KINETIC INVESTIGATION OF ELECTRONICALLY EXCITED TIN ATOMS, Sn(5^1S_0), BY TIME-RESOLVED ATTENUATION OF ATOMIC RESONANCE RADIATION

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Summary

A kinetic study of electronically excited tin atoms in the $(5p^2 \ ^1S_0)$ state, 2.128 eV above the 5^3P_0 ground state, is described. These optically metastable species were generated by the pulsed irradiation of $SnCl_4$ at relatively low wavelength ($\lambda > 165$ nm) and monitored photochemically in absorption by time-resolved attenuation of the atomic resonance transition at $\lambda = 291.45$ nm $[6d(^3D_1^0) \leftarrow 5p^2(^1S_0)]$. The resulting method, involving the use of a rapid response precision logarithmic signal converter which permitted $\ln (I_0/I_{tr})$ to be measured directly, was found to be sensitive and yielded reliable kinetic data for the ^1S state. Collisional quenching rate constants are given for the gases He, Xe, H_2, O_2 and $SnCl_4$, constituting the first reported kinetic data for this atomic state. The data are compared with those for the low lying ^1D state of the atom as well as with those of the analogous states of other atoms in Group IV, namely, carbon and lead. The data are discussed in terms of correlations based on both the weak and strong (J, Ω coupling) spin orbit coupling approximations.

Introduction

We have recently described direct investigations of the collisional behaviour of electronically excited tin atoms in the $(5p^2 \ ^1D_2)$ state [1, 2], 1.068 eV above the $(5p^2 \ ^3P_0)$ electronic ground state [3]. Studies of this type constitute part of a wider programme concerned with investigating the chemistry of atoms in specific electronic states, particularly all the optically metastable states arising from the overall gross electronic structure of the ground state configuration [4, 5], in order to elucidate the relationship between electronic structure and reactivity [6]. Within this context, we report the first kinetic data on the higher singlet state arising from the $5p^2$ configuration, Sn($5p^2 \ ^1S_0$), 2.128 eV above the 5^3P_0 ground state [3].

A comparison of the collisional behaviour of the low lying ^1S and ^1D states of atoms in both Groups IV and VI is of both practical and fundamental interest. Clearly, in Group VI, the chemistry of O($2p^4 \ ^1S_0$) and

$O(2p^4\ ^1D_2)$ is of especial relevance to aeronomy [4 - 6]. Kinetic investigations of $S(3p^4\ ^1S_0)$ [7] and $S(3p^4\ ^1D_2)$ [8 - 10] lead to interesting comparisons with the analogous states of atomic oxygen especially in terms of the influence of an increased spin orbit coupling or correlations based on the weak spin orbit coupling approximation. Such pairs of atomic states often give rise to reactions which are both spin allowed and exothermic but which differ from the viewpoint of orbital symmetry [6]. For Group IV, such considerations have been applied to the chemistry of the light atomic states, $C(2p^2\ ^1S_0)$ [6, 11] and $C(2p^2\ ^1D_2)$ [6, 12], where the effects of spin orbit coupling are clearly minimized. Kinetic investigations on the heavy atomic states, $Pb(6p^2\ ^1S_0)$ [13, 14] and $Pb(6p^2\ ^1S_0)$ [15, 16], on the other hand, indicate that the collisional behaviour of these species is governed by spin orbit interaction. The absolute rate data obtained here for $Sn(5^1S_0)$ and those reported previously for $Sn(5^1D_2)$ [1, 2] are compared with the data for the ^1S and ^1D states of carbon and lead, there being no data for the analogous states of silicon and germanium. Correlations based on both the weak and strong spin orbit coupling approximation are discussed.

Experimental

A similar experimental arrangement to that described hitherto for the study of $Sn(5^1D_2)$ was employed [1]. Thus, $Sn(5^1S_0)$ was generated by pulsed irradiation and monitored photoelectrically in absorption by time-resolved attenuation of atomic resonance radiation. In the earlier investigation [1], it was found that only $Sn(5^1D_2)$ and *not* $Sn(5^1S_0)$ was produced on photolyzing $SnMe_4$ in the quartz region ($\lambda > 200$ nm). In this study, it was found that $Sn(5^1S_0)$ could be generated on flash photolyzing $SnCl_4$ through high purity quartz (Spectrosil) ($\lambda > 165$ nm) yielding concentrations of this atomic species sufficient for kinetic analysis in the "single-shot" mode. Hence, a coaxial lamp and vessel assembly, whose geometry has been described hitherto [1], was employed, with the common wall separating the lamp and vessel constructed of the Spectrosil material. The pulse energy dissipated in the annular space of the coaxial system (*viz*. the photolysis lamp) was similar to that employed in the studies on $Sn(5^1D_2)$ ($C = 10\ \mu F$, $V = 10$ kV, $E = 500$ J; $p_{Kr} = 1.3$ kN/m^2 (1 Torr = 133 N/m^2); pulse duration = ~ 20 μs).

The highly optically metastable $Sn(5^1S_0)$ atom [17] was monitored by means of the resonance transition $Sn[(6d\ ^3D_1^0) \leftarrow 5p^2\ ^1S_0)]$ ($\lambda = 291.45$ nm, $gA = 9.5 \times 10^8$ s^{-1}) [18] derived from a microwave discharge through a flow system of $SnCl_4$ in helium ($p_{SnCl_4} = 4.0$ N/m^2, $p_{total\ with\ He} = 400$ N/m^2). The line intensity of this transition from this source was weaker than that of the line at $\lambda = 285.06$ nm [$Sn(5d\ ^3F_2^0) \leftarrow (5p^2\ ^1D_2)$] used for the study of the ^1D state [1], notwithstanding the comparable transition probabilities (gA (285.06 nm) = 11×10^8 s^{-1} [18]), and hence a greater incident power was necessary (120 W). The resonance transition was optically separated with a grating monochromator (Hilger and Watts, Monospek 1000) and resonance

absorption monitored by means of a photomultiplier (E.M.I. 9783QB) mounted on the exit slit of this instrument. The photoelectric output was fed into a current-to-voltage converter [19] and then into a rapid response precision logarithmic circuit and an a.c.-coupled amplifier with one directional clamping [20]. This system measures $\ln(I_0/I_{tr})$ directly (where the symbols have their usual significance) in the time-resolved mode. Whilst this type of arrangement has been designed for repetitive pulsed experiments involving weak absorption signals with rapid decays and requiring signal averaging [20], it may also be used to advantage in the "single-shot" mode. In particular, the I_0 signal is obtained with this circuitry without spreading the absorption signal over a long time range in order to reach the infinite time value. The result is a measured attenuation of considerably improved signal-to-noise ratio. After passage through the logarithmic circuitry, the signal was fed into a transient recorder (Biomation Model 610 B), the contents of which were subsequently transferred to an XY-recorder (Bryans) for kinetic analysis.

Materials

All materials were prepared as described hitherto [1].

Results and discussion

Figure 1(a) shows a typical concentration–time profile for $Sn(5^1S_0)$ obtained by monitoring $\ln(I_0/I_{tr})$ at $\lambda = 291.45$ nm following the pulsed irradiation of $SnCl_4$ in the presence of excess helium. As with the measurement on the ^1D state [1], we employ the modified Beer–Lambert law [21]:

$$I_{tr} = I_0 \exp\left[-\epsilon(cl)^\gamma\right] \tag{i}$$

where γ is characterized for the 291.45 nm transition by the standard procedure [1, 21] shown in Fig. 2. This yields $\gamma = 0.51 \pm 0.07$, which is somewhat surprising for a transition that would not be expected to show a high degree of self reversal in the spectroscopic source. The scatter in Fig. 2 is relatively low for a measurement of this type and indeed, the first-order plots (see, for example, Fig. 3) from which Fig. 2 is constructed were particularly good over the entire decay of the excited atom. Figures 1(b) - (c) show modification to the signals by the addition of molecular oxygen, the first-order kinetic plots for these being given in Fig. 3. The slopes of these first-order plots ($-\gamma k'$) may then be translated into overall first-order decay coefficients, k', by means of the above γ-value and expressed in the standard form [1]:

$$k' = K + k_Q[Q] \tag{ii}$$

The nature of the contributions to K, which may be taken to be a constant in a given series of kinetic runs, have been discussed for $Sn(5^1D_2)$ [1]. Figures 4 - 6 show the variation of k' ($\gamma k'$) with O_2, H_2 and $SnCl_4$, respectively. The slopes of these plots in turn yield k_Q, the absolute quenching
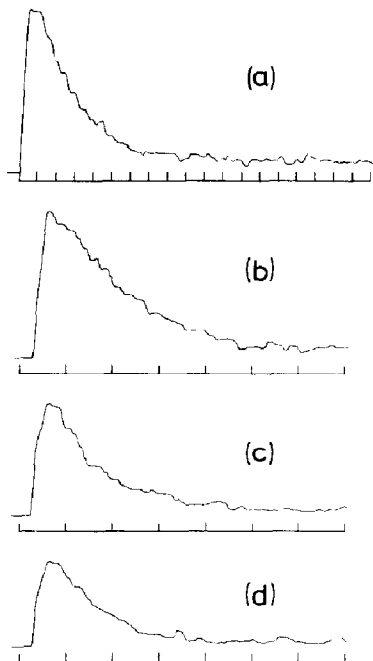
Fig. 1. Typical transient recorder traces for the decay of $Sn(5^1S_0)$ obtained by directly monitoring $\ln(I_0/I_{tr})$ at $\lambda = 291.45$ nm in the presence of oxygen. $E = 980$ J; $p_{SnCl_4} = 0.06$ N/m^2, $p_{total\ with\ He} = 3.33$ kN/m^2. Time scale = 50 μs/div. for all traces starting at $t = 50$ μs. Leading edge = scattered light from photolysis pulse. p_{O_2} (N/m^2): (a) 0.0; (b) 0.25; (c) 0.66; (d) 0.81.
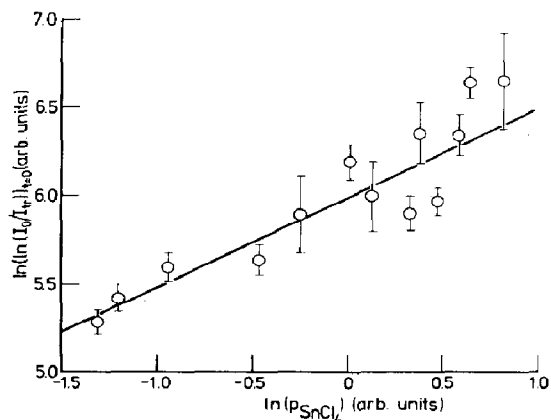

Fig. 2. Beer—Lambert plot for the variation in the light transmitted from an atomic resonance lamp, attenuated by $Sn(5^1S_0)$, at $\lambda = 291.45$ nm [$Sn(6d\ ^3D_1^0) \leftarrow Sn(5p^2\ ^1S_0)$]. $p_{total\ with\ He} = 3.33$ kN/m^2.

constants for $Sn(5^1S_0)$ by these gases. These data, as well as the appropriate data for $Sn(5^1D_2)$ together with those for $C(2^1D_2, 2^1S_0)$ and $Pb(6^1D_2, 6^1S_0)$, are given in Table 1. We may note the high value for $SnCl_4$ which we simply report as the collision number. Indeed, it is this rapid quenching by the parent
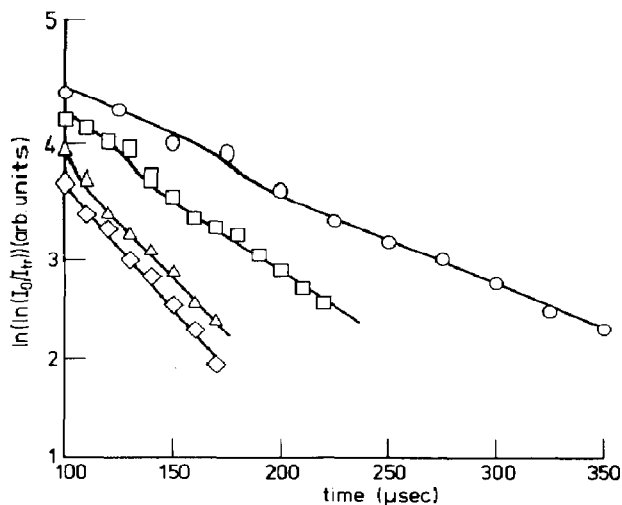
Fig. 3. Pseudo first-order plots for the decay of $Sn(5^1S_0)$ in the presence of oxygen obtained by monitoring the absorption of light at λ = 291.45 nm. p_{SnCl_4} = 0.06 N/m^2; $p_{total\ with\ He}$ = 3.33 kN/m^2; E = 980 J. p_{O_2}(N/m^2): $\circ$, 0.0; $\square$, 0.25; $\triangle$, 0.66; $\diamond$, 0.81.
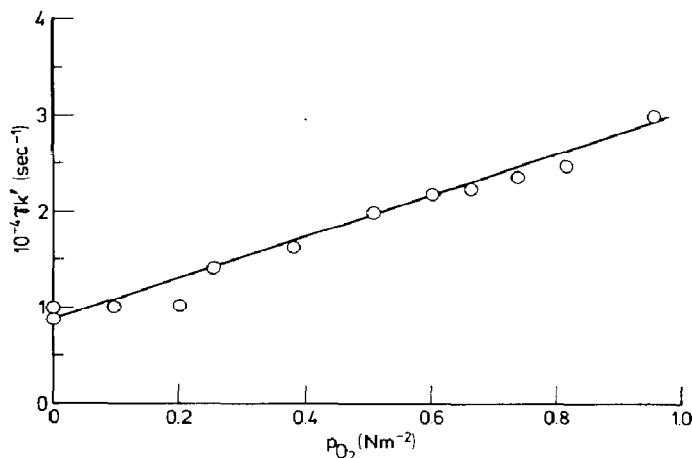

Fig. 4. Pseudo first-order rate coefficients (k') for the decay of $Sn(5^1S_0)$ in the presence of oxygen. p_{SnCl_4} = 0.06 N/m^2; $p_{total\ with\ He}$ = 3.33 kN/m^2; E = 980 J.

molecule that limits the pressures over which the effect of added gases may be investigated.

Collisional quenching data for $C(2^1D_2)$ and $C(2^1S_0)$, including those for H_2 and O_2 (Table 1), have been found to be essentially in accord with correlations of reactants and products based on the weak spin orbit coupling approximation [12]. This procedure has been shown to be inadequate for discussing the rate data for the ^1D and ^1S states of lead [16]. The data for the heavy lead atom must clearly be reconsidered in terms of (J, Ω) coupling using the theory of double groups [26], as must the results for the electronically excited tin atom.

With the hydrogen molecule, chemical reaction to yield the lower spin orbit component of the ground state of $PbH(X^2II_{1/2})$ would be endothermic
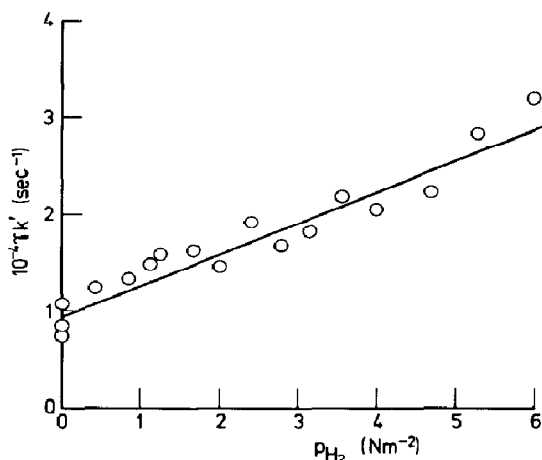
Fig. 5. Pseudo first-order rate coefficients (k') for the decay of $Sn(5^1S_0)$ in the presence of hydrogen. $p_{SnCl_4} = 0.06\ N/m^2$; $p_{total\ with\ He} = 3.33\ kN/m^2$; $E = 980\ J$.
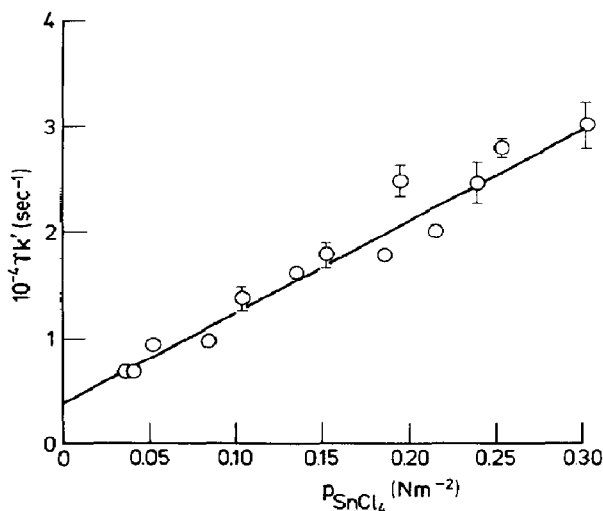

Fig. 6. Pseudo first-order rate coefficients (k') for the decay of $Sn(5^1S_0)$ in the presence of $SnCl_4$. $p_{total\ with\ He} = 3.33\ kN/m^2$; $E = 980\ J$.

($\Delta H \geqslant 0.32$ eV) [3, 26] and exothermic ($\Delta H \geqslant -0.67$ eV) [3, 26] for $Pb(6^1D_2)$ and $Pb(6^1S_0)$, respectively. A correlation diagram based on (J, Ω) coupling indicates that there are no correlations with energetically accessible products for either atomic state and that reaction or relaxation result from non-adiabatic transition following surface crossing. The slow quenching rates exhibited by these two states of the lead atom (Table 1) are in accord with this. A similar (but not identical [16]) argument may be applied to the tin atom. Again, only the lower spin orbit component of SnH need be considered from the viewpoint of possible chemical reaction:

TABLE 1

Rate constants (k_Q, cm^3 molecule^{-1} s^{-1}, 300 K) for the removal of the ($np^2\,^1D_2$) and ($np^2\,^1S_0$) states of some atoms in Group IV on collision with various gases

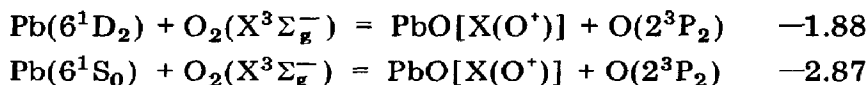| Gas	*Sn($5\,^1S_0$)(2.128 eV)	Sn($5\,^1D_2$)(1.068 eV)	C($2\,^1S_0$)(2.684 eV)	C($2\,^1D_2$)(1.263 eV)	Pb($6\,^1S_0$)(3.65 eV)	Pb($6\,^1D_2$)(2.66 eV)
He	$<5 \times 10^{-15}$	$<2 \times 10^{-15}$ [1]	$<2 \times 10^{-15}$ [11]	$<3 \times 10^{-16}$ [24]		$<2 \times 10^{-16}$ [13]
Xe	$<10^{-15}$	$<1.7 \times 10^{-15}$ [1]		$1.1 \pm 0.3 \times 10^{-10}$ [24]	$<2 \times 10^{-15}$ [15]	$<10^{-15}$ [13]
H$_2$	$2.4 \pm 0.4 \times 10^{-11}$	$5.5 \pm 0.1 \times 10^{-11}$ [1]	$\leqslant 4 \times 10^{-14}$ [11] $<5 \times 10^{-12}$ [22] $\sim 2 \times 10^{-14}$ [23]	$2.6 \pm 0.3 \times 10^{-10}$ [25] 4.15×10^{-11} [22]	$<10^{-14}$ [15]	$<10^{-14}$ [13]
O$_2$	$1.6 \pm 0.2 \times 10^{-10}$	$9.0 \pm 0.9 \times 10^{-11}$ [1]	$\sim 5 \times 10^{-14}$ [23]	$\sim 2.6 \times 10^{-11}$ [12] $<5 \times 10^{-12}$ [22]	$1.2 \pm 0.3 \times 10^{-10}$ [15]	$1.1 \pm 0.3 \times 10^{-10}$ [13]
SnMe$_4$		$2.0 \pm 0.2 \times 10^{-10}$ [1]				
SnCl$_4$	$\sim 6 \times 10^{-10}$					

*This work.

$$\Delta H(eV)[3, 26]$$

$$\text{Sn}(5^1S_0) + H_2(X^1\Sigma_g^+) = \text{SnH}(X^2\Pi_{1/2}) + H(^2S_{1/2}) \geqslant -0.842$$

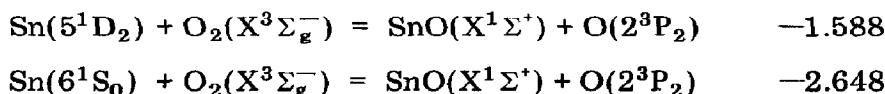$$\text{Sn}(5^1D_2) + H_2(X^1\Sigma_g^+) = \text{SnH}(X^2\Pi_{1/2}) + H(^2S_{1/2}) \geqslant 0.208$$

Reaction with the ^1S state would be exothermic whereas that with the ^1D state endothermic. However, neither in the case of a crude, low order correlation in which the spin orbit splitting in SnH is neglected nor in that involving (J, Ω) coupling are there correlations to chemical products with exothermic routes, and again, non-adiabatic transitions must take place for either reaction or relaxation. The rapid quenching rates for the ^1D and ^1S states of tin are in marked contrast to the results for the analogous states of lead (Table 1). We may only presume that this arises, in part, from the lowering in the appropriate potential surfaces by chemical interaction arising from an SnH_2 intermediate.

Quenching of the ^1D and ^1S states of both tin and lead by molecular oxygen is rapid (Table 1) and the discussion in terms of (J, Ω) coupling is similar for both atoms. Chemical reaction by both $\text{Pb}(6^1D_2)$ and $\text{Pb}(6^1S_0)$ is sufficiently exothermic:

$$\Delta H(eV)[3, 26]$$

$$\text{Pb}(6^1D_2) + O_2(X^3\Sigma_g^-) = \text{PbO}[X(O^+)] + O(2^3P_2) \quad -1.88$$

$$\text{Pb}(6^1S_0) + O_2(X^3\Sigma_g^-) = \text{PbO}[X(O^+)] + O(2^3P_2) \quad -2.87$$

as to involve low lying electronic states of PbO. The energies and Hund's case (c) components of a number of low lying states of this molecule have been reported by Barrow *et al.* [28], the results of which we have employed in constructing a correlation diagram. The resulting diagram is complex. There are 64 surfaces up to and including those correlating with $\text{Pb}(6^1D_2) + O_2(X^3\Sigma_g^-)$ ($7A' + 8A''$, total) and 82 up to and including those connecting $\text{Pb}(6^1S_0) + O_2(X^3\Sigma_g^-)$ ($A' + 2A''$, total). On the side of chemical products, there are 68 surfaces up to states which are accessible following reaction of $\text{Pb}(6^1S_0)$ ($\text{PbO}[B(1)] + O(2^3P_0)$) [28]. Thus the number of possible surface crossings are large. In neither the case of $\text{Pb}(6^1D_2)$ nor $\text{Pb}(6^1S_0)$ do correlations lead to energetically accessible states, and quenching in terms of either chemistry or physical relaxation must involve such crossings. We may emphasize that in (J, Ω) coupling, the formal spin quantum number is not restrictive and hence quenching of $\text{Pb}(6^1D_2)$ to the ^3P_J ground state will only involve mixing of A' and A'' states, and may, as here (Table 1), yield an efficient collisional process.

Reaction of the excited tin atoms:

$$\Delta H(eV)[3, 26]$$

$$\text{Sn}(5^1D_2) + O_2(X^3\Sigma_g^-) = \text{SnO}(X^1\Sigma^+) + O(2^3P_2) \quad -1.588$$

$$\text{Sn}(6^1S_0) + O_2(X^3\Sigma_g^-) = \text{SnO}(X^1\Sigma^+) + O(2^3P_2) \quad -2.648$$

similarly involves low lying states of SnO about which there is uncertainty. Smith and Meyer [29, 30] attribute the band at 20,900 cm^{-1} observed from spectroscopic studies on a matrix at 20 K containing SnO to the system, a$^3\Pi$ − X$^1\Sigma^+$, analogous to the Cameron bands in CO [26]. On the other hand, Barrow and Deutsch [31] suggest that the A(O$^+$) and B(1) bands they have observed in the gas phase, respectively at 24,200 and 24,760 cm^{-1}, are the B$^3\Pi_1$ and A$^3\Pi_{O^+}$ components of the SnO analogue of the Cameron bands. In assigning the case (c) components for the purpose of (J, Ω) coupling, Barrow and Deutsch's suggestion [31] appears to be more attractive as the components were characterized in work that was spectroscopically more detailed. Further, Smith and Meyer [29] do consider that the $^3\Sigma$ and $^3\Pi$ states could be reversed for the heavy SnO molecule. Assuming that the band at 20,900 cm^{-1} arises from the transition a$'$ $^3\Sigma^+$ ← X$'\Sigma^+$, the reaction between Sn(5^1S_0) + O$_2$ to yield the a$'$ state is marginally endothermic (ΔH = 0.06 eV). On the above ordering of states, the correlation diagram is found to be complex, there being no correlations leading exothermically to chemical products for either the ^{1}D or ^{1}S state. As with the lead atom, there are a large number of surfaces up to and including Sn(5^1S_0) + O$_2$ (72) and Sn(5^1D_2) + O$_2$ (41), and hence removal by the collision partner would again involve non-adiabatic transitions following surface crossings.

Clearly, correlations based on (J, Ω) coupling for these highly energized states are of limited use, especially on account of the large number of surfaces involved. On the other hand, only such correlations are relevant here in view of the large atomic and molecular spin orbit splittings, and the Hund's case (c) nature of many of the diatomic molecules involved. This type of correlation is better suited to considering the reactivities of spin orbit states of the ground states of heavy atoms, where the number of surfaces involved will be much smaller. As an example, we may note that whilst chemical reaction of Sn(5^3P_J) + O$_2$ is exothermic for the three J levels, Sn(5^3P_2) + O$_2$(X$^3\Sigma_g^-$) do *not* correlate with SnO(X$^1\Sigma^+$) + O($2^3P_{2, 1\ or\ 0}$). Hence future work on the individual spin orbit components of the ground state tin atom may reveal a difference in the reactivities of the J components which arises from considerations which are not simply energetic.

We may finally note that (J, Ω) correlations provide a direction for considering the reactivities of diatomic molecules in different *rotational* states by means of the standard Hund's coupling cases for the diatomic molecules [26]. In extreme situations there may, for example, be a change of coupling case with rotational quantum number or a change in the ordering of the Ω values, as in the ordering of the O$^+$ and O$^-$ components of the a$^3\Pi$ state with odd and even J$_{rot}$ values [26]. This would, in turn, affect the resulting *electronic* correlations or, in other words, the potential surfaces that reactants would experience. In some cases, potential surfaces may also, as Shuler has pointed out [32], be affected by *vibronic* coupling. These two considerations thus provide the basis, in principle, for bringing together within a single framework the electronic and nuclear dynamics of chemical reactions.

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Acknowledgements

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