

KINETIC STUDY OF ELECTRONICALLY EXCITED TIN ATOMS, $\text{Sn}(5^1\text{D}_2)$, BY ATOMIC ABSORPTION SPECTROSCOPY

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Summary

The method of spectroscopically studying transient atoms in absorption by time-resolved attenuation of atomic resonance radiation has been applied to electronically excited tin atoms, $\text{Sn}(5^1\text{D}_2)$. This atomic state was generated by the pulsed irradiation of tin tetramethyl in the presence of excess helium buffer gas and monitored photoelectrically *via* the resonance transition at $\lambda = 285.06 \text{ nm}$ { $\text{Sn}[5d(^3\text{F}_2^0) \leftarrow [5p^2(^1\text{D}_2)]]$ }. The resulting technique is found to be highly sensitive and has been used to investigate the collisional behaviour of $\text{Sn}(5^1\text{D}_2)$ in the presence of the gases He, Xe, H_2 , O_2 , and SnMe_4 , for which quenching rate constants at 300 K are reported. These rate constants are compared with analogous data for other atomic states in Group IV, namely, $\text{C}(2p^2\ ^1\text{D}_2)$ and $\text{Pb}(6p^2\ ^1\text{D}_2)$, and briefly considered from the viewpoint of spin and orbital symmetry on collision.

Introduction

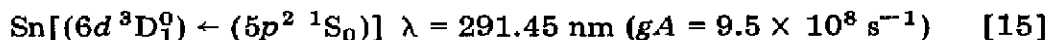
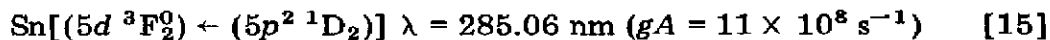
There is an extensive current interest in the reactivity of electronically excited atoms in low lying ^1D states above the ^3P ground state [1 - 3]. Much of the experimental work on the ^1D state has hitherto been primarily concerned with Group VI atoms, and especially the electronically excited oxygen atom, $\text{O}(2p^4\ ^1\text{D}_2)$, on account of its importance in the chemistry of the earth's upper atmosphere [1 - 3]. However, a more general concern in recent years with the relationship between electronic structure and atomic reactivity, guided by considerations of spin and orbital symmetry for atom-molecule collisions [1], has stimulated experimental investigations to be carried out on a wider range of atomic states. One practical objective of such studies is to characterize the collisional behaviour of atoms with the same gross electronic structure in a given group of the Periodic Table. Direct studies of the reactivity of atoms in Group IV, especially in the $(np^2\ ^1\text{D}_2)$ state, are a growing point in this field and the concern of this paper. In particular, we describe a highly sensitive method for monitoring electronically excited tin atoms, $\text{Sn}(5p^2\ ^1\text{D}_2)$,

1.068 eV above the ($5p^2\ ^3P_0$) ground state [4], and for studying its kinetic behaviour on a time-resolved basis.

Detailed kinetic investigations of Group IV atoms, in which the 1D state has been monitored spectroscopically, have hitherto dealt mainly with carbon and lead. Braun *et al.* [5] have monitored $C(2^1D_2)$ photographically in absorption by means of kinetic spectroscopy following flash photolysis, and Wolf *et al.* [6] have detected this state in a flow system by attenuation of atomic emission subsequent to the plasmolysis of a number of organic compounds. However, kinetic data were not reported for this latter study. Husain and Kirsch [7 - 9] have developed the method of time-resolved attenuation of atomic resonance radiation for the study of this atomic state following its production by pulsed irradiation. Husain and Littler [10, 11] employed a similar method for studying $Pb(6^1D_2)$. We now describe a comparable technique for investigating the kinetic behaviour of $Sn(5^1D_2)$. The method is highly sensitive and has been used to obtain collisional quenching data for this atomic state, for which there have been no previous investigations. Earlier kinetic spectroscopic work on the tin atom has been restricted to photographic detection of the ground state in absorption during the variable high temperatures of explosions [12]. Callear and Oldman [13] have detected $Ge(4^1D_2)$ following flash photolysis but have not reported kinetic data. The present results for the collisional quenching of $Sn(5^1D_2)$ are compared with those for the analogous states of carbon and lead.

Experimental

$Sn(5^1D_2)$ was generated by the pulsed irradiation of tin tetramethyl, $SnMe_4$, in the presence of excess helium buffer gas to ensure no significant rise in temperature on photolysis. A coaxial lamp and vessel assembly, similar to that described in the study of $Pb(6^1D_2)$ [10, 11], was employed. The inner cylinder comprised the reaction vessel and the annular space, of thickness ~ 2 mm to facilitate an intense plasma discharge between machined brass electrodes, the photolysis lamp. The common wall was constructed of standard quartz and permitted photolysis to a lower wavelength limit of $\sim \lambda = 200$ nm. High voltage switching by means of ignitron circuitry (BK66, B.T.H., U.K.) was used to fire the photolysis lamp at an energy of 500 J ($C = 10\ \mu F$, $V = 10$ kV) through krypton gas ($p_{Kr} = 1.3$ kN/m², 1 Torr = 133 N/m²). Following irradiation, both $Sn(5^1D_2)$, and also the highest state within the $5p^2$ configuration, $Sn(5^1S_0)$, 2.128 eV above the 5^3P_0 ground state [4], were monitored by atomic absorption spectroscopy, as both of these states are highly optically metastable [14]: the sum of the Einstein coefficients for the 1D and 1S states to all lower levels are given by Garstang [14] as 1.0 and $8.5\ s^{-1}$, respectively. The following resonance transitions were monitored:



The most intense source of the resonance lines was found to be that obtained from a microwave discharge (incident power 80 W) through a flow system of SnCl_4 in helium ($p_{\text{SnCl}_4} = 2.7 \text{ N/m}^2$, $p_{\text{total with He}} = 270 \text{ N/m}^2$) rather than by using a sealed metallic source as described in the study of $\text{Pb}(6^1\text{D}_2)$ [10, 11]. The atomic lines were separated with a 1 m grating monochromator (Hilger and Watts "Monospek" 1000, Czerny-Turner mount, blaze wavelength = 300 nm, 1200 lines/mm), used in the first order.

The time-dependent light absorption representing the temporal variation of $\text{Sn}(5^1\text{D}_2)$ and $\text{Sn}(5^1\text{S}_0)$ subsequent to photolysis, was detected by means of a photomultiplier (E.M.I. 9783QB) mounted on the exit slit of the monochromator. The output was fed into a current-to-voltage converter employing a fast settling operational amplifier [16] as described in recent experiments on the kinetic study of $\text{C}(2^1\text{S}_0)$ [17]. The time constant used in the detection circuit was $2 \mu\text{s}$. Whilst the duration of the photoflash discharge was approximately $20 \mu\text{s}$, the effect of the scattered light on the photomultiplier tube was to prevent kinetic measurements being made during the first $60 \mu\text{s}$ at the slit widths employed in the time-resolved measurements. The photoelectric pulses were displayed on a storage oscilloscope (Tektronix type 564B, time base 2B67, type 3A7 differential comparator) and photographed (D. Schackman Co. camera) for kinetic analysis.

Materials

SnMe_4 liquid (Aldrich Chemicals Co.) was cooled to -196°C and degassed by freeze-pump-thaw cycles. The material was then fractionally distilled from room temperature to -196°C before use. SnCl_4 liquid (Fison Laboratory Reagent) was cooled to -196°C and degassed and purified as described for SnMe_4 before use in the atomic flow lamp. Cylinder He (British Oxygen Company Ltd), for use both as the buffer gas and in the atomic flow lamp, was purified by passage through a standard B.O.C. purifier, capable of purifying both He and Ar. Kr, Xe, H_2 and O_2 (B.O.C. Grade X gases) were used directly.

Results and Discussion

Figure 1(a) shows a typical oscilloscopic trace indicating the production and decay of $\text{Sn}(5^1\text{D}_2)$ obtained by monitoring the absorption of light at $\lambda = 285.06 \text{ nm}$ following the photolysis of SnMe_4 in the quartz region ($\lambda > 200 \text{ nm}$). Negligible absorption at $\lambda = 291.45 \text{ nm}$ was detected, demonstrating an insignificant photolysis yield of $\text{Sn}(5^1\text{S}_0)$ when considered in terms of the gA value for this transition [15]. Thus the oscilloscopic traces at $\lambda = 285.06 \text{ nm}$ may be interpreted in terms of a single kinetic decay for the ^1D atom without including relaxation into this state from the $^1\text{S}_0$ state. The leading edge of the trace represents the effect of scattered light and measurements on the traces were not carried out until the decays fell outside this region of interference. Figure 1(b) gives an example of the decay of $\text{Sn}(5^1\text{D}_2)$ in the

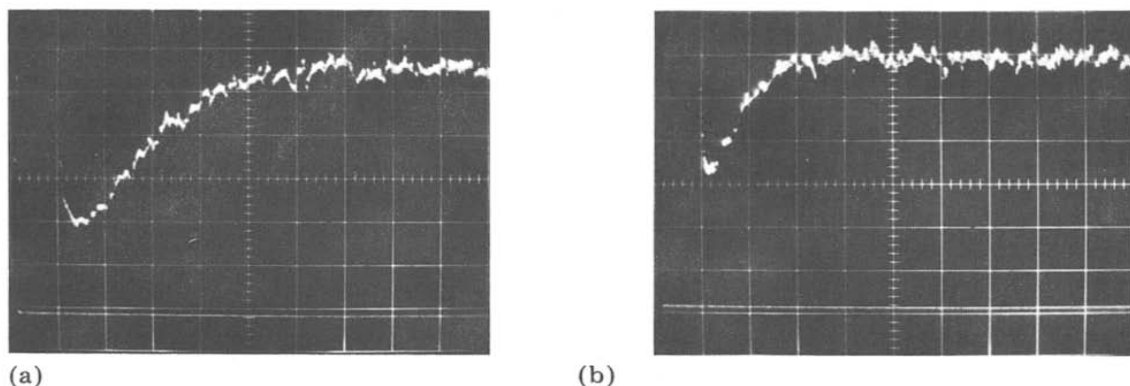


Fig. 1. Typical oscilloscopic traces indicating the decay of $\text{Sn}(5^1\text{D}_2)$ in the presence of oxygen obtained by monitoring the absorption of light at $\lambda = 285.06 \text{ nm}$ $\{\text{Sn}[5d(^3\text{F}_2^0)] \leftarrow \text{Sn}[5p^2(^1\text{D}_2)]\}$. $p_{\text{SnMe}} = 0.40 \text{ N/m}^2$; $p_{\text{total with He}} = 3.33 \text{ kN/m}^2$; $E = 500 \text{ J}$; time scale = $50 \mu\text{s}$ per division. $p_{\text{O}_2} (\text{N/m}^2)$: (a) 0.0; (b) 0.53.

presence of the quenching gas oxygen. The appropriate quenching rate constants were determined from modification to the trace in Fig. 1(a) by a range of pressures of the deactivating gas.

We employ the modified Beer–Lambert law [18]:

$$I_{\text{tr}} = I_0 \exp[-\epsilon(\text{cl})^\gamma] \quad (\text{i})$$

(where the symbols have their usual significance) in order to measure the *relative* concentrations of $\text{Sn}(5^1\text{D}_2)$ and hence the *absolute* values of the overall first-order decay coefficients, k' , for the decay of the excited atom in a given reaction mixture. Equation (i) has been used in measurements on the attenuation of resonance radiation by various transient atoms [2, 3], recent examples being the series of investigations on $\text{Pb}(6^3\text{P}_{0,1,2}, 6^1\text{D}_2, 6^1\text{S}_0)$ [10, 11, 19 - 21] and $\text{As}(4^2\text{D}_{3/2,5/2}, 4^2\text{P}_{1/2,3/2})$ [22]. Figure 2 shows the so-called Beer–Lambert plot for the resonance transition at $\lambda = 285.06 \text{ nm}$, the slope of this plot yields, in this case, $\gamma = 1.3 \pm 0.1$. The use and limitations of eqn. (i) has been discussed in detail in a number of papers involving measurements of this type [2, 3], particularly in the recent kinetic studies on lead atoms [10, 11, 19 - 21]. We adopt the procedure of taking the value of γ to be unity, especially as self reversal in the spectroscopic source should be relatively small for the excited atom.

Figure 3 shows typical first-order plots for the decay of $\text{Sn}(5^1\text{D}_2)$ in the presence of oxygen, obtained from oscilloscopic traces of the kind indicated in Figs. 1(a) and 1(b) using eqn. (i). In general, the slopes of plots of this type shown in Fig. 3 are given by $-\gamma k'$, where we have taken γ to be unity. k' is then expressed in the form:

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

where k_{Q} is the second-order rate constant for collisional quenching by an

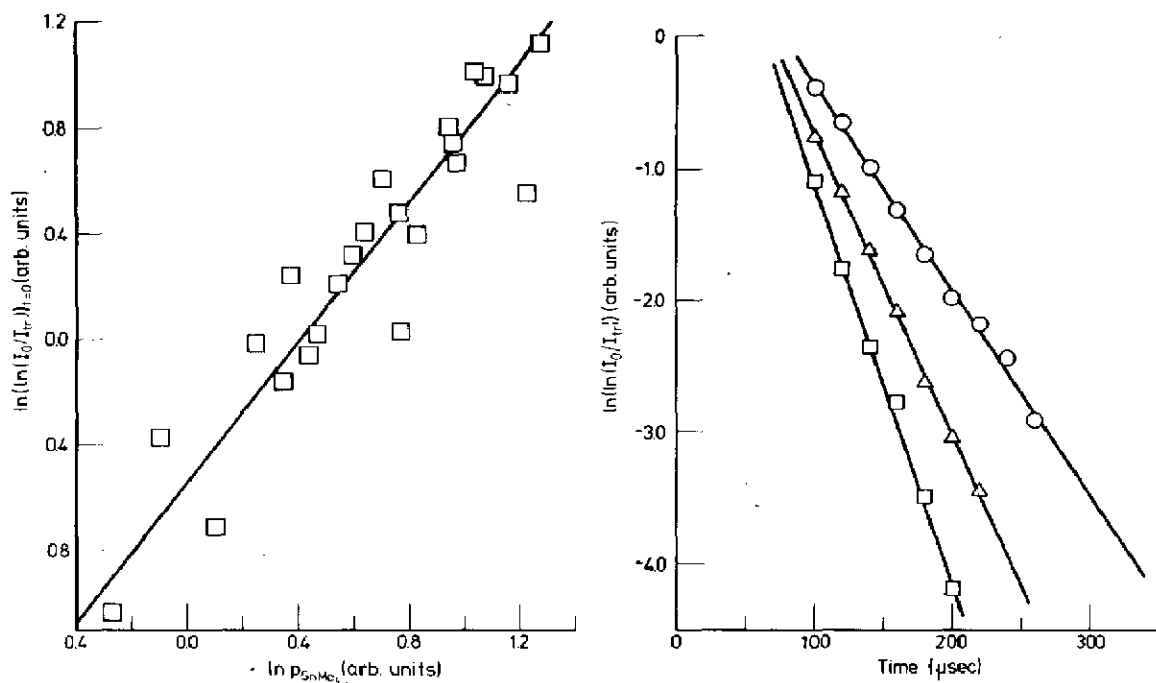


Fig. 2. Beer-Lambert plot for the variation in the light transmitted from an atomic resonance lamp, attenuated by $\text{Sn}(5^1\text{D}_2)$, at $\lambda = 285.06 \text{ nm}$ $\text{Sn}[5d(^3\text{F}_2^0)] \leftarrow \text{Sn}[5p^2(^1\text{D}_2)]$. $P_{\text{total with He}} = 3.33 \text{ kN/m}^2$.

Fig. 3. Pseudo first-order plots for the decay of $\text{Sn}(5^1\text{D}_2)$ in the presence of oxygen obtained by monitoring the absorption of light at $\lambda = 285.06 \text{ nm}$. $p_{\text{SnMe}_4} = 0.40 \text{ N/m}^2$; $P_{\text{total with He}} = 3.33 \text{ kN/m}^2$; $E = 500 \text{ J}$. $p_{\text{O}_2} (\text{N/m}^2)$: \circ , 0.0; \triangle , 0.30; \square , 0.52.

added gas Q . K is taken to be a constant in a given series of kinetic experiments in which $[Q]$ is varied and includes losses by diffusion, weak spontaneous emission and collisional quenching by impurities and products of photolysis. Figure 4 shows quenching data for the decay of $\text{Sn}(5^1\text{D}_2)$, plotted in the form of eqn. (ii), for hydrogen and oxygen, and Fig. 5, for the parent molecule, the slopes of these plots yielding the second-order rate constants for quenching by these gases. The results of the present investigation are given in Table 1 where the data have been compared with those for $\text{C}(2^1\text{D}_2)$ and $\text{Pb}(6^1\text{D}_2)$.

In general, the relative reaction rates exhibited by the three low lying states of the carbon atom in the $2p^2$ configuration are in accord with correlations between specific electronic states of reactants and products based on the weak spin orbit coupling approximation [9]. The data on $\text{C}(2^1\text{D}_2)$ in Table 1 fall within this context. By contrast, the collisional behaviour of the lead atom in the analogous states in general is not in accord with correlations constructed on this basis [11]. Indeed, the property of Hund's case (*c*) coupling in the electronic states of diatomic molecules such as PbO [23] is a spectroscopic expression of the large spin orbit coupling. This prevents the

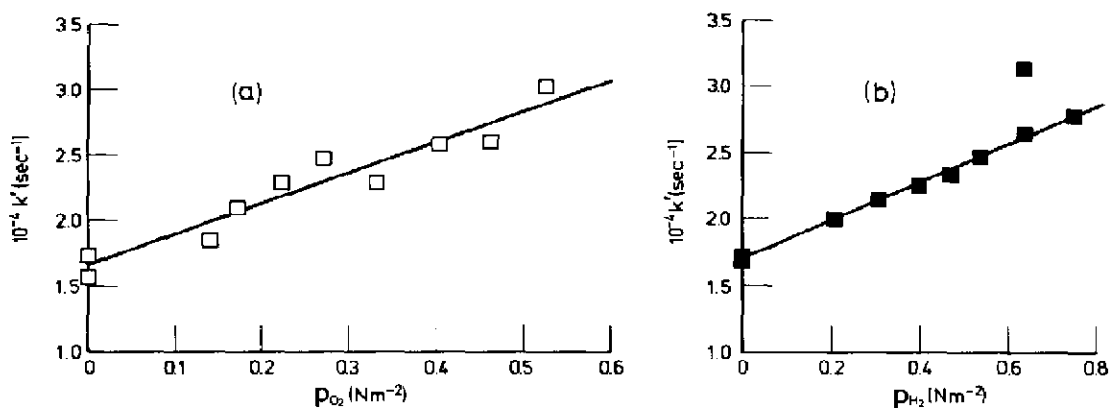


Fig. 4. Pseudo first-order rate coefficients (k') for the decay of $\text{Sn}(5^1\text{D}_2)$ in the presence of (a) oxygen and (b) hydrogen, $p_{\text{SnMe}_4} = 0.40 \text{ N/m}^2$; $p_{\text{total with He}} = 3.33 \text{ kN/m}^2$; $E = 500 \text{ J}$.

construction of such correlation diagrams, not only in terms of the designation of the symmetry of the states associated with the collision complex but also as a result of the ordering of the states of reactants and products at infinite separation. In the case of $\text{Pb} + \text{O}_2$ [11], this is manifest by the fact that from the viewpoint of energy, $\text{O}_2(a^1\Delta_g)$ lies within the manifold of $\text{Pb}(6^3\text{P}_J)$; in the case of $\text{Sn} + \text{O}_2$, $\text{Sn}(5^1\text{D}_2) + \text{O}_2(X^3\Sigma_g^-)$ lies within the J states of $\text{Sn}(5^3\text{P}_J) + \text{O}_2(a^1\Delta_g)$ [4, 24].

Further, whilst chemical reaction between $\text{Sn}(5^1\text{D}_2) + \text{O}_2(X^3\Sigma_g^-)$ to yield SnO is exothermic ($\Delta H = -1.59 \text{ eV}$) [24] even if one could crudely neglect the effect of spin orbit coupling on the ordering of states, $\text{Sn}(5^1\text{D}_2) + \text{O}_2(X^3\Sigma_g^-)$ would not correlate with ground state products. Indeed, these reactants would only correlate with higher, energetically inaccessible states

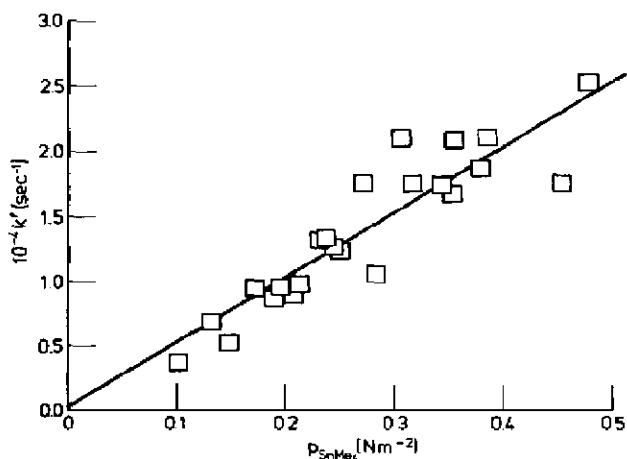


Fig. 5. Variation of the pseudo first-order rate coefficient (k') for the decay of $\text{Sn}(5^1\text{D}_2)$ with the pressure of tin tetramethyl. $p_{\text{total with He}} = 3.33 \text{ kN/m}^2$.

TABLE 1

Second order rate constants (k_Q cm³ molecule⁻¹ s⁻¹, 300 K) for the collisional removal of Sn(⁵1D₂), C(²1D₂) and Pb(⁶1D₂) by various gases

Gas	Sn(⁵ 1D ₂) (1.068 eV)*	C(² 1D ₂) (1.263 eV)	Pb(⁶ 1D ₂) (2.66 eV)
He	$< 2 \times 10^{-15}$	$< 3 \times 10^{-16}$ [8]	$< 2 \times 10^{-16}$ [10]
Xe	$< 1.7 \times 10^{-15}$	$1.1 \pm 0.3 \times 10^{-10}$ [8]	$< 10^{-15}$ [10]
H ₂	$5.5 \pm 0.1 \times 10^{-11}$	$2.6 \pm 0.3 \times 10^{-10}$ [7] 4.15×10^{-11} [5]	$< 10^{-14}$ [10]
O ₂	$9.0 \pm 0.9 \times 10^{-11}$	$< 2.6 \times 10^{-11}$ [9] 5×10^{-12} [5]	$1.1 \pm 0.3 \times 10^{-10}$ [10]
SnMe ₄	$2.0 \pm 0.2 \times 10^{-10}$	-	

* Data from this work

[24, 25]. Thus the collisional behaviour of the tin atom with oxygen is clearly seen to be governed by the effect of spin orbit coupling.

Abstraction of a hydrogen atom from H₂ by Sn(⁵1D₂) is endothermic ($\Delta H > 0.2$ eV) [24]. Thus the relatively rapid collisional removal by this molecule presumably arises from the effect of the strong spin orbit coupling [$T_e(\text{SnH}(X^2\Pi_r)) = 0, 2182$ cm⁻¹] [24] on the so-called "non-adiabatic transition" [1] yielding physical relaxation to Sn(⁵3P₁). This would be facilitated further by chemical interaction associated with an intermediate SnH₂.

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