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Collisional quenching of electronically excited germanium atoms, Ge[$4p^2(^1S_0)$], by small molecules investigated by time-resolved atomic resonance absorption spectroscopy

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Abstract

The collisional quenching of electronically excited germanium atoms, Ge[$4p^2(^1S_0)$], 2.029 eV above the $4p^2(^3P_0)$ ground state, has been investigated by time-resolved atomic resonance absorption spectroscopy in the ultraviolet at $\lambda = 274.04$ nm [$4d(^1P_1^\circ) \leftarrow 4p^2(^1S_0)$]. In contrast to previous investigations using the 'single-shot mode' at high energy, Ge($^1S_0$) has been generated by the repetitive pulsed irradiation of $Ge(CH_3)_4$ in the presence of excess helium gas and added gases in a slow flow system, kinetically equivalent to a static system. This technique was originally developed for the study of Ge[$4p^2(^1D_2)$] which had eluded direct quantitative kinetic study until recently. Absolute second-order rate constants obtained using signal averaging techniques from data capture of total digitised atomic decay profiles are reported for the removal of Ge($^1S_0$) with the following gases (k_R in cm^3 molecule^{-1} s^{-1}, 300 K): Xe, $7.1 \pm 0.4 \times 10^{-13}$; N_2, $4.7 \pm 0.6 \times 10^{-12}$; O_2, $3.6 \pm 0.9 \times 10^{-11}$; NO, $1.5 \pm 0.3 \times 10^{-11}$; CO, $3.4 \pm 0.5 \times 10^{-12}$; N_2O, $4.5 \pm 0.5 \times 10^{-12}$; CO_2, $1.1 \pm 0.3 \times 10^{-11}$; CH_4, $1.7 \pm 0.2 \times 10^{-11}$; CF_4, $4.8 \pm 0.3 \times 10^{-12}$; SF_6, $9.5 \pm 1.0 \times 10^{-13}$; C_2H_4, $3.3 \pm 0.1 \times 10^{-10}$; C_2H_2, $2.9 \pm 0.2 \times 10^{-10}$; $Ge(CH_3)_4$, $5.4 \pm 0.2 \times 10^{-11}$. The results are compared with previous data for Ge($^1S_0$) derived in the single-shot mode where there is general agreement though with some exceptions which are discussed. The present data are also compared with analogous quenching rate data for the collisional removal of the lower lying Ge[$4p^2(^1D_2)$] state (0.883 eV), also characterised by signal averaging methods similar to that described here. © 1997 Elsevier Science S.A.

Keywords: Ge atoms; Electronically excited; Collisional quenching; Time-resolved atomic absorption

1. Introduction

Absolute rate data are now available on the collisional behaviour of atomic germanium in all the low lying states arising from the overall $4p^2$ ground state configuration within the chemistry framework of Group IV atom. The experimental objective of such work is to elucidate the atomic reactivity of all states arising from the np^2 ground state electronic configuration ($^3P_{0,1,2}$, $^1D_2$, $^1S_0$) where the $^1D_2$ and $^1S_0$ states are optically metastable. One general approach for considering such data, apart from the detailed construction of potential surfaces in each case, is to employ symmetry arguments on the nature of the potential surfaces involved on collision using the weak spin–orbit coupling approximation for the light atoms [1] and (J,Ω) coupling for heavy atom collisions [2]. Indeed, this latter approach is still required when considering the collisional behaviour of atomic germanium in specific spin–orbit states within the ^3P_J manifold even though the splittings are relatively small [3] and for which rate data have been reported with a range of added gases [4–12]. In fact, such studies indicate that Boltzmann equilibrium in Ge(^3P_J) is normally maintained in bulk kinetic measurements. In recent years, we have developed a time-resolved resonance absorption method to study the kinetic behaviour of Ge[$4p^2(^1D_2)$], 0.883 eV above the $^3P_0$ electronic ground state [3] using signal averaging techniques [13–16] and yielding a wide body of absolute collisional rate data. Indeed, direct kinetic studies on this state had not been feasible hitherto. The collisional behaviour of Ge[$4p^2(^1S_0)$], 2.029 eV above the $4p^2(^3P_0)$ ground state, with a range of simple molecules has been reported using time-resolved atomic resonance absorption spectroscopy at high energy in the single-shot mode [17]. Consideration of these various studies on Ge($4^3P_{0,1,2}$, $^1D_2$, $^1S_0$) indicated that, in terms of such symmetry arguments, germanium falls between the two extreme coupling cases of the weak spin–orbit coupling approxima-

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tion and (J,Ω) coupling, where the latter was found to be of limited application as this type of coupling does not often lead to strongly restricted pathways [2].

Symmetry arguments on the collisional behaviour of these low lying states of atomic germanium have been addressed in the kinetic studies indicated above. In this paper, we extend the method developed for the study of Ge[$4p^2(^1D_2)$] using signal averaging methods [15,16,18–20], with some further modifications, especially in data capture and analysis, to the kinetic investigation of Ge[$4p^2(^1S_0)$]. Ge($^1S_0$) has thus been generated photochemically by the low energy repetitive pulsed irradiation from a germanium-containing precursor at low energy on a slow flow system and monitored by time-resolved atomic resonance absorption spectroscopy with signal averaging. The advantages of this method are described. Absolute rate constants are reported for collisional quenching of the $^1S_0$ state with a wide range of simple gases and the results compared with previous kinetic data for Ge($^1S_0$) obtained in the single-shot mode [17]. Whilst the results are similar, quantitative differences are seen to arise and, in some cases, qualitative differences have been found and are discussed in terms of the single-shot mode and signal averaged methods. The present results are also compared with analogous quenching data for the lower lying $^1D_2$ state.

2. Experimental

The experimental method is a variant of that employed for the time-resolved atomic resonance absorption spectroscopic technique developed initially for the study of Ge(4^1D_2) [13–16]. Ge(4^1S_0) was generated from the repetitive pulsed photolysis of $Ge(CH_3)_4$ in the presence of excess helium buffer gas ($p_{He}:p_{GeMe_4}$: ca. 3000:1) using a coaxial lamp and vessel assembly with a common wall of high purity quartz ('Spectrosil', $\lambda > 160$ nm). This type of reactor was employed hitherto for the kinetic study of Ge(4^1S_0) where the excited atom was derived from the higher energy pulsed initiation of $Ge(CH_3)_4$ ($E = 1225$ J) with spectroscopic monitoring in the single-shot mode [17]. Lower pulse energies ($E = 88$ J), minimising the effect of secondary products from photolysis, are employed in the present investigation with monitoring at shorter decay times using signal averaging to improve the signal-to-noise ratio. As with the investigation on Ge($^1D_2$), this is a slow flow system, kinetically equivalent to a static system [15,16]. Repetitive pulsing was effected by means of thyratron pulser (0.1 Hz) and the resulting Ge(4^1S_0) monitored in absorption using an atomic emission resonance source at $\lambda = 274.04$ nm [$4d(^1P^\circ_1) - 4p^2(^1S_0)$, $gA = 2.4 \times 10^9$ s^{-1}] [21]. This was derived from a microwave-powered discharge (E.M.S. Microwave Generator, 'Microtron 200', incident power = ca. 100 W) through a flow of ca. 1% $GeCl_4$ in He ($p_{total} = 133$ N m^{-2}) as hitherto in the study of Ge(4^1D_2) [13,14]. The resonance transition was optically isolated using a small grating monochromator (Grubb Parsons, type M2) onto whose exit slit a high gain photomultiplier tube (E.M.I. 9816QB) was mounted and where quartz optics were used throughout.

The resulting photoelectric signal at $\lambda = 274.04$ nm representing resonance absorption by Ge(4^1S_0) was amplified without distortion using a current-to-voltage converter [22] prior to transfer to the data handling and analysis system. Unlike the kinetic studies on Ge(4^1D_2) [13,14], the data analysis system has been modified to replace the combination of a transient recorder and a BBC computer, which effectively analyses as a computerised boxcar integrator, by a system which captures the complete decay profiles. Thus, decay profiles were captured with a 'Digital Storage Adaptor' (Thurlby DSA 524) interfaced to a computer, triggered by the thyratron pulser operating at 0.1 Hz. The DSA is effectively a transient digitiser which is capable of a resolution of 50 ns but this is not required in the present measurements. This unit is capable of capturing 255 decay profiles but normally 16 profiles are used as this represents a physical limit to the consistent operation of the pulsing flash lamp system. This technique requires a separate computer programme for both recording the unattenuated signal at $\lambda = 274.04$ nm, I_0, prior to the capture of the absorption signal, and the subsequent capture of the decay trace, I_{tr}, as a function of time. The resonance absorption signals were analysed using the standard Beer–Lambert law, $I_{tr}(274\,\text{nm}) = I_0\exp(-\epsilon cl)$, where the symbols have their usual meaning and not a modified form [17] and where $c = [Ge(4^1S_0)]_t$. This is combined with the first-order decay of the $^1S_0$ atom:

$$[Ge(4^1S_0)]_t = [Ge(4^1S_0)]_{t=0}\exp(-k't) \qquad (1)$$

and hence a plot of ln [ln (I_0/I_{tr})] versus time yields a straight line of slope k', the overall first-order decay coefficient of the atom which is the object of the profile analysis and from which the appropriate collisional rate data are subsequently obtained.

2.1. Materials

$Ge(CH_3)_4$ was prepared by the reaction of the Grignard reagent, CH_3MgBr, with $GeCl_4$ as described by Parry [23]. The $Ge(CH_3)_4$ was always subjected to many freeze–pump–thaw cycles and fractional distillation from −80°C (CO_2 + acetylene slush) to −196°C (liquid nitrogen) before use with each set of kinetic experiments. All other materials were prepared essentially as given in earlier paper (He, Xe, Kr, N_2, O_2, NO, CO, N_2O, CO_2, CH_4, CF_4, SF_6, C_2H_4 and C_2H_2) [24–26].

3. Results and discussion

Following an earlier procedure described for the kinetic study of Ge(4^1D_2) [15,16] and also C(2^3P_J) in the vacuum ultraviolet [18–20], a single flow of a mixture of fixed fractional composition of the photochemical precursor of Ge(4^1S_0) and the added reactant in excess helium buffer gas is employed for all rate measurements rather than the combination of three separate calibrated mass flows. Measurements were carried out at varying total pressures (p_T) of this single flow of constant relative composition in which the diffusional loss term, whose functional form is clear, i.e. $\propto 1/p_T$, is permitted to vary but which can be quantified in principle. Of course, the initial photochemical yields of $Ge(4^1S_0)$ from the precursor $Ge(CH_3)_4$ also vary at different total pressures but the first-order kinetic decays only require a knowledge of relative atomic densities as a function of time. The procedure adopted for measuring the absolute second-order rate constant for the collisional removal of $Ge(4^1S_0)$ by $Ge(CH_3)_4$ itself was thus to prepare a dilute mixture of $Ge(CH_3)_4$ in He of fixed composition ($f=[Ge(CH_3)_4]/([Ge(CH_3)_4]+[He])=4.0\times10^{-4}$) and to monitor the decay of $Ge(4^1S_0)$ following the repetitive pulsed irradiation of different total pressures in the flow. The value of f was governed by both the lower pressures of $Ge(CH_3)_4$ which yield initial atomic concentrations that can be studied in absorption, on the one hand, and the time-scale over which atomic germanium be monitored at higher pressures due to rapid loss by collisional removal. This procedure, including measurements with added reactant gases, themselves of defined fractional composition, avoids the onerous and difficult procedure of controlling the three separate flows at constant total pressure to keep the diffusional loss term constant, which is small, and at a constant low concentration of $Ge(CH_3)_4$ with varying reactant concentration.

Fig. 1 gives examples of first-order decay profiles for $Ge(4^1S_0)$ taken for two different total pressures for a mixture of $Ge(CH_3)_4$ of $f=4.0\times10^{-4}$ in He by time-resonance absorption in the ultraviolet at $\lambda=274.04$ nm $\{Ge[4d(^1P^o_1)\leftarrow4p^2(^1S_0)]\}$ with signal averaging. We may note immediately that the decay profiles, indicating initial resonance absorption of ca. 10%, may be monitored over time scales a factor of ca. three greater than those employed at high energy in the single-shot mode [17]. The slopes of these plots thus yield the first-order decay coefficients for the removal of $Ge(4^1S_0)$. The overall first-order decay coefficient for the removal of $Ge(4^1S_0)$ in this case can be expressed as the sum of two terms, namely that due to diffusion and chemical reaction. In the units of pressure, this can be expressed as:

$$k'=\beta/p_T+k_R f p_T \tag{2}$$

which can be recast as:

$$k'p_T=\beta+k_R f p_T^2 \tag{3}$$

where k_R ($=k_1$, see later) is the absolute second-order rate constant for the collisional removal of $Ge(4^1S_0)$ by $Ge(CH_3)_4$. In theory, the diffusional loss term, β/p_T, could be expressed in terms of the 'long-time solution' of the diffusion equation for a cylinder (length 1, radius r, where $1\gg r=1$ cm) [27,28]. In practice this term is very small compared with collisional loss and the diffusion coefficient of $Ge(4^1S_0)$ in He, D_{12}, cannot be quantified with any accuracy from the relevant kinetic plots (see later). Fig. 2(a) shows the plot for the removal of $Ge(4^1S_0)$ by $Ge(CH_3)_4$ based on Eq. (3) which, from the slope of $k_R f$ (correlation coefficient = 0.9919) and the appropriate value of f, yields $k_R=5.2\pm0.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (300 K). Fig. 2(b) shows an analogous plot (correlation coefficient = 0.9985) to that given in Fig. 2(a) (for $f=2.0\times10^{-4}$) yielding $k_R=5.6\pm0.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (300 K) from which we take the average value of $5.4\pm0.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (300 K). As can be seen from Table 1, the previous value for the second-rate constant for the removal of $Ge(4^1S_0)$ by $Ge(CH_3)_4$ from measurements with the single-shot mode was found to be very large, namely $k_R=8.0\times10^{-10}$ cm^3 molecule^{-1} s^{-1} [17].

In the presence of an added gas, such as O_2, the overall first-order decay coefficient for the removal of $Ge(4^1S_0)$ can be expressed as the sum of three terms, namely that due to diffusion and to collisional quenching by the precursor,

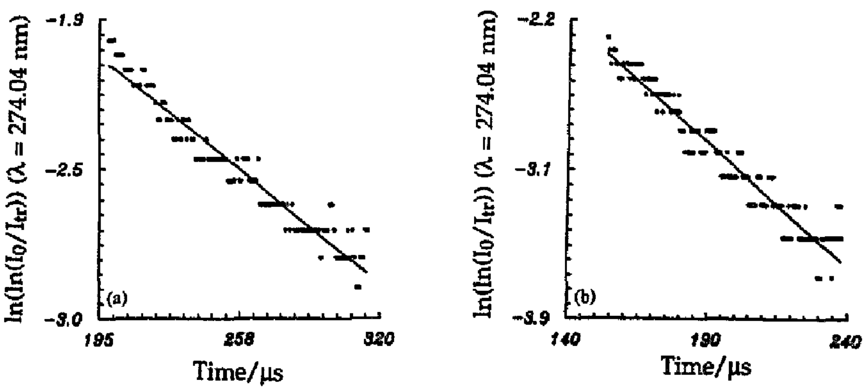

Fig. 1. Examples of computerised fitting indicating the first-order kinetic decay of $Ge[4p^2(^1S_0)]$ obtained by time-resolved atomic resonance absorption spectroscopy in the ultraviolet $\{\lambda=274.04$ nm, $Ge[4d(^1P_1^o)\leftarrow4p^2(^1S_0)]\}$ following the repetitively pulsed irradiation of $Ge(CH_3)_4$ in the presence of excess helium buffer gas. $f=[Ge(CH_3)_4]/([Ge(CH_3)_4]+[He])=4.0\times10^{-4}$; $E=88$ J; repetition rate = 0.1 Hz; No. of experiments for averaging = 16; p_{Total} (Torr): (a) 6.0; (b) 18.0.

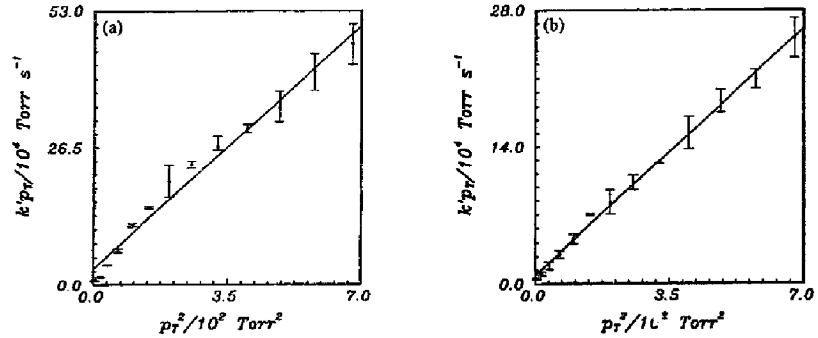

Fig. 2. Variation of the pseudo-first-order rate coefficient (k') for the decay of Ge(4^1S_0) obtained by time-resolved atomic resonance absorption spectroscopy in the ultraviolet ($\lambda = 274.04$ nm, Ge[4d($^1P_1^o$) ← 4p^2($^1S_0$)]) following the repetitively pulsed irradiation of $Ge(CH_3)_4$ in the presence of excess helium buffer gas. $k'p_T$ versus p_T^2; $T = 300$ K; $f = [Ge(CH_3)_4]/([Ge(CH_3)_4] + [He])$: (a) $f = 4.0 \times 10^{-4}$; (b) $f = 2.0 \times 10^{-4}$.

$Ge(CH_3)_4$, and the added reactant. Thus the characterisation of the absolute second-order rate constant for the collisional quenching of Ge(4^1S_0) with oxygen, for example, involved the preparation of a mixture of fixed composition of the form $f_1 = [Ge(CH_3)_4]/([Ge(CH_3)_4] + [O_2] + [He])$, $f_2 = [O_2]/([Ge(CH_3)_4] + [O_2] + [He])$. Hence, in this case, the measured first-order rate coefficient (k') can then be written as:

$$k' = \beta/p_T + k_1 f_1 p_T + k_2 f_2 p_T \qquad (4)$$

where k_1 and k_2 represent the absolute second-order rate constants for the collisional removal of Ge(4^1S_0) by $Ge(CH_3)_4$ and O_2, respectively, in appropriate units involving pressure. k' is measured from slopes of first-order plots of the type given in Fig. 3 with O_2 as the added quenching gas for $f_1 = 4.0 \times 10^{-4}$ and $f_2 = 5.0 \times 10^{-5}$ for two different total pressures, p_T. Eq. (4) can thus be recast in the form:

$$k'p_T = \beta + (k_1 f_1 + k_2 f_2) p_T^2 \qquad (5)$$

In the special case, of $f_1 = f_2 = f$, Eq. (5) becomes

$$k'p_T = \beta + (k_1 + k_2) f p_T^2 \qquad (6)$$

Fig. 4(c) shows the plots for the decay of Ge(4^1S_0) in the presence of O_2 based on Eq. (5), the slope of which, coupled with the values of k_1 (above), f_1 and f_2 yields k_2(300 K) = $3.6 \pm 0.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Fig. 4(a), 4(b) and 4(d) give the analogous plots based on Eq. (5) for the removal of Ge(4^1S_0) with N_2, Xe and NO. Correlation coefficients for Fig. 4(a)–4(d) were found to be 0.9856, 0.9947, 0.9912 and 0.9909, respectively. The resulting rate constants for quenching of Ge(4^1S_0) by N_2, Xe, O_2 and NO are given in Table 1.

One may also see that the intercepts (β) based on Eq. (5) are small in comparison to the magnitudes of the ordinates of such plots (Fig. 4) and that diffusional loss is small in this type of system, dominated by collisional quenching. This can be seen by estimates of β through the long-time solution for the diffusion equation for a cylinder based on the geometry of the reactor and a sensible estimate of D_{12}(Ge(4^1S_0)–He). Following the earlier analogous procedure for C(2^3P_J) [29]

Table 1

Absolute second-order rate constants (k_R(300 K) in cm^3 molecule^{-1} s^{-1}) for the collisional quenching of Ge[4p^2($^1S_0$)] (2.029 eV) by small molecules (R) determined by pulsed irradiation coupled with time-resolved atomic resonance absorption spectroscopy using signal averaging methods and the 'single-shot mode' and comparison with analogous data quenching of Ge[4p^2($^1D_2$)] (0.883 eV)

R	Ge($^1S_0$)	Ge($^1S_0$)	Ge($^1D_2$)
Xe	$(7.1 \pm 0.4) \times 10^{-13}$ [a]	1.8×10^{-11} [17]	$(2.0 \pm 0.1) \times 10^{-12}$ [13]
N_2	$(4.7 \pm 0.6) \times 10^{-12}$ [a]	1.8×10^{-12} [17]	$(5.9 \pm 0.3) \times 10^{-12}$ [14]
O_2	$(3.6 \pm 0.9) \times 10^{-11}$ [a]	4.2×10^{-11} [17]	$(2.5 \pm 0.1) \times 10^{-10}$ [14]
NO	$(1.5 \pm 0.3) \times 10^{-11}$ [a]	2.0×10^{-11} [17]	$(9.0 \pm 0.5) \times 10^{-11}$ [14]
CO	$(3.4 \pm 0.5) \times 10^{-12}$ [a]	1.8×10^{-12} [17]	$(1.8 \pm 0.1) \times 10^{-11}$ [14]
N_2O	$(4.5 \pm 0.5) \times 10^{-12}$ [a]	3.1×10^{-12} [17]	$(2.1 \pm 0.1) \times 10^{-11}$ [14]
CO_2	$(1.1 \pm 0.3) \times 10^{-11}$ [a]	3.9×10^{-13} [17]	$(7.0 \pm 0.4) \times 10^{-13}$ [14]
CH_4	$(1.7 \pm 0.2) \times 10^{-11}$ [a]	1.3×10^{-11} [17]	$(5.7 \pm 0.3) \times 10^{-11}$ [14]
CF_4	$(4.8 \pm 0.3) \times 10^{-12}$ [a]	1.6×10^{-12} [17]	$(4.3 \pm 0.2) \times 10^{-12}$ [14]
SF_6	$(9.5 \pm 1.0) \times 10^{-13}$ [a]	8.5×10^{-14} [17]	$(1.0 \pm 0.1) \times 10^{-12}$ [14]
C_2H_4	$(3.3 \pm 0.1) \times 10^{-10}$ [a]	2.3×10^{-10} [17]	$(3.6 \pm 0.2) \times 10^{-10}$ [15]
C_2H_2	$(2.9 \pm 0.2) \times 10^{-10}$ [a]	1.1×10^{-10} [17]	$(2.4 \pm 0.1) \times 10^{-10}$ [16]
$Ge(CH_3)_4$	$(5.4 \pm 0.2) \times 10^{-11}$ [a]	8.0×10^{-10} [17]	$(4.2 \pm 0.2) \times 10^{-10}$ [13]

[a] This work (signal averaging, errors 2σ); [17] single-shot mode (errors ca. 30%); [13–16], signal averaging.

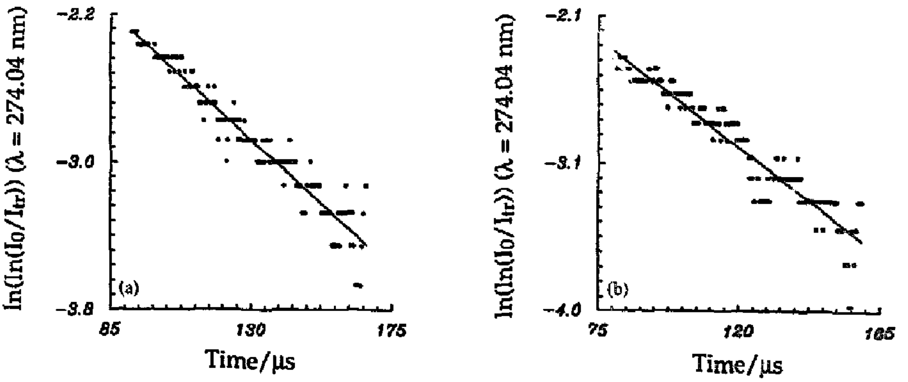

Fig. 3. Examples of computerised fitting indicating the first-order kinetic decay of Ge[$4p^2(^1S_0)$] obtained by time-resolved atomic resonance absorption spectroscopy in the ultraviolet {$\lambda = 274.04$ nm, Ge[$4d(^1P_1^o) \leftarrow 4p^2(^1S_0)$]} following the repetitively pulsed irradiation of $Ge(CH_3)_4$ in the presence of oxygen and excess helium buffer gas. $f_1 = [Ge(CH_3)_4]/([Ge(CH_3)_4] + [O_2] + [He]) = 4.0 \times 10^{-4}$; $f_2 = [O_2]/([Ge(CH_3)_4] + [O_2] + [He]) = 5.0 \times 10^{-5}$; $E =$ 88 J; repetition rate = 0.1 Hz; No. of experiments for averaging = 16; p_{Total} (Torr): (a) 14.0; (b) 22.0.

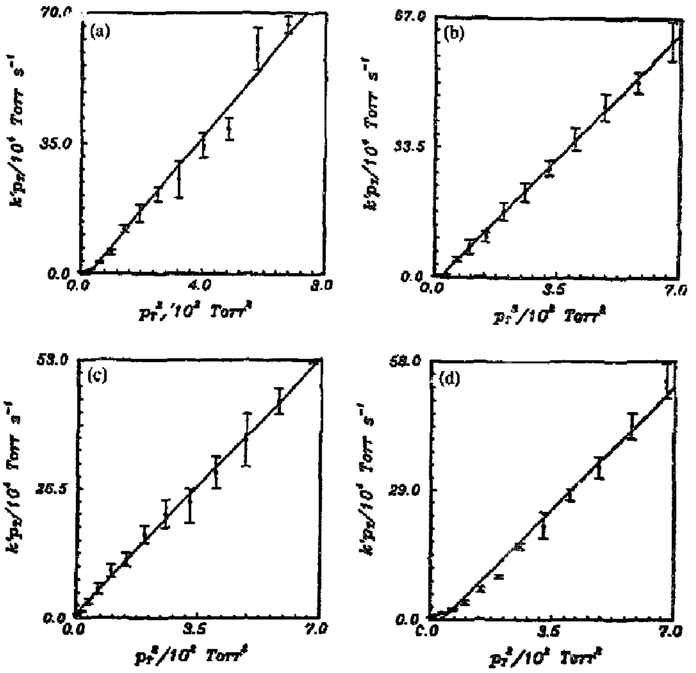

Fig. 4. Variation of the pseudo-first-order rate coefficient (k') for the decay of $Ge(4^1S_0)$ obtained by time-resolved atomic resonance absorption spectroscopy in the ultraviolet {$\lambda = 274.04$ nm, Ge[$4d(^1P_1^o) \leftarrow 4p^2(^1S_0)$]} following the repetitively pulsed irradiation of $Ge(CH_3)_4$ in the presence of excess helium buffer gas. $k'p_T$ versus p_T^2; $T = 300$ K; $f_1 = [Ge(CH_3)_4]/([Ge(CH_3)_4] + [R] + [He]) = 4.0 \times 10^{-4}$; $f_2 = [R = N_2, Xe, O_2, NO]/([Ge(CH_3)_4] + [R] + [He])$; (a) N_2, $f_2 = 2.0 \times 10^{-3}$; (b) Xe, $f_2 = 1.0 \times 10^{-2}$; (c) O_2, $f_2 = 5.0 \times 10^{-5}$; (d) NO, $f_2 = 2.0 \times 10^{-4}$.

and $Ge(4^1D_2)$ in He [15], the magnitude of β can be estimated from the simplified form of long-term solution of the diffusion equation for a long cylinder ($k_{diff} = \beta/p_T \approx 5.81D_{12}$ where $D_{12} = D_{12}^0/p_T$ and where $r = 1$ cm) using the reported estimate for $D_{12}(Si(3^3P_J)\text{-}He)) = 0.48 \pm 0.04$ cm^2 s^{-1} at 1 atm (300 K) [30]. Assuming that the diffusion coefficients of $Ge(4^1S_0)$ and $Si(3^3P_J)$ in He are similar, the intercepts β in plots of the type given in Fig. 4 should be the order of 2.1×10^3 Torr s^{-1}. This can be compared with the range in the ordinate of $(0\text{–}5.3) \times 10^5$ Torr s^{-1} for Fig. 4(a). Similar considerations apply to other plots based on Eq. (5) where such plots effectively pass through the origin, within experimental error, and the removal of $Ge(4^1S_0)$ is dominated by collisional removal.

Fig. 5 shows plots based on Eq. (5) for the collisional quenching of $Ge(4^1S_0)$ by the simple gases CO, N_2O, CO_2

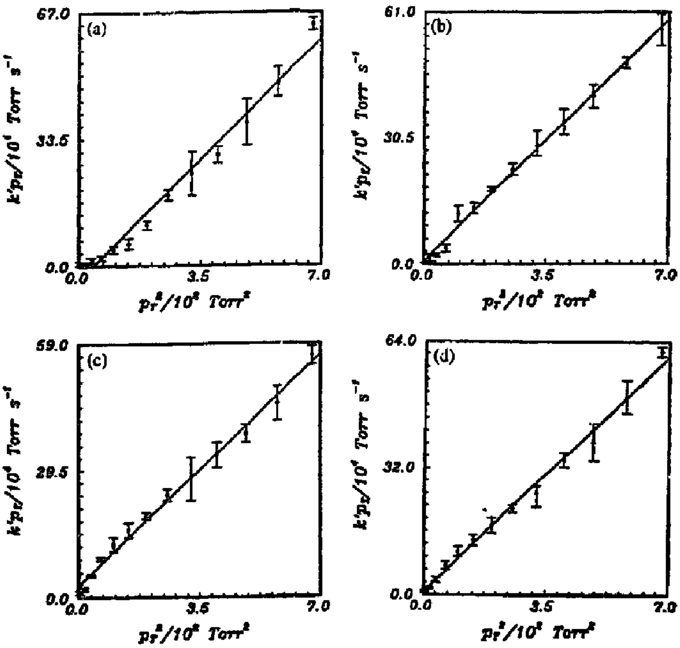

Fig. 5. Variation of the pseudo-first-order rate coefficient (k') for the decay of Ge(4^1S_0) obtained by time-resolved atomic resonance absorption spectroscopy in the ultraviolet {$\lambda = 274.04$ nm, Ge[$4d(^1P_1^o) \leftarrow 4p^2(^1S_0)$]} following the repetitively pulsed irradiation of $Ge(CH_3)_4$ in the presence of excess helium buffer gas. $k'p_T$ versus p_T^2; $T = 300$ K; $f_1 = [Ge(CH_3)_4]/([Ge(CH_3)_4] + [R] + [He]) = 4.0 \times 10^{-4}$; $f_2 = [R = CO, N_2O, CO_2, CH_4]/([Ge(CH_3)_4] + [R] + [He])$; (a) CO, $f_2 = 2.0 \times 10^{-3}$; (b) N_2O, $f_2 = 1.0 \times 10^{-3}$; (c) CO_2, $f_2 = 2.0 \times 10^{-4}$; (d) CH_4, $f_2 = 3.0 \times 10^{-4}$.

and CH_4. The slopes of these plots (correlation coefficients = 0.9840, 0.9937, 0.9907 and 0.9914, respectively) together with the above value of k_1 and the values of f_1 and f_2 given in the figure caption, yield the absolute second-order quenching rate constants (Table 1). The slopes of the analogous plots (Fig. 6) for the large spherical molecules CF_4 and SF_6 based on Eq. (5) (correlation coefficients = 0.9943 and 0.9858, respectively) and the values of k_1, f_1 and f_2 yield the appropriate absolute second-order quenching constants given in Table 1. Finally, Fig. 7 shows the plots (Eq. (5)) for the quenching of Ge(4^1S_0) by the simple unsaturated hydrocarbons C_2H_4 and C_2H_2 (correlation coefficients = 0.9919 and 0.9849) with the resulting rate data given in Table 1. Errors are quoted as 2σ. The present rate data are compared with analogous rate data derived from kinetic measurements made at high energy on Ge(4^1S_0) in the single-

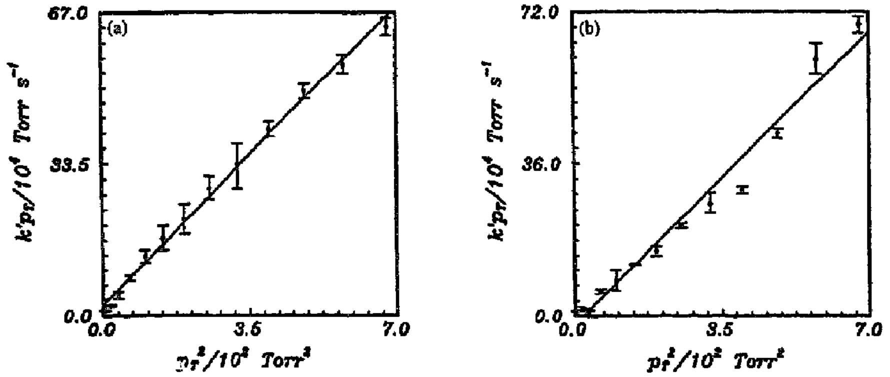

Fig. 6. Variation of the pseudo-first-order rate coefficient (k') for the decay of Ge(4^1S_0) obtained by time-resolved atomic resonance absorption spectroscopy in the ultraviolet {$\lambda = 274.04$ nm, Ge[$4d(^1P_1^o) \leftarrow 4p^2(^1S_0)$]} following the repetitively pulsed irradiation of $Ge(CH_3)_4$ in the presence of excess helium buffer gas. $k'p_T$ versus p_T^2; $T = 300$ K; $f_1 = [Ge(CH_3)_4]/([Ge(CH_3)_4] + [R] + [He]) = 4.0 \times 10^{-4}$; $f_2 = [R = CF_4, SF_6]/([Ge(CH_3)_4] + [R] + [He])$; (a) CF_4, $f_2 = 2.0 \times 10^{-3}$; (b) SF_6, $f_2 = 1.0 \times 10^{-2}$.

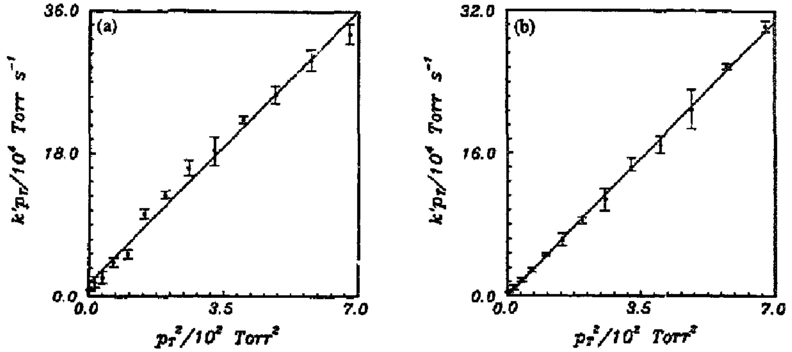

Fig. 7. Variation of the pseudo-first-order rate coefficient (k') for the decay of Ge(4^1S_0) obtained by time-resolved atomic resonance absorption spectroscopy in the ultraviolet {λ = 274.04 nm, Ge[4d($^1P_1{}^o$) ← $4p^2$($^1S_0$)]} following the repetitively pulsed irradiation of Ge(CH_3)$_4$ in the presence of excess helium buffer gas. $k'p_T$ versus p_T^2; T = 300 K; f_1 = [Ge(CH_3)$_4$]/([Ge(CH_3)$_4$] + [R] + [He]) = 4.0×10^{-5}; f_2 = [R = C_2H_4, C_2H_2]/([Ge(CH_3)$_4$] + [R] + [He]) = 4.0×10^{-5}; (a) C_2H_4; (b) C_2H_2.

shot mode [17], where the errors are quoted generally as ca. 30%, and with analogous data for the quenching of Ge[$4p^2$($^1D_2$)] (0.883 eV [3]) also characterised by signal averaging methods analogous to those employed here.

Inspection of the absolute rate data for the collisional quenching of Ge(4^1S_0) by the present method using repetitive pulsed irradiation at low energy with signal averaging and that of Chowdhury and Husain [17] employing high energy with monitoring at short times in the single-shot mode, shows sensible accord for most collision partners. Those authors quote errors in the rate data of ca. 30%. CO_2 and SF_6 are the only two gases for which the absolute second-order rate constants have found to be significantly more rapid and these were repeated a number of times. In both cases, chemical reaction with Ge(4^1S_0) is highly exothermic:

$$\mathrm{Ge}(4^1S_0) + CO_2 \rightarrow \mathrm{GeO} + CO \quad \Delta H = -3.36\ \mathrm{eV}$$

[3,31,32]

$$\mathrm{Ge}(4^1S_0) + SF_6 \rightarrow \mathrm{GeF} + SF_5 \quad \Delta H = -3.68\ \mathrm{eV}$$

[3,32–34] though, for the reaction between Ge(4^1S_0 + CO_2, the ^{1}A′ surface arising from these species does not correlate with ground state products on the basis of C_s symmetry in the 'least symmetrical complex' or on the basis of the weak spin–orbit coupling approximation, nor does this correlate with ground state products using (J,Ω) coupling. Surface crossings and non-adiabatic transitions are again required for chemical reaction or physical quenching [17]. In general, the greater accuracy with the present kinetic method arising from the use of low energies and of a signal averaging method, now extended from kinetic studies on C(2^3P_J) [18,19] and Ge(4^1D_2) [15,16] to Ge(4^1S_0), favours the present results. Similar quenching rates are observed with those for the lower lying Ge($^1D_2$) in many cases (Table 1) notwithstanding the smaller energy to be transferred for the latter.

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