KINETIC STUDY OF ELECTRONICALLY EXCITED ANTIMONY ATOMS, Sb($5^2D_{3/2, \, 5/2}$), BY TIME-RESOLVED ATTENUATION OF ATOMIC RESONANCE RADIATION

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Summary

A method is described for the direct kinetic study of electronically excited antimony atoms, Sb($5^2D_{3/2}$) and Sb($5^2D_{5/2}$), respectively 1.055 and 1.222 eV above the ($5^4S_{3/2}$) ground state. These optically metastable atoms were generated by the pulsed irradiation of $SbMe_3$ and monitored photoelectrically by time-resolved absorption spectroscopy of resonance transitions at $\lambda = 259.81$ nm [$6s(^2P_{1/2}) \leftarrow 5p^3(^2D_{3/2})$] and $\lambda = 252.85$ nm [$6s(^2P_{3/2}) \leftarrow 5p^3(^2D_{5/2})$]. These two spin orbit levels, in general, showed different kinetic decays and were clearly not in a Boltzmann equilibrium throughout the rate measurements. Absolute quenching constants for the collision partners He, H_2, O_2, CO, CO_2 and $SbMe_3$ are reported and compared with the analogous data for the ^2D_J states of atomic nitrogen, phosphorus and arsenic. Unlike the data for these lighter atoms, which were considered hitherto in terms of symmetry arguments involving the weak spin orbit coupling approximation, the present data are discussed using (J, Ω) coupling which is seen to be a more suitable vehicle for interpreting the collisional behaviour of heavy metal atoms in the gas phase.

Introduction

There is an extensive current interest in direct studies of the collisional behaviour of low lying states of Group V atoms arising from the np^3 ground state electronic configuration. Recent work includes investigation on N(2^2D_J, 2^2P_J) [1 - 3], P(3^2D_J, 3^2P_J) [4 - 6] and As(4^2D_J, 4^2P_J) [7 - 9], the majority of which have been carried out by atomic absorption spectroscopy using attenuation of resonance radiation following pulsed photolytic initiation. In practical terms, the overall objective is to characterize the kinetic properties of the atoms in these excited states for the complete periodic Group and to study the influence of increasing atomic weight. The fundamental aim of such work is to understand the relationship between electronic structure and reactivity within a broader programme of atomic kinetics [10,

11]. The rate data for the electronically excited nitrogen and phosphorus atoms [1, 2, 4, 5] have been found to be in accord with symmetry arguments based on the weak spin orbit coupling approximation [12, 13]. Correlation diagrams which depend on the separation of spin and orbital motion have been found to be only of limited use in interpreting the data for arsenic atoms in the ^{2}D and ^{2}P states [7, 8]. With arsenic, spin orbit coupling influences collisional behaviour to a much greater extent than in the light atoms. Clearly, a much larger effect from spin orbit coupling will be expected for the heavier antimony atoms, including a tendency towards Hund's coupling case (c) for the appropriate diatomic molecules. Hence, the present study is concerned with kinetic measurements particular to the excited antimony atom, for which no data have been reported, and the more general problem of the importance of spin orbit coupling on heavy metal atom chemistry in the gas phase. The only detailed kinetic data for antimony atoms in a specific electronic state are those reported by Strausz *et al.* [14] on half pressures for quenching of the emission from $Sb(6s^2P_{3/2})$. This general field has received recent impetus by the search for a laser operating in the visible region of the spectrum, resulting from the reaction of a heavy metal atom. An example of such an investigation is the study of Broida *et al.* [15, 16] on the reactions of barium atoms.

This paper describes kinetic measurements on Sb atoms in the individual spin orbit levels ($5p^3\ ^2D_{3/2}$) and ($5p^3\ ^2D_{5/2}$), respectively, 1.055 and 1.222 eV above the ($5p^3\ ^4S_{3/2}$) electronic ground state [17]. These optically metastable species [18] were monitored in absorption following flash photolysis and the resulting absolute rate constants for collisional quenching by added gases were obtained and compared with the analogous data for N, P and As atoms. The rate data for the antimony atoms are discussed in terms of correlation diagrams based on (J, Ω) coupling, a vehicle which has recently been found suited for considering the collisional behaviour of tin and lead atoms in specific electronic states [19, 20].

Experimental

By contrast with the kinetic studies on $As(4^2D_J)$ and $As(4^2P_J)$ [7, 8], considerable experimental difficulties were encountered with electronically excited antimony atoms. The photochemical source of the transient atoms, in particular, the combination of the choice of parent molecule and the design of the photochemical reactor which would yield concentrations of the atoms sufficiently large for direct measurement, proved the basic limitation of this investigation. This is especially reflected in the larger scatter in the kinetic plots for $Sb(5^2D_{5/2})$ which arises from smaller degrees of light absorption than normally employed in "single-shot" measurements [7, 8], and rapid quenching by the parent molecule. Nevertheless, we have succeeded in carrying out the first direct, detailed kinetic investigation of $Sb(5^2D_{3/2})$ and $Sb(5^2D_{5/2})$ in the gas phase, generated by pulsed irradiation of antimony trimethyl and monitored photoelectrically in absorption by attenuation of atomic resonance radiation.

A number of parent molecules were investigated as photochemical sources, including SbH_3 and $SbCl_5$, but only antimony trimethyl, $SbMe_3$, proved sufficiently stable and yielded atomic concentrations suitable for measurement. Various types of reactor were also investigated. These included: (1) a conventional flash photolysis arrangement with a separate quartz lamp and vessel separated by air (this resulted in huge scattered light signals); (2) a coaxial lamp and vessel assembly [7], with both the inner and outer tubes constructed of quartz and employing optical coupling by means of aluminium foil on the outermost surface; (3) a reactor of the type described by Husain and Kirsch [21] in which photolysis was effected through sapphire port-holes ($\lambda > 144$ nm). However, the standard coaxial assembly [7] with the common wall constructed of high purity quartz ('Spectrosil', $\lambda > 165$ nm) and the outer tube of Pyrex, with a narrow annular space (~ 2 mm) to facilitate an intense plasma discharge ($E = 1125$ J) in this case, through nitrogen [7], triggered by means of an ignition circuit (BK66, B.T.H., U.K.), proved to be the optimum arrangement.

Resonance lines of the antimony atom were derived from a microwave discharge through a flow system of $SbMe_3$ in He ($p_{SbMe_3} = 1.3$ N m^{-2}, $p_{total\,with\,He} = 133$ N m^{-2}, incident power = 100 W). This yielded the most stable discharge when compared with other sources used in the flow (SbH_3 and $SbCl_5$), and was considerably more reliable and intense in comparison with a sealed source similar to those employed for the study of arsenic [7] and lead atoms [22]. The atomic lines were isolated by means of a Seya–Namioka grating monochromator [7]. Following irradiation, resonance absorption by the transient atoms was monitored by means of a photo-multiplier tube (E.M.I. 9783B) mounted on the exit slit. Antimony atoms in the low lying ^2D and ^2P states are highly optically metastable, as seen from the sum of the Einstein coefficients (ΣA) to all lower states

Atomic state	$E(\text{cm}^{-1})$ [17]	$\Sigma A(\text{s}^{-1})$ [18]
$5p^3\,^2P_{3/2}$	18,465	11.27
$5p^3\,^2P_{1/2}$	16,397	4.70
$5p^3\,^2D_{5/2}$	9,854	0.11
$5p^3\,^2D_{3/2}$	8,512	1.11

and from this aspect, are amenable to study by absorption spectroscopy in allowed electronic transitions to higher states. The detection system for the photoelectric pulses was similar to that employed hitherto [7]. The principal differences were, firstly, that the transient recorder was operated in the pre-trigger mode. Secondly, unlike the later measurements on $As(4^2D_J, 4^2P_J)$ [8], the present system did not employ the logarithmic signal converter on account of the lower degrees of absorption and the faster decay rates.

The spectrum of atomic antimony from the resonance source was taken with a Hilger and Watts 'Monospek' 1000 grating monochromator. We are indebted to Mr. Adam Brown for the use of this instrument.

Materials

He, Kr, H_2, O_2, N_2, CO and CO_2 were used essentially as hitherto [7, 8]. $SbCl_5$ (British Drug Houses) was thoroughly degassed at $-130\ ^\circ C$ (n-pentane slush) and used directly. SbH_3 was prepared by the action of potassium antimony tartrate with sodium borohydride following Kleinberg [23]. $SbMe_3$ for the flow lamp was prepared by the action of $SbCl_3$ and MeLi and separated from ethereal solution as solid $SbMe_3Br_2$ using bromine. The $SbMe_3Br_2$ was then mixed with zinc powder and slowly heated under vacuum, liberating gaseous $SbMe_3$ which was trapped at $-196\ ^\circ C$. Commercial $SbMe_3$ (Alfa Inc.) was used directly for reaction mixtures.

Results and Discussion

Figure 1 shows a portion of the spectrum of atomic antimony taken from the microwave discharge through the $SbMe_3$/He mixture. Whilst this lamp employs relatively large quantities of $SbMe_3$ during kinetic measurements, it is only the high intensity of the resulting atomic lines from this source that permits the monochromator slits to be narrowed to widths which cause a suitable and necessary reduction in the noise level from the scattered light. The following transitions were employed in this investigation:

Transition	λ (nm) [24]	$10^{-8}\ gA\ (s^{-1})$ [24]
$6s^2P_{1/2} \rightarrow 5p^3\ ^2D^0_{3/2}$	259.81	64
$6s^2P_{3/2} \rightarrow 5p^3\ ^2D^0_{5/2}$	252.85	56
$6s^2P_{3/2} \rightarrow 5p^3\ ^2P^0_{1/2}$	302.98	10
$6_s^2P_{1/2} \rightarrow 5p^3\ ^2P^0_{1/2}$	326.75	11
$6s^2P_{3/2} \rightarrow 5p^3\ ^2P^0_{3/2}$	323.25	22

Despite the use of different chemical sources, various reactor designs (see experimental) and the use of different gas fillings in the photolysis sources to achieve different distributions in the wavelength outputs from the high intensity pulses, we were unable to detect antimony atoms in the ^2P state at concentrations sufficiently high for kinetic measurements. Only very low yields were barely detectable following photolysis. Measurements on the two spin orbit components of the ^2D state could be readily made, as shown in Figs. 2 and 3, which give the digitized time variation of the transmitted light intensity, respectively, at $\lambda = 259.81$ and 252.85 nm, following the photolysis of $SbMe_3$ in the presence of excess helium. Figures 4 and 5 show examples of first order kinetic plots for the decay of $Sb(5^2D_{3/2})$ and $Sb(5^2D_{5/2})$ from the data contained respectively in Figs. 2 and 3.

Unfortunately, γ-values for the modified Beer–Lambert law [25]

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

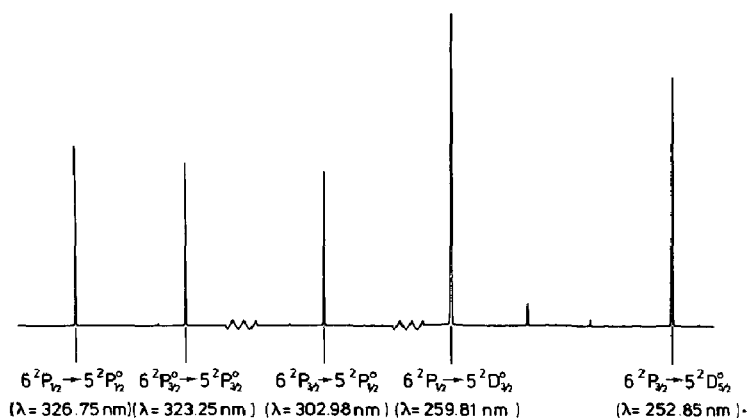could not be determined for the atomic transitions employed. This would

Fig. 1. Portion of the emission spectrum of atomic antimony from the microwave-powered flow lamp. $p_{SbMe_3} = 1.3$ N m^{-2}, $p_{total\ with\ He} = 133$ N m^{-2}; incident power = 100 W. Scan speed = 2.5 nm/min. Width of slits = 0.01 mm.

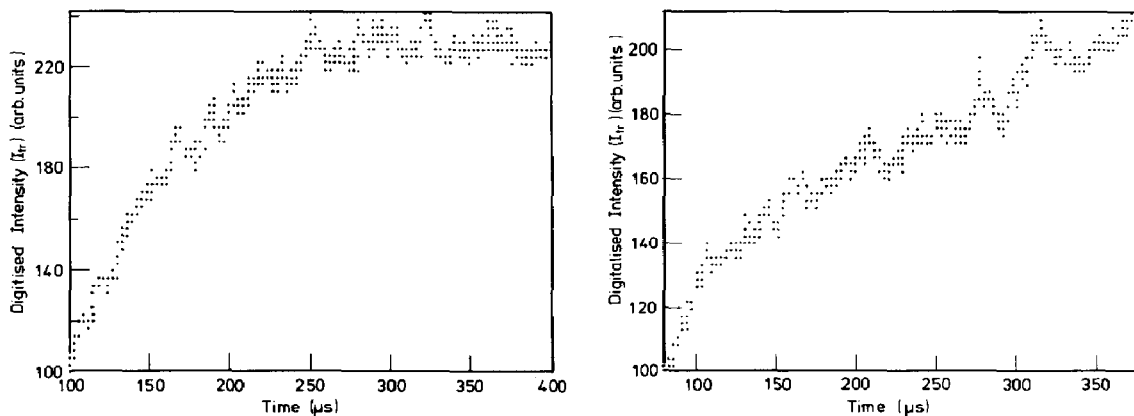Fig. 2. Digitized time-variation of the transmitted light intensity at $\lambda = 259.81$ nm [Sb($6\,^2P_{1/2}$) → Sb($5\,^2D^0_{3/2}$)] indicating the decay of resonance absorption by Sb($5\,^2D_{3/2}$). $p_{SbMe_3} = 0.20$ N/m^2, $p_{total\ with\ He} = 3.33$ kN/m^2; $E = 1125$ J; recording delayed by 80 μs.

Fig. 3. Digitized time-variation of the transmitted light intensity at $\lambda = 252.85$ nm [Sb($6\,^2P_{3/2}$) → Sb($5\,^2D^0_{5/2}$)] indicating the decay of resonance absorption by Sb($5\,^2D_{5/2}$). $p_{SbMe_3} = 0.20$ N/m^2, $p_{total\ with\ He} = 3.33$ kN/m^2; $E = 1125$ J; recording delayed by 100 μs.

have required an accuracy and reproducibility in the intercepts of the first-order plots of the type given in Figs. 4 and 5 considerably better than those for the slopes. We therefore employ γ-values of unity for the transitions at $\lambda = 259.81$ and 252.85 nm. This approximation should not be too serious in the present context as a high degree of self reversal by the excited atoms would not be expected in the spectroscopic source [26]. γ-values for the resonance transitions employed to monitor the ^2D levels of the arsenic were of magnitude ~ 0.8 [7]. Thus, the absolute values of the quenching rate constants (k_Q) reported here for both Sb($5^2D_{3/2}$) and Sb($5^2D_{5/2}$) could conceivably be low by $\sim 25\%$ if the transition were characterized by γ-values of comparable magnitude. The relative values of k_Q for different gases with
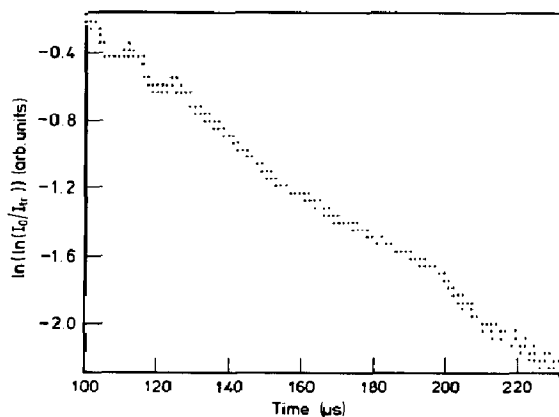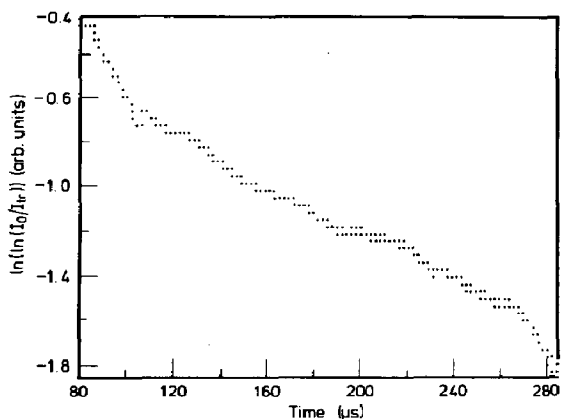
Fig. 4. Typical pseudo first-order plots for the decay of $Sb(5^2D_{3/2})$ obtained by monitoring the absorption of light at λ = 259.81 nm [$Sb(6^2P_{1/2}) \leftarrow Sb(5^2D^0_{3/2})$]. p_{SbMe_3} = 0.20 N/m^2, $p_{total\ with\ He}$ = 3.33 kN/m^2; E = 1125 J.

Fig. 5. Typical pseudo first-order plots for the decay of $Sb(5^2D_{5/2})$ obtained by monitoring the absorption of light at λ = 252.85 nm [$Sb(6^2P_{3/2}) \leftarrow Sb(5^2D^0_{5/2})$]. p_{SbMe_3} = 0.20 N/m^2, $p_{total\ with\ He}$ = 3.33 kN/m^2; E = 1125 J.

a given ^2D_J level would remain correct and only a small difference would arise when comparing data for $J = 3/2$ and $J = 5/2$ resulting from a small difference in γ for the two transitions.

The slopes in the first-order plots are given by $-\gamma k'$, where γ is taken as unity. A linear relationship between k' and the pressure of added quenching gas (Q) is employed. Figure 6 shows the variation of the first-order rates with respect to the blank, $k' - K$, for $Sb(5^2D_{3/2})$ and $Sb(5^2D_{5/2})$ with added hydrogen. The slopes of these plots yield the absolute values of the rate constants for the quenching of the two levels by this added gas; the values of K describe contributions to removal, principally by weak spontaneous emission and collisional quenching by the parent molecule and products of photolysis, which are assumed to be constant in a given series of kinetic runs. Table 1 lists the collisional quenching rate constants for $Sb(5^2D_{3/2,5/2})$, for which there are no previous data, and these are compared with analogous data for the other ^2D states in Group V.

An initial, fundamental conclusion for the quenching data of $Sb(5^2D_{3/2})$ and $Sb(5^2D_{5/2})$, is that the observed rates are *not*, in general, equal for the two spin orbit states. This may be contrasted with the data for $As(4^2D_{3/2})$ and $As(4^2D_{5/2})$ where the overall decays were found to be equal [7]. An observation of that type can result from the maintenance of an equilibrium during kinetic measurements between the J levels and can be expected for a splitting of this magnitude ($\Delta E[As(4^2D_{5/2}) - As(4^2D_{3/2})] = 322$ cm^{-1}) [17] simply in terms of the energy to be transferred to translation only [28]. A similar conclusion can be made from the observed equal quenching rates for $P(3^2P_{1/2})$ and $P(3^2P_{3/2})$ [5] ($\Delta E = 25.7$ cm^{-1}) [17]. Acuna *et al.* [5] were unable to resolve the J levels in $P(3^2D_J)$ during kinetic experiments but the small splitting between $J = 3/2$ and $J = 5/2$ ($\Delta E = 14.8$ cm^{-1}) [17] leads one
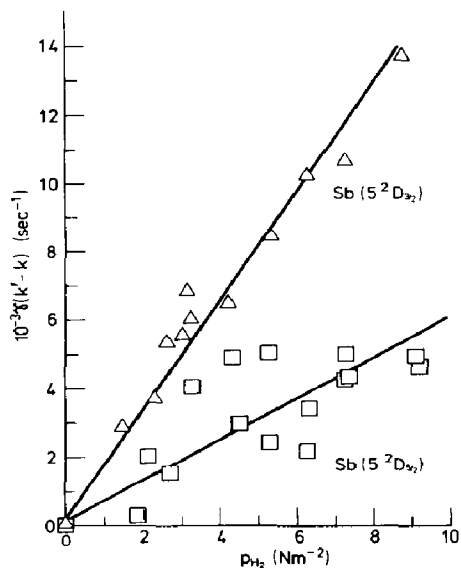
Fig. 6. Plots of first-order rate coefficients ($\gamma(k' - K)$) for the decay of $Sb(5^2D_{3/2})$ and $Sb(5^2D_{5/2})$ in the presence of hydrogen. $P_{SbMe_3} = 0.20$ N/m^2, $P_{total\,with\,He} = 3.33$ kN/m^2; $E = 1125$ J.

to expect the maintenance of a Boltzmann equilibrium between the spin orbit levels in that state. We may emphasize that equality in the observed quenching rates for the spin orbit levels may also result from equal removal rates out of the ^2D state. An observed difference in quenching rates for $Sb(5^2D_{3/2})$ and $Sb(5^2D_{5/2})$ clearly requires the use of a formal framework which differentiates between the J levels and thus implies (J, Ω) coupling.

A correlation diagram for Sb + H_2 = SbH + H necessitates knowledge of the bond dissociation energy of SbH but its accurate value is not critical in the present context. Bollmark and Lindgren [29] have observed SbH and SbD in absorption *via* the system $^3\Pi_i - ^3\Sigma^-$ following flash photolysis. They describe a tendency towards Hund's case (c) coupling from an analysis restricted to the (0,0) band and do not report a bond dissociation energy. We employ D(SbH) = ~ 4 eV from Pauling's additive and geometric rules which both yield values of 4.1 eV using D(H_2) = 4.4763 and D(Sb_2) = 3.7 eV given by Herzberg [31]. This latter value is in accord with an upper limit of 3.9 eV that may be calculated (by the authors) from the recent vibrational data for the ground state given by Sfeila *et al.* [32]. Collisional quenching by molecular hydrogen is significantly slower for $Sb(5^2D_{5/2})$ and this result is in accord with the correlation diagram (Fig. 7). There are no surfaces leading exothermically to chemical products for the J = 5/2 level and thus removal, either by reaction or physical quenching, must involve non-adiabatic transitions (N.A.T.) following surface crossing. There is a surface leading exothermically to ground state products for J = 3/2 (Fig. 7). As the present system did not involve the very difficult experimental problem of monitoring the small yields of molecular products, the production of SbH + H

TABLE 1

Rate constants (k_Q, cm^3 molecule^{-1} s^{-1}, 300 K) for the collisional removal of Group V atoms (N, P, As and Sb) in the ($np^{3\,2}D_J$) state by various gases

Gas	Sb($5^2D_{3/2}$)	Sb($5^2D_{5/2}$)	As(4^2D_J)	P(3^2D_J)	N(2^2D_J)
He	<(−16)*	≤6 (−15)*	≤3.6 ± 0.4 (−15) [8]	<5 (−16) [4]	≤2 (−16) [1] ≤1.6 (−16) [3]
H$_2$	6.6 ± 0.2 (−12)*	2.5 ± 0.3 (−12)*	5.1 ± 0.8 (−12) [7] 2.8 ± 0.3 (−11) [9]	3.1 ± 0.8 (−13) [4]	2.1 ± 0.3 (−12) [1] 1.7 ± 0.5 (−12) [2] 5 (−12) [3] 5 (−12) [27]
O$_2$	1.7 ± 0.1 (−11)*	1.8 ± 0.2 (−11)*	2.2 ± 0.4 (−12) [8]	2.6 ± 0.2 (−11) [4]	5.2 ± 0.4 (−12) [1] 9.3 ± 0.2 (−12) [2] 6 ± 2 (−12) [3]
CO	1.3 ± 0.1 (−11)*	7.5 ± 1.1 (−12)*	4.0 ± 0.8 (−11) [7] 4.7 ± 0.6 (−11) [9]	1.5 ± 0.4 (−11) [5]	2.1 ± 0.2 (−12) [19] 6 (−12) [27]
CO$_2$	2.1 ± 0.5 (−13)*	<1 (−13)*	3.3 ± 0.5 (−13) [8] 7.8 ± 1.2 (−13) [9]	3.3 ± 1.0 (−12) [5]	1.8 ± 0.2 (−13) [1] 5 ± 2 (−13) [3] 6 (−13) [27]
SbMe$_3$	9.4 ± 1.1 (−11)*	1.8 ± 0.3 (−10)*			

*This work. Powers of ten in parentheses.
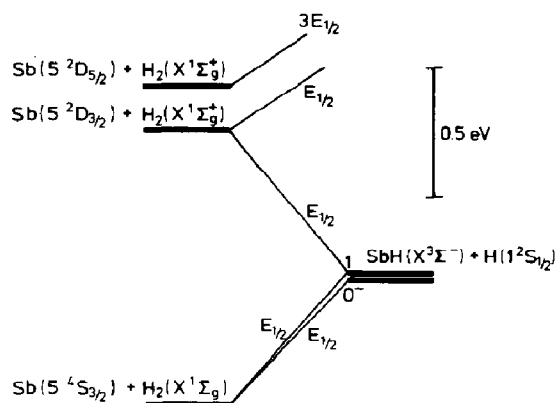
Fig. 7. Correlation diagram for Sb + H₂ = SbH + H using (J, Ω) coupling.
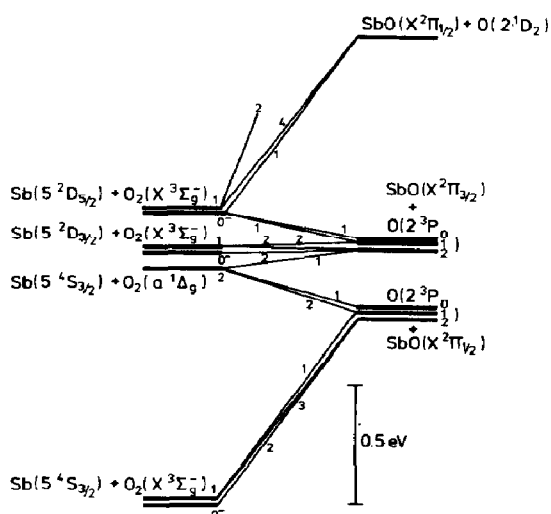
Fig. 8. Correlation diagram for Sb + O₂ = SbO + O using (J, Ω) coupling. (All surfaces are of the type $E_{1/2}$. Correlations indicated by the number of $E_{1/2}$ surfaces.)

from $Sb(5\,^2D_{3/2})$ constitutes conjecture but supported by the symmetry arguments. Further, the experimental accuracy did not permit us to monitor any effects of $J = 5/2 \rightarrow 3/2$ during observed decays of the latter.

By contrast with the discussion of the data for molecular hydrogen, that for quenching by molecular oxygen requires a relatively accurate value for $D(SbO)$ which is, unfortunately, not available. Gaydon [33] gives $D(SbO) = 4 \pm 1$ eV from linear Birge–Sponer extrapolations reported in the literature, ranging from 3.8 to 4.5 eV. We employ a value of 4 eV following Gaydon [33], this being in accord with an upper limit reported recently by Rai et al. [34] ($D(SbO) < 4.2865$ eV). Using Gaydon's value, chemical reaction of $Sb(5\,^2D_{5/2})$ and $Sb(5\,^2D_{3/2})$ is in accord with the appropriate correlation diagram (Fig. 8) which is self-explanatory. On the other hand, a significantly smaller value for $D(SbO)$ would require collisional removal for either reaction or relaxation by means of a N.A.T. An alternative explanation
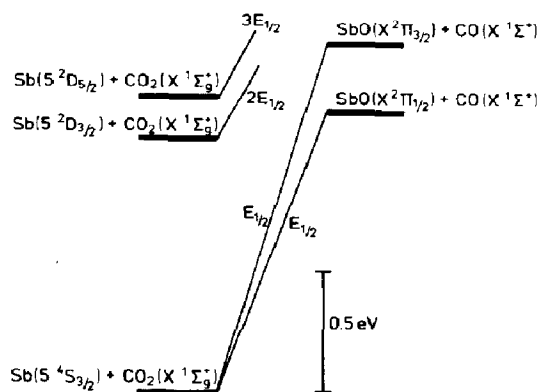
60

$3E_{1/2}$ $SbO(X^2\Pi_{3/2}) + CO(X\ ^1\Sigma^+)$

$Sb(5\ ^2D_{5/2}) + CO_2(X\ ^1\Sigma_g^+)$ $2E_{1/2}$

$Sb(5\ ^2D_{3/2}) + CO_2(X\ ^1\Sigma_g^+)$ $SbO(X^2\Pi_{1/2}) + CO(X\ ^1\Sigma^+)$

$E_{1/2}$ $E_{1/2}$

0.5 eV

$Sb(5\ ^4S_{3/2}) + CO_2(X\ ^1\Sigma_g^+)$

Fig. 9. Correlated diagram in C_s symmetry for Sb + CO_2 = SbO + CO using (J, Ω) coupling for reactants and products.

for the equal quenching rate constants would involve a mechanism in which various N.A.T.'s between one or more of the $6E_{1/2}$ surfaces correlating with $Sb(5^2D_{3/2}) + O_2$ and the $9E_{1/2}$ surfaces correlating with $Sb(5^2D_{5/2}) + O_2$ would maintain a Boltzmann equilibrium between the J = 3/2 and 5/2 levels.

As chemical reaction between $Sb(^2D_J)$ and carbon monoxide is highly endothermic [17, 31, 33], collisional removal must take place by means of physical relaxation and involve N.A.T.'s following crossing of surfaces correlating with $CO(X^1\Sigma^+)$ and $Sb(5^2D_{5/2})$ ($3E_{1/2}$), $Sb(5^2D_{3/2})$ ($2E_{1/2}$) and $Sb(5^4S_{3/2})$ ($2E_{1/2}$). Further, the crossings must clearly take place at low or negative energies. With $As(4^2D_J)$, $P(3^2D_J)$ and $N(2^2D_J)$, rapid deactivation of these states by CO (Table 1) also took place via N.A.T.'s [1, 5, 7] where it was presumed that surface crossings were facilitated by intermediates such as NCO [12].

Figure 9 shows the correlation diagram in (J, Ω) coupling for Sb + CO_2 = SbO + CO, assuming C_s symmetry in the collision intermediate and presented here as an example for a triatomic collision partner. Despite an exothermic route to $SbO(X^2\Pi_{1/2})$ for $Sb(5^2D_{5/2})$, there is no adiabatic pathway for this reactant and the inefficient quenching behaviour of CO_2 towards both J levels is in accord with the diagram. Further, whilst the ν_1 mode in CO_2 (1388 cm^{-1}) [35] presents a near-resonance pathway (ΔE = +46 cm^{-1}) for electronic-to-vibrational energy involving a single vibrational quantum jump for J = 5/2 → 3/2, crossing of the surfaces correlating with the two spin orbit components must presumably take place at unfavourable energies as endorsed by the slow quenching rate for $Sb(5^2D_{5/2})$.

Acknowledgements

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