

TEMPERATURE-DEPENDENT STUDIES OF THE COLLISIONAL BEHAVIOUR OF $\text{Ge}(4p^2(^3P_{0,1}))$

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Summary

The kinetic behaviour of $\text{Ge}(4p^2(^3P_0))$ and $\text{Ge}(4p^2(^3P_1))$ (557 cm^{-1}) is investigated over a wide temperature range by the method of resonance line absorption in the time-resolved single-shot mode following pulsed irradiation. Collisional removal by the molecules N_2O , CO_2 , CO and N_2 are described. A comparison of the overall first order decay coefficients for the collisional removal of $\text{Ge}(4^3P_0)$ and $\text{Ge}(4^3P_1)$ in a wide range of experiments indicates that these two close-lying spin-orbit states are in Boltzmann equilibrium throughout the kinetic decays. No strong temperature dependence of the rates was observed in the cases of N_2O and CO_2 . Removal of germanium atoms by CO and N_2 showed negative temperature rate coefficients, expressed in the Arrhenius form (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$k(^3P_1 + \text{CO}) = 1.8 \pm 1.3 \times 10^{-16} \exp\{(4.6 \pm 0.5 \text{ kcal})/RT\}$$

$$k(^3P_1 + \text{N}_2) = 4.7 \pm 2.1 \times 10^{-15} \exp\{(391 \pm 150 \text{ cal})/RT\}$$

The strong negative temperature dependence for the removal of Ge by CO is attributed to a strong chemical interaction, and this is supported by evidence from previous matrix-isolation studies on a species attributed to GeCO. It is noted that the rate expression for the removal of Ge by N_2 could equally be described by an overall temperature dependence of the form $T^{-1/2}$. Where possible, the rate data reported here are compared with the results of previous resonance line absorption studies derived from measurements on flow discharge systems.

1. Introduction

A number of investigations have been reported on the collisional behaviour of atomic germanium in specific electronic states arising from the overall $4p^2$ ground state configuration. Callear and Oldman [1] have

detected $\text{Ge}(4^3\text{P}_{0,1,2})$ and $\text{Ge}(4^1\text{D}_2)$ by kinetic absorption spectroscopy using photographic detection following flash photolysis but did not report detailed rate measurements. Husain and coworkers [2 - 4] have employed resonance line absorption in the single-shot time-resolved mode at a single temperature to study the collisional removal of $\text{Ge}(4^3\text{P}_{0,1,2})$ and $\text{Ge}(4^1\text{S}_0)$ by a wide range of gases following pulsed irradiation. However, despite the sensitivity afforded by the experimental arrangement described by Husain and Norris using repetitive pulsing, pre-trigger photomultiplier gating and signal averaging and employed for investigating rate processes undergone by all the atomic states of $\text{Si}(3\text{p}^2(^3\text{P}_{0,1,2}, ^1\text{D}_2, ^1\text{S}_0))$ [5 - 10], these authors have been unable to detect $\text{Ge}(4^1\text{D}_2)$ by resonance line absorption following photolysis [11]. More recently, Swearingen and coworkers [12, 13] have described resonance line absorption measurements on $\text{Ge}(4^3\text{P}_{0,1})$ in a flow discharge system which includes the temperature dependence of the reaction rate of atomic germanium with N_2O . In the present study we describe rate measurements of $\text{Ge}(4^3\text{P}_{0,1})$ in the presence of N_2O , CO_2 , CO and N_2 over a relatively wide temperature range using time-resolved resonance line absorption in the single-shot mode following flash photolysis. The overall fundamental background of this work falls within the general concern for the relation between electronic structure and atomic reactivity [14].

2. Experimental

The experimental arrangement was similar to that described hitherto in previous studies of $\text{Ge}(4^3\text{P}_{0,1,2})$ and $\text{Ge}(4^1\text{S}_0)$ [2 - 4] with modification to the photolysis lamp and vessel assembly for rate measurements at different temperatures and for the use of an improved data handling system. Thus, $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$ (557 cm^{-1}) [15] were generated by the pulsed irradiation of GeBr_4 [3] in the presence of excess buffer gas to ensure no significant temperature rise on photolysis. The two atomic states were then monitored photoelectrically in the single-shot mode by resonance line absorption at $\lambda = 249.8\text{ nm}$ ($5\text{s}(^1\text{P}_1^o) \leftarrow 4\text{p}^2(^3\text{P}_0)$, $gA = 2.4 \times 10^8\text{ s}^{-1}$ [16]) and $\lambda = 259.3\text{ nm}$ ($5\text{s}(^3\text{P}_2^o) \leftarrow 4\text{p}^2(^3\text{P}_1)$, $gA = 11 \times 10^8\text{ s}^{-1}$ [16]). The spectroscopic source comprised a microwave-powered atomic flow lamp as previously described [3] and the relation between the extent of resonance absorption and atomic particle density employed the modified Beer-Lambert law, $I_{\text{tr}} = I_0 \exp(-\epsilon cl)^\gamma$ [17], using the previously determined γ values ($\lambda = 249.8\text{ nm}$, $\gamma = 0.75 \pm 0.06$ and $\lambda = 259.3\text{ nm}$, $\gamma = 0.68 \pm 0.04$ [2]).

A standard arrangement of a quartz flash lamp and reaction vessel, separated by an air gap ($\lambda \gtrsim 185\text{ nm}$), as used in conventional flash photolysis and kinetic spectroscopy, was employed. The lamp and vessel assembly was heated electrically from room temperature up to about 670 K, lagged and the temperature monitored by measurement of the thermoelectric e.m.f. (copper-constantan). The temperature was controlled to $\pm 1\text{ K}$ during the course of a series of experiments using a standard eurotherm unit. The

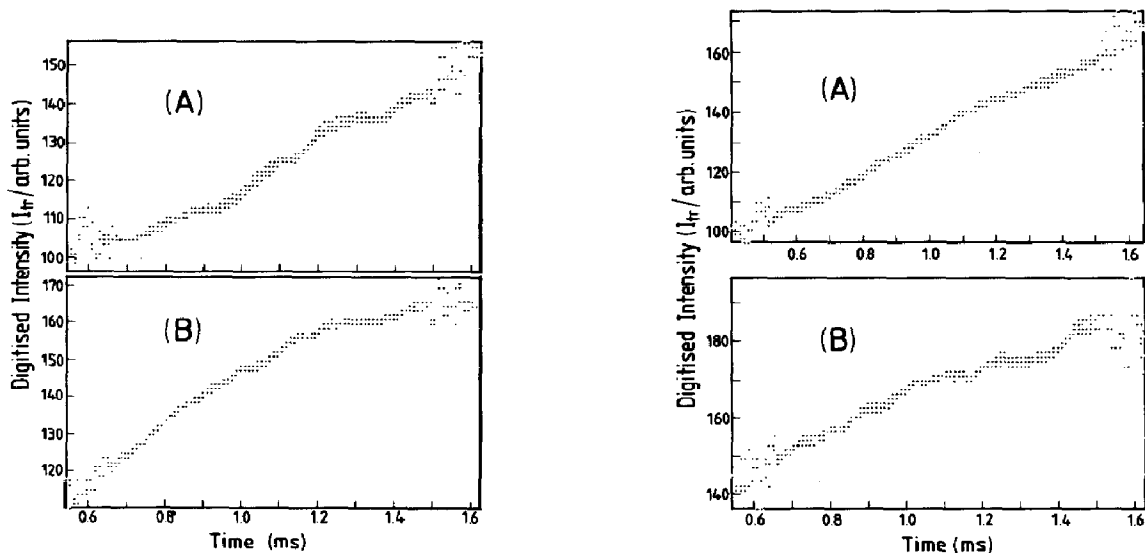


Fig. 1. Smoothed digitized time variation of the transmitted light intensity at $\lambda = 249.8$ nm ($\text{Ge}(5s(^1P_1^o)) \rightarrow \text{Ge}(4p(^3P_0))$) indicating the decay of resonance absorption by $\text{Ge}(4^3P_0)$ in the presence of N_2O : $p(\text{GeBr}_4) = 0.064 \text{ N m}^{-2}$, $p(\text{total with He}) = 5.6 \text{ kN m}^{-2}$; $E = 500 \text{ J}$; $T = 297 \text{ K}$. $p(\text{N}_2\text{O}) (\text{N m}^{-2})$: (a) 0.0; (b) 1.81.

Fig. 2. Smoothed digitized time variation of the transmitted light intensity at $\lambda = 259.3$ nm ($\text{Ge}(5s(^3P_2^o)) \rightarrow \text{Ge}(4p(^3P_1))$) indicating the decay of resonance absorption by $\text{Ge}(4^3P_1)$ in the presence of N_2O : $p(\text{GeBr}_4) = 0.064 \text{ N m}^{-2}$, $p(\text{total with He}) = 5.6 \text{ kN m}^{-2}$; $E = 500 \text{ J}$; $T = 297 \text{ K}$. $p(\text{N}_2\text{O}) (\text{N m}^{-2})$: (a) 0.0; (b) 1.81.

measurements on both states of atomic germanium with this experimental arrangement involved monitoring at lower degrees of resonance absorption than observed in similar experiments hitherto [3] on account of the necessarily smaller reaction vessel length ($l \approx 15 \text{ cm}$) required to achieve the appropriate temperature control. Hence an improved sensitivity in the detection and data handling system was required than that used previously [3].

Unlike the previous measurements on $\text{Ge}(4^3P_j)$ in which the photoelectric pulses representing resonance absorption signals following pulsed irradiation were analysed in analogue form using an XY recorder [2, 3], the present measurements involved data handling in digital form coupled with computerized analysis. Thus, following optical excitation of the resonance absorption signals (Hilger and Watts Monospek 1000 grating monochromator, photomultiplier tube E.M.I. 9783B), the photoelectric pulses were amplified without distortion [18], digitized and stored in a transient recorder (Data Laboratories DL905), and transferred onto paper tape (Data-dynamics punch 1133) in ASCII code for direct input into the University of Cambridge IBM 370 computer. The digitized decays were smoothed according to the numerical data smoothing procedure of Savitsky and Golay [19].

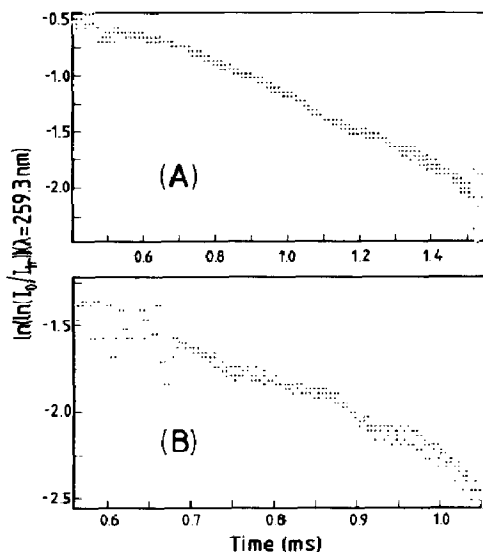
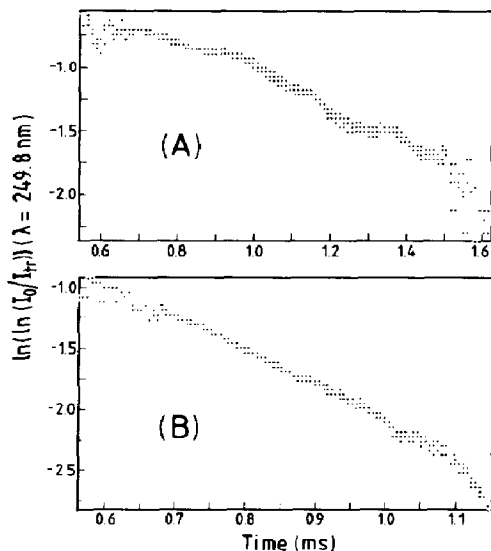


Fig. 3. Pseudo first order plots for the decay of $\text{Ge}(4^3\text{P}_0)$ obtained by monitoring the absorption of light at $\lambda = 249.8 \text{ nm}$ ($5s(^1\text{P}_1^o) \leftarrow 4p^2(^3\text{P}_0)$) in the presence of N_2O : $p(\text{GeBr}_4) = 0.064 \text{ N m}^{-2}$, $p(\text{total with He}) = 5.6 \text{ kN m}^{-2}$; $E = 500 \text{ J}$; $T = 297 \text{ K}$. $p(\text{N}_2\text{O})$ (N m^{-2}): (a) 0.0; (b) 1.81.

Fig. 4. Pseudo first order plots for the decay of $\text{Ge}(4^3\text{P}_1)$ obtained by monitoring the absorption of light at $\lambda = 259.3 \text{ nm}$ ($5s(^3\text{P}_2^o) \leftarrow 4p^2(^3\text{P}_1)$) in the presence of N_2O : $p(\text{GeBr}_4) = 0.064 \text{ N m}^{-2}$, $p(\text{total with He}) = 5.6 \text{ kN m}^{-2}$; $E = 500 \text{ J}$; $T = 297 \text{ K}$. $p(\text{N}_2\text{O})$ (N m^{-2}): (a) 0.0; (b) 1.81.

2.1. Materials

All materials (GeBr_4 , He, Kr (for the photoflash lamp), N_2 , CO, N_2O and CO_2) were prepared essentially as described in previous publications [2, 3].

3. Results and discussion

Figure 1(a) gives an example of the computerized output, following smoothing [19], of the digitized time variation of the transmitted light intensity at $\lambda = 249.8 \text{ nm}$ indicating the decay of resonance absorption by $\text{Ge}(4^3\text{P}_0)$ following the pulsed irradiation of GeBr_4 . Figure 1(b) shows the effect of the addition of a quantity of N_2O . Figure 2 shows examples of analogous results for $\text{Ge}(4^3\text{P}_1)$ obtained by monitoring of the $\lambda = 259.3 \text{ nm}$ transition. The computerized forms of the first order kinetic plots for the two atomic states, derived from the data of Figs. 1 and 2, are shown respectively in Figs. 3 and 4. The first order plots clearly indicate some scatter, but the least squares errors from the computerized analyses show that in general these lie in the range 1 - 2%. Following the use of the modified Beer-Lambert law [17] (see Section 2), the slopes of the plots of $\ln\{\ln(I_0/I_{tr})\}$ against time

TABLE 1

Second order rate constants k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the collisional removal of $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$ by N_2O

$\text{Ge}(4^3\text{P}_0)$	$\text{Ge}(4^3\text{P}_1)$
$5.7 \pm 0.6 \times 10^{-12}$ (297 K) ^a	$3.6 \pm 0.6 \times 10^{-12}$ (297 K) ^a
$5.8 \pm 0.8 \times 10^{-12}$ (300 K) [3] ^b	$5.3 \pm 0.1 \times 10^{-12}$ (300 K) [3] ^b
$9.9 \pm 0.9 \times 10^{-12}$ (300 K) [20] ^b	
$6.7 \pm 2.5 \times 10^{-13}$ (300 K) [12] ^c	
$1.2 \pm 0.6 \times 10^{-12}$ (350 K) [13] ^c	$1.3 \pm 0.6 \times 10^{-12}$ (350 K) [13] ^c
$4.2 \pm 1 \times 10^{-12}$ (350 K) [21] ^c	$8.4 \pm 3 \times 10^{-12}$ (350 K) [21] ^c

^aThis work.

^bFlash photolysis with resonance line absorption.

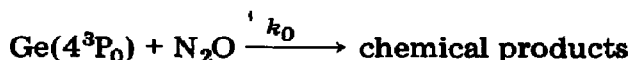
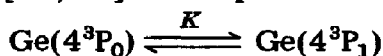
^cFlow discharge system with resonance line absorption

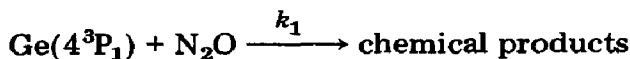
are given by $-\gamma k'$, where k' is the overall first order decay coefficient for the given electronic state in a particular experiment. Hence the slopes of the plots of the type given in Figs. 3 and 4, coupled with the γ values given earlier (see Section 2), yield the values of k' for $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$. We have previously given plots of the linear variation of k' for $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$ with the pressure of added N_2O [3] and do not repeat such plots here. These linear variations are expressed in the form

$$k' = K + k_R [R] \quad (\text{I})$$

which in turn yields the absolute second order rate constants for the collisional removal of $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$ by an added gas R, in this particular case N_2O .

Table 1 gives the second order rate constants at $T = 300 \text{ K}$ and $T = 350 \text{ K}$ that have been reported for the collisional removal of $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$ by N_2O obtained by resonance line absorption coupled with (a) flash photolysis and (b) a flow discharge system. For a given temperature of 300 K, the weight of results (Table 1) indicates that the value for $k(4^3\text{P}_0 + \text{N}_2\text{O})$ obtained from a flow discharge system [12] is rather low. This may possibly result from the effects of atomic reformation arising from species in the discharge. Inspection of the data in Table 1 shows that, for a given experimental method, the rate constants reported for removal of the two atomic states by N_2O are essentially equal. This is in accord with the maintenance of a Boltzmann equilibrium between $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$ (557 cm^{-1} [15]) during kinetic measurements which could be expected simply in terms of the relatively small amount of electronic energy to be transferred on collision [22, 23]. A simple mechanism of the type





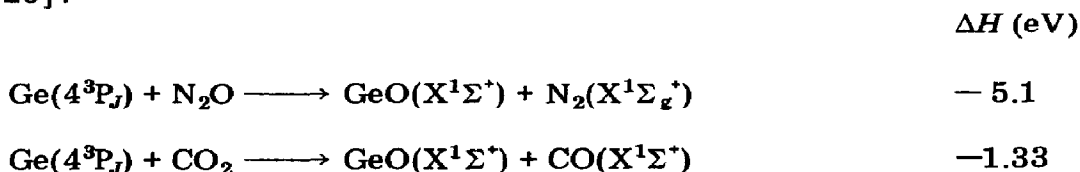
clearly generates an equality in "apparent" second order rate constants and first order decay coefficients, namely

$$\begin{aligned} -\frac{d \ln\{\text{Ge}(4^3\text{P}_0)\}}{dt} &= -\frac{d \ln\{\text{Ge}(4^3\text{P}_1)\}}{dt} \\ &= \frac{k_0 + k_1 K}{1 + K} [\text{N}_2\text{O}] \\ &= k' \end{aligned}$$

The apparent second order rate constants for reaction of either atomic state is thus given by $(k_0 + k_1 K)/(1 + K)$. Of course such a mechanism does not preclude the participation by N_2O in the collisional establishment of the Boltzmann equilibrium. k_0 and k_1 simply refer to rate constants for the chemical channels. Hence, in any experiment, the overall first order decay coefficients k' for either atomic state should be equal.

We have studied the first order rate coefficients for the $^3\text{P}_0$ and $^3\text{P}_1$ states over the temperature range $T = 295 - 470$ K in order to investigate whether either of the fundamental rate constants k_0 or k_1 could be so altered by the effect of temperature as to disturb significantly the equilibrium. The variation of the two measured first order rate coefficients k' for each atomic state, for various experimental conditions and at various temperatures is shown in Fig. 5. The data are scattered but the slope of the resulting plot of k' (for $^3\text{P}_0$) against k' (for $^3\text{P}_1$) (γ corrected) is given by 1.09 ± 0.34 , showing that the quality is not sensibly disturbed. A similar result is shown in Fig. 6 for CO_2 (slope, 1.01 ± 0.35). In chemical terms one would not expect a large difference in the reactivities of $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$ once a physical equilibrium has been established following spin-orbit relaxation of the $^3\text{P}_1$ state. Hence, assuming $k_0 = k_1$, monitoring of either the $^3\text{P}_1$ or $^3\text{P}_0$ states will yield rate data for the effectively degenerate level $\text{Ge}(4^3\text{P}_{0,1})$. Indeed, the equality in the apparent second order rate constants for the collisional removal of $\text{Ge}(4^3\text{P}_{0,1,2})$ ($^3\text{P}_2$, 1410 cm^{-1} [15]) by a number of gases [2, 3] indicates that monitoring of any of the three spin-orbit levels yields rate data for $\text{Ge}(4^3\text{P}_j)$. Clearly, study of any significant differences in the collisional rate data for the individual spin-orbit levels would require investigation at shorter time domains before the establishment of the Boltzmann equilibrium.

Reaction of atomic germanium with N_2O and CO_2 is exothermic [24, 25]:



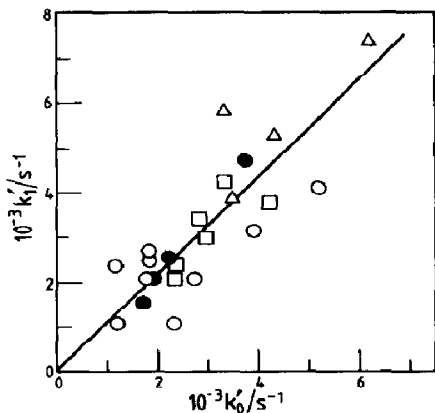


Fig. 5. Plot of the pseudo first order rate coefficient for the collisional removal of $\text{Ge}(4^3\text{P}_1)$ by N_2O (k'_1) against that for $\text{Ge}(4^3\text{P}_0)$ (k'_0) at various temperatures $T(\text{K})$: \circ , 297; \square , 327; \triangle , 408; \bullet , 466.

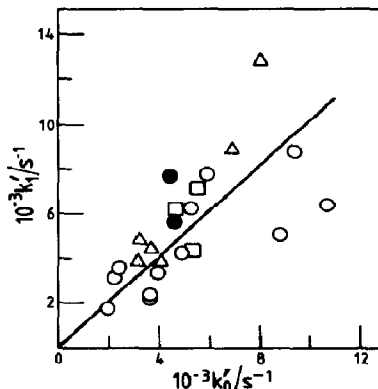


Fig. 6. Plot of the pseudo first-order rate coefficient for the collisional removal of $\text{Ge}(4^3\text{P}_1)$ by CO_2 (k'_1) against that for $\text{Ge}(4^3\text{P}_0)$ (k'_0) at various temperatures $T(\text{K})$: \circ , 297; \triangle , 339; \square , 417; \bullet , 468.

the former reaction is particularly so. Indeed, $\text{GeO}(a^3\Sigma^+ - X^1\Sigma^+)$ emission has been observed from a flow discharge containing $\text{Ge} + \text{N}_2\text{O}$ [26, 27]. The feasibility of creating a population inversion between the $a^3\Sigma^+$ and $X^1\Sigma^+$ states from the above reaction, given the optical metastability of the former state resulting from the spin selection rule, is an attractive proposition and, in part at least, is a practical impetus to the study of this reaction. We have investigated the temperature dependence of the reaction of $\text{Ge}(4^3\text{P}_0)$ with N_2O up to $T = 580$ K. The flow tube experiments of Swearingen and coworkers [12, 13] on the rate of this overall reaction were performed at two temperatures, 300 and 350 K, in separate studies (Table 1), and, whilst this indicated a small positive temperature coefficient, the two measured rates overlapped within the error limits ($k = 6.7 \pm 2.5 \times 10^{-13}$ (300 K) and $1.2 \pm 0.6 \times 10^{-12}$ (350 K) $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [12, 13]). We confirm the lack of any significant temperature dependence in the reaction rate up to $T \approx 580$ K (Fig. 7). The values of $k(^3\text{P}_0 + \text{N}_2\text{O})$ at given temperatures were

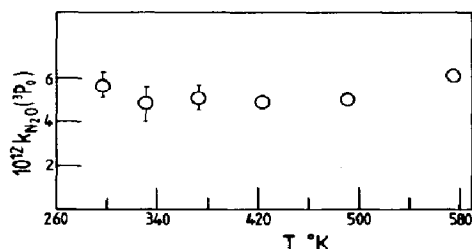


Fig. 7. Variation of the second order rate constant ($k(\text{N}_2\text{O})(^3\text{P}_0)$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)) for the collisional removal of $\text{Ge}(4^3\text{P}_0)$ by N_2O at various temperatures.

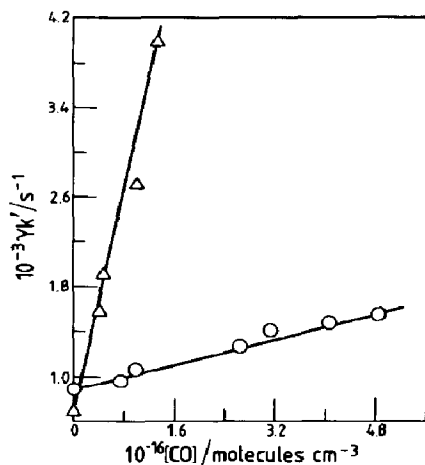


Fig. 8. Plots of the variation of the pseudo first order rate coefficients ($\gamma k'$) for the collisional removal of $\text{Ge}(4^3\text{P}_1)$ by CO at different temperatures T K: Δ , 296 \circ , 478.

obtained taking full account of Charles law corrections in the calculation of $[\text{N}_2\text{O}]$. Similar experiments on the reaction rate determination of $\text{Ge}(4^3\text{P}_0) + \text{CO}_2$ were unsuccessful. We were unable to obtain a consistent trend in the overall effective reaction rate constant with temperature for this species. The absence of a significant energy barrier in the reaction of $\text{Ge}(4^3\text{P}_j) + \text{N}_2\text{O}$, as seen both from this work and the flow tube experiments [12, 13], is somewhat surprising as atom-molecule reactions involving N_2O or CO_2 , including those that are highly exothermic, are generally characterized by large energy barriers [28, 29]. This is normally attributed to the effect of the closed shell 18-electron structures of these two linear molecules.

Previous measurements at $T = 300$ K on the collisional removal of $\text{Ge}(4^3\text{P}_0)$ and $\text{Ge}(4^3\text{P}_1)$ by CO and N_2 [2, 3] indicate rate constants sufficiently close in magnitude to employ a Boltzmann equilibrium between the two spin-orbit states during kinetic decays (CO: $k(^3\text{P}_0) = 3.6 \pm 0.4 \times 10^{-13}$, $k(^3\text{P}_1) = 4.0 \pm 0.4 \times 10^{-13}$ [2]; N_2 : $k(^3\text{P}_0) = 2.5 \pm 0.2 \times 10^{-13}$, $k(^3\text{P}_1) = 3.6 \pm 0.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [3]). The decay of $\text{Ge}(4^3\text{P}_1)$ by CO and N_2 was investigated over a wide temperature range. The removal of $\text{Ge}(4^3\text{P}_1)$ by CO shows a strong negative temperature dependence on reaction rate as illustrated, for example, by the variation of $k'(^3\text{P}_1)$ with $[\text{CO}]$ at temperatures of 296 and 479 K (Fig. 8). The Arrhenius plots expressing the temperature dependence in terms of the collisional removal of $\text{Ge}(4^3\text{P}_1)$ by CO and N_2 are shown in Figs. 9 and 10 respectively. Both plots yield apparent "negative activation energies", namely (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

$$k(^3\text{P}_1 + \text{CO}) = (1.8 \pm 1.3) \times 10^{-16} \exp\left(\frac{4.6 \pm 0.5 \text{ kcal}}{RT}\right)$$

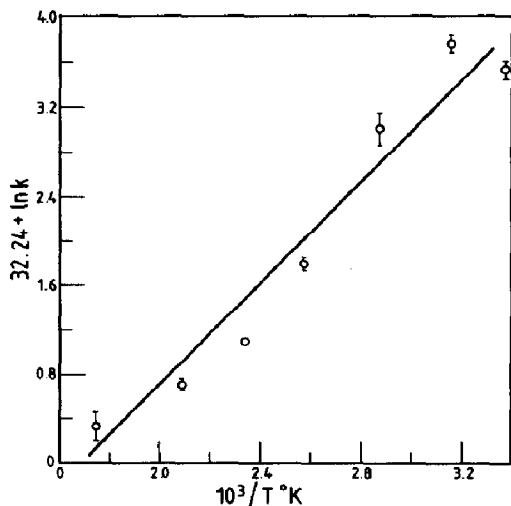


Fig. 9. Arrhenius plot for the rate constant k for the collisional removal of $\text{Ge}(4^3\text{P}_1)$ by CO.

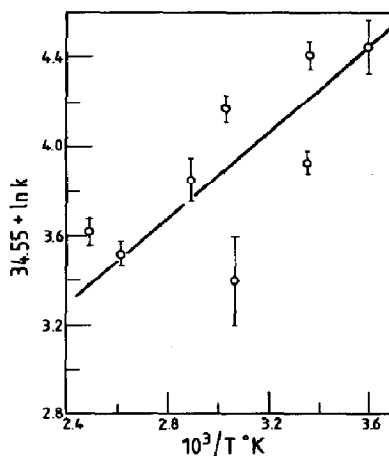


Fig. 10. Arrhenius plot for the rate constant k for the collisional removal of $\text{Ge}(4^3\text{P}_1)$ by N_2 .

$$k(4^3\text{P}_1 + \text{N}_2) = (4.7 \pm 2.1) \times 10^{-15} \exp\left(\frac{391 \pm 150 \text{ cal}}{RT}\right)$$

(1 cal = 4.3363×10^{-5} eV molecule⁻¹)

The magnitude of the positive exponent in the rate expression for $\text{Ge}(4^3\text{P}_1) + \text{CO}$, representing a strong interaction between these two colliding species, is in accord with previous work on matrix-isolation studies of species resulting from the co-codensation at 20 K of Ge atoms, evaporated from a Knudsen cell, with CO in krypton [30]. The observed IR peak at 1908 cm^{-1} is attributed to the species GeCO , analogous to CCO [31]. The positive exponent in the rate expression for $\text{Ge}(4^3\text{P}_1) + \text{N}_2$, by contrast, is small and could equally be accounted for by an overall temperature dependence of the order of $T^{-1/2}$.

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