

THE COLLISIONAL BEHAVIOUR OF ATOMIC SILICON IN THE ELECTRONIC STATES $\text{Si}(3p^2(^3P_J, ^1D_2, ^1S_0))$ WITH SF_6 BY TIME-RESOLVED ATOMIC RESONANCE ABSORPTION SPECTROSCOPY

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Summary

We present a kinetics study of the three states of atomic silicon arising from the overall ground state configuration, namely $\text{Si}(3p^2(^3P_J))$, $\text{Si}(3p^2(^1D_2))$ (0.781 eV) and $\text{Si}(3p^2(^1S_0))$ (1.909 eV) with the molecule SF_6 . These atoms, generated by the repetitive pulsed irradiation of SiCl_4 in the presence of SF_6 and helium buffer gas, were monitored photoelectrically by time-resolved atomic resonance absorption spectroscopy at the following wavelengths: $\lambda = 251.6$ nm ($\text{Si}(4^3P_1) \leftarrow \text{Si}(3^3P_J)$), $\lambda = 288.16$ nm ($\text{Si}(4^1P_1) \leftarrow \text{Si}(3^1D_2)$) and $\lambda = 390.53$ nm ($\text{Si}(4^1P_1) \leftarrow \text{Si}(3^1S_0)$). Of the three states, $\text{Si}(3^1D_2)$ showed marked effects due to cascading from $\text{Si}(3^1S_0)$ on collision with SF_6 . The following absolute rate constants k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (300 K) are obtained: $k(\text{Si}(3^3P_J) + \text{SF}_6) = (3.2 \pm 0.5) \times 10^{-11}$, $k(\text{Si}(3^1D_2) + \text{SF}_6) = (8.4 \pm 0.6) \times 10^{-11}$ and $k(\text{Si}(3^1S_0) + \text{SF}_6) = (2.0 \pm 0.5) \times 10^{-10}$. These are compared with the results for the removal of atomic silicon with other fluorinated compounds that have been investigated as collision partners, namely F_2 and CF_4 . Subsequent production of SiF in various electronic states is considered as is the feasibility of constructing a laser operating on the transition $\text{SiF}(a^4\Sigma^-) \rightarrow \text{SiF}(A^2\Sigma^+) + h\nu$ (1.4 μm) and resulting from the reaction of $\text{Si}(3^1D_2)$ and $\text{Si}(3^1S_0)$ generated photochemically from SiCl_4 in the single-shot pulsed mode and in the presence of fluorine-containing molecules.

1. Introduction

Interest in the collisional behaviour of atomic silicon with fluorinated compounds is strongly influenced by attempts to correlate the relationship between the rate of fluorine atom abstraction from such molecules with the feasibility of constructing a molecular electronic transition laser based on SiF and arising from a population inversion in the product states of this

diatomic molecule [1, 2]. Armstrong and Davis [1] have reported a value for the reaction rate constant of ground state $\text{Si}(3p^2(^3P_J))$ with molecular fluorine in a flow system at 600 K where reaction is highly exothermic ($D_0^0(\text{F}_2(\text{X } ^1\Sigma_g^+)) = 1.602 \text{ eV}$; $D_0^0(\text{SiF}(\text{X } ^2\Pi_r)) = 5.57 \text{ eV}$ [3]). More recently, we have presented a detailed investigation [4] of the collisional behaviour with this molecule studied by time-resolved atomic resonance absorption spectroscopy of both the 3^3P_J ground state and the low-lying optically metastable electronically excited atomic states $\text{Si}(3p^2(^1D_2))$ and $\text{Si}(3p^2(^1S_0))$ [5], 0.781 eV and 1.909 eV respectively above the $3p^2(^3P_J)$ ground state [6]. As well as demonstrating the increase in the absolute second-order rate constant for removal of $\text{Si}(3^3P_J)$, $\text{Si}(3^1D_2)$ and $\text{Si}(3^1S_0)$ with F_2 with increasing electronic energy [4], thermochemistry alone clearly indicates that a much larger number of electronic states of SiF are accessible on collision. Indeed, reaction to yield electronically excited states as high as $\text{SiF}(\text{D}'^2\Pi)$, 5.7791 eV above the $\text{X } ^2\Pi_r$ ground state [3], is still exothermic for collisions between $\text{Si}(3^1S_0)$ and F_2 . A molecular electronic transition laser would be based on the optically metastable state $\text{SiF}(\text{a } ^4\Sigma^-)$ [6] and would operate on the transition $\text{SiF}(\text{a } ^4\Sigma^- \rightarrow \text{A } ^2\Sigma^+ + h\nu (\lambda = 1.4 \mu\text{m}))$.

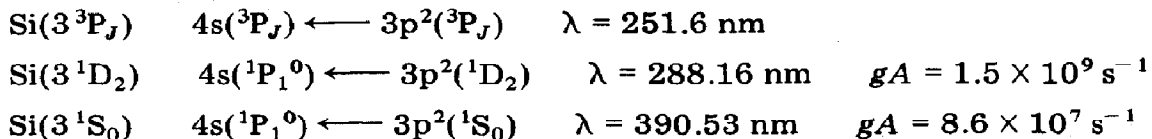
In this paper, we describe the kinetics study of $\text{Si}(3^3P_J)$, $\text{Si}(3^1D_2)$ and $\text{Si}(3^1S_0)$ with the molecule SF_6 by time-resolved atomic resonance absorption spectroscopy. Fluorine atom abstraction will be exothermic ($D(\text{SF}_5-\text{F}) = 3.33 \text{ eV}$ [7]) for all three atomic states and restrictions to product electronic states of SiF arising from orbital correlations of the type encountered with $\text{Si} + \text{F}_2$ [4] will be overcome by collisions with this polyatomic species. Husain and Norris [8-10] have studied the collisional removal of $\text{Si}(3^3P_J)$, $\text{Si}(3^1D_2)$ and $\text{Si}(3^1S_0)$ with CF_4 , the only other polyatomic molecule of the type $\text{R}-\text{F}$ whose reaction with atomic silicon has been investigated. No significant difference was observed between the second-order rate constants for the removal of each of these three electronic states of the silicon atom [8-10]. By contrast, the absolute second-order rate constants reported here indicate increasing removal rates of silicon with the electronic energy of the atom, that for $\text{Si}(3^1S_0) + \text{SF}_6$, in particular, proceeding at essentially every collision. In this case, reaction into $\text{SiF}(\text{a } ^4\Sigma^-)$, 3.9653 eV above the $\text{X } ^2\Pi_r$ ground state [3] is thermochemically favourable. A comparison is presented of the absolute rate data for the removal of $\text{Si}(3^3P_J)$, $\text{Si}(3^1D_2)$ and $\text{Si}(3^1S_0)$ with F_2 , CF_4 and SF_6 .

2. Experimental details

The experimental arrangement used to monitor the three states of atomic silicon (3^3P_J , 3^1D_2 and 3^1S_0) is similar to that used for the analogous study of atomic silicon with F_2 [4]. The salient features are presented here with emphasis on those modifications, where they arise, especially in dealing with the numerical analysis of the data.

Atomic silicon was generated by the repetitive photolytic pulsing ($E = 63 - 140 \text{ J}$ at 1 Hz) of low pressures of SiCl_4 (typically $(1 - 3) \times 10^{13}$

molecules cm^{-3}) in the presence of excess helium buffer gas ($[\text{He}]:[\text{SiCl}_4]$, about $5 \times 10^4:1$) in a slow flow system, kinetically equivalent to a static system [4, 11]. The reaction mixture consisted of a combination of three flows: (1) $\text{SiCl}_4 + \text{He}$, (2) $\text{SF}_6 + \text{He}$ and (3) He alone. The following atomic transitions were employed for the time-resolved monitoring measurements [12]:



As indicated in the measurements on $\text{Si} + \text{F}_2$ [4], it was found to be more convenient in terms of signal-to-noise ratio to use the unresolved multiplet at $\lambda = 251.6 \text{ nm}$ rather than the $\text{Si}(4s(3^3\text{P}_1)) \leftarrow \text{Si}(3p^2(3^3\text{P}_0))$ transition at $\lambda = 251.43 \text{ nm}$ [12]. There is a reduction in the sensitivity encountered when the unresolved multiplet is used, characterized by $\gamma = 0.51 \pm 0.04$ as observed by Husain and Norris [13] when employing the modified Beer-Lambert law, $I_{\text{tr}} = I_0 \exp\{-(ecl)^\gamma\}$ [14] compared with $\gamma = 0.98 \pm 0.15$ [13] for the transition at $\lambda = 251.43 \text{ nm}$. However, this is more than offset by the increase in the I_0 signal and the subsequent improvement in the signal-to-noise ratio. Husain and Norris [13] have demonstrated that the decay coefficients for $\text{Si}(3^3\text{P}_0)$, $\text{Si}(3^3\text{P}_1)$ and $\text{Si}(3^3\text{P}_2)$, and also for $\text{Si}(3^3\text{P}_J)$, are identical within experimental error and that the spin-orbit components are in Boltzmann equilibrium throughout the kinetics decays.

The photoelectric resonance absorption signals representing the decays of the three atomic states following pulsed irradiation employed the "pre-trigger photomultiplier gating" circuitry [11] used in the study of $\text{Si}(3^3\text{P}_J)$, $\text{Si}(3^1\text{D}_2)$ and $\text{Si}(3^1\text{S}_0)$ with F_2 [4]. Even so, the electronic effects of remnants of the scattered light pulse from the photoflash were detected at the earlier parts of the decay signal and were eliminated in the computing procedure. The photoelectric signals were thus amplified without distortion using a current-to-voltage converter employing a fast-settling operational amplifier [15] and were captured in a transient recorder (Data Laboratories DL 920). A typical procedure in the measurements was to use the last 100 of the 1024 available channels of the transient recorder to determine the unattenuated resonance intensity I_0 after a time lapse of 4 ms, compared with the measurement of the decay with the remaining 924 channels over a time interval of 0.5 - 1 ms, depending on the atomic state. The photomultiplier analogue signal, resolved and digitized in the transient recorder, was then transferred to a signal averager (Data Laboratories DL 4000) and subsequently punched onto paper tape output in ASCII code (Datadynamics punch 1183) for analysis in the University of Cambridge IBM 3081 computer. Particular effort was undertaken in improving the numerical analysis routines. This involved the computerized fit of a third-order Chebychev polynomial to the data to help to distinguish the decay of atomic states from the electronic "rise time" of the photomultiplier tube and associated amplification and current-to-voltage conversion components. Typically, the

polynomial least-squares fit would provide an uncertainty of less than 4% using data associated solely with the decay of the atomic state. First-order decay coefficients k' were derived from fitting the form of I_{tr} versus t to a double-exponential equation (i.e. $I_{tr} = I_0 \exp(-c t)$ and $c = c_0 \exp(-k' t)$ in simple terms, where the symbols have their usual significance). This is considered in further detail in Section 3. All materials were essentially prepared as described in previous publications [4, 8, 11].

3. Results and discussion

Examples of the data obtained for the decay profiles of the three states of atomic silicon are given in Figs. 1 - 3. They show the digitized form of the time variation in the transmitted light intensity which represents temporal resonance absorption by Si(3^3P_J), Si(3^1D_2) and Si(3^1S_0) in the presence of SF₆. The digitized data presented here are derived by monitoring the photo-electrical signals for either 0.5 ms or 1 ms subsequent to pulsed irradiation (see Section 2), which gives a resolution of 0.35 μ s or 0.9 μ s respectively. For diagrammatic purposes only every fifth data point is plotted in Figs. 1 - 3. The straight line parallel to the abscissa represents the computed I_0 values averaged from a 100 point "sweep" 2 - 10 ms after the high voltage discharge. Finally a least-squares fit of a third-order Chebychev polynomial to the data indicates the convergence of the transmitted light intensity to the I_0 value. The collection of data points at the smallest time interval is the

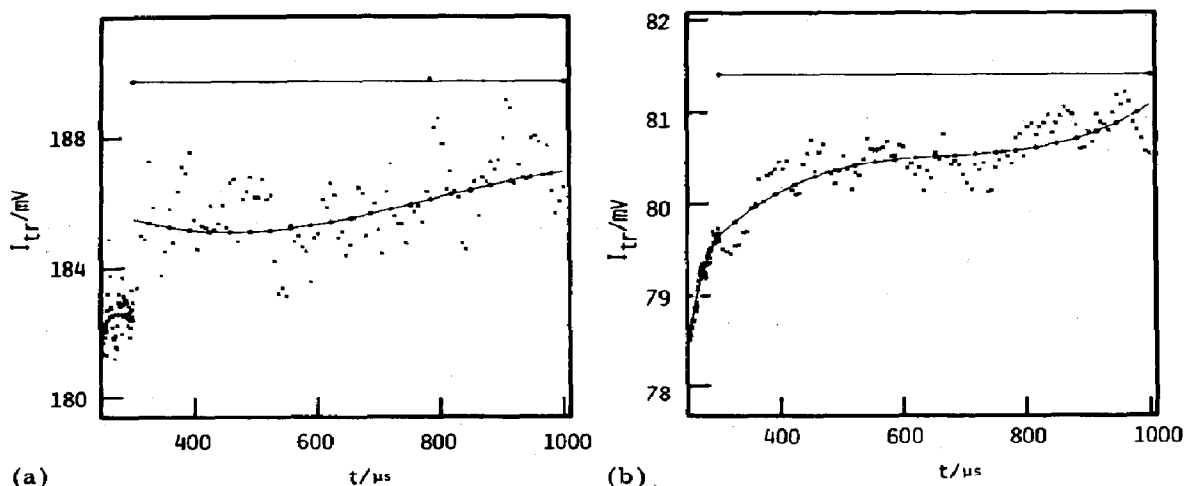


Fig. 1. Digitized time variation in the transmitted light intensity I_{tr} at $\lambda = 251.6$ nm (Si($4^3P_J \rightarrow 3^3P_J$)) indicating the decay of resonance absorption by ground state silicon atoms Si(3^3P_J) following the pulsed irradiation of SiCl₄ in the presence of SF₆ for (a) [SF₆] = 4.0×10^{13} molecules cm⁻³ and (b) [SF₆] = 6.9×10^{13} molecules cm⁻³ ([SiCl₄] = 1.9×10^{13} molecules cm⁻³; [He] $\approx 9.6 \times 10^{17}$ atoms cm⁻³; $E = 62$ J; repetition rate, 1 Hz; number of experiments for averaging, 256): x, data points; —, computerized least-squares third-order Chebychev polynomial fit.

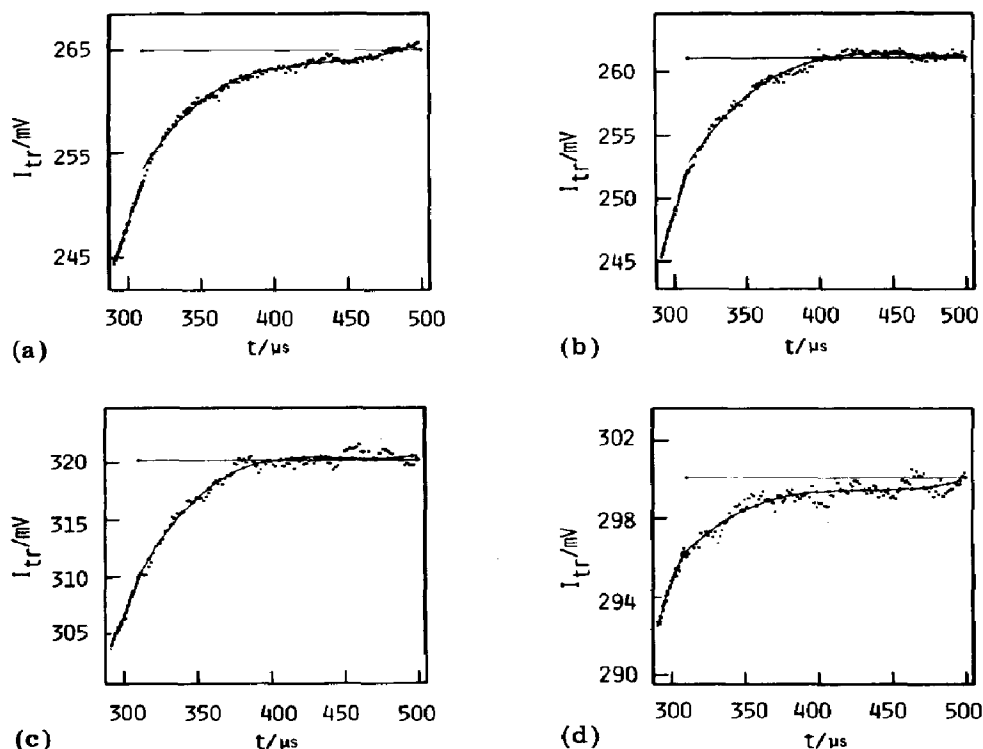


Fig. 2. Digitized time variation in the transmitted light intensity I_{tr} at $\lambda = 288.16$ nm ($\text{Si}(4^1\text{P}_1 \rightarrow 3^1\text{D}_2)$) indicating the decay of resonance absorption by electronically excited silicon atoms $\text{Si}(3^1\text{D}_2)$ following the pulsed irradiation of SiCl_4 in the presence of SF_6 for (a) $[\text{SF}_6] = 1.8 \times 10^{13}$ molecules cm^{-3} , (b) $[\text{SF}_6] = 3.5 \times 10^{13}$ molecules cm^{-3} , (c) $[\text{SF}_6] = 5.1 \times 10^{13}$ molecules cm^{-3} and (d) $[\text{SF}_6] = 8.2 \times 10^{13}$ molecules cm^{-3} ($[\text{SiCl}_4] = 2.0 \times 10^{13}$ molecules cm^{-3} ; $[\text{He}] \approx 9.6 \times 10^{17}$ atoms cm^{-3} ; $E = 120$ J; repetition rate, 1 Hz; number of experiments for averaging, 256): \times , data points; —, computerized least-squares third-order Chebychev polynomial fit.

remnant of the scattered light pulse which is separated and eliminated from the subsequent analysis.

Particular care was taken with the resonance absorption measurements on $\text{Si}(3^1\text{D}_2)$ at $\lambda = 288.16$ nm ($4^1\text{P}_1 \rightarrow 3^1\text{D}_2$) which is presented in most detail here (see Fig. 2) since, of the three states investigated, this is the most prone to complexities of growth resulting from cascading from the $\text{Si}(3^1\text{S}_0)$ state accompanying the decay of $\text{Si}(3^1\text{D}_2)$. Husain and Norris [9] have presented the results of calculations on the relevant coupled differential equations for the ^3P , ^1D and ^1S concentrations which demonstrate this effect quantitatively. The quality of the raw data is very good (Fig. 2), the degree of light absorption being about 5% and thus the first-order decay coefficients obtained for this atomic state and their variation with SF_6 concentration (see later) may be confidently employed. Examples of raw data for the decay of $\text{Si}(3^1\text{S}_0)$ in the presence of SF_6 are presented in Fig. 3 and indicate the variation in the transmitted radiation at $\lambda = 390.53$ nm ($4^1\text{P}_1 \leftarrow 3^1\text{S}_0$). These are of marginally inferior quality to those for $\text{Si}(3^1\text{D}_2)$, involving

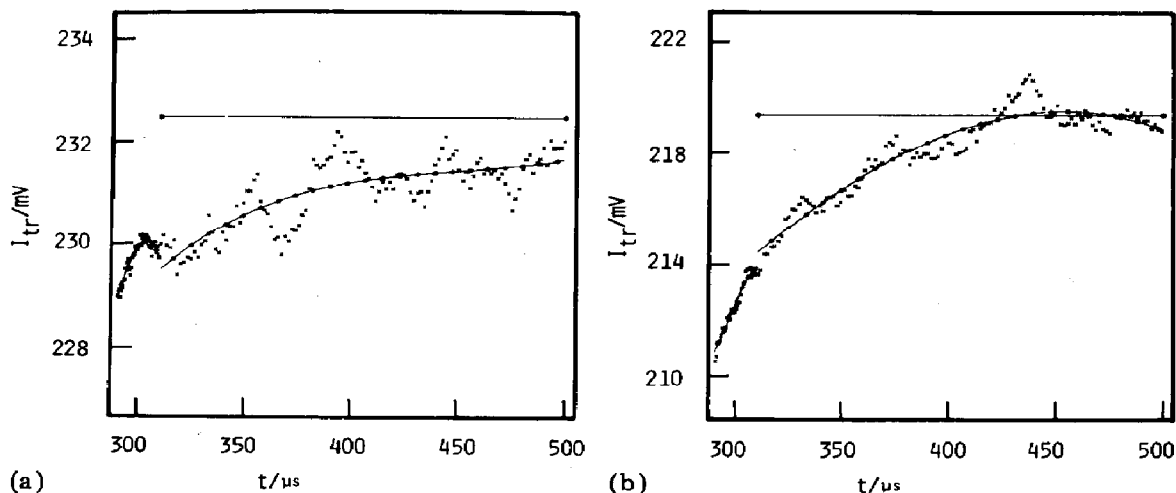


Fig. 3. Digitized time variation in the transmitted light intensity I_{tr} at $\lambda = 390.53$ nm ($\text{Si}(4^1P_1 \rightarrow 3^1S_0)$) indicating the decay of resonance absorption by electronically excited silicon atoms $\text{Si}(3^1S_0)$ following the pulsed irradiation of SiCl_4 (a) in the absence of SF_6 and (b) in the presence of SF_6 ($[\text{SF}_6] = 3.1 \times 10^{13}$ molecules cm^{-3}) ($[\text{SiCl}_4] = 1.3 \times 10^{13}$ molecules cm^{-3} ; $[\text{He}] \approx 9.6 \times 10^{17}$ atoms cm^{-3} ; $E = 140$ J; repetition rate, 1 Hz; number of experiments for averaging, 256): x, data points; —, computerized least-squares third-order Chebychev polynomial fit.

degrees of light absorption of about 4%. It is also clear from the scatter about the Chebychev polynomial fit (Fig. 3) that the noise is not totally random and is presumed to result from high frequency fluctuations in the intensity of the light output from the microwave-powered resonance source.

Following the procedure described in the study of $\text{Si}(3^3P_J)$, $\text{Si}(3^1D_2)$ and $\text{Si}(3^1S_0)$ with F_2 [4], we use the method similar to that of Clark and Husain [16, 17] for the data analysis where the digitized output is subjected to an iterative two-parameter fit (A and k') of the following equation:

$$I_{tr} = I_0 \exp\{-A \exp(-k't)\} \quad (1)$$

Equation (1) represents the combination of the standard Beer-Lambert law and a first-order kinetics decay of the relevant atomic state. For resonance absorption on $\text{Si}(3^3P_J)$ at $\lambda = 251.6$ nm, the analysis yields $\gamma k'$ via the modified Beer-Lambert law [14] where $\gamma = 0.51 \pm 0.04$ [13] for this transition. This procedure overcomes the generation of large scatter in the data for smaller degrees of light absorption that occur when an alternative solution to eqn. (1), i.e. $k' = -d[\ln\{\ln(I_0/I_{tr})\}]/dt$, is used.

Figures 4, 5 and 6 show, respectively, the variation in k' for the removal of $\text{Si}(3^3P_J)$, $\text{Si}(3^1D_2)$ and $\text{Si}(3^1S_0)$ with $[\text{SF}_6]$. The variation for $\text{Si}(3^1D_2)$, for which the best parabolic fit is arbitrarily presented, demonstrates the effect of cascading from $\text{Si}(3^1S_0)$ and, of course, illustrates that the removal of the most energized of these atomic states with SF_6 is not totally chemical. The rate constant for total removal of $\text{Si}(3^1D_2)$ with SF_6 is taken from the

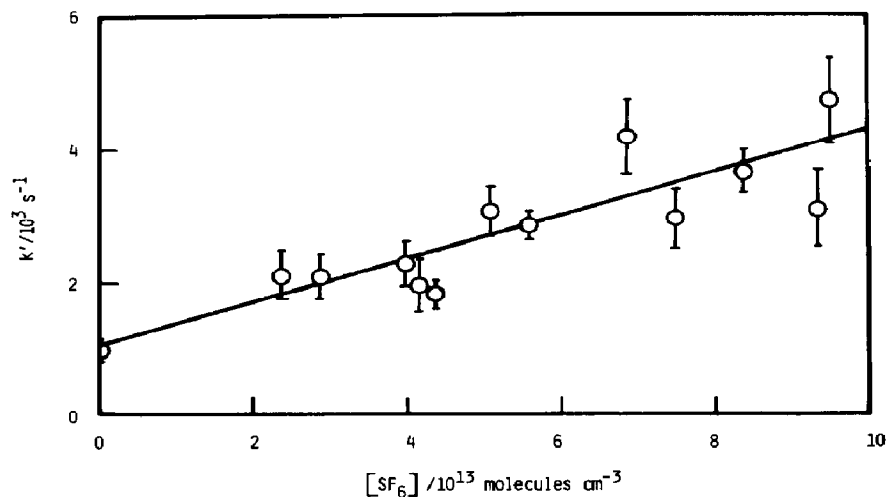


Fig. 4. Variation in the pseudo-first-order rate coefficient k' for the decay of $\text{Si}(3^3\text{P}_J)$ in the presence of SF_6 ($[\text{He}] \approx 9.6 \times 10^{17} \text{ atoms cm}^{-3}$).

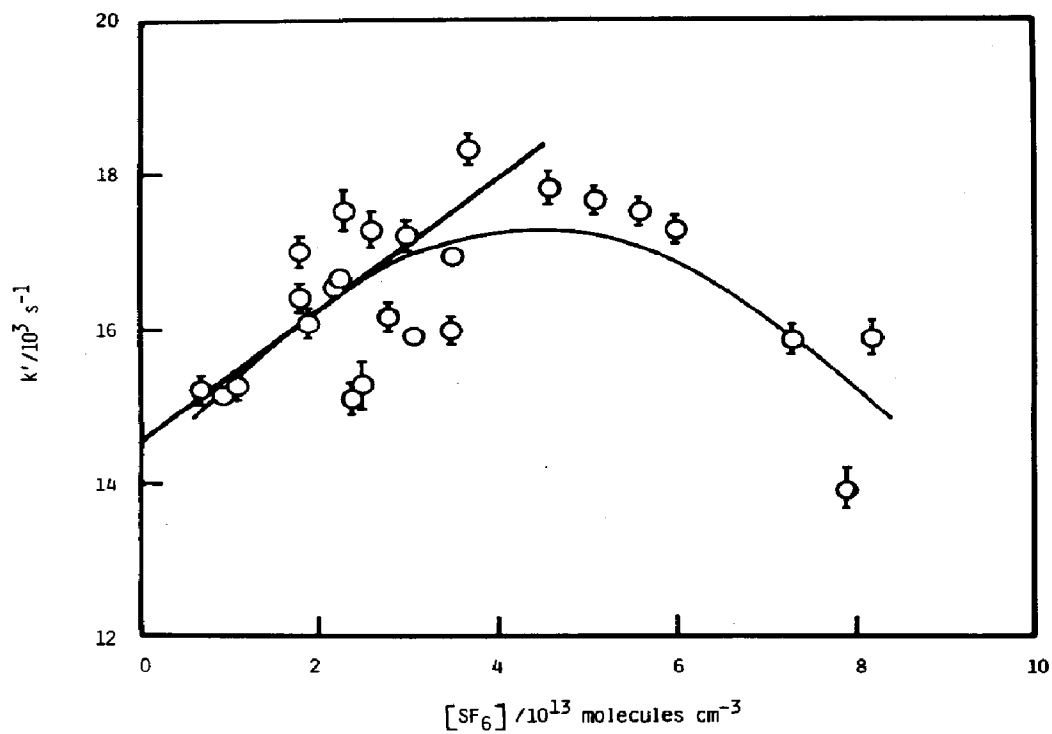


Fig. 5. Variation in the pseudo-first-order rate coefficient k' for the decay of $\text{Si}(3^1\text{D}_2)$ in the presence of SF_6 ($[\text{He}] \approx 9.6 \times 10^{17} \text{ atoms cm}^{-3}$).

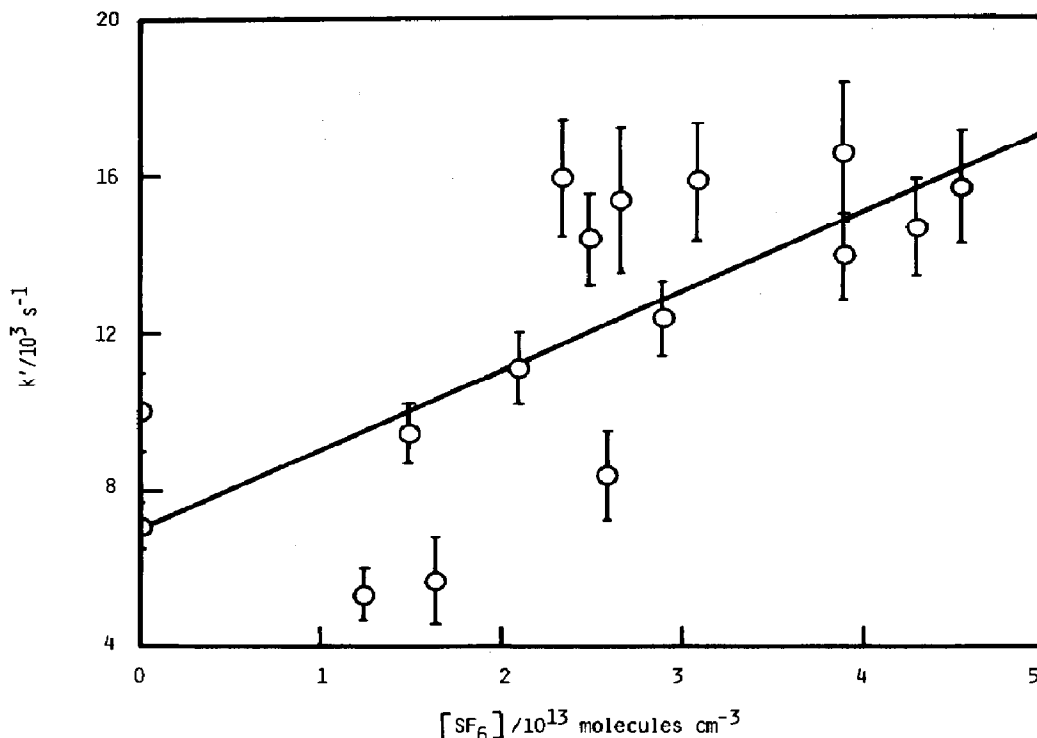


Fig. 6. Variation in the pseudo-first-order rate coefficient k' for the decay of $\text{Si}(3^1\text{S}_0)$ in the presence of SF_6 ($[\text{He}] \approx 9.6 \times 10^{17}$ atoms cm^{-3}).

computed initial slope in Fig. 5, which is then described by the standard form:

$$k' = K + k_2[\text{SF}_6] \quad (2)$$

The same form is taken to hold for $\text{Si}(3^3\text{P}_J)$ and $\text{Si}(3^1\text{S}_0)$, the absolute second-order rate constants for removal being derived respectively from the slopes of Figs. 4 and 6 (errors, 2σ).

The resulting values for the absolute second-order rate constants for the total removal of $\text{Si}(3^3\text{P}_J)$, $\text{Si}(3^1\text{D}_2)$ and $\text{Si}(3^1\text{S}_0)$ with SF_6 are presented in Table 1 together with the analogous data for F_2 and CF_4 , these being the only fluorine-containing species with which we may compare our results. Both the absolute values and the trend in the reactivities of $\text{Si}(3^3\text{P}_J)$, $\text{Si}(3^1\text{D}_2)$ and $\text{Si}(3^1\text{S}_0)$ with SF_6 are similar to those reported for the diatomic molecule F_2 (Table 1 [4]), namely $k(^1\text{S}) > k(^1\text{D}) > k(^3\text{P})$ with the rate for $\text{Si}(3^1\text{S}_0) + \text{SF}_6$ approaching that of the collisional number. By contrast, the rates for the three atomic states of CF_4 are comparable, removal taking place in about one in every 100 collisions. Clearly, the branching ratios for chemical reaction and energy transfer would be desirable for the ^1D and ^1S states with the species F_2 , CF_4 and SF_6 , where reaction is highly exothermic in all cases. This constitutes part of the present work that is being undertaken in the study of SiF in such systems.

TABLE 1

Absolute second-order rate constants k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (300 K) for the collisional removal of $\text{Si}(3^3\text{P}_J)$, $\text{Si}(3^1\text{D}_2)$ and $\text{Si}(3^1\text{S}_0)$ with SF_6 , CF_4 and F_2 derived from time-resolved atomic resonance absorption spectroscopy measurements

	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference
<i>SF</i> ₆		
$\text{Si}(3^3\text{P}_J)$	$(3.2 \pm 0.5) \times 10^{-11}$	
$\text{Si}(3^1\text{D}_2)$	$(8.4 \pm 0.6) \times 10^{-11}$	
$\text{Si}(3^1\text{S}_0)$	$(2.0 \pm 0.5) \times 10^{-10}$	
<i>CF</i> ₄		
$\text{Si}(3^3\text{P}_J)$	$(2.4 \pm 0.3) \times 10^{-12}$	[8]
$\text{Si}(3^1\text{D}_2)$	4.2×10^{-12}	[9]
$\text{Si}(3^1\text{S}_0)$	$(4.3 \pm 0.8) \times 10^{-12}$	[10]
<i>F</i> ₂		
$\text{Si}(3^3\text{P}_J)$	$(1.2 \pm 0.5) \times 10^{-11}$	[4]
	$(1.2 \pm 0.6) \times 10^{-10\text{a}}$	[1]
$\text{Si}(3^1\text{D}_2)$	$(8.2 \pm 2.1) \times 10^{-11}$	[4]
$\text{Si}(3^1\text{S}_0)$	$(1.9 \pm 0.8) \times 10^{-10}$	[4]

^aAtomic resonance absorption measurements on a flow system (600 K).

Apart from the general interest in product states of SiF (see Section 1), the production of $\text{SiF}(a^4\Sigma^-)$ is of particular interest. For F_2 , we have shown that correlations with defined states of $\text{SiF} + \text{F}$ are more restrictive [4], and population of $\text{SiF}(a^4\Sigma^-)$, particularly from chemical reaction with $\text{Si}(3^1\text{D}_2)$ and $\text{Si}(3^1\text{S}_0)$, must involve non-adiabatic transitions. Whilst fluorine atom abstraction from CF_4 is exothermic for the three atomic states ($D(\text{CF}_3-\text{F}) = 4.0 \pm 0.2 \text{ eV}$ [7]), reaction to yield $\text{SiF}(a^4\Sigma^-)$ is not energetically accessible even to $\text{Si}(3^1\text{S}_0)$, a process that would still be endothermic ($\Delta H = 0.216 \text{ eV}$ [3, 6, 7]). Reaction to lower-lying states ($\text{SiF}(A^2\Sigma^+, X^2\Pi_r)$) is energetically favourable and these product states are being investigated. Of the three atomic states of silicon, reaction of $\text{Si}(3^1\text{S}_0)$ with SF_6 to yield $\text{SiF}(a^4\Sigma^-)$ is energetically favourable ($\Delta H = -0.46 \text{ eV}$ [3, 6, 7]), although spin forbidden, and non-adiabatic transitions would still be involved. Apart from the general interest in the behaviour of silicon atoms in specific electronic states, as far as a chemical laser based on the transition $\text{SiF}(a^4\Sigma^- \rightarrow A^2\Sigma^+ + h\nu)$ is concerned, we believe that the best direction in which to proceed is one employing the chemistry of the ^1D and ^1S states. This would be facilitated in the pulsed mode, using high energy irradiation of mixtures of $\text{SiCl}_4 + \text{RF}$ within a laser cavity as it has been demonstrated that the photochemical yields of the ^1D and ^1S states are relatively high.

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