

## COLLISIONAL BEHAVIOUR OF $\text{Ge}(4^3\text{P}_{0,1,2})$ BY ATOMIC ABSORPTION SPECTROSCOPY

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### Summary

A gas phase kinetic study of atomic germanium in the three individual spin orbit states,  $\text{Ge}(4p^2(^3\text{P}_{0,1,2}))$ , is presented. The transient atoms were generated by pulsed irradiation of  $\text{GeBr}_4$  at  $\lambda > 165$  nm and monitored photoelectrically in absorption by time-resolved attenuation of atomic resonance radiation at  $\lambda = 275.5$  nm ( $5s(^3\text{P}_1^0) \leftarrow 4p^2(^3\text{P}_2)$ ),  $\lambda = 259.3$  nm ( $5s(^3\text{P}_2^0) \leftarrow 4p^2(^3\text{P}_1)$ ) and  $\lambda = 249.8$  nm ( $5s(^1\text{P}_1^0) \leftarrow 4p^2(^3\text{P}_0)$ ) in the "single shot" mode. The decays of the atomic states were studied in the presence of the gases  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  and absolute rate constants for the collisional removal of each of the three spin orbit states are presented for all gases. These data and those obtained in an earlier investigation are compared with analogous data for the collisional behaviour of other  $np^2$  spin orbit states in Group IV that have been studied hitherto, namely the heavy atoms  $\text{Sn}(5^3\text{P}_{0,1,2})$  and  $\text{Pb}(6^3\text{P}_{0,1,2})$  and, in the cases of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ , with previous rate data for carbon atoms. Various reaction pathways, including E (electronic)  $\rightarrow$  V (vibrational) transfer and chemical reaction, are considered and, in some cases, the effects of both the weak spin orbit coupling approximation and ( $J, \Omega$ ) coupling on the nature of the potential surfaces are discussed.

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### Introduction

Kinetic studies of Group IV elements constitute one of the main general areas concerned with the investigation of the collisional behaviour of atoms in specific electronic states and their relationship with electronic structure [1 - 3]. An overall experimental objective of such work is to elucidate the atomic reactivity of all states arising from the  $np^2$  ground state electronic configuration ( $^3\text{P}_{0,1,2}$ ,  $^1\text{D}_2$ ,  $^1\text{S}_0$ ). Thus there has been detailed direct kinetic study of the light atomic states  $\text{C}(2^3\text{P}_J, 2^1\text{D}_2, 2^1\text{S}_0)$  [4 - 11], and also of the heavy atomic states  $\text{Sn}(5^3\text{P}_{0,1,2}, 5^1\text{D}_2, 5^1\text{S}_0)$  [12 - 17] and  $\text{Pb}(6^3\text{P}_{0,1,2}, 6^1\text{D}_2, 6^1\text{S}_0)$  [18 - 26]. The structure on which rate data resulting from such studies have

been based is to employ symmetry arguments on the nature of the associated potential surfaces using the weak spin orbit coupling approximation for light atoms [27] and  $(J, \Omega)$  coupling for heavy atom collisions [3]. It was within this context that the preliminary work on the three spin orbit states of germanium,  $\text{Ge}(4p^2(^3P_{0,1,2}))$ , was placed [28]. Although these states involved relatively small spin orbit splittings (as shown in Table 1), it was necessary to employ  $(J, \Omega)$  coupling in order to make detailed statements of the influence of electronic structure of the individual  $J$  levels on the kinetics. As Ge is an atom of "intermediate" atomic weight, it was found that  $(J, \Omega)$  coupling was of limited application, especially as this type of coupling does not often lead to heavily restrictive pathways [3]. The present paper extends this earlier work and describes the collisional removal of  $\text{Ge}(4^3P_J)$  by a range of added gases. The data are compared, where available, with analogous data for absolute removal rates of individual spin orbit states of the heavy atoms  $\text{Pb}(6^3P_{0,1,2})$  and  $\text{Sn}(5^3P_{0,1,2})$  as well as with those for carbon atoms.

TABLE 1

Atomic states of  $\text{Ge}(4p^2(^3P_J))$ 

	Energy ( $\text{cm}^{-1}$ ) [29]	Einstein coefficient $A_m$ ( $\text{s}^{-1}$ ) [30]
$\text{Ge}(4^3P_2)$	1410	$8.2 \times 10^{-3}$
$\text{Ge}(4^3P_1)$	557	$3.1 \times 10^{-3}$
$\text{Ge}(4^3P_0)$	0	—

## Experimental

The experimental arrangement was similar to that employed previously [28].  $\text{Ge}(4^3P_{0,1,2})$  were generated by the pulsed irradiation of  $\text{GeBr}_4$  in a coaxial lamp and vessel assembly ( $E = 980 \text{ J}$ ,  $p_{\text{Kr}} = 1.4 \text{ kN m}^{-2}$ ,  $\lambda > 165 \text{ nm}$ ) in the presence of excess helium buffer gas to ensure that there was significant temperature rise on photolysis ( $p_{\text{He}} : p_{\text{GeBr}_4} \approx 40\,000 : 1$ ). The high optical metastability of the  $^3P_1$  and  $^3P_2$  states, whose radiative lifetimes ( $\tau_e = 1/A_{nm}$ ) (Table 1) arise principally from magnetic dipole emission [30], permits their study as well as that of the  $^3P_0$  ground state by atomic absorption spectroscopy. The states were monitored by means of the resonance transitions shown in Table 2, which were derived from a microwave-powered atomic emission source of a flow system of  $\text{GeCl}_4$  in He ( $p_{\text{GeCl}_4} = 4.0 \text{ N m}^{-2}$ ,  $p$  (total with He) =  $400 \text{ N m}^{-2}$ , incident power =  $100 - 140 \text{ W}$ ). The time-resolved attenuation of atomic resonance radiation, representing resonance absorption by the particular spin orbit state, was detected by means of a photomultiplier tube (EMI 9783 B) mounted on the exit slit of a grating monochromator

TABLE 2

Resonance transitions employed in the kinetic investigation of  $\text{Ge}(4p^2(^3P_J))$ 

Transition	$\lambda(\text{nm})$ [31]	$10^{-8}gA$ ( $\text{s}^{-1}$ ) [31]	$\gamma$ [28]*
$5s(^3P_1^0) \leftarrow 4p^2(^3P_2)$	275.5	9.8	$0.58 \pm 0.02$
$5s(^3P_2^0) \leftarrow 4p^2(^3P_1)$	259.3	11	$0.68 \pm 0.04$
$5s(^1P_1^0) \leftarrow 4p^2(^3P_0)$	249.8	2.4	$0.75 \pm 0.06$

\*Based on the modified Beer–Lambert law [32] :  $I_{\text{tr}} = I_0 \exp \{-\epsilon(cl)^\gamma\}$ .

(Hilger and Watts, Monospek 1000). The resulting signals were amplified by means of a current-to-voltage converter employing a fast settling operational amplifier [33]. Hitherto [28] these pulses were fed into rapid response precision logarithmic amplification circuitry [10, 34, 35] in order to measure effectively  $\ln(I_{\text{tr}}/I_0)$  (the symbols have their usual significance). However, in this study the signals were transferred directly to and stored in a transient recorder (Biomation, model 610B), displayed on an oscilloscope for the purpose of visual inspection and transferred to an XY recorder (Bryans Ltd.) for subsequent kinetic analysis. As described previously [28], kinetic measurements were restricted to times of approximately 100  $\mu\text{s}$  following the photolytic flash in order to avoid complications due to the scattered light accompanying the high intensity discharge.

Regarding the use of the modified Beer–Lambert law  $I_{\text{tr}} = I_0 \exp \{-\epsilon(cl)^\gamma\}$  [32], we have discussed the general significance of  $\gamma$  elsewhere [36, 37]. In particular, “curves of growth” [38] for attenuation of resonance radiation based on “three layer” models [39] are consistent with the logarithmic form of the modified Beer–Lambert law as used in experiments of the present kind both for cases in which there is no nuclear hyperfine splitting [40] and for cases in which nuclear hyperfine interaction is significant [41, 42]. In the case of the resonance transitions of germanium, of the five atomic isotopes only one has a nuclear spin  $I$  ( $^{70,72,74,76}\text{Ge}$  (92.1% total)  $I = 0$ ;  $^{73}\text{Ge}$  (7.9%)  $I = 9$  [2, 43]. Using the simple vector model for nuclear hyperfine interaction [44] and the standard selection rules ( $\Delta F = 0, \pm 1$ ) [44], the  $^{73}\text{Ge}$  component will contribute nine lines to both the  $\lambda = 275.5$  nm and the  $\lambda = 259.3$  nm transitions and three lines to the  $\lambda = 249.8$  nm transition (Table 2).

### Materials

He, Kr,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{GeCl}_4$  and  $\text{GeBr}_4$  were prepared essentially as described previously [13, 19, 28].

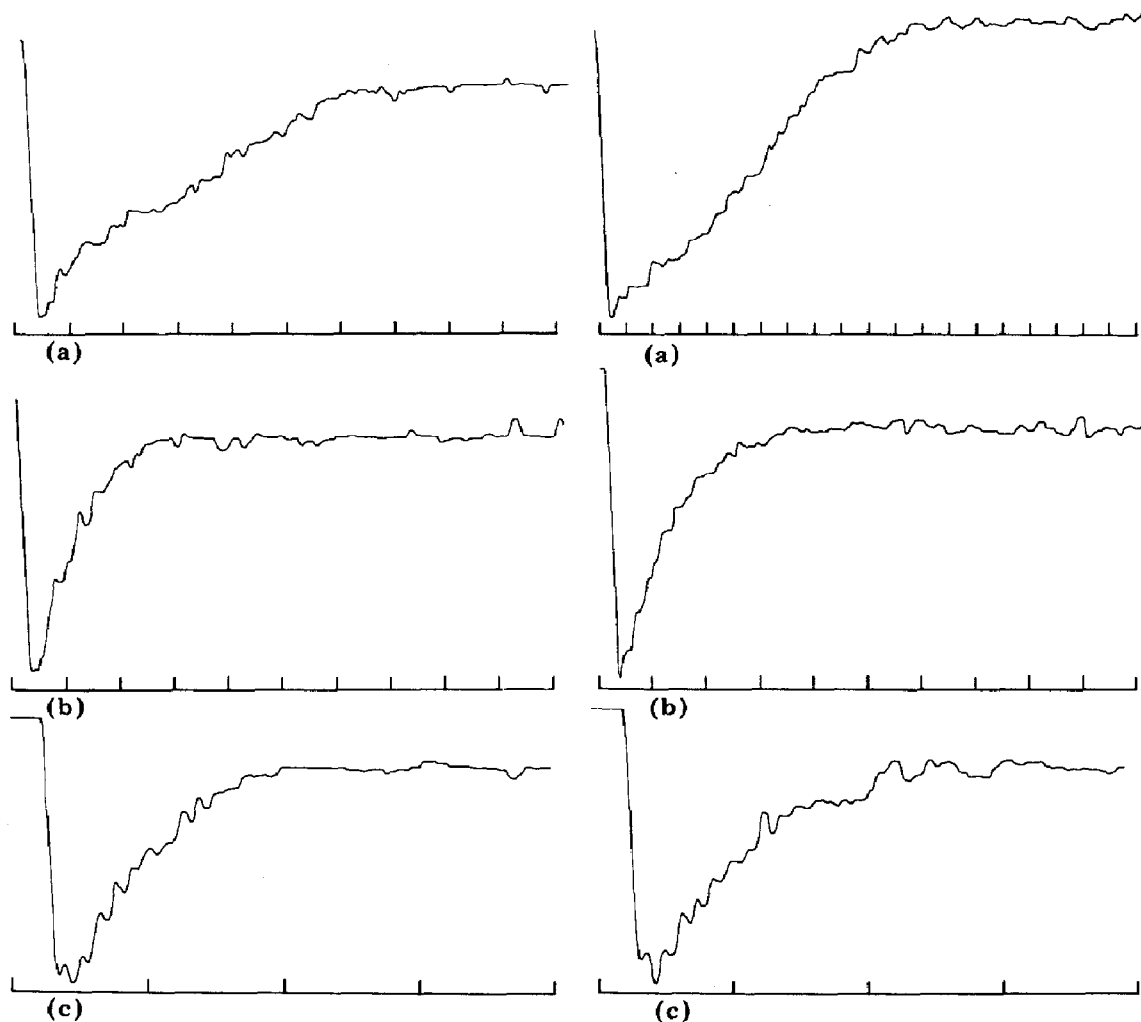


Fig. 1. Typical transient recorder traces  $I_{tr}$  for the decay of  $\text{Ge}(4^3\text{P}_2)$  in the presence of  $\text{N}_2\text{O}$ , which were obtained by attenuation of the atomic resonance radiation at  $\lambda = 275.5$  nm associated with the transition  $\text{Ge}(5s(^3\text{P}_1^0)) \rightarrow \text{Ge}(4p^2(^3\text{P}_2))$ . The pressures were:  $p(\text{GeBr}_4)$   $0.16 \text{ N m}^{-2}$ ;  $p(\text{total with He})$   $4.67 \text{ kN m}^{-2}$ ;  $p(\text{N}_2\text{O})$  ( $\text{N m}^{-2}$ ) (a) 0.0, (b) 7.8 and (c) 12.9.  $E = 980 \text{ J}$  and the time scale is  $100 \mu\text{s}$  per division for all traces, starting at  $t = 25 \mu\text{s}$ . The leading edge results from scattered light from the photolysis pulse.

Fig. 2. Typical transient recorder traces  $I_{tr}$  for the decay of  $\text{Ge}(4^3\text{P}_1)$  in the presence of  $\text{N}_2\text{O}$ , which were obtained by attenuation of the atomic resonance radiation at  $\lambda = 259.3$  nm associated with the transition  $\text{Ge}(5s(^3\text{P}_1^0)) \rightarrow \text{Ge}(4p^2(^3\text{P}_1))$ . The pressures were:  $p(\text{GeBr}_4)$   $0.16 \text{ N m}^{-2}$ ;  $p(\text{total with He})$   $4.67 \text{ kN m}^{-2}$ ;  $p(\text{N}_2\text{O})$  ( $\text{N m}^{-2}$ ) (a) 0.0, (b) 9.6 and (c) 15.2. Other information is as in Fig. 1.

## Results and discussion

Figures 1 and 2 show examples of transient recorder traces indicating the decay of resonance absorption by  $\text{Ge}(4^3\text{P}_2)$  ( $\lambda = 275.5 \text{ nm}$ ) and  $\text{Ge}(4^3\text{P}_1)$  ( $\lambda = 259.3 \text{ nm}$ ) in the presence of added nitrous oxide. A similar set of traces

was obtained for  $\text{Ge}(4^3\text{P}_0)$ . Examples of first order kinetic plots ( $\ln \{ \ln (I_0/I_{tr}) \} \propto \ln [\text{Ge}(4^3\text{P}_j)]$  versus time) derived from the data given in Figs. 1 and 2 are shown in Figs. 3(a) and 3(b), respectively. The slopes of these first order plots are given by  $-\gamma k'$ , where  $k'$  is the overall first order decay coefficient in a given experiment which may then be expressed in the form

$$k' = K + k_Q [Q] \quad (1)$$

$K$  is a constant in a series of kinetic runs in which only  $[Q]$  is varied, first order contributions to which have been described hitherto [28].  $k_Q$  is the absolute second order rate constant for the total collisional removal, *i.e.* physical quenching and chemical reaction, by the added gas  $Q$ . Figure 4 shows the variation of  $k'$  ( $\gamma k'$ ) with added nitrous oxide for the three spin orbit states in the form of eqn. (1). Similar plots were obtained for the decay of  $\text{Ge}(4^3\text{P}_{0,1,2})$  with other added gases. The data were, in fact, generally

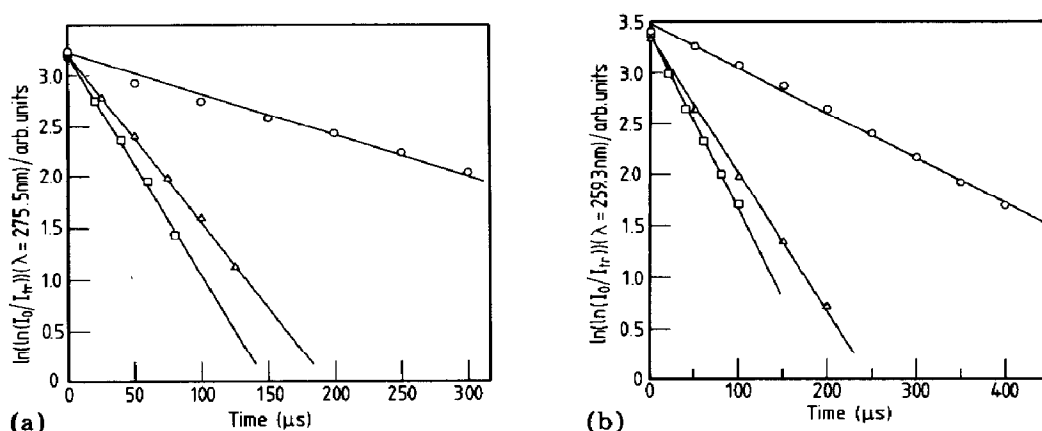


Fig. 3. Pseudo first order plots for the decay of  $\text{Ge}(4^3\text{P}_2)$  in the presence of  $\text{N}_2\text{O}$ . In (a)  $p(\text{GeBr}_4)$  was  $0.16 \text{ N m}^{-2}$ ,  $p(\text{total with He})$  was  $4.67 \text{ kN m}^{-2}$ ,  $E$  was  $980 \text{ J}$  and  $p(\text{N}_2\text{O})$  took the following values (in  $\text{N m}^{-2}$ ):  $\circ$  0.0,  $\triangle$  7.8,  $\square$  12.9. In (b)  $p(\text{GeBr}_4)$  was  $0.12 \text{ kN m}^{-2}$ ,  $p(\text{total with He})$  was  $3.47 \text{ kN m}^{-2}$ ,  $E$  was  $980 \text{ J}$  and  $p(\text{N}_2\text{O})$  took the following values (in  $\text{N m}^{-2}$ ):  $\circ$  0.0,  $\triangle$  9.6,  $\square$  15.2.

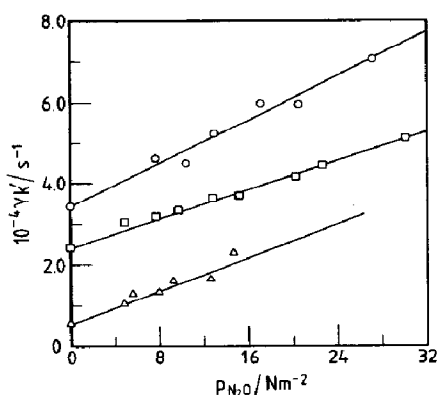


Fig. 4. Pseudo first order rate coefficients  $\gamma k'$  for the decay of  $\text{Ge}(4^3\text{P}_j)$  in the presence of  $\text{N}_2\text{O}$ :  $\circ$   $\text{Ge}(4^3\text{P}_2)$ ,  $\gamma k' + 3.0 \times 10^4 \text{ s}^{-1}$ ;  $\square$   $\text{Ge}(4^3\text{P}_1)$ ,  $\gamma k' + 2.0 \times 10^4 \text{ s}^{-1}$ ;  $\triangle$   $\text{Ge}(4^3\text{P}_0)$ .

plotted with the ordinate in the form  $\gamma(k' - K)$ . This is to allow for small variations in  $K$  which is constant in a given series but varies from batch to batch on account of the difficulty in dispensing exactly equal low pressures of  $\text{GeBr}_4$ . Since  $\text{GeBr}_4$  quenches both  $\text{Ge}(4^3\text{P}_2)$  and  $\text{Ge}(4^3\text{P}_1)$  with efficiencies approaching those of the respective collision numbers [28], small variations in  $p_{\text{GeBr}_4}$  generate differences in the intercepts of plots in the form of eqn. (1) but not, of course, in the slopes. The slopes of plots of the type shown in Fig. 4, together with the above values of  $\gamma$  (Table 2), yield the total absolute quenching constants  $k_Q$ . The resulting values for all the states,  $\text{Ge}(4^3\text{P}_{0,1,2})$ , obtained in this study and from the previous investigation are given in Table 3.

TABLE 3

Second order rate constants ( $k_Q \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 300 K) for the collisional removal of  $\text{Ge}(4^3\text{P}_2)$ ,  $\text{Ge}(4^3\text{P}_1)$  and  $\text{Ge}(4^3\text{P}_0)$  by various gases Q

Q	$4^3\text{P}_2$	$4^3\text{P}_1$	$4^3\text{P}_0$
He	$< 5 \times 10^{-15}$ [28]	$< 5 \times 10^{-16}$ [28]	$< 10^{-15}$ [28]
Xe	$< 10^{-14}$ [28]	$< 2 \times 10^{-16}$ [28]	$< 10^{-16}$ [28]
$\text{O}_2$	$1.5 \pm 0.3 \times 10^{-10}$ [28]	$1.3 \pm 0.1 \times 10^{-10}$ [28]	$1.2 \pm 0.1 \times 10^{-10}$ [28]
$\text{N}_2$	$2.4 \pm 0.1 \times 10^{-13*}$	$3.6 \pm 0.1 \times 10^{-13*}$	$2.5 \pm 0.2 \times 10^{-13*}$
CO	$3.6 \pm 0.3 \times 10^{-13}$ [28]	$4.0 \pm 0.4 \times 10^{-13}$ [28]	$3.6 \pm 0.4 \times 10^{-13}$ [28]
NO	$2.1 \pm 0.2 \times 10^{-12}$ [28]	$2.5 \pm 0.2 \times 10^{-12}$ [28]	$3.8 \pm 0.6 \times 10^{-12}$ [28]
$\text{CO}_2$	$8.0 \pm 0.2 \times 10^{-12*}$	$3.6 \pm 0.1 \times 10^{-12*}$	$6.0 \pm 0.5 \times 10^{-12*}$
$\text{N}_2\text{O}$	$9.5 \pm 0.7 \times 10^{-12*}$	$5.3 \pm 0.1 \times 10^{-12*}$	$5.8 \pm 0.8 \times 10^{-12*}$
$\text{CH}_4$	about $1.3 \times 10^{-10*}$		
$\text{CF}_4$	$2.0 \pm 0.2 \times 10^{-13*}$	$2.6 \pm 0.2 \times 10^{-13*}$	$1.5 \pm 0.1 \times 10^{-13*}$
$\text{SF}_6$	$3.7 \pm 0.6 \times 10^{-13*}$	$9.0 \pm 0.9 \times 10^{-14*}$	$1.3 \pm 0.1 \times 10^{-13*}$
$\text{C}_2\text{H}_2$	$2.5 \pm 0.2 \times 10^{-10*}$	$4.9 \pm 0.3 \times 10^{-10*}$	$2.7 \pm 0.4 \times 10^{-10*}$
$\text{C}_2\text{H}_4$	$4.3 \pm 0.2 \times 10^{-12*}$	$4.2 \pm 0.2 \times 10^{-12*}$	$8.3 \pm 0.4 \times 10^{-12*}$
$\text{GeBr}_4$	$2.1 \pm 0.2 \times 10^{-10}$ [28]	$2.9 \pm 0.3 \times 10^{-10}$ [28]	$1.5 \pm 0.1 \times 10^{-10}$ [28]

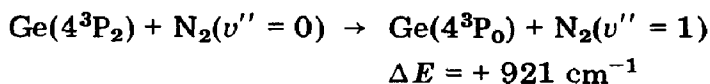
\* This work.

Before proceeding with a discussion of the individual quenching constants, we must stress two general points which have been made before [28]. Firstly, the first order plots which yield satisfactory straight lines are not sufficiently sensitive to detect growth due to any cascading from collisional quenching superimposed on the decays. The state most liable to error in the quenching data is the  $^3\text{P}_1$  state. Neither of the higher states,  $\text{Ge}(4^1\text{D}_2)$  and  $\text{Ge}(4^1\text{S}_0)$ , were detected in this type of experiment [28]. Secondly, whilst some of the values for  $k_Q$  are close in magnitude for the different spin orbit states, the kinetics do not, in general, indicate behaviour consistent with the

maintenance of a Boltzmann equilibrium between states [28]. One can show from a formal kinetic analysis given previously for  $\text{Sn}(5^3\text{P}_J)$  and  $\text{Pb}(6^3\text{P}_J)$  [17] that, on this basis, low and high pressure limits for the decay of  $\text{Ge}(4^3\text{P}_J)$  with  $[\text{Q}]$  should yield rates determined solely by the parent molecule  $\text{GeBr}_4$ . This was not generally observed in these experiments [28].

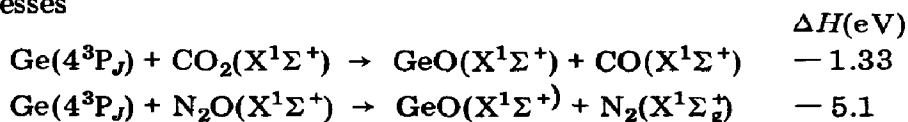
An overall comparison of the present rate data for  $\text{Ge}(4^3\text{P}_{1,2})$  (Table 3) and those obtained hitherto for the more highly energised states  $\text{Sn}(5^3\text{P}_1)$  (0.210 eV) and  $\text{Sn}(5^3\text{P}_2)$  (0.425 eV) [29] ( $1 \text{ eV} = 8068.3 \text{ cm}^{-1}$  [45]) shows that large differences in the collisional behaviour (*i.e.* a factor of about 10) for the two spin orbit states with a given quenching gas are rare and are only seen with the tin atom [16]. By contrast, very large differences (*i.e.* factors of about  $10^3 - 10^4$ ) are observed for  $\text{Pb}(6^3\text{P}_1)$  (0.969 eV) and  $\text{Pb}(6^3\text{P}_2)$  (1.320 eV) [24 - 26, 29]. The restrictive nature of reaction pathways derived from  $(J, \Omega)$  coupling will clearly become more important with increasing spin orbit coupling in the atom; this constitutes the basis of the general reason for this behaviour. The reader is referred to Table 1 of ref. 16 for a detailed presentation of the rate data for Sn and  $\text{Pb}(^3\text{P}_{1,2})$  and a discussion of quenching by those molecules whose collisional behaviour with  $\text{Ge}(4^3\text{P}_{1,2})$  is presented in this paper.

Before proceeding with a consideration, where appropriate, of the nature of the potential surfaces involved in the collision of  $\text{Ge}(4^3\text{P}_2)$  and  $\text{Ge}(4^3\text{P}_1)$ , one may note that, for most of the gases studied, near resonant E (electronic)  $\rightarrow$  V (vibrational) energy transfer can be invoked from the appropriate vibrational spectroscopic data [45, 46]. This will necessarily involve non-adiabatic transitions. As with the previous measurements on CO [28], the quenching of  $\text{Ge}(4^3\text{P}_2)$  by  $\text{N}_2$  (Table 3) is consistent with the process



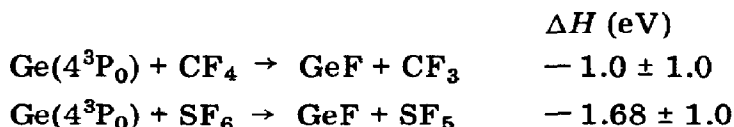
This represents a transfer probability of about 0.1 for those collisions with the energy defect in translation (T). We may also note the similar rates for the removal of the  $^3\text{P}_2$  and  $^3\text{P}_0$  states by  $\text{N}_2$  (Table 1) which could arise from the maintenance of a Boltzmann equilibrium between these two atomic levels via the above E-V exchange process. For the  $^3\text{P}_1$  level, however, as with CO [28], E  $\rightarrow$  R (rotational) or T transfer must be invoked as the energy defect for E  $\rightarrow$  V transfer ( $\Delta E = + 1774 \text{ cm}^{-1}$ ) would require a quenching constant at least a factor of 10 lower than that observed (Table 3). For the remaining molecules ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{SF}_6$ ,  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ ) inspection of the vibrational data [46] indicates that one can readily invoke near resonant E  $\rightarrow$  V transfer processes for quenching of both  $\text{Ge}(4^3\text{P}_2)$  and  $\text{Ge}(4^3\text{P}_1)$ . We feel that further speculation on this aspect would not be profitable.

As regards chemical reaction with the molecules  $\text{CO}_2$  and  $\text{N}_2\text{O}$ , the processes



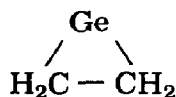
are clearly exothermic [47, 48] but spin forbidden on the basis of the weak spin orbit coupling approximation. Using ( $J, \Omega$ ) coupling and  $C_s$  symmetry in the least symmetrical complex,  $\text{Ge}(4^3\text{P}_1) + \text{CO}_2(\text{X}^1\Sigma^+(0^+))$  would, in fact, correlate with ground state products via an  $A'$  surface but  $\text{Ge}(4^3\text{P}_0)$  and  $\text{Ge}(4^3\text{P}_2)$  would only correlate with thermally inaccessible states. The same symmetry considerations will apply to  $\text{N}_2\text{O}$  except that one presumes the existence of correlations for  $\text{Ge}(4^3\text{P}_{0,1,2}) + \text{N}_2\text{O}$  to states of  $\text{GeO}$ , as yet unassigned [49], within an energy manifold of the high reaction exothermicity. In the event of a breakdown on collision both of  $C_s$  symmetry and of the weak spin orbit coupling approximation, the principal consideration will be that of energy.

With respect to the polyatomic molecules  $\text{CH}_4$ ,  $\text{CF}_4$  and  $\text{SF}_6$ , reaction with  $\text{CH}_4$  to form  $\text{GeH}$  would be endothermic ( $\Delta H = +1.3$  eV) [48, 50]. The datum for  $\text{CH}_4$  (Table 3) should be viewed with caution. The kinetics did not exhibit consistent behaviour, as was found in the earlier study using  $\text{H}_2$  [28], and may reflect the effect of a chain reaction involving bromine atoms generated on photolysis. Reaction with both  $\text{CF}_4$  and  $\text{SF}_6$  is exothermic [48, 50]:



and may well describe the removal of all the  $4^3\text{P}_J$  states. Classical flash photolysis employing absorption kinetic spectroscopy with photographic detection could partly resolve this question through observation of  $\text{GeF}$  via the strong  $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi$  system [51].

Removal of  $\text{Ge}(4^3\text{P}_J)$  by  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  (Table 3) may involve insertion, at least with  $\text{C}_2\text{H}_4$ , to form an intermediate of the type



One may note analogous reactions of carbon atoms.  $\text{C}(2^1\text{D}_2)$  certainly reacts at an efficiency close to that of gas kinetic collisions with  $\text{C}_2\text{H}_4$  ( $k \approx 3.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 300 K) [8]; CNDO calculations indicate a relatively stable singlet species [8, 52]. Early experiments on  $\text{C}(2^3\text{P}_J)$  led to a negligible reaction rate with ethylene [53] but Wolfgang *et al.* [54, 55] have observed that the insertion of  $^{11}\text{C}$  into the C—C bond in ethylene yields, amongst other products, centre-labelled allene. Clearly, the detection of germanium analogues from the present system would pose severe analytical problems.

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