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Collisional Behaviour of Atomic Silicon in Specific Electronic States, Si($3\,^3P_J$, $3\,^1D_2$, $3\,^1S_0$), with Molecular Fluorine Studied by Time-resolved Atomic Resonance Absorption Spectroscopy

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We present a kinetic study of atomic silicon in the three low-lying electronic states arising from the overall $3p^2$ ground-state configuration, namely Si($3\,^3P_J$) (0 eV), Si($3\,^1D_2$) (0.781 eV) and Si($3\,^1S_0$) (1.909 eV). Si($3\,^3P_J$, $3\,^1D_2$ and $3\,^1S_0$) were generated by the repetitive pulsed irradiation of $SiCl_4$ in the presence of an excess of helium buffer gas in a slow-flow system, kinetically equivalent to a static system. The photochemically generated transient atoms were monitored photoelectrically by time-resolved resonance absorption at $\lambda = 251.6$ nm [Si($4\,^3P_J \leftarrow 3\,^3P_J$)], $\lambda = 288.16$ nm [Si($4\,^1P_1 \leftarrow 3\,^1D_2$)] and $\lambda = 390.53$ nm [Si($4\,^1P_1 \leftarrow 3\,^1S_0$)] using pre-trigger photomultiplier gating with signal averaging. The decays of these atoms were investigated in the presence of molecular fluorine, leading to the following absolute second-order rate constants (k_2):

	k_2/cm^3 molecule^{-1} s^{-1} ($T = 300$ K)
Si($3\,^3P_J$)+F_2	$(1.2 \pm 0.5) \times 10^{-11}$
Si($3\,^1D_2$)+F_2	$(8.2 \pm 2.1) \times 10^{-11}$
Si($3\,^1S_0$)+F_2	$(1.9 \pm 0.8) \times 10^{-10}$

The result for Si($3\,^3P_J$)+F_2 is compared with data derived from previous measurements carried out at 600 K on a flow system, and the data as a whole are compared with the results of earlier kinetic studies on Si($3\,^3P_J$, $3\,^1D_2$, $3\,^1S_0$)+Cl_2. Reaction pathways to defined product states of SiF+F are considered in terms of symmetry arguments based on the weak spin–orbit coupling approximation. Discussion is also presented on the use of time-resolved spontaneous emission from product states of SiF+F as spectroscopic markers for kinetic investigations of defined electronic states of atomic silicon and the feasibility of investigating stimulated emission from SiF($a\,^4\Sigma$) – SiF($A\,^2\Sigma^+$) + $h\nu$ in the 1.4 μm region in the pulsed mode following the reaction of the electronically excited Si($3\,^1D_2$) and Si($3\,^1S_0$) with F_2.

The $3p^2$ overall ground-state electronic configuration of atomic silicon gives rise to the three electronic states, Si($3\,^3P_J$), Si($3\,^1D_2$) and Si($3\,^1S_0$), the latter two states lying, respectively, 0.781 and 1.909 eV above the $3p^2(^3P_0)$ ground state.[1] The $^1D_2$ and $^1S_0$ states are optically metastable with respect to spontaneous emission,[2] and hence the removal of all these three states, once generated in a chemical system, is determined by collisional processes and by diffusion. The spin–orbit splitting in the $3p^2(^3P_J)$ manifold is small ($J_{0-1} = 77$ cm^{-1}, $J_{2-3} = 28$ cm^{-1}).[1] In chemical systems Boltzmann equilibrium is normally sustained between these J levels *via* collisions during kinetic experiments,[3] and hence each spin–orbit state will show identical kinetics characterised by a combination of rate constants specific to each spin–orbit component and the standard equilibrium constants connecting them.[3] Electronic interactions between any of these spin–orbit components and a colliding reactant molecule may be assumed to be equal within the bounds of experimental measurements, and hence absolute rate constants for each spin–orbit state are assumed to be identical and ascribed to a 'Boltzmannised' Si($3\,^3P_J$).

Two experimental methods may be highlighted as having contributed broadly to the investigation of the collisional behaviour of atomic silicon in the gas phase. Gaspar and coworkers have employed fast neutron irradiation of phosphine *via* a $^{31}(n, p)^{31}$Si nuclear transformation to study reaction pathways of atomic silicon with a range of large molecules.[4-7] This general area of hot-atom chemistry has been extensively reviewed recently by Gaspar and Root,[8] with particular reference to silicon atom chemistry. The principal method involving direct monitoring of atomic silicon, leading to absolute rate data for collisional behaviour in specific quantum states, is that employing the combination of pulsed irradiation with time-resolved atomic resonance absorption spectroscopy. By this technique Husain and Norris have reported absolute rate constants for reactions of Si($3\,^3P_J$),[3,9] Si($3\,^1D_2$)[10,11] and Si($3\,^1S_0$)[12,13] with a range of collisional partners. Whilst these investigations included the study of Si($3\,^3P_J$, $3\,^1D_2$, $3\,^1S_0$)+Cl_2,[9,11,13] reaction with molecular fluorine has not been examined by this method. Armstrong and Davis[14] have reported a rate constant for the reaction of Si($3\,^3P_J$)+F_2 in a flow system. Atomic silicon was generated thermally by evaporation of solid silicon at 2173 K and the reaction rate with fluorine at 600 K was studied by resonance line absorption as a function of distance along the flow. In the present paper we describe not only a kinetic study of Si($3\,^3P_J$)+F_2 determined by time-resolved atomic resonance absorption spectroscopy, in order to compare absolute rate data obtained by this method with those from the flow technique,[14] but also the analogous absolute rate data for Si($3\,^1D_2$)+F_2 and Si($3\,^1S_0$)+F_2, in order to investigate further the relationship between collisional behaviour and electronic structure.[15,16] We have demonstrated hitherto[3,9-12] that correlations based on the weak spin–orbit coupling approximation[17] constitute a useful basis for discussion of the collisional behaviour of atomic silicon in specific electronic states with a range of molecules, and this is extended here to reaction with molecular fluorine. This automatically includes consideration of channels leading to specific electronic states of SiF+F *via* the correlation diagram connecting the states of Si+F_2 and SiF+F, a matter of interest to possible laser applications discussed by Armstrong and Davis.[14,18-21]

EXPERIMENTAL

The experimental arrangement broadly employed the systems described previously for the kinetic study of Si($3\,^3P_J$),[3,9] Si($3\,^1D_2$)[10,11] and Si($3\,^1S_0$)[12,13] with a limited number of modifications. These include improvements in optical baffling to reduce scattered light (a major factor in these investigations) and screening of the data-handling systems to prevent spurious triggering of the electronics and also to reduce noise effects. This apparatus is essentially a modification of that described in detail by Husain and Norris[22] for the kinetic study of $P(3\,^4S_{3/2})$ in the vacuum ultraviolet region. Thus atomic silicon in the relevant electronic state was generated by the repetitive pulsed irradiation ($E \approx 80$–160 J, repetition rate = 0.2 Hz) of low pressures of $SiCl_4$ in the presence of an excess of helium buffer gas (typically $[He]:[SiCl_4] \approx 10^5:1$) in a slow-flow system, kinetically equivalent to a static system following Heidner *et al.*[23,24] The reaction mixture was thus prepared from the combination of three gaseous flows, (*a*) $SiCl_4$+He, (*b*) F_2+He and (*c*) He alone, which entered a mixing vessel (at approximately equal pressures) *via* three coplanar capillaries orthogonal to the flow to avoid mutual pumping before entry into the reactor. Furthermore the coaxial lamp and vessel assembly, employing a common wall of high-purity quartz (Spectosil), was used here as previously described.[3,9-13] Kinetic investigations of Si($3\,^3P_J$), Si($3\,^1D_2$) and Si($3\,^1S_0$), sufficiently free from cascading effects within the energy manifold, were then achieved as follows.

First, in principle, photolysis from the annular pulsed discharge through the Spectrosil common wall should yield actinic radiation at $\lambda > ca.$ 165 nm. In practice the wall requires regular maintenance as the mildest deposit from the electrodes causes rapid deterioration in the light-transmission characteristics. Hence Si($3\,^1S_0$) can only be generated for a limited period of operation of the reactor, after which only Si($3\,^1D_2$) and Si($3\,^3P_J$) are produced in concentrations sufficiently high for absorption measurements. In any event there is no cascading into the Si($3\,^1S_0$) state from higher-lying Rydberg states during measurements of its kinetic decay, and experimentally the practical requirement is to cause photolysis of $SiCl_4$ at sufficiently low wavelengths to yield Si($3\,^1S_0$) at suitable concentrations. Secondly, the relatively large photolytic yields of Si($3\,^3P_J$) and the longer time-scales over which the decay of the ground state is monitored compared with the $^1D_2$ and $^1S_0$ states[3,9-13] clearly indicate that kinetic measurements can be ascribed to the ground-state atoms that are free of kinetic complexities arising from the optically metastable singlet states. These complexities are attributed to the cascading effect, which would be most marked for Si($3\,^1D_2$). This is borne out by the numerical solutions of the appropriate differential equations for the excited states of silicon.[12] Finally, the energetically favourable and symmetry-allowed pathways to accessible states of SiF+F would indicate removal of all the states of atomic silicon by chemical reaction.

Following pulsed irradiation the three states of atomic silicon were monitored in absorption *via* the following resonance transitions:[25]

transition	λ/nm	gA/s^{-1}
$Si[4s(^3P_J)] \leftarrow Si[3p^2(^3P_J)]$	251.6	
$Si[4s(^3P_1)] \leftarrow Si[3p^2(^3P_0)]$	251.43	5.7×10^8
$Si[4s(^3P_2)] \leftarrow Si[3p^2(^3P_1)]$	250.69	6.3×10^8
$Si[4s(^3P_2)] \leftarrow Si[3p^2(^3P_2)]$	251.61	1.3×10^9
$Si[4s(^1P_1^0)] \leftarrow Si[3p^2(^1D_2)]$	288.16	1.5×10^9
$Si[4s(^1P_1^0)] \leftarrow Si[3p^3(^1S_0)]$	390.53	8.6×10^7

Whilst kinetic measurements on the individual spin–orbit levels of the ground state, Si($3\,^3P_{0,1,2}$), have been described, we employ the method of monitoring the sum of these lines as indicated above. This follows the earlier procedure used in kinetic studies of Si($3\,^3P_J$) with various molecules.[3,9] Husain and Norris[3] have described the determination of the value of γ in the modified Beer–Lambert law[26]

$$I_{tr} = I_0 \exp[-(\varepsilon c l)^\gamma] \qquad \text{(i)}$$

(where the symbols have their usual significance)[26] for this sum of lines as $\gamma = 0.51 \pm 0.04$ for this type of experimental arrangement.[3] Thus, whilst the degree of resonance absorption would be less than that obtained by monitoring a specific spin–orbit state [*i.e.* Si($3\,^3P_0$) at $\lambda = 251.43$ nm; $\gamma = 0.98 \pm 0.15$], this is more than offset by the reduction in the noise level using the larger I_0 signal resulting from widening the slits of the grating monochromator (Czerny–Turner mount, McPherson Instrument Corporation, U.S.A.). The atomic-resonance transitions were derived from a microwave-powered emission flow lamp (*ca.* 1% $SiCl_4$ in He, $p_{total} \approx 70$ N m^{-2}, typical incident power = 75 W, Microtron 200 microwave generator plus reflected power meter, Electromedical Supplies) of the type described by Davis and Braun[27] for various other atomic transitions using an air-cooled Fehsenfeld cavity.[28]

Thus, following pulsed irradiation Si($3\,^3P_J$, $3\,^1D_2$, $3\,^1S_0$) were monitored photoelectrically by the technique of pre-trigger photomultiplier gating. We have hitherto[22] described in detail the use of the E.M.I. photomultiplier tube (E.M.I. 9816QB) specifically designed for operation in the gated mode (1.8 kV, Wallis power supply, 5 kV, 6 mA). All measurements involved a 'gate-on'[22] duration of 250 μs. Hence, using a thyratron double-pulser a pulse separation of 75 μs between defocussing the gating electrode of the photomuliplier tube and firing the discharge circuitry was obtained. Consequently measurements on atomic silicon began $250-75=175$ μs after the initiation-flash discharge. Subsequent to previous kinetic measurements on atomic silicon, a honeycombe collimator and baffle system at the enterance slit of the monochromator was found to be necessary to reduce the effect of scattered light. This is of special concern owing to the high gain of the photomultiplier tube and the short duration of the reaction.

The photoelectric signals representing resonance absorption were amplified by means of a current-to-voltage converter employing a fast-settling operational amplifier[29] to avoid signal distortion. The data-handling system [Data Laboratories transient recorder DL920 in the A/B mode and signal averager (Data Laboratories DL 4000)] with paper-tape output (Datadynamics 1183 in ASCII code) has been described previously.[12] By contrast with earlier kinetic measurements on atomic silicon, the complete data-handling system, including all input connections, was fully encased and shielded in a Faraday cage. This prevented spurious triggering of the electronics. The digitised output was analysed on the University of Cambridge IBM 3081 computer using the data-smoothing procedure of Savitsky and Golay[30] where appropriate. With the exception of fluorine (B.O.C. cylinder, 5%F_2 in He)† all materials were prepared essentially as previously described.[3,9-13]

RESULTS AND DISCUSSION

The quality of the raw data obtained by direct monitoring of the transient silicon atom resulting from photodissociation of a stable molecule such as $SiCl_4$, as with analogous studies on atomic carbon,[31] is primarily determined by the degree of light absorption from the atomic resonance radiation source.[3,9-13] A complementary consideration is the relatively short times subsequent to photomultiplier gating procedures (despite their efficiency and complexity) over which Si($3\,^3P_J$, $3\,^1D_2$, $3\,^1S_0$) may be monitored. This is governed by the concentrations of the $SiCl_4$ precursor molecules, as these three states each react with this molecule at rates approaching the collision number.[11] There is therefore a narrow 'chemical window' of concentrations of $SiCl_4$ for each atomic state which yields the combination of resonance absorption and decay time suitable for kinetic studies.

Fig. 1-3 show, respectively, examples of the digitised forms of the computerised output for the transmitted light intensity at $\lambda=251.6, 288.2$ and 390.5 nm, indicating the decay of resonance absorption by Si($3\,^3P_J$), Si($3\,^1D_2$) and Si($3\,^1S_0$). Those computer points representing output while the gating system is switched off constitute electronic noise and hence have been removed from these figures for clarity of presentation. Apart from this, the data are the actual computer output. Note that, while the magnitude of I_0 varies with each experiment (owing to the nature of the flow lamp), this does not affect the measured first-order rate coefficients. It is sufficient that there be an I_0 signal between 20 and 300 mV which is constant for the duration of the experiment.

As with the previous studies,[3,9-13] first-order kinetic plots {ln [ln (I_0/I_{tr})] plotted against time} were used to determine the overall first-order decay coefficients, k', for the removal of the appropriate electronic state. However, because of the small degree of light absorption, particularly by Si($3\,^1S_0$) and Si($3\,^1D_2$) (in some cases as low as 1 to 2%) and the possibility of large fluctuations in the limit $\lim_{I_0-I_{tr}}$ {ln [ln (I_0/I_{tr})]}, an alternative method was used to confirm values of k'. This took the form of a direct fit of the digitised output of the type indicated in

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† We are indebted to Dr I. W. M. Smith for samples of this material.

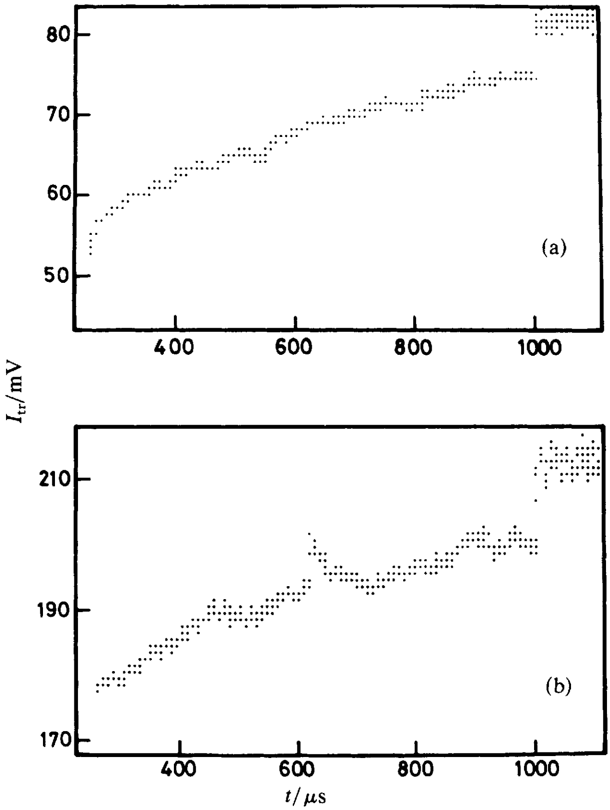

Fig. 1. Digitised time-variation of the transmitted light intensity at $\lambda = 251.6$ nm [$Si(4\,^3P_J \rightarrow 3\,^3P_J)$] indicating the decay of resonance absorption by ground-state silicon atoms, $Si(3\,^3P_J)$, following the pulsed irradiation of $SiCl_4$ in the presence of molecular fluorine. $[SiCl_4] = 7.0 \times 10^{12}$ molecule cm^{-3}, $[He] \approx 8.3 \times 10^{17}$ atom cm^{-3}, $E = 76$ J, repetition rate = 0.2 Hz, no. of experiments for averaging = 64, smoothed data. $[F_2]/10^{13}$ molecule cm^{-3} = (*a*) 0.0 and (*b*) 5.7.

fig. 1–3 to the equation

$$I_{tr} = I_0 \exp[-A \exp(-k't)] \qquad \text{(ii)}$$

following the procedures of Clark and Husain.[32,33] Eqn (ii) follows from the combination of the standard Beer–Lambert law [$I_{tr} = I_0 \exp(-\varepsilon cl)$] and a first-order kinetic profile. k' is the object of experimental interest for each atomic state. Not unexpectedly both computational techniques agreed within their limits of uncertainty; however, the former method was favoured and used predominantly in the calculation of the first-order rate coefficients reported in table 1, this being simply for ease of operation as both procedures have in this instance comparable error limits. In the case of measurements at $\lambda = 251.6$ nm for $Si(3\,^3P_J)$, the analysis yields $\gamma k'$ *via* eqn (i). Hence, k' is determined through the use of the previously determined value of $\gamma[\lambda = 251.6\text{ nm for } Si(3\,^3P_J)] = 0.51 \pm 0.04$.[3] Fig. 4 shows examples of the results of curve-fitting procedures based on eqn (ii) for $Si(3\,^3P_J)$, $Si(3\,^1D_2)$ and $Si(3\,^1S_0)$ in the presence of various concentrations of F_2.

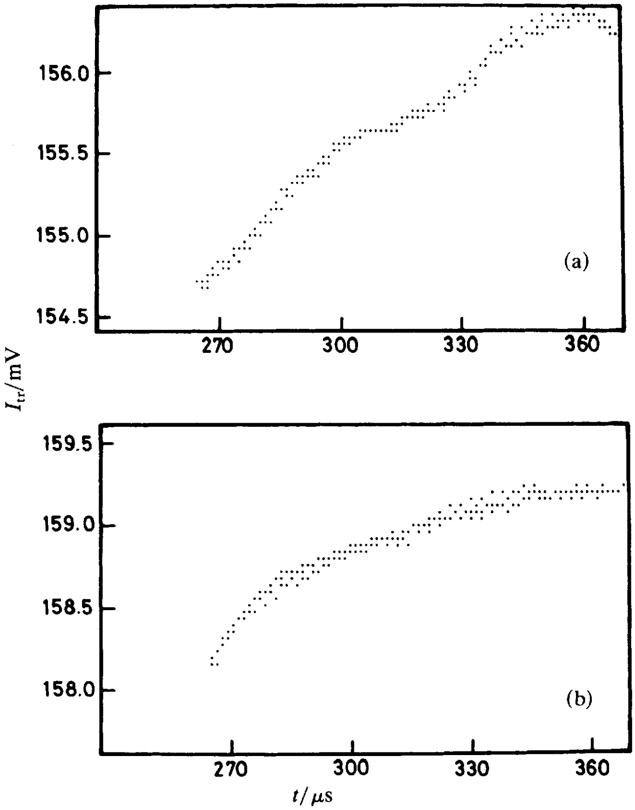

Fig. 2. Digitised time-variation of the transmitted light intensity at $\lambda = 288.16$ nm [$Si(4\,^1P_1^0 \rightarrow 3\,^1D_2)$] indicating the decay of resonance absorption by electronically excited silicon atoms, $Si(3\,^1D_2)$, following the pulsed irradiation of $SiCl_4$ in the presence of molecular fluorine. $[SiCl_4] = 8.2 \times 10^{12}$ molecule cm^{-3}, $[He] \approx 8.3 \times 10^{17}$ atm cm^{-3}, $E = 160$ J, repetition rate = 0.2 Hz, no. of experiments for averaging = 64, smoothed data, $[F_2]/10^{13}$ molecule cm^{-3} = (*a*) 7.7 and (*b*) 14.3.

The resulting values of k' are expressed in the form

$$k' = K + k_2[F_2] \qquad \text{(iii)}$$

where k_2 represents the absolute second-order rate constant for the removal of $Si(3\,^3P_J)$, $Si(3\,^1D_2)$ and $Si(3\,^1S_0)$ on collision with fluorine. K is principally determined by the magnitude of the term k_{SiCl_4} $[SiCl_4]$ for each atomic state[11] and is a constant in a series of experiments with varing $[F_2]$ and in which $[SiCl_4]$ is held constant. Following the procedure employed by Armstrong and Davis,[14] the resulting values of k' and k_2 are presented in tabular form (table 1) for the purpose of data compilation in view of the importance of reaction with this molecule. The intercept, K, used in the calculations of k_2 through eqn (iii) and determined by a least-squares extrapolation of the results of these investigations (k' against $[F_2]$) is indicated in fig. 5–7. The resulting absolute second-order rate constants were

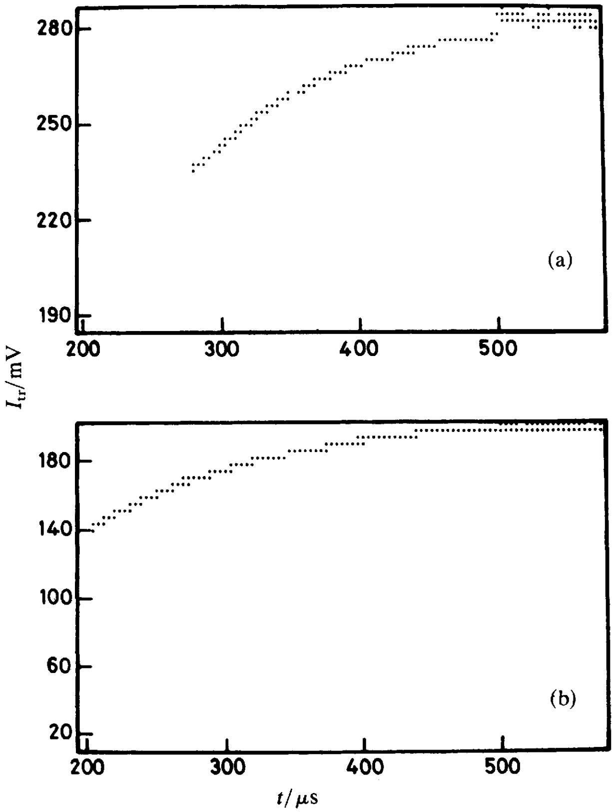

Fig. 3. Digitised time-variation of the transmitted light intensity at $\lambda = 390.53$ nm [Si($4\,^1P_1^0 \rightarrow 3\,^1S_0$)] indicating the decay of resonance absorption by electronically excited silicon atoms, Si($3\,^1S_0$), following the pulsed irradiation of $SiCl_4$ in the presence of molecular fluorine. $[SiCl_4] = 8.1 \times 10^{12}$ molecule cm^{-3}, $[He] \approx 8.3 \times 10^{17}$ atom cm^{-3}, $E = 160$ J, repetition rate = 0.2 Hz, no. of experiments for averaging = 64 smoothed data. $[F_2]/10^{13}$ molecule cm^{-3} = (*a*) 0.0 and (*b*) 11.8.

obtained by weighted least-squares analyses, yielding

	k_2/cm^3 molecule^{-1} s^{-1} ($T = 300$ K)
Si($3\,^3P_J$) + F_2	$(1.2 \pm 0.5) \times 10^{-11}$
Si($3\,^1D_2$) + F_2	$(8.2 \pm 2.1) \times 10^{-11}$
Si($3\,^1S_0$) + F_2	$(1.9 \pm 0.8) \times 10^{-10}$
Si($3\,^3P_J$) + Cl_2 [9]	$(3.3 \pm 0.3) \times 10^{-10}$
Si($3\,^1D_2$) + Cl_2 [9]	$(6.1 \pm 0.7) \times 10^{-11}$
Si($3\,^1S_0$) + Cl_2 [9]	$(7.3 \pm 0.1) \times 10^{-11}$

which are compared with the analogous data reported hitherto[9] for removal by Cl_2.

Table 1. Summary of rate data for the collisional removal of Si($3\,^3P_J$), Si($3\,^1D_2$) and Si($3\,^1S_0$) by molecular fluorine at $T = 300$ K $\{k_2 = (k' - K)/[F_2]$ cm^3 molecule^{-1} s^{-1}, [He] $= 8.3 \times 10^{17}$ atom cm$^{-3}\}$. (*a*) Si($3\,^3P_J$) : [SiCl$_4$] $= 7.5 \times 10^{12}$ molecule cm^{-3}; (*b*) Si($3\,^1D_2$) : [SiCl$_4$] $= 8.5 \times 10^{12}$ molecule cm^{-3}; (*c*) Si($3\,^1S_0$) : [SiCl$_4$] $= 8.7 \times 10^{12}$ molecule cm^{-3}.

(*a*) Si($3\,^3P_J$)

$[F_2]/10^{13}$ molecule cm^{-3}	$k'/10^3$ s^{-1}	$k_2/10^{-12}$ cm^3 molecule^{--} s^{-1}
0.0	2.8 ± 0.1	—
4.1	3.6 ± 0.1	22.3 ± 0.6
6.3	3.4 ± 0.2	11.1 ± 0.7
5.7	3.3 ± 0.05	11.3 ± 0.2
6.7	3.4 ± 0.1	11.4 ± 0.4
8.2	2.9 ± 0.2	3.3 ± 0.3
10.2	3.8 ± 0.2	11.5 ± 0.6
10.6	4.3 ± 0.1	15.5 ± 0.4
12.1	3.4 ± 0.2	5.9 ± 0.4
17.0	4.5 ± 0.2	10.8 ± 0.5
22.1	6.3 ± 0.3	16.6 ± 0.7
26.5	5.2 ± 0.3	9.5 ± 0.6

$k_2[\mathrm{Si}(3\,^3P_J) + F_2] = (1.2 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(*b*) Si($3\,^1D_2$)

$[F_2]/10^{13}$ molecule cm^{-3}	$k'/10^3$ s^{-1}	$k_2/10^{-11}$ cm^3 molecule^{-1} s^{-1}
0.0	1.3 ± 0.4	—
0.0	2.1 ± 0.3	—
0.0	2.4 ± 0.4	—
4.9	5.9 ± 0.9	8.5 ± 1.3
5.1	5.0 ± 1.0	6.6 ± 1.3
5.8	5.6 ± 1.1	6.9 ± 1.3
6.2	4.1 ± 0.8	3.9 ± 0.8
6.5	6.3 ± 0.3	7.2 ± 0.3
6.7	8.9 ± 0.9	10.8 ± 1.1
7.7	7.6 ± 0.8	7.7 ± 0.8
8.8	10.3 ± 1.1	9.8 ± 1.0
9.9	9.8 ± 0.5	8.2 ± 0.4
9.9	13.6 ± 1.4	12.1 ± 1.2
11.4	8.6 ± 0.9	6.1 ± 0.6
11.9	12.3 ± 1.0	8.9 ± 0.7
14.3	14.5 ± 2.9	9.0 ± 1.8
25.5	14.1 ± 2.1	8.0 ± 1.2
17.3	12.2 ± 1.5	6.1 ± 0.7
18.4	18.8 ± 1.9	9.3 ± 0.9

$k_2[\mathrm{Si}(3\,^1D_2 + F_2)] = (8.2 \pm 2.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(*c*) $Si(3\,^1S_0)$

$[F_2]/10^{13}$ molecule cm^{-3}	$k'/10^4$ s^{-1}	$k_2/10^{-10}$ cm^3 molecule^{-1} s^{-1}
0.0	1.7 ± 0.1	—
0.0	1.8 ± 0.1	—
0.0	2.1 ± 0.1	—
6.0	2.7 ± 0.2	1.7 ± 0.1
7.7	3.1 ± 0.2	1.9 ± 0.1
7.9	2.9 ± 0.1	1.6 ± 0.1
8.6	2.6 ± 0.4	1.1 ± 0.2
9.0	3.2 ± 0.1	1.8 ± 0.1
9.8	3.7 ± 0.2	2.1 ± 0.1
10.5	3.9 ± 0.1	2.2 ± 0.1
11.0	4.0 ± 0.2	2.1 ± 0.1
11.1	2.6 ± 0.3	0.9 ± 0.2
11.8	4.2 ± 0.3	2.2 ± 0.1
13.1	4.1 ± 0.6	1.9 ± 0.3
13.5	4.1 ± 0.3	1.8 ± 0.1
15.8	4.9 ± 0.2	2.1 ± 0.1
18.1	4.1 ± 0.4	1.4 ± 0.1
20.2	6.3 ± 0.5	2.3 ± 0.2

$k_2[Si(3\,^1S_0)+F_2] = (1.9 \pm 0.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

The errors quoted for the results here represent the reproducibility of the second-order rate constant as well as an estimate of the accuracy of the analysis.

The only data with which we can directly compare our results are those for $Si(3\,^3P_J)+F_2$ described for $T = 600$ K from the flow measurements of Armstrong and Davis,[14] who reported $k_2[Si(3\,^3P_J)+F_2] = (1.2 \pm 0.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} ($T = 600$ K). There is comparable scatter in the analogous plot to fig. 5 for the flow measurement [fig. 2, ref. (14)]. Combination of the higher-temperature flow data with the present results for $Si(3\,^3P_J)$ would indicate a small activation energy of *ca.* 12 kJ mol^{-1} for the reaction. This latter estimate yields an Arrhenius form given by

$$k_2[Si(3\,^3P_J)+F_2] = (1.2 \pm 0.8) \times 10^{-10} \exp(-1382/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The present results for reactions with F_2, which indicate $k_2[Si(3\,^3P_J)] < k_2[Si(3\,^1D_2)] < k_2[Si(3\,^1S_0)]$, may be contrasted with the results indicated above for removal by chlorine. Whilst the reverse order of reactivity is observed for Cl_2, the rates are all rapid and lie within a factor of five. Furthermore, there are symmetry-allowed exothermic routes to SiCl+Cl for the three atomic states [$Si(3\,^3P_J)+Cl_2 \rightarrow SiCl+Cl$, $\Delta H = -1.59$ eV].[34,35] The correlation diagram connecting the states of $Si+Cl_2$ and SiCl+Cl, constructed on the basis of C_s symmetry and the weak spin–orbit coupling approximation,[17] indicating these pathways has been given by Husain and Norris.[11] Fig. 8 shows the correlation diagram connecting the states of $Si+F_2$ and SiF+F at infinite separation constructed on the basis of C_s symmetry in the 'least-symmetrical complex' and employing the weak spin–orbit coupling approximation.[1,17,34] There are symmetry-allowed routes for chemical reaction of

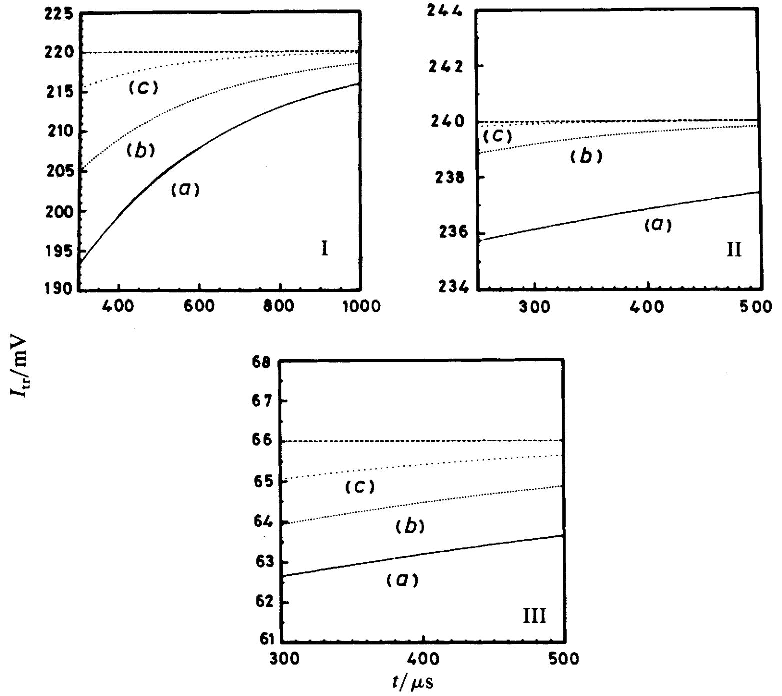

Figure 4. Examples of computerised fitting of the digitised time-variation of the transmitted light intensity (I_{tr}) at (I) $\lambda = 251.6$ nm [$Si(4\,^3P_J \rightarrow 3\,^3P_J)$], (II) $\lambda = 288.16$ nm [$Si(4\,^1P_1^0 \rightarrow 3\,^1D_2)$] and (III) $\lambda = 390.53$ nm [$Si(4\,^1P_1^0 \rightarrow 4\,^1S_0)$], indicating the decay of resonance absorption by $Si(3\,^3P_J)$, $Si(3\,^1D_2)$ and $Si(3\,^1S_0)$, respectively, following the pulsed irradiation of $SiCl_4$ in the presence of molecular fluorine to the form: $I_{tr} = I_0 \exp\{A[\exp(-Bt)]\}$. $[SiCl_4] \approx 8 \times 10^{12}$ molecule cm^{-3}, $[He] \approx 8.3 \times 10^{17}$ atom cm^{-3}, top line in each diagram = I_0 signal.

	I			II			III		
	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)
$[F_2]/10^{13}$ molecule cm^{-3}	0.0	5.7	17.0	0.0	6.5	15.6	0.0	7.7	13.1
$k'/10^3$ s^{-1}	2.8	3.3	4.5	2.1	6.9	14.1	18	31	41

the three species; however, only $Si(3\,^1S_0)$ correlates in this manner with an electronially excited state of SiF:

channels	ΔH/eV^{1,17,34}
$Si(3\,^3P_J) + F_2(X\,^1\Sigma_g^+) \xrightarrow{^3A'+2\,^3A''} SiF(X\,^2\Pi_r) + F(2\,^2P_J)$	−3.968
$Si(3\,^1D_2) + F_2(X\,^1\Sigma_g^+) \xrightarrow{3\,^1A'+2\,^1A''} SiF(X\,^2\Pi_r) + F(2\,^2P_J)$	−4.749
$Si(3\,^1S_0) + F_2(X\,^1\Sigma_g^+) \xrightarrow{^1A'} SiF(A\,^2\Sigma^+) + F(2\,^2P_J)$	−5.043

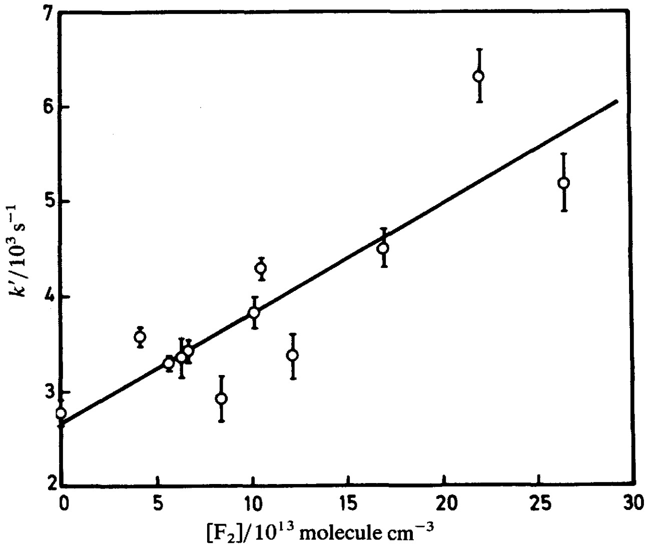

Fig. 5. Variation of the pseudo-first-order rate coefficient (k') for the decay of Si($3\,^3P_J$) in the presence of fluorine ([He] ≈ 8.3×10^{17} atom cm^{-3}).

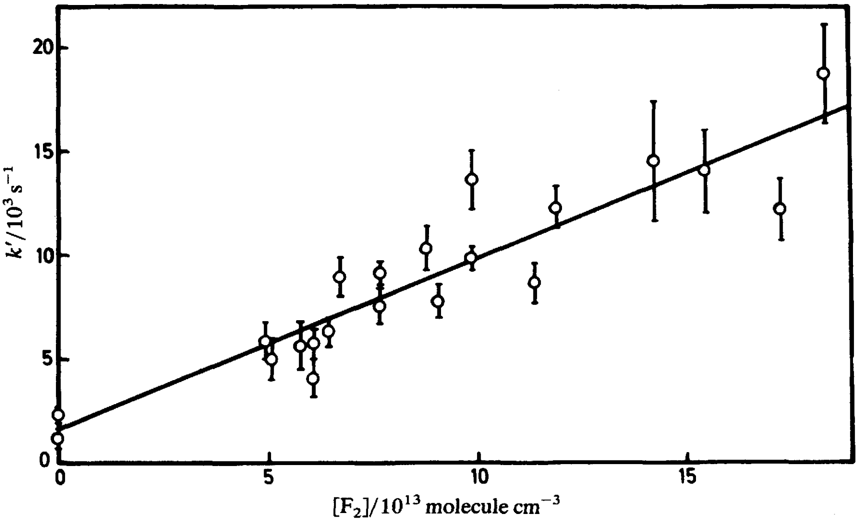

Fig. 6. Variation of the pseudo-first-order rate coefficient (k') for the decay of Si($3\,^1D_2$) in the presence of fluorine ([He] ≈ 8.3×10^{17} atom cm^{-3}).

Inspection of fig. 8 shows that on energetic grounds a number of electronic states of SiF would be thermochemically accessible but population of these would require either the breakdown of the weak spin–orbit coupling approximation and correlations based on J–Ω coupling[16] or surface crossing, of which there should be many, together with non-adiabatic transitions. Clearly, the rapid removal of Si($3\,^3P_J$, $3\,^1D_2$, $3\,^1S_0$) by F_2 is in accord with fig. 8, which, it must be stressed, is a

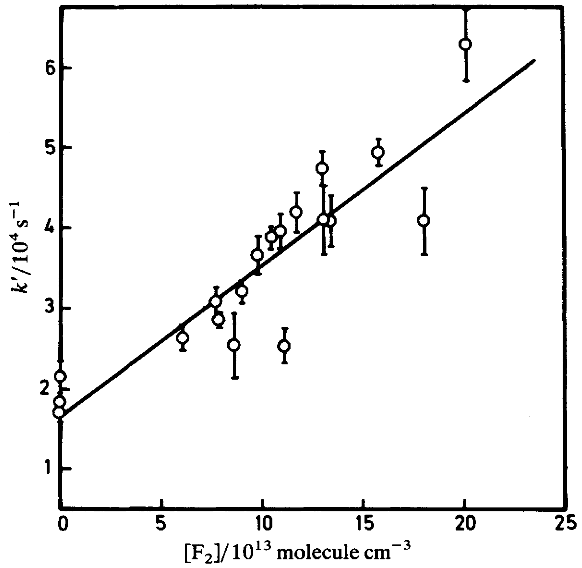

Fig. 7. Variation of the pseudo-first-order rate coefficient (k') for the decay of $Si(3\,^1S_0)$ in the presence of fluorine ($[He] \approx 8.3 \times 10^{17}$ atom cm^{-3}).

correlation diagram and not a potential-energy diagram and therefore does not indicate energy barriers or the energies at which surface crossings take place. It has been emphasised in previous publications[15,16] that a complete state manifold to the energy level of interest, such as of SiF_2, is required for correlation. Schaeffer and coworkers[36] have recently calculated the energies of the three lowest electronic states of SiF_2 with full geometrical optimisation. They find the $\tilde{a}\,^3B_1$ and $\tilde{A}\,^1B_1$ states to lie, respectively, 2.998 and 6.110 eV above the $\tilde{X}\,^1A_1$ ground state, in good accord with the spectroscopically determined values of Rao,[37] who reports 3.262 and 5.469, respectively. Using $D(SiF—F) = 8.28 \pm 0.607$ eV,[38] $D_0^\circ[Si—F(X\,^2\Pi_r)] = 5.57$ eV[34] and $D_0^\circ[F_2(X^1\Sigma_g^+)] = 1.602$ eV[34] the $\tilde{X}\,^1A_1$, $\tilde{a}\,^3B_1$ and $\tilde{A}\,^1B_1$ states of SiF_2 lie at, respectively, −12.25, −8.99 and −6.78 eV with respect to $Si(3\,^3P_J) + F_2(X^1\,\Sigma_g^1)$. Thus the $\tilde{X}\,^1A_1$ and $\tilde{A}\,^1B_1$ states of SiF_2 provide potential wells for correlating $Si(3\,^1D_2) + F_2(X\,^1\Sigma_g^+)$ with ground-state products of SiF+F *via*, respectively, $^1A'$ and $^11A''$ surfaces. $SiF_2(\tilde{a}\,^3B_1)$ yields the potential well leading $Si(3\,^3P_J) + F_2$ to ground-state products of SiF+F *via* a $^3A''$ surface (fig. 8). Clearly, a fuller state manifold of SiF_2 is required for an analogous correlation diagram of the type presented hitherto for $Si + H_2 \rightarrow SiH + H$[11] based on the lowest eight states of SiH_2 calculated by Wirsam.[39]

Finally, the electronic states of product SiF not only provide a guide to reaction pathways as indicated on fig. 8 but may also be used as a spectroscopic marker. For example, the system $SiF(A\,^2\Sigma^+) - SiF(X\,^2\Pi_r) + h\nu$ may in principle be used to monitor the kinetics of the $^1S_0$ state. Thus the time-dependence of the A–X emission resulting from the reaction between $Si(3^1S_0) + F_2$ (fig. 8) could be used to determine k' for the $^1S_0$ state, including its value in the presence of added gases, provided that the decay coefficient is significantly less than $A_{nm}\{A_{nm}[SiF(A\,^2\Sigma^+) - SiF(X\,^2\Pi_r)]$, (0, 0), $\lambda = 436.82$ nm $= 4.3 \times 10^6\ s^{-1}\}$.[19] Similar considerations will apply to other product electronic states of SiF where $A_{nm} \gg k'$ for a given atomic state. In the

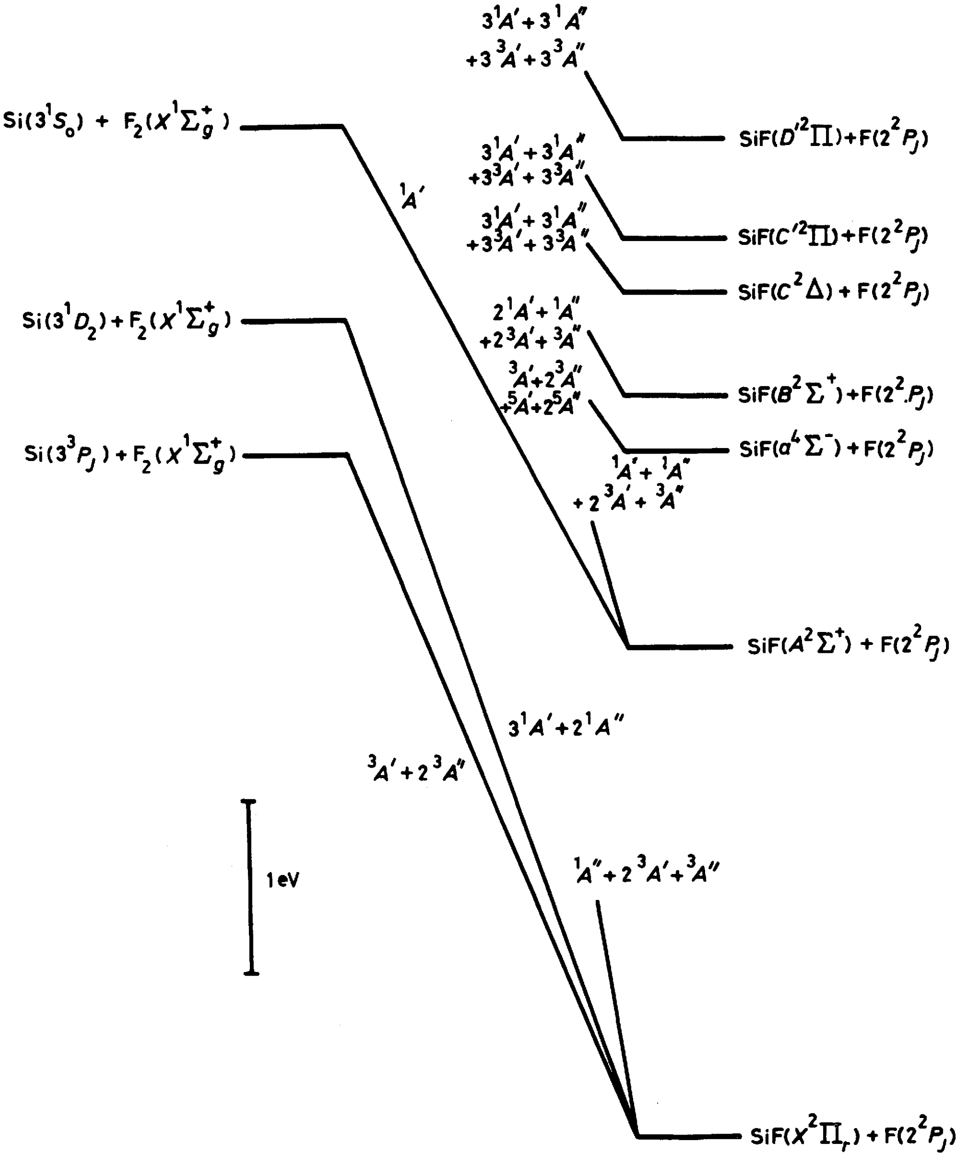

Fig. 8. Correlation diagram connecting the states of Si + F_2 and SiF + F.

case of the optically metastable SiF($a\ ^4\Sigma^-$) state, even though population *via* reaction of Si($3\ ^3P_J$, $3\ ^1D_2$, $3\ ^1S_0$) + F_2 will arise, in the weak spin–orbit coupling approximation, at least, from non-adiabatric transitions, there are six surfaces correlating with SiF($a\ ^4\Sigma^-$) + F($2\ ^2P_J$). Further, product SiF($A\ ^2\Sigma^+$) will be rapidly depleted by A–X spontaneous emission as indicated above ($\tau_0 = 0.23\ \mu$s).[19] Hence a population inversion between SiF($a\ ^4\Sigma^-$) and SiF($A\ ^2\Sigma^+$), particularly facilitated by reactions of the electronically excited Si($3\ ^1D_2$) and Si($3\ ^1S_0$), is feasible in the pulsed mode.

This in turn provides the initial basis of a pulsed photochemical laser system operating in the 1.4 μm region which we propose to investigate together with the spontaneous emission from other product states and molecular resonance absorption measurements on the ground-state product, SiF($X\ ^2\Pi_r$).

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