

Short Communication

A kinetic study of electronically excited lead atoms, Pb (6^1S_0), by absorption spectroscopy using attenuation of atomic resonance radiation $\{\lambda = 500.5 \text{ nm, Pb}[7s(^1P^0_1) \leftarrow 6p^2(^1S_0)]\}$

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Electronically excited lead atoms in the $6p^2(^1S_0)$ state, 3.65 eV above the lowest spin orbit level ($J = 0$) of the $6p^2(^3P)$ ground state, have been generated by the low wavelength pulsed irradiation of lead tetraethyl. The optically metastable atoms have been monitored photoelectrically in absorption by time-resolved attenuation of atomic resonance radiation at $\lambda = 500.5 \text{ nm}$ $\{\text{Pb}[7s(^1P^0_1) \leftarrow 6p^2(^1S_0)]\}$. Rate constants (300 K) for the total quenching of Pb (6^1S_0) by the gases Xe, H₂, O₂ and PbEt₄ are reported and compared with the data for Pb(6^1D_2).

Introduction

A direct method for the kinetic investigation of electronically excited lead atoms in the $6p^2(^1D_2)$ state, 2.66 eV above the lowest spin orbit level ($J = 0$) of the $6p^2(^3P)$ ground state¹, has recently been reported². A detailed study of the collisional quenching of these optically metastable atoms³ has subsequently been described⁴ using the technique of monitoring the excited atoms in absorption by time-resolved attenuation of atomic resonance radiation at $\lambda = 374.0 \text{ nm}$ $\{\text{Pb}[7s(^3P^0_2) \leftarrow 6p^2(^1D_2)]\}$. Within the $6p^2$ configuration, the 1S_0 state, 3.65 eV above the ground state¹, is also highly optically metastable, the sum of all the transition probabilities for radiation to lower states being 88.5 sec^{-1} ,³ by comparison with 22 sec^{-1} for spontaneous emission from Pb(6^1D_2)³. No rate data have been reported for Pb(6^1S_0) hitherto. Previous work on 1S_0 states of atoms in both np^2 and np^4 configurations^{5,6} has shown that the 1S_0 states are generally more *collisionally* metastable than the 1D_2 states. This principally arises from the restrictions on orbital symmetry when correlating specific sets of states of reactants and products for the weak spin orbit coupling approximation^{5,6}. We have now thus succeeded in generating photochemically Pb(6^1S_0) and monitoring this species in absorption by a method similar to that described for the lower lying singlet state^{2,4}. The kinetic study of different electronic states of a given heavy atom is of particular interest with regard to the relationship between chemical reactivity and the electronic

structure of atoms and the extent to which correlation diagrams based on weak spin orbit coupling⁵ break down.

The experimental arrangement was similar to that described previously^{2,4}. $\text{Pb}(6^1\text{S}_0)$ was generated by the low wavelength ($\lambda > 165 \text{ nm}$) pulsed irradiation of lead tetraethyl in the presence of excess helium buffer gas ($\sim 4000:1$) using a coaxial lamp and vessel assembly^{2,7} with a constricted, high intensity plasma for photolytic initiation⁴ ($E = 562 \text{ J}$, $\tau^{\pm} = 25 \mu\text{s}$). The spectroscopic source comprised light, taken radially from a microwave-powered atomic lead lamp (incident power = 100 W), and focused through the reaction vessel onto the slit of a monochromator with the grating blazed at 500 nm (Spex Industries "Minimate" model 1650). This was employed to isolate the resonance line at $\lambda = 500.5 \text{ nm}$ $\{\text{Pb}[7s(^1\text{P}^0_1) \leftarrow 6p^2(^1\text{S}_0)]\}$. $\text{Pb}(6^1\text{S}_0)$ was monitored photoelectrically in absorption by the variation in the transmitted light intensity from the atomic emission lamp, attenuated by the transient, metastable atoms. The resulting photoelectric pulses were recorded in a transient recorder ("Biomation" model 610B) and expanded onto an XY recorder (Bryans Ltd.) for subsequent kinetic analysis.

For the absorption of light at $\lambda = 500.5 \text{ nm}$, it was found necessary initially to investigate in some detail the modified Beer-Lambert law⁸:

$$I_{\text{tr}} = I_0 \exp [-\varepsilon (c D)^{\gamma}] \quad (\text{i})$$

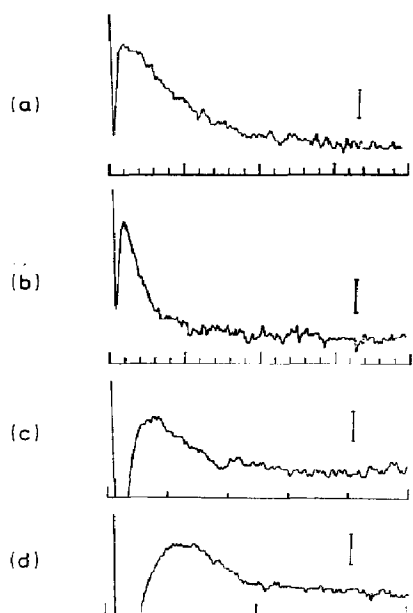


Fig. 1. Typical transient recorder traces for the decay of $\text{Pb}(6^1\text{S}_0)$ obtained by monitoring the absorption of light at $\lambda = 500.5 \text{ nm}$ in the presence of oxygen. $E = 562 \text{ J}$; $p_{\text{PbEt}_4} = 0.27 \text{ N m}^{-2}$, $p_{\text{total with He}} = 1.06 \text{ kN m}^{-2}$. $I = 20\%$ absorption of light; time scale = $200 \mu\text{s}$ per division for all traces. p_{O_2} (N m^{-2}): (a) 0.0; (b) 0.13; (c) 0.36; (d) 0.53. (Leading edge = scattered light from photolysis pulse.)

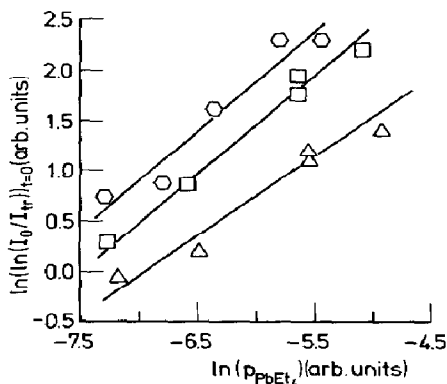


Fig. 2. Beer-Lambert plots as a function of pressure for the variation in the light transmitted from an atomic resonance lamp, attenuated by $\text{Pb}(6^1\text{S}_0)$, at $\lambda = 500.5 \text{ nm}$ $\{\text{Pb}[7s(1^1\text{P}^0_1) \leftarrow 6p^2(1^1\text{S}_0)]\}$. $E = 562 \text{ J}$. p_{total} with He: Δ , 1.6 kN m^{-2} ($\gamma = 0.73 \pm 0.25$); \square , 798 N m^{-2} ($\gamma = 1.1 \pm 0.1$); \circ , 5.85 kN m^{-2} ($\gamma = 1.0 \pm 0.2$).

where the symbols have their usual significance. For the atomic line at $\lambda = 374.0 \text{ nm}$, employed previously for monitoring $\text{Pb}(6^1\text{D}_2)^2$, a γ value of unity was found to hold over a range of pressure^{2,4}. This is in accord with the general arguments of Braun and Carrington⁹, where the concentration of $\text{Pb}(6^1\text{D}_2)$ in the lamp would be expected to be low and where the optical arrangement for removing light radially from the atomic emission source minimised light reversal in the lamp. By contrast, the γ value for attenuation of the line at $\lambda = 500.5 \text{ nm}$ was found to vary significantly with pressure. Figure 1 (a) shows a typical recorder trace indicating the production and decay of $\text{Pb}(6^1\text{S}_0)$. We employ, as hitherto², the general method described by Donovan *et al.*⁸. Thus we assume a proportionality between $[\text{Pb}(6^1\text{S}_0)]_{t=0}$ and p_{PbEt_4} (initial). Following eqn. (i), the intercepts of first-order decay plots, $\ln[\ln(I_0/I_{\text{tr}})]_{t=0}$, versus $\ln(p_{\text{PbEt}_4})$ yield straight lines of slope γ . Figure 2 indicates such plots for $p_{\text{He}} = 0.798, 5.85$ and 1.6 kN m^{-2} , the first two of which yield γ values of unity and the third, $\gamma = 0.73$. Considerable scatter in these plots may reasonably be expected as the intercepts are critically sensitive to small departures in linearity in the first-order plots $\{\ln[\ln(I_0/I_{\text{tr}})]_t \text{ vs. } t\}$ and also on account of the difficulty in measuring p_{PbEt_4} directly in this range (Fig. 2).

When γ may be readily determined, total collisional quenching constants k_Q may be obtained from the slopes of first-order plots ($-\gamma k'$) using the expression:

$$k' = K + k_Q[Q] \quad (\text{ii})$$

where k' is the overall first-order decay coefficient in the presence of a given concentration of quenching gas Q, and K is a constant in a set of kinetic runs and includes losses by spontaneous emission, diffusion and deactivation by impurity. Figure 3 gives a plot of k' versus p_{PbEt_4} , derived from conditions where $\gamma = 1$ ($p_{\text{He}} = 798 \text{ N m}^{-2}$) and $\gamma = 0.25$ (2.66 kN m^{-2}), yielding the same value for k_{PbEt_4} . In general, conditions of pressure where γ is unity are chosen for collisional

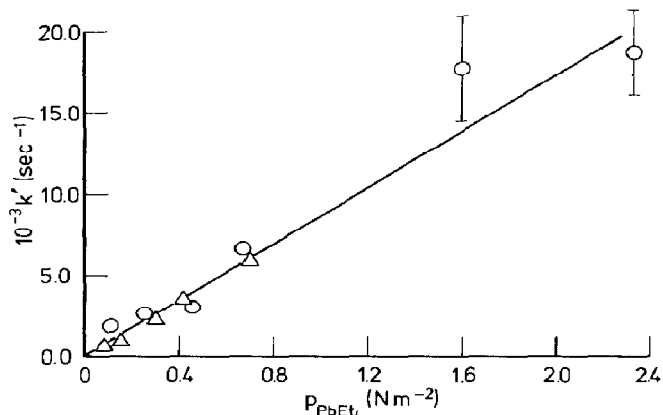


Fig. 3. Variation of the pseudo first-order rate coefficient (k') for the decay of $\text{Pb}(6^1\text{S}_0)$ with the pressure of lead tetraethyl ($E = 562 \text{ J}$). p_{total} with He: Δ , 798 N m^{-2} ($\gamma = 1.1 \pm 0.1$); \circ , 2.66 kN m^{-2} ($\gamma = 0.25$).

quenching studies to maximize the sensitivity of the detection system. Whilst it is interesting to speculate on factors that may influence the variation of γ , such as the effect of collision broadening, too complex to be included in the analysis of Braun and Carrington⁹, detailed studies under high resolution are clearly required to approach this aspect experimentally. The rate constant for the collisional quenching of $\text{Pb}(6^1\text{S}_0)$ by He cannot be determined on account of this variation of γ with the pressure of helium. The photochemical yield of $\text{Pb}(6^1\text{S}_0)$ appears higher than that of $\text{Pb}(6^1\text{D}_2)$. Up to 90% absorption is observed at $\lambda = 500.5 \text{ nm}$ in some cases. Further, "gf values"¹⁰ of 0.53 and 5.3 have been found¹⁰, respectively, for the lines at $\lambda = 500.5$ and 374.0 nm .

Figures 1(b)–(d) show examples of transient recorder traces for the decay of $\text{Pb}(6^1\text{S}_0)$ in the presence of molecular oxygen. Figure 4 comprises first-order plots constructed from the traces of Fig. 1, the slopes of which plots may be ex-

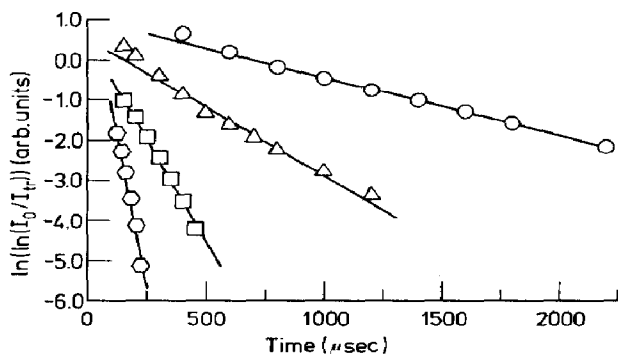


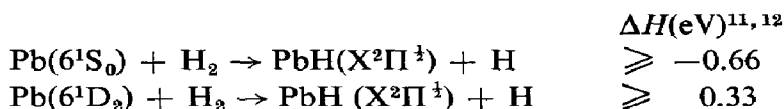
Fig. 4. First-order plots indicating the decay of $\text{Pb}(6^1\text{S}_0)$ in the presence of oxygen obtained by monitoring the absorption of light at $\lambda = 500.5 \text{ nm}$ [$\text{Pb}[7s(^1\text{P}^{\circ}) \leftarrow 6p^2(^1\text{S}_0)]$]. $E = 562 \text{ J}$; $p_{\text{PbEt}_4} = 0.27 \text{ N m}^{-2}$, p_{total} with He = 1.06 kN m^{-2} . p_{O_2} (N m^{-2}): \circ , 0.0; Δ , 0.13; \square , 0.36; \diamond , 0.53.

TABLE 1

SECOND ORDER RATE CONSTANTS (k_Q , CM³ MOLECULE⁻¹ SEC⁻¹, 300 K) FOR THE COLLISIONAL REMOVAL OF Pb(⁶S₀) AND Pb(⁶D₂) BY VARIOUS GASES (M)

	Pb(⁶ S ₀)	Pb(⁶ D ₂) ^a
He	—	$< 2 \times 10^{-10}$
Xe	$< 2 \times 10^{-15}$	$< 10^{-15}$
H ₂	$< 10^{-14}$	$< 10^{-14}$
PbEt ₄	$3.7 \pm 0.4 \times 10^{-11}$	$5.6 \pm 1.2 \times 10^{-11}$
O ₂	$1.2 \pm 0.3 \times 10^{-10}$	$1.1 \pm 0.3 \times 10^{-10}$

pressed in the form of eqn. (ii) to yield the rate constant for quenching by O₂ (Table 1). Table 1 lists other rate data derived by this method compared with that for Pb(⁶D₂)². Removal of both Pb(⁶S₀) and Pb(⁶D₂) by molecular oxygen proceed at rates comparable with the collision numbers. Chemical reaction to yield PbO(X¹Σ⁺(O⁺)) + O(2³P_J) is highly exothermic for both states, namely, -3.51 and -4.50 eV for the ¹D and ¹S states, respectively^{11,12}. A correlation diagram⁵ cannot be readily constructed for this system as O₂(a¹Δ_g) lies energetically¹¹ amongst the J states of Pb(6³P_J)¹, and the states of PbO are best described in terms of Hund's case (c) coupling¹³. The comparably slow rates of removal of both Pb(⁶S₀) and Pb(⁶D₂) by H₂ are in approximate accord with a low order correlation diagram. Thus, whilst chemical reaction of the former is exothermic and the latter is not:



crudely neglecting the large spin orbit coupling in both Pb(6³P_J)¹ and PbH(X²Π^{½, ¾})¹¹, Pb(⁶S) + H₂(X¹Σ_g⁺) does not correlate with PbH(X²Π) + H(1²S).

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