

THE MODIFIED BEER-LAMBERT LAW AND THE CURVE OF GROWTH FOR THE ATOMIC RESONANCE TRANSITION $\text{Pb}(7s(^3\text{P}_1^o) \leftarrow 6p^2(^3\text{P}_0))$

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Summary

We describe an experimental study of the modified Beer-Lambert law

$$I_{\text{tr}} = I_0 \exp\{-\epsilon(c l)^\gamma\}$$

or

$$I_{\text{tr}} = I_0 \exp\{-(\epsilon c l)^\gamma\}$$

applied to the resonance transition of atomic lead at $\lambda = 283.3$ nm ($\text{Pb}(7s(^3\text{P}_1^o) \leftarrow 6p^2(^3\text{P}_0))$). γ is determined experimentally by two methods. The first involves the standard empirical procedure for time-resolved resonance line absorption following, in this case, the pulsed irradiation of lead tetraethyl in the presence of a buffer gas, yielding $\gamma = 0.41 \pm 0.04$. The second employs a direct calibration of I_0/I_{tr} against the absolute concentration of atomic lead vapour in the temperature range $T = 600 - 783$ K, in equilibrium with solid lead, using the technique of phase sensitive detection. This yields $\gamma = 0.54 \pm 0.01$. γ is also generated by calculation from the slope of the logarithmic form of the curve of growth using the three-layer model. Whilst such calculations can generate γ values considerably less than unity at high optical densities, they do *not* yield such values using realistic parameters at the optical densities at which the calibration using absolute atomic concentrations was carried out. It is therefore concluded that the disagreement between the measured and calculated values arises from limitations in the three-layer model. The time-resolved resonance absorption signals obtained in the empirical measurements of γ permit one to estimate a rate constant k for the reaction



of $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (300 K).

1. Introduction

The study of the collisional behaviour of atoms in specific electronic states by time-resolved resonance line absorption, following the generation of the atoms by pulsed irradiation, is a well-established experimental method [1 - 4]. The extent of resonance line absorption is often described by a modified Beer-Lambert law of the form [5]

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

or

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

From the viewpoint of the many kinetic experiments that have been reported [1 - 4], the choice of the forms of eqns. (I) or (II) is not of prime importance. In eqn. (I), ϵ will be a variable of floating dimensions $(cl)^{-\gamma}$. Neither eqn. (I) nor eqn. (II) will lead to the correct limiting form of the curve of growth [6], *i.e.* the calculated relation between I_0/I_{tr} and the atomic concentration c , as has been pointed out by Bemand and Clyne [7]. However, for time-resolved experiments involving decays of the atom which are kinetically first order, it is the *logarithmic* forms of eqns. (I) or (II) which are of concern, namely

$$\ln\{\ln(I_0/I_{tr})\}_t = \gamma \ln c + \text{constant} \quad (III)$$

Thus γ is seen to be the slope of the curve of growth when presented in logarithmic form. Ideally, γ is itself a function of concentration, but for practical purposes it can be taken to be sensibly constant over a limited concentration range, as will become evident (see later). It is immediately obvious from eqn. (III) that the values of measured absolute rate constants derived from the resonance absorption technique will depend on the reciprocal of γ , and differences in rate data resulting from the use of various techniques including resonance absorption have been ascribed to the effect of the magnitude of γ and its empirical determination (see later) [8 - 10]. It is, indeed, the empirical determination of γ on which much of the controversy rests. In practical terms, this arises because, for most of the atomic states whose kinetics are investigated [1 - 4], one does not usually have a convenient technique for calibrating I_0/I_{tr} against the absolute atomic concentration. This may be contrasted with the calibration of resonance absorption by N and O atoms in a flow discharge system where absolute concentrations can be determined by the N + NO chemical titration technique [7]. The empirical determination of γ in time-resolved absorption measurements generally involves the assumption of a linear relation between an initial atomic concentration generated on irradiation and the concentration of the photochemical precursor [5].

In this paper resonance absorption by ground state lead atoms, $\text{Pb}(6p^2 \text{ } ^3\text{P}_0)$, which have been the object of a number of kinetic investigations [11 - 15], is studied in detail using the transition at $\lambda = 283.3 \text{ nm}$ ($7s(^3\text{P}_1^o) \leftarrow$

$6p^2(^3P_0)$). The empirical measurement of γ [5, 11] has been re-investigated in detail and has been shown to result in a value for this quantity which is considerably less than unity, *i.e.* the standard Beer-Lambert law is *not* obeyed. Further, an absolute calibration yielding γ has been carried out by measurement of the extent of resonance absorption by atomic lead in the vapour phase in equilibrium with solid lead over the temperature range $T = 600 - 783$ K, and the resulting value for γ is also considerably less than unity. Finally, we describe curve of growth calculations for the $\lambda = 283.3$ nm transition which includes the effects of nuclear hyperfine interaction.

2. Experimental

Two experimental arrangements were employed in this investigation. The empirical determination of γ [5] for the $\lambda = 283.3$ nm transition was carried out essentially with an apparatus similar to that described for previous time-resolved studies of $Pb(6^3P_0)$ [13 - 15] but with some modifications. Ground state lead atoms were generated by the low energy ($E = 38 - 61$ J) photolysis of low concentrations of lead tetraethyl ($PbEt_4$) in the presence of excess nitrogen to prevent any significant temperature rise on irradiation. A conventional quartz photolysis lamp and reaction vessel, separated by air, were employed. The system was deliberately designed to avoid any strong optical coupling between the photolysis lamp and the vessel. In order to achieve low degrees of photolysis and, more importantly, to minimize the photochemical production of the optically metastable excited states $Pb(6p^2(^3P_{1,2}, ^1D_2, ^1S_0))$ that are normally generated in this type of system [16 - 22], no kind of reflection system to increase the incidence of actinic radiation from the flash onto the reaction vessel was employed. This experimental arrangement may be contrasted with those employed in previous kinetic studies of ground state lead atoms by the resonance absorption technique [13, 15] which involved higher pulse energies and a high degree of optical coupling, which was effected by means of a coaxial lamp and vessel assembly. The objective of the present procedure is to ensure that measurements of $[Pb(6^3P_0)]$, extrapolated to $t = 0$, are sensibly uncomplicated by the effects of relaxation of higher lying atomic states into the ground state at longer times.

The $Pb(6^3P_0)$ atoms generated by the photolysis pulse were monitored in the single-shot mode by use of the resonance line at $\lambda = 283.3$ nm ($Pb(7s(^3P_1^o) \leftarrow 6p^2(^3P_0))$, $gA = 1.8 \times 10^8 \text{ s}^{-1}$ [23]), derived from a hollow cathode source (High Spectral Output, Westinghouse, U.S.A.) [13]. The optical transition was isolated by means of a Seya-Namioka grating monochromator [14, 24 - 26]. The resonance absorption signals were detected photoelectrically (E.M.I. 9783 B), amplified without distortion [27], transferred to and digitized in a transient recorder (Data Laboratories, DL 905) employed in the A/B mode [14] and punched onto paper tape in ASCII code (Data-dynamics punch 1133) for direct input into the University of Cambridge

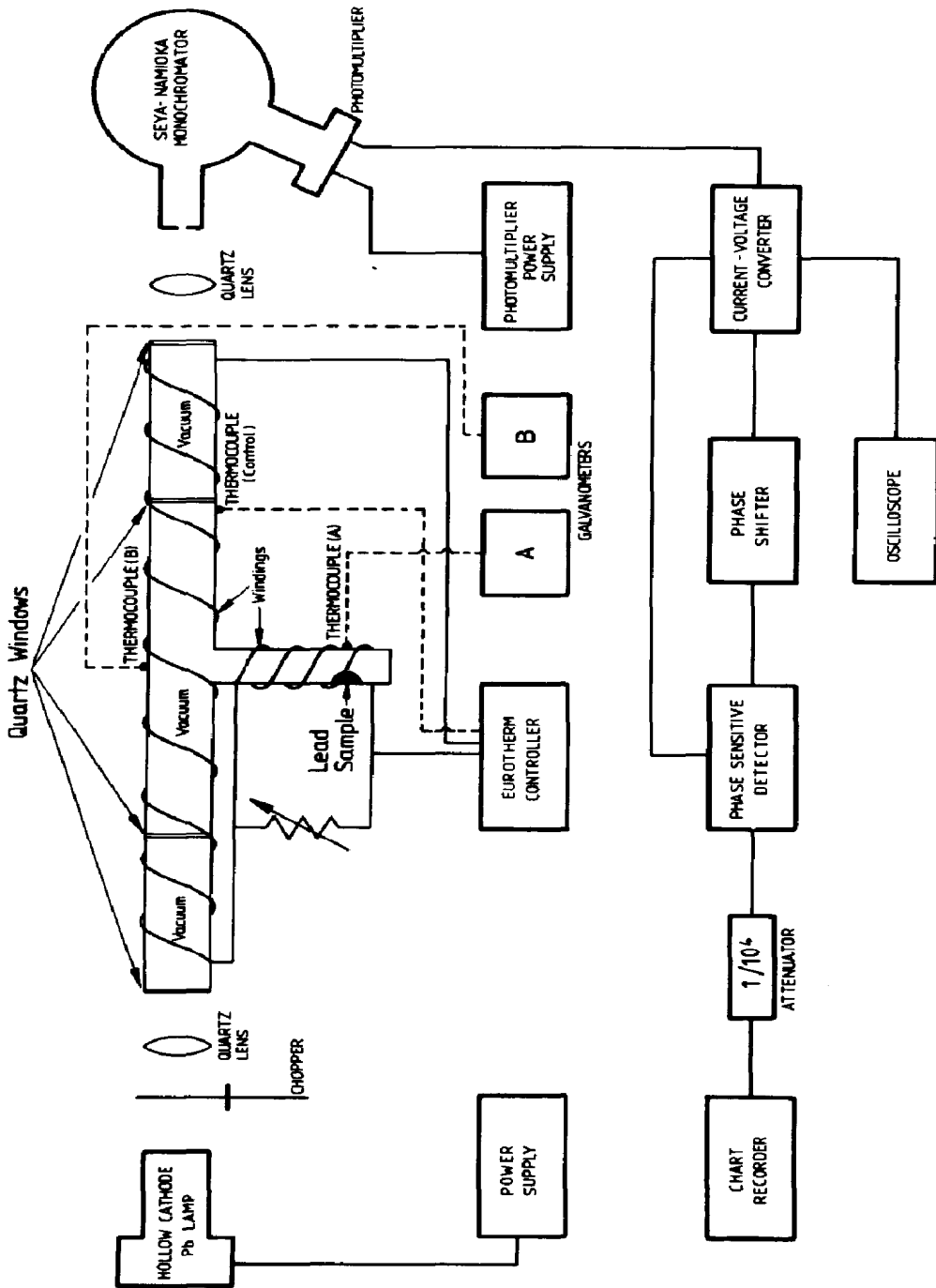


Fig. 1. Block diagram of the apparatus for measuring the extent of absorption of atomic lead resonance radiation by lead vapour in equilibrium with solid lead.

IBM 370 computer. The raw data were subjected to the standard numerical smoothing procedure of Savitsky and Golay [28].

The second apparatus employed the same optical system for measurement of the extent of resonance absorption at $\lambda = 283.3$ nm by the atomic vapour of lead in equilibrium with solid lead over a defined temperature range. We employ the standard procedure of phase sensitive detection. A block diagram of the system is shown in Fig. 1. Light from the lead hollow cathode resonance source was mechanically chopped at 75 Hz, focused through the heated absorption cell onto the entrance slit of the monochromator and detected by means of the E.M.I. 9783B photomultiplier tube mounted on the exit slit. The modulated output was fed to the fast-settling electrometer amplifier [13, 27] which provided both the signal and reference channels for a phase-sensitive detector (Brookdeal Type 411). A variable phase shift was introduced into the reference channel (Brookdeal Phase Shifter Type 321). The output from the detector was fed onto a chart recorder (Leeds and Northrop Speedomax H) and the signal was maximized by varying the phase shift so that the actual signal and the reference signal were in phase. Use of this system enabled very low noise levels to be attained, the signal to noise ratio being typically 100:1.

The heated cell employed consisted of a quartz tube ($l = 35$ cm; outer diameter, 23 mm) divided into three parts by internal quartz windows. Of these three compartments, the outer two, each of length 10 cm, were evacuated to about 10^{-4} Torr (1 Torr = 133 N m^{-2}) and sealed. The central section carried a side arm ($l \approx 10$ cm; outer diameter, about 10 mm) into which a small amount of lead was sublimed. This section was also evacuated. Heating wire (Nichrome; diameter, 0.075 in; $R = 9.96 \Omega \text{ m}^{-1}$) was then wound around the complete assembly. One winding was placed around the main tube and a separate winding, connected in series with the first, around the side arm. Independent control over the current in the side-arm winding was provided by connecting a variable resistance ($R_{\text{max}} \approx 75 \Omega$) in parallel with it. On the main tube the winding density was slightly greater near the windows of the central compartment in order to prevent condensation of solid lead onto these windows. The lagging consisted of one layer of asbestos immediately over the heating wire, followed by a thick (about 15 cm) layer of fibreglass.

Temperature measurement was effected by means of three T_1/T_2 thermocouples housed in quartz sleeves and mounted on the main tube and on the side arm. One thermocouple was placed very close to the lead sample and the second at the centre of the main tube near the junction with the side arm; the thermoelectric e.m.f.s were measured on galvanometers (Cambridge Instruments model 7504 R). The third thermocouple, which provided the controlling signal to a Eurotherm regulator, was mounted above one of the windows of the central part of the cell. Two of the thermocouples (those mounted on the main tube) could be moved along in their quartz sleeves parallel to the main tube, and provided a convenient means of checking the axial temperature distribution which was found to be uniform

to within ± 15 K of the set temperature (typically 700 K). During an experiment the variable resistance in parallel with the side-arm winding was adjusted so that the equilibrium temperature near the lead droplet was about 40 K below that of the main tube, thus providing a further safeguard against deposition of lead onto the windows. The temperature near the lead sample was used to calculate the particle density of the lead atoms [29].

As the present arrangement did not permit measurement of the unattenuated light intensity I_0 throughout the series of measurements at different temperatures, it was essential to ensure that the hollow cathode lamp was free from systematic variations in intensity over a time period of about 2.5 h. It was found that this stable operation could be readily achieved provided that a warm-up period of about 20 min was allowed. In all cases, therefore, the lamp was operated for at least this time before the furnace was switched on. When the hollow cathode lamp had warmed up, the furnace was allowed to pre-equilibrate at $T = 520 - 570$ K, at which temperature the vapour pressure of lead is negligible [29], and the I_0 signal was rechecked before proceeding with the light absorption measurements. The temperature was then increased slowly in steps of about 20 K and absorption measurements were taken when equilibrium had been established. When the extent of light absorption had reached 95 - 97%, the furnace was allowed to cool, again in steps of about 20 K, and the measurements were repeated during the cooling process. Complete series of measurements were repeated on three separate days. All the resulting data were found to fit onto the same line to an accuracy of about 2% (see Section 3).

2.1. Materials

PbEt_4 , krypton (for the photoflash lamp) and nitrogen were prepared as described previously [13 - 15]. Solid lead (Analar) was used for sublimation into the absorption cell.

3. Results and discussion

3.1. Empirical determination of γ

A detailed description has been given in previous papers [13 - 15] of the handling of the raw experimental data representing time-resolved resonance absorption at $\lambda = 283.3$ nm following the pulsed irradiation of PbEt_4 in the presence of excess buffer gas. Thus one obtains (a) a computer-generated plot representing the digitized form of $I_{\text{tr}}(\lambda = 283.3 \text{ nm})$ versus time, (b) a computerized plot of I_{tr} versus time following the smoothing procedure of Savitsky and Golay [28] and (c) good linear plots, with slope errors of the order of typically 1% [14] of the digitized form of $\ln\{\ln(I_0/I_{\text{tr}})\}$ versus time. These plots were regularly obtained in the present investigation. Reference may be made to the earlier work [13 - 15] for examples of the form of the data. The intercepts of these first-order plots (c), $\ln\{\ln(I_0/I_{\text{tr}})\}$ ($t = 0$), are then employed in the construction of the so-called Beer-Lambert plots. The intercepts are determined for varying initial concentrations of PbEt_4 . The assumption of a linear relation between $[\text{Pb}(6^3\text{P}_0)]$

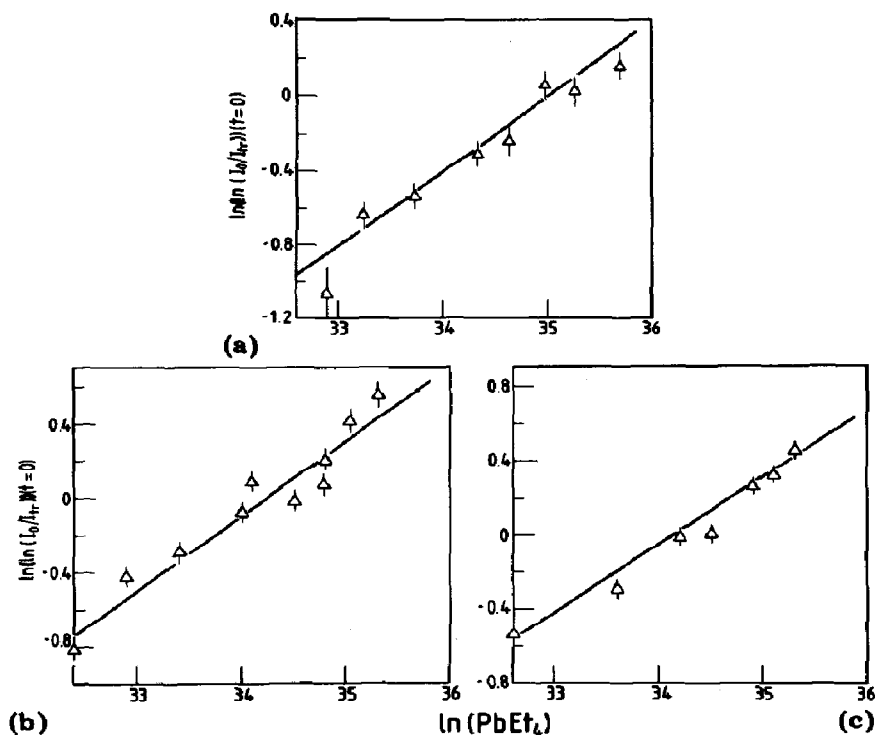


Fig. 2. Beer-Lambert plots for the absorption of resonance radiation by lead atoms at $\lambda = 283.3$ nm ($\text{Pb}(7s(^3P_1^o) \leftarrow 6p^2(^3P_0))$): $[\text{N}_2] = 3.1 \times 10^{17} - 2.8 \times 10^{18}$ molecules cm^{-3} ; (a) $E = 38$ J ($\gamma = 0.41 \pm 0.04$); (b) $E = 53$ J ($\gamma = 0.41 \pm 0.04$); (c) $E = 61$ J ($\gamma = 0.37 \pm 0.03$).

$(t = 0) \propto \ln\{\ln(I_0/I_{tr})\}(t = 0)$ and $[\text{PbEt}_4]$, coupled with eqn. (I) or eqn. (II), yields the Beer-Lambert plot [5, 11]. Hence, for a constant value of γ the plot of $\ln\{\ln(I_0/I_{tr})\}(t = 0)$ versus $\ln[\text{PbEt}_4]$ should be a straight line of slope γ . In the present investigation, series of measurements were carried out at three different flash energies (38 J, 53 J and 61 J) to see if there was any significant effect arising from any relaxation from optically metastable atomic states into the ground state. Further, it must be emphasized that perhaps the main inaccuracy in the measurement of γ by the present procedure results from the errors in the measurement of low pressures of materials such as PbEt_4 in the millitorr region. The γ plot itself depends only upon the ratio of PbEt_4 concentrations. Accordingly, we employ the procedure of using varying aliquots from a stock PbEt_4/N_2 mixture. Thus we forego the constancy of total pressure with N_2 , the variation of which in the present experiments has a very minor Lorentzian-broadening effect on the atomic line shape, which is principally determined by Doppler broadening [6], and an even smaller effect on the logarithmic form of the curve of growth which is a function of many parameters [6]. The gain in this procedure is the accurate determination of relative concentrations of PbEt_4 . The centre of the concentration range of nitrogen that was employed was approximately that used (with helium) by Husain and Littler in their earlier determination of γ for this particular resonance transition [11]. The resulting γ plots are given in Fig. 2, and yield

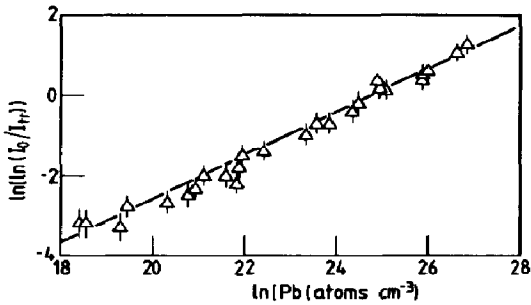


Fig. 3. Experimental curve of growth for the absorption of resonance radiation at $\lambda = 283.3$ nm ($\text{Pb}(7s(^3\text{P}_1^0) \leftarrow 6p^2(^3\text{P}_0))$) by lead atomic vapour in equilibrium with solid lead in the temperature range $T = 600 - 783$ K.

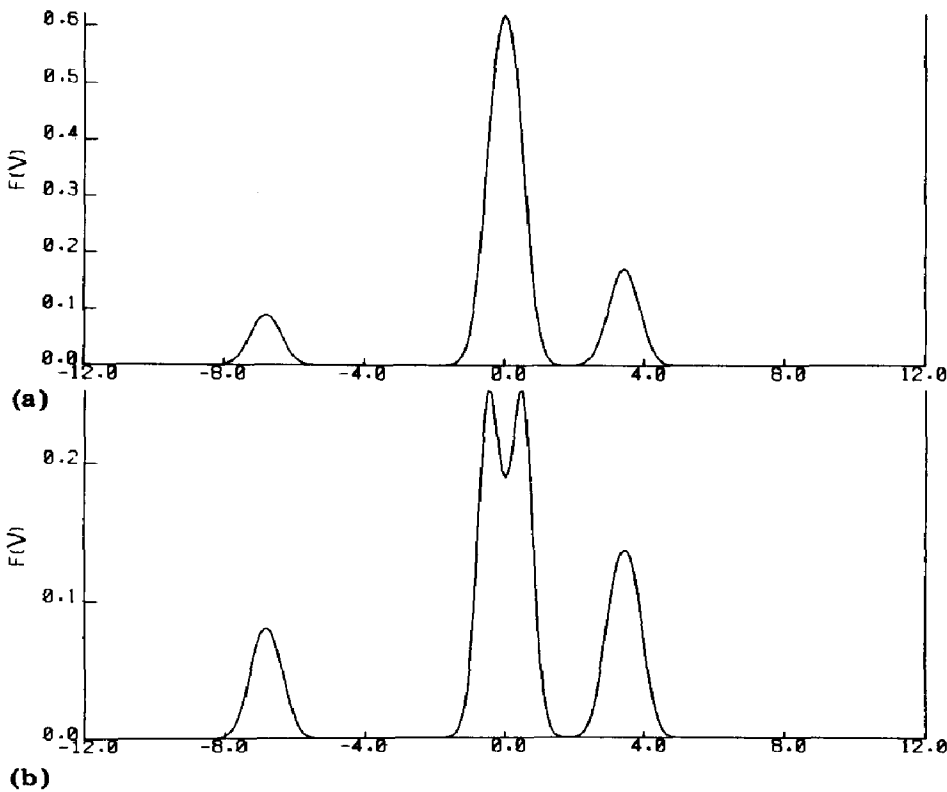


Fig. 4. Example of the computer simulation of the atomic transition at $\lambda = 283.3$ nm ($\text{Pb}(7s(^3\text{P}_1^0) \rightarrow 6p^2(^3\text{P}_0))$) for lead atom emission derived from a hollow cathode source showing separate Doppler profiles associated with individual nuclear hyperfine components. Isotopic abundances for generating spectral intensities: ^{207}Pb ($I = \frac{1}{2}$) (21.11%); ^{204}Pb , ^{206}Pb , ^{208}Pb ($I = 0$) (total 78.89%). The Doppler width was calculated for the mean atomic mass. The components were measured in Doppler widths from the line centre taken exactly as $\lambda = 283.306$ nm. The nuclear magnetic dipole hyperfine interaction constant $A(7s(^3\text{P}_1^0)) = 8813$ MHz. (a) Unreversed lamp: $T_E = 600$ K; $\Delta\nu_D^E = 1289.7$ MHz. (b) Reversed lamp: $T_E = 600$ K; $T_F = 400$ K; $L_E = 1$ cm; $L_F = 1$ cm; $\Delta\nu_D^E = 1289.7$ MHz; $\Delta\nu_D^F = 1053.1$ MHz. The atomic densities in the source (E) and the filter (F) were 10^{11} atoms cm^{-3} .

$E = 38 \text{ J}$	$\gamma = 0.41 \pm 0.04$
$E = 53 \text{ J}$	$\gamma = 0.41 \pm 0.04$
$E = 61 \text{ J}$	$\gamma = 0.37 \pm 0.04$

The results are clearly independent of energy. The close agreement with the result of Husain and Littler ($\gamma = 0.38 \pm 0.04$) [11], who used an optically coupled coaxial lamp and vessel assembly, higher flash energy ($E = 562 \text{ J}$) and a different optical system, is striking.

3.2. Determination of γ from light absorption by lead atomic vapour

Figure 3 shows the curve of growth in logarithmic form for the $\lambda = 283.3 \text{ nm}$ transition using the absolute atomic lead densities in the temperature range $T = 600 - 783 \text{ K}$ following Hultgren *et al.* [29]. There is no significant concentration of molecular lead (Pb_2) in equilibrium with the solid at these temperatures [30]. The slope of Fig. 3 yields $\gamma = 0.54 \pm 0.01$. We can offer no quantitative explanation for the difference in the two experimental values of γ , namely the empirical result and the present result which disagree by about 20%, but we can emphasize that γ is not unity. We must clearly favour the absolute calibration. Figure 3, as with all such measurements of curves of growth employing equilibrium atomic densities of vapours above solids, is not strictly a curve of growth as the temperature is varying. However, the variation of the Doppler width for the transition associated with the atoms in the vessel, resulting from this limited temperature variation, will have a negligible effect on the curve of growth in logarithmic form as line-shape calculations clearly show (see later).

3.3. Curve of growth calculations

The present experiments have clearly demonstrated both by empirical calibration [5] and by absolute calibration that a γ value considerably less than unity must be employed in eqns. (I) or (II) to describe the relation between the extent of resonance absorption at $\lambda = 283.3 \text{ nm}$ and the particle density of lead atoms. Furthermore, empirically determined values of γ which are less than unity have been found to be in accord with rate data for $\text{Bi}(6^4\text{S}_{3/2})$, $\text{Sb}(5^4\text{S}_{3/2})$, $\text{As}(4^4\text{S}_{3/2})$ and $\text{P}(3^4\text{S}_{3/2})$ determined on the one hand by time-resolved resonance absorption [31 - 35] and on the other hand by time-resolved resonance fluorescence [36 - 39]. The former method depends on the form of eqn. (I) or (II) whereas the latter method only depends on the functional relation, preferably linear, between the resonance fluorescence intensity and the atomic particle density. It can readily be seen that a comparison of a rate constant k_R for the reaction of a given atom with a given molecule R studied by the two techniques yields γ for the transition employed in the resonance absorption measurements. Thus,

$$k_R(\text{res. abs., assuming } \gamma = 1)/k_R(\text{res. fluor.}) = \gamma$$

The whole series of investigations [31 - 39] showed that γ was less than unity for each resonance transition involved in the absorption studies and

the comparison of the rate data obtained by the absorption and fluorescence techniques generally substantiated the empirically measured values of γ in each case.

Within this broad context, a controversy has developed over rate data for the electronically excited oxygen atom $O(2^1D_2)$ determined (a) by time-resolved resonance absorption at $\lambda = 115.2$ nm ($O(3^1D_2) \leftarrow O(2^1D_2)$) using the empirically measured value of $\gamma = 0.41$ [8, 9] and (b) by the weak forbidden emission at $\lambda = 630$ nm ($O(2^1D_2) \rightarrow O(2^3P_2)$) [10]. In the absence of an absolute calibration technique for $[O(2^1D_2)]$, Phillips [40] has used the three-layer model [41 - 43] in order to determine γ for the $\lambda = 115.2$ nm transition by curve of growth calculations [6]. Phillips concludes that γ is essentially unity for the optical densities at $\lambda = 115.2$ nm generally encountered in time-resolved resonance absorption measurements on $O(2^1D_2)$ [40] and hence concludes further that the rate data for $O(2^1D_2)$ that are obtained from the absorption measurements are high [40]. In this paper we describe three-layer model curve of growth calculations for the $\lambda = 283.3$ nm transition which may be compared with the absolute calibration presented here. The objective of the calculations described here is to show that the three-layer model is too idealized for the type of experimental system generally encountered in time-resolved atomic absorption measurements and generates γ values of unity when absolute calibration shows the γ value to be much lower than this at the appropriate optical densities.

The line shapes in the present calculations are restricted to Doppler profiles [6] as in the earlier calculations of Braun and Carrington [43] and in those of Phillips [40]. Even at the buffer gas densities typically encountered in time-resolved resonance absorption measurements, say 10^{19} particles cm^{-3} , the effect of Lorentzian broadening on the logarithmic form of the curve of growth is minor [34]. For the present purposes, the density of neon gas in the hollow cathode lamp is about 3.5×10^{17} atoms cm^{-3} (we are indebted to the Westinghouse Corporation, U.S.A., for this information) and no buffer gas was employed for the measurements on the light absorption by the atomic lead vapour in equilibrium with the solid (see Section 2).

In the three-layer model the resonance lamp is viewed as being composed of two layers: (1) the first layer at temperature T_E and of effective length L_E is the primary emitting layer; (2) the second layer at temperature T_F ($T_F < T_E$) and of effective length L_F is the absorbing layer and takes account of partial light reversal in the lamp. It is customary in such calculations [34, 40, 43] to make the arbitrary choice of equality in the emitting and reversing lengths ($L_E = L_F$), and also in the particle densities in these two regions ($n_E = n_F$). Layer (3) of this model is then the absorption cell at temperature T_C and of length L_C which is situated between the spectroscopic source and the detection system. In the present calculations, the total line shape is obtained from the summation of the Doppler profiles for the individual nuclear hyperfine components, weighted according to the isotopic abundances. The ^{207}Pb (21.1%) isotope is characterized by a nuclear spin $I = \frac{1}{2}$ and therefore gives rise to a nuclear magnetic dipole hyperfine

interaction; the remaining isotopes, ^{204}Pb , ^{206}Pb and ^{208}Pb , possess no nuclear spin [44]. In these calculations we employ an average Doppler width for the mean atomic mass.

The $7s(^3\text{P}_1^o) \leftarrow 6p^2(^3\text{P}_0)$ transition comprises two nuclear hyperfine components for the ^{207}Pb isotope arising from the nuclear magnetic dipole hyperfine interaction. The $7s(^3\text{P}_1^o)$ state comprises two levels for this isotope ($F = \frac{1}{2}, \frac{3}{2}$) [44] whereas the $6p^2(^3\text{P}_0)$ state ($F = \frac{1}{2}$) is unsplit. The splitting in the $^3\text{P}_1^o$ state can be expressed in the standard form [45] and two components will arise in the electronic transition from the selection rule $\Delta F = 0, \pm 1$ [45]. Kopferman [46, 47] gives the nuclear magnetic dipole hyperfine interaction constant A in the $7s(^3\text{P}_1^o)$ state for ^{207}Pb as 8813 MHz. The mathematical details of the curve of growth calculations based on the three-layer model have been given in previous papers [34, 40, 43]. The appropriate integrals were evaluated using the standard method of Gaussian quadrature [48, 49].

Figure 4 gives an example of the computerized simulation of the atomic line shape for the $7s(^3\text{P}_1^o) \rightarrow 6p^2(^3\text{P}_0)$ transition. The line centre ν_0 is taken as exactly at $\lambda = 283.306$ nm [50] as the curve of growth is not sensitive to the exact position of the atomic line beyond this accuracy. As described in Section 2, we have employed $gA = 1.8 \times 10^8 \text{ s}^{-1}$ [23] for the transition and a Doppler width calculated for a mean atomic mass from the isotopic distribution [44]. The hyperfine components are situated at $\nu_0 + 44.065$ MHz and $\nu_0 - 8813$ MHz. The abscissa of Fig. 4 is presented in units of Doppler widths. The ordinate $F(\nu)$ in Fig. 4 is the integrand of the integral expression describing the intensity distribution of a partially reversed line source. The intensity ratio for the hyperfine components is taken from the standard angular momentum relations given by Condon and Shortley [51] (intensity ratio $F(\frac{3}{2}, \frac{1}{2}) : F(\frac{1}{2}, \frac{1}{2}) = 2:1$). Figure 4 shows line shapes for reversed and unreversed sources using the arbitrary parameters given in the figure caption.

Figure 5 shows the logarithmic form of the calculated curves of growth using the parameters characterizing the hollow cathode source described in Fig. 4 for the reversed and unreversed conditions, and for the two extremes of the temperature range used for the absolute experimental curve of growth calibration (Fig. 3). It is clear that the effect of the variation of the Doppler width with temperature on the curve of growth is negligible. The slope of Fig. 5 is unity in the linear region and curves towards a value of about 0.5 at higher optical densities. As with other calculations of this type [34], it would be necessary to ascribe a set of unrealistic parameters to the spectroscopic source in order to generate logarithmic curves of growth of slope about 0.5 or lower at lower optical densities. The absolute calibration is clearly of good accuracy (Fig. 3). The sensible accord between the empirical result for γ and the slope of Fig. 3 indicates that the assumptions inherent in the former procedure, namely the constancy of γ over the optical density ranges investigated and the linear relation between $[\text{Pb}(6^3\text{P}_0)]$ ($t = 0$) and $[\text{PbEt}_4]$ (initial), are reasonably justified. Given the absolute calibration, we

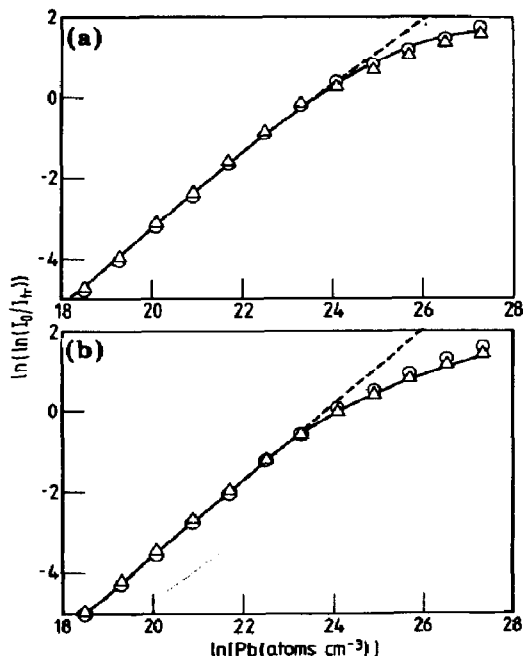


Fig. 5. Examples of calculated curves of growth for the lead atom at $\lambda = 283.3$ nm ($7s$ ($^3P_1^o$) \leftarrow $6p^2$ (3P_0)) indicating the effect of temperature in the reaction vessel ($L_G = 15.5$ cm). Vessel temperature (K): \circ , 783 ($\Delta\nu_D = 1472.6$ MHz); \triangle , 600 ($\Delta\nu_D = 1289.7$ MHz). (a) Using unreversed source: $T_E = 600$ K. (b) Using reversed source: $T_E = 600$ K; $T_F = 400$ K; $L_E = L_F = 1$ cm. $[\text{Pb}] = 10^{11}$ atoms cm^{-3} in source (E) and filter (F).

must conclude that the difficulty in generating by calculation γ values considerably less than unity in the low optical density range is an artifact of the model. However, it is difficult to speculate on the aspect of the model which is responsible for this, be it for example the oversimplification of the two-layer model in the spectroscopic source or the use of Doppler or Voigt profiles [6] for what might be a highly reversed source with the main absorption in the wings of the line.

One aspect that has not received detailed attention in reported curve of growth calculations is Stark splitting. This is an extremely complicated subject [52] and beyond the scope of this paper. We would not expect the effect in the present type of system to be significant as the field gradient in the hollow cathode source is not large because the nominal potential gradient between the electrodes is reduced by space charge. As a purely arbitrary type of calculation, various curves of growth were generated for a single line at $\lambda = 283.3$ nm, neglecting hyperfine interaction and using an unreversed source but shifting the line centre of the transition associated with the atoms in the vessel up to one Doppler width relative to that associated with the source. The effect (Fig. 6) is only to shift the curve and reduce the sensitivity but not to alter the slope significantly.

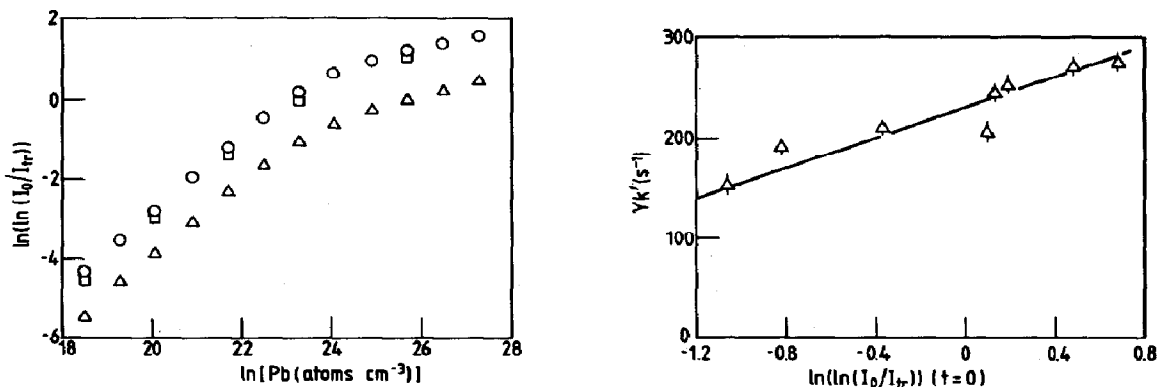


Fig. 6. Examples of calculated curves of growth for the lead atom at $\lambda = 283.3$ nm ($7s({}^3P_1) \leftarrow 6p^2({}^3P_0)$) indicating the effect of an arbitrary shift in line centres for atomic lines associated with the atoms in the source and in the vessel, and neglecting the effects of nuclear hyperfine interaction. Unreversed source: $T_E = 600$ K; T_C (vessel) = 600 K. Shifts of source line centre (in units of $\Delta\nu_D$) relative to vessel line centre: \circ 0.3; \square 0.5; \triangle 1.0.

Fig. 7. Variation of the pseudo first order rate coefficients ($\gamma k'$) for the decay of Pb(6^3P_0) with the initial photochemical yield of lead atoms resulting from the use of different flash energies: $[PbEt_4] = 1.1 \times 10^{16}$ molecules cm^{-3} ; $[N_2] = 3.5 \times 10^{17}$ molecules cm^{-3} ; $E = 21.125$ J.

Finally, we note that for a series of experiments at a fixed concentration of $PbEt_4$ and varying flash energy the first order decay coefficient $\gamma k'$ for $Pb(6^3P_0)$ (*i.e.* the slope of the plot of $\ln\{\ln(I_0/I_{tr})\}_t$ ($\lambda = 283.3$ nm) against time) showed a sensibly linear relation with $\ln\{\ln(I_0/I_{tr})\} (t = 0)$, namely with $[Pb(6^3P_0)] (t = 0)$ (Fig. 7). In view of the deliberate lack of optical coupling between the light flash and the reactant system (see Section 2), the degree of photolysis of $PbEt_4$ is negligible. Hence, the first-order decay coefficient $k_{PbEt_4}[PbEt_4]$ can be taken as constant in this series of experiments. We can use the calibration of Fig. 3 to estimate the absolute concentrations of $Pb(6^3P_0)(t = 0)$ from the observed values of $\ln\{\ln(I_0/I_{tr})\} (t = 0)$. Assuming that $[C_2H_5] (t = 0) = 4[Pb(6^3P_0)] (t = 0)$, which is partially justified by the use of very low pressures of $PbEt_4$ and the very slow rate of radical recombination, we can then use the slope of Fig. 7 to estimate the rate constant for the reaction



as $k_1 \approx 2 \times 10^{-10}$ cm^3 molecule $^{-1}$ s $^{-1}$ (300 K). This is entirely in accord with our previous failure to measure the rate of recombination of two $Pb(6^3P_0)$ atoms by resonance line absorption using departures from linearity at short times in the first order kinetic plots [15]. Such departures could be ascribed entirely to the reaction of $Pb(6^3P_0)$ with fragments of photolysis proceeding at a rate commensurate with the collision number, and not to third order atomic recombination. The present results echo the historical experiments of

Paneth and Hofeditz [53], performed half a century ago, in which the rate of removal of a metallic lead mirror in a flow system was used to estimate alkyl radical concentrations derived from the thermal decomposition of lead alkyls.

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