption of resonance radiation at $\lambda$ = 286.3 nm ($Sn(6s(^3P_1^o) \leftarrow 5p^2(^3P_0))$) by tin atomic vapour in equilibrium with solid tin in the temperature range $T$ = 943 - 1238 K.

## 3.2. Curve of growth calculations

We describe curve of growth calculations [2], *i.e.* the calculated relation between $I_0/I_{tr}$ and the atomic concentration $c$, which are presented here in logarithmic form for the purpose of comparison with the experimental curve of growth (Fig. 1). As with the analogous calculations on the resonance transition of $Pb(6^3P_0)$ [8], we employ the three-layer model [15], restricting the line shapes to Doppler profiles [8, 16, 17] as the effect of Lorentzian broadening [16] will be very minor at the pressures employed in these experiments [8, 18].

The line shape of the $6s(^3P_1^o) \leftarrow 5p^2(^3P_0))$ transition includes the effect of nuclear magnetic dipole hyperfine interaction for the principal isotopes of tin with nuclear spin $I$. The isotopic abundances of this atom are taken to be as follows [19]: ($I$ = 0) $^{112}Sn$ (0.9%), $^{114}Sn$ (0.61%), $^{116}Sn$ (14.07%), $^{118}Sn$ (23.98%), $^{120}Sn$ (33.03%), $^{122}Sn$ (4.78%) and $^{124}Sn$ (6.11%); ($I = \frac{1}{2}$) $^{115}Sn$ (0.35%), $^{117}Sn$ (7.54%) and $^{119}Sn$ (8.62%). The $^3P_0$ ground state is unsplit ($F = \frac{1}{2}$) [20]. We neglect nuclear hyperfine structure in the minor isotope $^{115}Sn$. To the best of our knowledge, the nuclear magnetic dipole hyperfine interaction constants $A$ have not been reported for the isotopes in the $^3P_1^o$ state, although the ratio $A(^{117}Sn(^3P_1^o))/A(^{119}Sn(^3P_1^o))$ = 0.9555 ± 0.0003 has been measured by level crossing spectroscopy [21]. For simplicity in the calculation, we assumed equality between these constants and parameterized the system by a variable interaction constant $A$ ascribed to an isotope of effective mass 118 and mean abundance 16.2% for the purpose of calculating a Doppler width. Similarly, for the remaining isotopes (83.8%) we employed a mean weighted mass of Sn(119.1). Various line shapes were generated using for $A(Sn(^3P_1^o))$ the value measured for $A(Pb(7^3P_1^o))$ (8813 MHz) [22, 23] and values smaller and greater than this. However, the main component of the $Sn(^3P_1^o \leftarrow ^3P_0)$ transition is unsplit by nuclear hyperfine interaction. The isotopes characterized by $I = \frac{1}{2}$ in this parameterized model give rise to two components, $F(\frac{3}{2}, \frac{1}{2})$ and $F(\frac{1}{2}, \frac{1}{2})$, arising from the application of the standard selection rule $\Delta F$ = 0, ±1 [20]. The total line shape is then calculated from the weighted summation of the Doppler profiles for
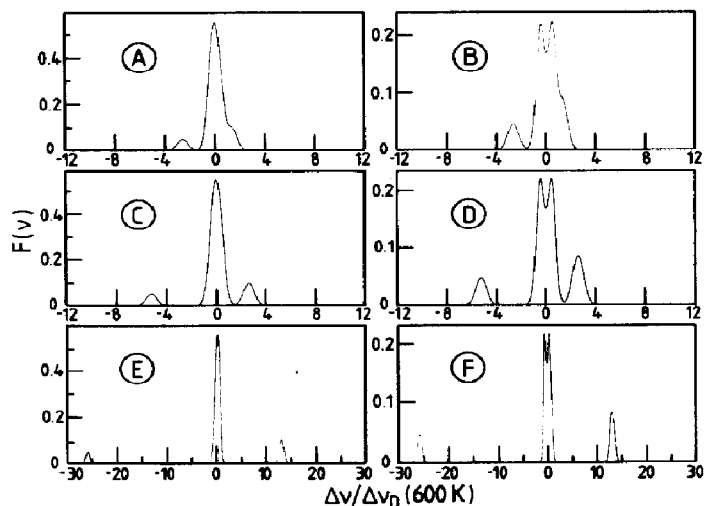
Fig. 2. Examples of computer simulation of model line shapes for the atomic transition at $\lambda = 286.3$ nm ($Sn(6s(^3P_1^o) \rightarrow 5p^2(^3P_0))$) for tin atom emission derived from a hollow cathode source showing separate Doppler profiles associated with individual nuclear hyperfine components. The Doppler width was calculated for the mean atomic mass. The components were measured in Doppler widths at $T = 600$ K ($\Delta\nu_D = 1686$ MHz) for the line centre taken exactly as at $\lambda = 286.333$ nm. (A), (C), (E) Unreversed sources ($L_F = 0$). (B), (D), (F) Partially reversed sources: $T_E = 600$ K; $\Delta\nu_D^E = 1686$ MHz; $T_F = 400$ K; $\Delta\nu_D^F = 1376.6$ MHz; $L_E = L_F = 1$ cm; $n_E = n_F = 10^{11}$ Sn atoms cm$^{-3}$. $A(^{117,119}Sn(6s(^3P_1^o)))$ (GHz): (A), (B) 4.406; (C), (D) 8.813; (E), (F) 44.06.

the various nuclear hyperfine components contributing to the overall transition.

For the purpose of presentation, we need to note the nomenclature associated with the parameters described in the emitting (E) and filter layers (F) in the two-layer hollow cathode source (temperatures $T_E$ and $T_F$ ($T_F < T_E$), effective lengths $L_E = L_F$ and particle densities $n_E = n_F$ [8]) and in the absorbing medium ($T_C$, $L_C$ and $c$), which have been described elsewhere [8, 16, 17, 18]. The line centre $\nu_0$ is taken exactly at $\lambda = 286.333$ nm [9, 10] which is sufficiently accurate for the sensitivity of the curve of growth to this parameter. All the integrations were carried out using the procedure of Gaussian quadrature [24, 25] on the University of Cambridge IBM 370 computer.

Figure 2 shows some computer simulations of the total line shape for the $Sn(^3P_1^o \leftarrow {}^3P_0)$ transition, for various values of $A(Sn(^3P_1^o))$, for unreversed and partially reversed spectroscopic sources using the chosen lamp parameters ($T_E$, $T_F$, $n_E = n_F$ and $L_E = L_F$). The abscissa is presented in units of Doppler widths for the mean atomic mass at $T = 600$ K. The ordinate $F(\nu)$ is the standard normalized intensity distribution function [6, 8] for the emission from the source, weighted according to isotopic abundance. The relative intensities of the hyperfine components are taken from the standard angular momentum relations given by Condon and Shortley [26].
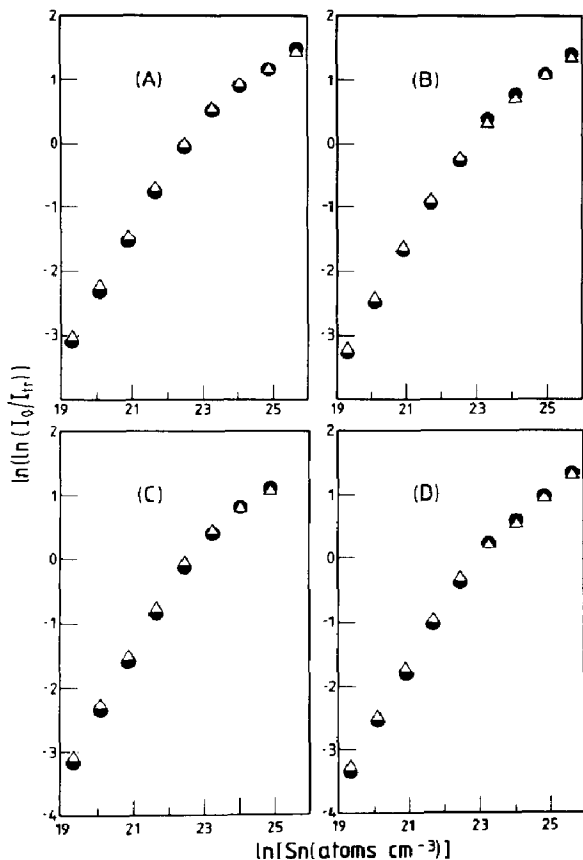
Fig. 3. Examples of calculated curves of growth for the tin atom at $\lambda$ = 286.3 nm $(Sn(6s(^3P_1^o) \leftarrow 5p^2(^3P_0)))$ indicating the effect of temperature in the absorption cell $(L_C = 15.5$ cm) and the effect of nuclear hyperfine interaction in $^{117,119}Sn(6s(^3P_1^o))$. $A(^{117,119}Sn(^3P_1^o)))$ (GHz): (A), (B) 4.406; (C), (D) 44.06; (A), (C) unreversed sources; (B), (D) partially reversed sources, $T_E$ = 600 K, $T_F$ = 400 K, $L_E = L_F = 1$ cm, $n_E = n_F = 10^{11}$ Sn atoms cm$^{-3}$. $T$ K (absorption cell): $\triangle$ 943; $\bullet$ 1238.

Figure 3 gives example of the curves of growth in logarithmic form for some of the lamp parameters given in Fig. 2 for the two extremes of temperature used in the experimental curve of growth calibration (Fig. 1). As we have emphasized previously [8], as with all such measurements on atomic vapours in equilibrium with solids, Fig. 1 is not strictly a curve of growth in view of the variation of temperature which should ideally be held constant. However, the effect of the Doppler width resulting from the limited temperature change on the curve of growth is seen to be negligible (Fig. 3). Similar curves of growth were obtained for the other lamp parameters given in Fig. 2, and further sensible variation in the parameters in Fig. 2 had no dramatic effect on the curves of growth.

As with previous calculations of this type [8, 17, 18], the slopes of plots of the type given in Fig. 3 are unity at low optical density in the linear

region and only become significantly less than unity, reaching values of about 0.5 and lower, at higher optical densities. Only unrealistic sets of spectroscopic lamp parameters will generate a slope of about 0.5 or lower in the low optical density region. Hence the three-layer model is too idealistic for generating a curve of growth in accord with the absolute atomic calibration curve, as seen both for the $Pb(6^3P_0)$ atom [8] and for the $Sn(5^3P_0)$ atom considered here (Fig. 1). Given the sensible agreement between the absolute curve of growth calibrations and the empirically determined $\gamma$ values both for the transitions involving $Pb(6^3P_0)$ [8] and $Sn(5^3P_0)$ (refs. 13 and 14 and this work), the three-layer model, by the same token, is not sufficiently realistic to describe kinetic systems designed for time-resolved resonance absorption spectroscopy. This conclusion, therefore, is not in accord with recent three-layer model calculations designed to consider collisional rate data for $O(2^1D_2)$ [17] derived from attenuation of atomic resonance radiation.

## Acknowledgments

## References

1 R. J. Donovan, D. Husain and L. J. Kirsch, Trans. Faraday Soc., 66 (1970) 2551.
2 A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge University Press, London, 1934.
3 P. P. Bemand and M. A. A. Clyne, J. Chem. Soc. Faraday Trans. 2, 69 (1973) 1643.
4 D. Husain, Ber. Bunsenges. Phys. Chem., 81 (1977) 168.
5 R. J. Donovan and D. Husain, Annu. Rep. Prog. Chem., Sect. A, 68 (1971) 123.
6 R. J. Donovan, D. Husain and L. J. Kirsch, Annu. Rep. Prog. Chem., Sect. A, 69 (1972) 19.
7 R. J. Donovan and H. M. Gillespie, in P. G. A. Ashmore (ed.), Specialist Periodical Reports, Reaction Kinetics, Vol. 1, The Chemical Society, London, 1975, p. 14.
8 P. J. Cross and D. Husain, J. Photochem., 10 (1979) 251.
9 C. H. Corliss and W. R. Bozman, Experimental transition probabilities for spectral lines of seventy elements, Nat. Bur. Stand. (U.S.), Monogr., 53, 1962.
10 C. E. Moore (ed.), Atomic Energy Levels, Vols. I - III, Nat. Bur. Stand. (U.S.A.), Circ., 467, 1958.
11 R. Hultgren, P. D. Desai, D. T. Hawkins, K. K. Kelley and P. D. Wagman, Am. Chem. Soc. Met., Metals Park, Ohio, 1973.
12 R. E. Honig, J. Chem. Phys., 21 (1953) 573.
13 P. D. Foo, J. R. Wiesenfeld and D. Husain, Chem. Phys. Lett., 32 (1975) 443.
14 M. A. Chowdhury and D. Husain, J. Chem. Soc. Faraday Trans. 2, 74 (1978) 1065.
15 W. Bleeker, Z. Phys., 52 (1929) 809.
16 W. Braun and T. Carrington, J. Quant. Spectrosc. Radiat. Transfer, 9 (1968) 1133.
17 L. F. Phillips, Chem. Phys. Lett., 37 (1976) 421.
18 P. E. Norris and D. Husain, J. Chem. Soc. Faraday Trans. 2, 73 (1977) 415.

19  W. Gordy, W. A. Smith and R. F. Trambarulo, Microwave Spectroscopy, Dover, New York, 1960.
20  C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York, 1955.
21  M. Britger and P. Zimmerman, Z. Naturforsch., Teil A, 22 (1967) 2001.
22  H. Kopferman, Z. Phys., 75 (1932) 363.
23  G. H. Fuller, Nuclear spins and moments, J. Phys. Chem. Ref. Data, 5 (1976) 835.
24  T. N. L. Patterson, Math. Comput., 22 (1968) 847.
25  NAG Library Routine DUlACF.
26  E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, London, 1934.