

The Si(³P_J) + O₂ reaction: A fast source of SiO at very low temperature; CRESU measurements and interstellar consequences

S. D. Le Picard¹, A. Canosa¹, G. Pineau des Forêts², C. Rebrion-Rowe¹, and B. R. Rowe¹

¹ UMR 6627: Physique des Atomes, Lasers, Molécules et Surfaces, Équipe Astrochimie Expérimentale, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France

² Observatoire de Paris, 92195 Meudon Principal Cedex, France
e-mail: Guillaume.PineauDesForets@obspm.fr

Received 8 March 2001 / Accepted 23 March 2001

Abstract. The rate coefficient of the reaction Si(³P_J) + O₂ → SiO + O has been measured at temperatures down to 15 K using a CRESU (Cinétique de Réaction en Écoulement Supersonique Uniforme) apparatus coupled with the PLP-LIF (Pulsed Laser Photolysis – Laser Induced Fluorescence) technique. The temperature dependence of the rate coefficient is well fitted using the expression: $1.72 \times 10^{-10} (T/300 \text{ K})^{-0.53} \exp(-17 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the temperature range 15–300 K. The silicon chemistry in interstellar clouds is reviewed and possible consequences of our study are stressed.

Key words. molecular processes – methods: laboratory – ISM: molecules

1. Introduction

The silicon monoxide molecule SiO is the most widespread silicon-bearing molecule in the interstellar medium. Its abundance, however, shows large variations under the differing physical conditions of interstellar objects. The largest fractional abundance ($\approx 2 \times 10^{-6}$) has been observed in star-forming regions (Martin-Pintado et al. 1992) whereas it is found to be extremely low in cold dense clouds such as TMC1 and L183 ($< 3 \times 10^{-12}$, Ziurys et al. 1989). Intermediate values of about 10^{-10} were also measured in several translucent molecular clouds (Turner 1998), in “spiral arm” clouds (Greaves et al. 1996), and in photodissociation regions (Schilke et al. 2001). Although several models have been elaborated to explain the large variations of the SiO abundance, this is still a matter of debate. Briefly, two main ideas can be found in the literature. It is first argued that silicon bearing molecules are strongly depleted onto grains in cold quiescent regions whereas in photodominated regions or in dynamical active regions their abundance increases due to photodesorption (Turner 1998; Walmsley et al. 1999) from grains or to local shocks inside which grains are partially destroyed, releasing silicon back to the gas phase (Gueth et al. 1998; Schilke et al. 1997). Alternatively, observations by

Ziurys et al. (1989) led these authors to propose that SiO production is dependent on the kinetic temperature of the gas. Their major guess was to suggest that the chemistry has an activation energy barrier of ≈ 90 K. Gas phase SiO production in available models occurs via a series of ion-molecule reactions (see for example Herbst et al. 1989) or/and neutral-neutral reactions amongst which



and



are used by almost all models and are the most straightforward. For instance, Langer & Glassgold (1990) proposed a simple model where SiO is formed mainly via these two reactions. Going deeply into the Ziurys et al. assumptions, Langer & Glassgold extended a theoretical study by Graff (1989) and used rate coefficients proportional to $\exp -111 \text{ K}/T$ where 111 K corresponds to the difference in energy between the first two spin-orbit levels of the silicon ground state: ³P₀ and ³P₁. This inferred temperature dependence was also used by Schilke et al. (1997) and Turner (1998). Other authors, however, preferred a $T^{0.5}$ dependence based on the collision theory (Herbst et al. 1989; MacKay 1995, 1996; Turner 1998; Walmsley et al. 1999). In every case, therefore, authors were expecting a lower rate coefficient as the temperature decreased but

Send offprint requests to: A. Canosa,
e-mail: andre.canosa@univ-rennes1.fr

obviously some clarification was required, as for example stressed by Pineau des Forêts & Flower (1997) who claimed: “*It should be noted that $Si + O_2 \rightarrow SiO + O$ is a key reaction for the production of SiO in dense clouds, and it would be interesting to measure the rate coefficient for this neutral-neutral reaction below 300 K*”.

From an experimental point of view, indeed, the reaction $Si(^3P) + O_2 \rightarrow SiO + O$ has only been studied by two groups (Husain & Norris 1978; Swearingen et al. 1978) and only close to room temperature. Husain & Norris (1978) used a slow He flow tube apparatus working at room temperature in which silicon atoms were produced by pulsed irradiation of SiCl₄ and detected in absorption in the ultraviolet using resonance radiation derived from a microwave-powered flow lamp. They obtained a fast rate of $(2.7 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K. In the fast flow tube experiment by Swearingen et al. (1978), silicon atoms were produced by flowing a mixture of argon and SiH₄ through a hollow cathode discharge and their detection was achieved using resonance absorption at 251.6 nm ($3p^2 \ ^3P_2 \rightarrow 4s \ ^3P_1$). Although this study was carried out at a slightly higher temperature (350 K) than that of Husain & Norris, Swearingen et al. measured a rate constant which was 30 times lower: $(9.8 \pm 4.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ than the value of Husain & Norris. In interstellar cloud models, most of the authors interested in the silicon chemistry used the value of Husain & Norris (with the exception of Langer & Glassgold 1990) in their simulations.

The aim of the present work was therefore to answer the request of Pineau des Forêts & Flower (1997) by studying the kinetics of the $Si(^3P) + O_2 \rightarrow SiO + O$ reaction in the temperature range 15–300 K. This work was carried out at the University of Rennes I using the CRESU facility associated to the PLP-LIF technique (Pulsed Laser Photolysis – Laser Induced Fluorescence). In recent years, experiments using this technique, in close collaboration between our laboratory at Rennes and Prof. Ian Smith’s laboratory at Birmingham, allowed us to measure the rate coefficients for many rapid neutral reactions at extremely low temperature involving radicals CN, OH, CH, C₂H (Smith & Rowe and references therein 2000), and atoms, Al(²P) (Le Picard et al. 1997) and C(³P) (Chastaing et al. 2000, 2001).

The apparatus will be briefly described in the next section followed by a presentation of the experimental results and their relevance to interstellar environments.

2. Experimental

The CRESU apparatus and the PLP-LIF technique have been extensively described elsewhere (Sims et al. 1994) so that only specific features will be reported here. Low temperatures were achieved via the isentropic expansion of a buffer gas (argon or helium) through a suitably designed Laval nozzle. The resulting supersonic flow was found to be axially and radially uniform in temperature, density and velocity (Sims et al. 1994). Due to the relatively high

density (10^{16} – 10^{18} cm^{-3}) of the expansion, thermal equilibrium is maintained along the flow. The Laval nozzle was mounted on a moveable reservoir into which the buffer gas as well as reagent gases were injected. Each nozzle is designed for a given set of temperature and pressure in the supersonic flow so that changes in temperature were achieved by using different nozzles. Our collection of nozzles (about 30) allowed us to work in the temperature range 15–300 K at a typical pressure of 0.2 mbar, although some of the nozzles work at a few mbar (1–6 mbar). Rate constants were measured using the Pulsed Laser Photolysis (PLP), Laser Induced Fluorescence (LIF) technique.

The silicon atoms were produced in the supersonic flow by multiphoton photolysis of tetramethylsilane, Si(CH₃)₄. Photolysis was achieved using a 266 nm YAG pulsed (10 Hz) laser beam, propagated along the flow axis through the throat of the Laval Nozzle and focused at the nozzle exit using a UV lens (37 cm focal length) located inside the moveable reservoir. A burst of silicon atoms was therefore produced in a small volume around the focal point. It then took several tens of microseconds to flow and reach the detection zone where a tuneable pulsed laser beam (MOPO 730, 10Hz), propagating perpendicularly to the flow, excited the $3p^2 \ ^3P_0 \rightarrow 4s \ ^3P_1$ transition of Si at 251.43 nm. After passing through a narrowband interference filter centred at 250 nm, the resonant fluorescence was then collected on the photocathode of a UV-sensitive photomultiplier tube set perpendicular both to the flow axis and the excitation laser beam.

The time delay between the two laser pulses was set equal to the time necessary for the silicon atoms formed at the focal point to reach the detection zone. The LIF signal from Si(³P₀) atoms was then measured and averaged over 200 laser shots for different oxygen flow rates. Figure 1 presents a typical decrease of the LIF signal as a function of the oxygen density for a given time delay (i.e. a given distance between the focal point and the detection zone). This decrease was well fitted using an exponential function $\exp^{-k_{1st}[O_2]}$ where k_{1st} is a first order rate coefficient expressed in $\text{cm}^3 \text{ molecule}^{-1}$ units. Such a set of measurements was then repeated for different focal point positions by moving the Laval nozzle so that several k_{1st} were obtained and plotted as a function of the time delay. This is illustrated in Fig. 2 where data are very well fitted using a straight line, crossing both axes at the origin. The slope of this line gave the second order rate coefficient k (expressed in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units) for the conditions of temperature and pressure for the particular Laval nozzle used.

Due to laser focusing, a large amount of energy was focused into the small volume where the silicon atoms were formed. The initial spin-orbit population of the Si(³P_J) ground state was therefore found to be strongly off-Boltzmann equilibrium. Furthermore, the first electronic excited state of silicon, Si (¹D₂), lying 0.78 eV (i.e. 9065 K) above the ground state was also detected resonantly by exciting the transition $3p^2 \ ^1D_2 \rightarrow 4s \ ^1P_1$ at

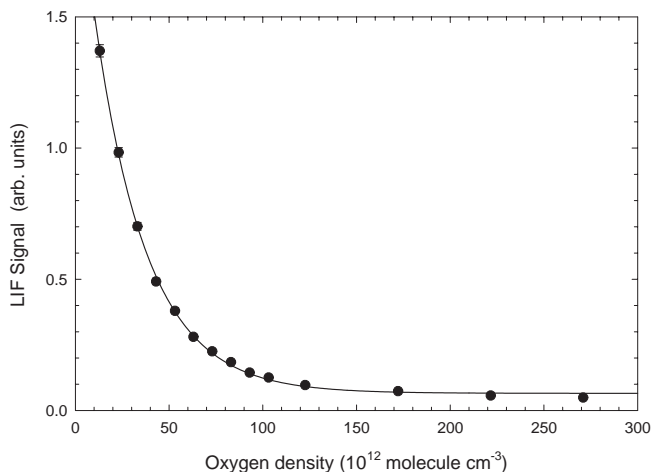


Fig. 1. Silicon atoms fluorescence signal as a function of oxygen density at 15 K for a time delay set to 130 μ s.

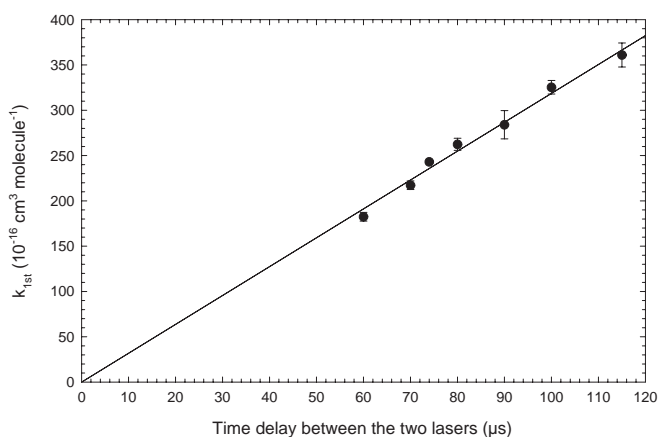


Fig. 2. First order rate coefficients k_{1st} plotted as a function of the time delay for the Laval nozzle working at 23 K.

288.16 nm. Collisional relaxation of the Si(¹D₂) state to the Si(³P_{*J*}) ground state presented different behaviour according to the nature of the buffer gas. Using argon, we observed a rapid decrease of the ¹D₂ LIF signal along the supersonic flow, indicating that collisional relaxation occurred rapidly as no ¹D₂ was ever detected after about 30 μ s. On the other hand, using helium as a buffer gas, the Si(¹D₂) state turned out to relax slowly on the time scale of the experiment. Therefore, for all Laval nozzles working in helium, we introduced a small amount of N₂ (\sim 1%) which was found to be a very efficient quencher of Si(¹D₂). To ensure the complete spin-orbit relaxation of the Si(³P) states, the three different levels ($J = 0, 1, 2$) were also individually probed as a function of time, exciting the transitions $3p^2\ ^3P_0 \rightarrow 4s\ ^3P_1$ (251.43 nm), $3p^2\ ^3P_1 \rightarrow 4s\ ^3P_2$ (250.69 nm), $3p^2\ ^3P_2 \rightarrow 4s\ ^3P_2$ (251.61 nm) respectively. In every condition, relative intensities of these transitions were found to be constant after about 40 μ s. Kinetic measurements, therefore, were only started after relaxation of Si(¹D₂) and Si(³P_{*J*}) had taken place. Consequently, the rate coefficients derived from our experiments concern Si(³P_{*J*}) atoms fully thermalised to the

temperature of the supersonic flow. It is worth noting, however, that at 15 K, only the $J = 0$ state was present, whereas at 23 K the signal arising from the $J = 1$ state was hardly detectable. This is consistent with the energy spacing between the fine structure levels of Si(³P_{*J*}) since Si(³P₁) and Si(³P₂) lie at energies equivalent to 111 K and 321 K above Si(³P₀) respectively. The lowest temperature measurement presented here can then be considered as a state-selected ($J = 0$) experiment. This is very specific as, usually, state-to-state studies are not possible using the CRESU apparatus since collisional relaxation time scales are much shorter than the reaction time scale. This is essentially due to the high density (10^{16} – 10^{18} cm⁻³ according to the nozzle used) prevailing in the CRESU supersonic flow.

3. Results and discussion

Our results for the rate coefficient measurements are summarised in Table 1, which also reports the main flow conditions for each experiment. Only statistical errors are quoted. Some systematic errors due to flow control inaccuracies or inaccuracies in the determination of the total buffer gas density should, however, also be taken into account. Every effort was made to minimize these, and we estimate that the additional error does not exceed 10%. A plot of the temperature dependence of the rate constant is presented in Fig. 3, indicating a slight increase of the rate coefficient when the temperature is lowered. Furthermore, a plateau seems to be reached at about 20–40 K followed by a slight decrease. Such a behaviour may result from a possible spin-orbit dependence of the reaction, as at 15 K, only the $J = 0$ was present (see Experimental section). Our results can be well fitted by the following expression in cm³ molecule⁻¹ s⁻¹ units

$$k(T) = 1.72 \times 10^{-10} \left(\frac{T}{300 \text{ K}} \right)^{-0.53} \exp \frac{-17 \text{ K}}{T} \quad (3)$$

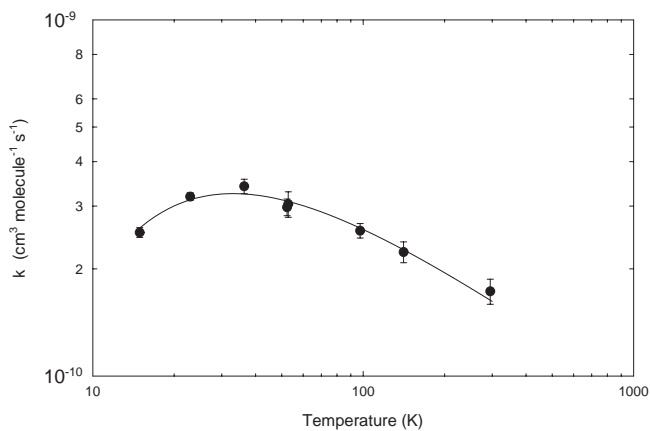
that we advise the reader to use only in the experimental temperature range (15–300 K).

Our measurement at room temperature was found to fall in between those of Husain & Norris and Swearingen et al., much closer, however, to the result obtained by the former. Nevertheless Husain & Norris were criticized by Swearingen et al. who claimed that in experiments using the flash lamp photolysis method, the temperature is not precisely known and hot atoms could be produced as well as some oxygen photolysis. In our experiment, the possibility of partial photolysis of the reactant gas O₂ due to laser focusing was examined. We returned to a previous study involving reactions of aluminum atoms with molecular oxygen (Le Picard et al. 1997). In this experiment, no focusing of the photolysis laser was required to produce aluminum atoms from the precursor Al(CH₃)₃. We then repeated that experiment for a given temperature (141 K) using the present protocol and found no significant differences between the measured rate coefficients.

t1

Table 1. Rate constants for the reaction Si(³P) + O₂ between 15 and 295 K.

T (K)	Buffer Gas	nb pts	Total Density (10 ¹⁶ cm ⁻³)	[O ₂] (10 ¹³ cm ⁻³)	Δt (μ s)	k (10 ⁻¹⁰ cm ³ molecule ⁻¹ s ⁻¹)
15	He	5	5.05	0.8–30	66–156	2.53 ± 0.08
23	He	7	4.73	1.1–35	60–115	3.19 ± 0.08
36	He	5	5.28	0.8–44	60–170	3.41 ± 0.16
52.3	Ar	6	10.3	2.3–23	45–122	2.98 ± 0.16
52.8	Ar	4	20.3	0.9–12	45–120	3.04 ± 0.25
97.4	Ar	5	15.5	0.9–5.6	260–420	2.56 ± 0.12
141	Ar	5	6.95	1.2–9.4	200–423	2.25 ± 0.15
295	Ar	5	6.25	0.4–2.0	100–470	1.73 ± 0.14

**Fig. 3.** Rate constant for the reaction of silicon atoms with O₂ as a function of temperature, displayed in a log-log scale. Experimental results are fitted using the following expression: $1.72 \times 10^{-10} (T/300 \text{ K})^{-0.53} \exp(-17 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, only valid in the temperature range 15–300 K.

We can therefore conclude that the oxygen density was not affected by the focusing of the photolysis laser.

4. Silicon in the interstellar medium

4.1. Dark clouds

The fraction of elemental silicon which is deduced from observations of the gas phase varies greatly amongst the different components of the interstellar medium. In the hot gas, from a few per cent to 70 per cent of the Si is observed to be in the gas phase in its ionized form (Si⁺, Si⁺⁺) (Sofia et al. 1994; Fitzpatrick 1996). In dark clouds, on the other hand, where atomic silicon reacts with O₂ and is rapidly transformed into SiO, as is now confirmed by the present study, most of the gas-phase silicon is expected to be in the form of SiO. This is essentially a result of the high dissociation energy of SiO (~8 eV) and consequent stability (Herbst et al. 1989). Thus, in steady state as well as in time dependent situations, it is difficult to construct realistic chemical models where SiO represents less than ten percent of gas phase silicon.

However, very low upper limits ($< 3 \times 10^{-12}$) have been established for the SiO/H₂ abundance ratio from observations in several well studied dark clouds (Ziurys et al. 1989; Martin-Pintado et al. 1992). This suggests a degree of depletion of silicon relative to the solar value by as much as six orders of magnitude. In quiescent clouds, silicon must then be present in the solid phase, most probably in the form of refractory silicate grains or, possibly, in the ice mantles of dust grains. An alternative to this assumption was proposed by Langer & Glassgold (1990) who suggested that reaction (1) would not proceed if the silicon atoms were in the ground fine-structure state but would have a dominant effect if the silicon atoms were in the first excited spin state, $J = 1$. Consequently, they used a rate coefficient for reaction (1) proportional to $\exp(-111 \text{ K}/T)$. The main interest of this model, at that time, was to explain both the non-detection of SiO in cold dense clouds and the much higher abundances found in star-forming regions. The present study, however, definitely rules out the assumption of a possible activation barrier for the reaction between Si and O₂. For a cloud of density 10⁵ cm⁻³ we have calculated the rate coefficient for the reaction Si(³P) + O₂ at 100 K using Eqs. (1) and (2) from the Langer & Glassgold paper and the experimental result from Swearengen et al. which was chosen by these authors. This is three orders of magnitude lower than our experimental work and the disagreement would be even larger at lower temperatures. The present study confirms that the reaction of Si(³P) with O₂ is still fast at low temperature and therefore cannot explain the low upper limit detection of SiO in dense clouds.

Indeed, SiO emission is mostly observed *only* from dynamically active regions: molecular outflows, supernovae remnants, the Galactic centre and more recently, in photodissociation regions, as we will see below.

4.2. Shock regions

Large enhancements of the gas-phase silicon abundance are observed in high velocity components, not only of diffuse clouds (Sofia et al. 1993; Gry et al. 1997), but also of dense clouds associated with supernova remnants (van Dishoeck et al. 1993). In molecular outflows, up to

10% of the silicon can be in the gas phase, in the form of SiO (see, for example, Gueth et al. 1998). The spatial and velocity distributions of the SiO emission suggest that SiO is formed in shocked layers, in which grains have been partially destroyed, releasing silicon into the gas phase. Another piece of evidence is the fine structure line emission at 68.5 μm from atomic silicon associated with the Orion KL flow observed by Gry et al. (1999) using the LWS spectrometer on the satellite ISO.

The most likely explanation is that the silicon is sputtered from the grains by the action of shocks, which are associated with bipolar outflows, in which case SiO emission is a good tracer of shock activity. Schilke et al. (1997) have considered the formation of Si and SiO through non-thermal sputtering of interstellar grain driven by two-fluid C-type shocks. The silicon is released from the grain cores, predominantly through impact by particles heavier than He, and then oxidised in the gas phase. More recently, Gry et al. (1999) have shown that the observed fine structure line of Si, together with the observed lines of SiO, is consistent with C-shock models.

To illustrate the silicon chemistry in a C-shock, we adopted a value for the density of the preshock gas, $n_{\text{H}} = 10^4 \text{ cm}^{-3}$, which is within the range of the estimates of densities in molecular outflows. The initial value of the magnetic induction, $B = 100 \mu\text{G}$, was obtained from the frequently-used scaling relation $B(\mu\text{G}) = [n_{\text{H}} (\text{cm}^{-3})]^{0.5}$. A shock speed of 30 km s^{-1} was adopted; this value is within the range of velocities derived from radio emission line profiles, particularly of SiO, and is sufficient to cause sputtering of refractory grain materials, such as silicates (Field et al. 1997). Other information on initial conditions is to be found in Schilke et al. (1997).

The mantles of the grains are rapidly removed in the shock wave, exposing the grain core. In the model presented here, about ten per cent of the elemental silicon is then released from the grain nucleus, by sputtering. Latest low energy sputtering yields on olivine (MgFeSiO_4), using the TRIM code and computed by May et al. (2000), have been used in this model. Once in the gas phase, the atomic silicon is oxidised, first to SiO via reaction (1) and (2) and subsequently to SiO₂, through the reaction



owing to the enhanced abundance of OH in the postshock gas. However, discrepancies exist in the rate constant of this latter reaction. Figures 4 and 5 compares fractional abundances, expressed as functions of the flow time (i.e. the time required by a fluid particle to flow through the shock), and illustrates the crucial role played by this second oxidation on the silicon chemistry.

In Fig. 4 a rate constant of $1 \times 10^{-12} (T/300 \text{ K})^{-0.70} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (4) has been used (Schilke et al. 1997). In this model, SiO₂ is the most abundant Si-bearing species for times comparable with the estimated lifetimes of molecular clouds (few 10^5 yr), when the fractional abundance of SiO is only of the order of 10^{-9} . SiO₂ is ultimately

destroyed in reactions with ions, yielding SiO in the far postshock gas. However, in molecular outflows associated with low-mass star formation, the dynamical timescales (10^3 – 10^4 yr) are too short for the oxidation of SiO to SiO₂ to be completed, and so Si and SiO are likely to be the most abundant silicon-bearing species in the hot gas. If adsorption processes are neglected, SiO₂ (which is a stable molecule) is practically the only Si-bearing species in the postshock gas for a time as long as $5 \times 10^5 \text{ yr}$, but is invisible as it does not possess a permanent dipole moment. It is eventually destroyed in reactions with atomic ions, and SiO becomes the main silicon bearing species, as predicted by steady-state models of the gas-phase chemistry in dark clouds (Herbst et al. 1989). SiO may then have a very low abundance in the postshock gas during its lifetime. This could explain why it appears to be absent from the gas phase of dark clouds (Ziurys et al. 1989).

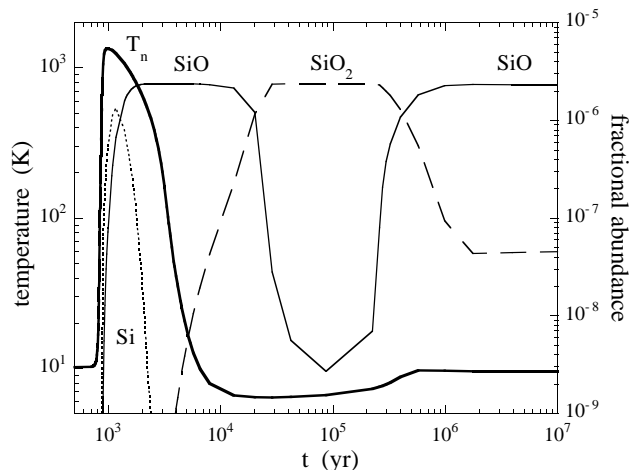


Fig. 4. Abundances of Si (dotted line), SiO (full line) and SiO₂ (dashed line) computed in the C-shock model, plotted as a function of the flow time along the direction of shock propagation. The temperature of neutral species (bold line) is shown for comparison (left-hand axis). The preshock gas is to the left. Calculations are for a model with preshock density 10^4 cm^{-3} , shock velocity 30 km s^{-1} , and preshock magnetic field $100 \mu\text{G}$. A rate constant of $1 \times 10^{-12} (T/300 \text{ K})^{-0.70} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (4) have been used.

Theoretical calculations have been made however by Zachariah & Tsang (1995) on chemical reactions involving silicon bearing molecules, leading to a rate constant for reaction (4) of $2.54 \times 10^{-12} (T/300 \text{ K})^{0.78} \exp(-613 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see their Table 7). As these calculations were made for a high temperature range (1000–2500 K), this rate constant, and more specifically the activation barrier, remains highly speculative for temperatures as low as 10 K that we are interested in. Figure 5 shows the same shock model as in Fig. 4, but using this rate constant. Owing to the activation barrier of reaction SiO + OH, no SiO₂ formation occurs and SiO remains the main silicon bearing molecule in the cold

postshock gas. If such an activation barrier exists, an explanation of the absence of SiO in dark clouds is still to be found. This is the reason why it would be extremely interesting to measure the rate coefficient of this second oxidation at low temperature.

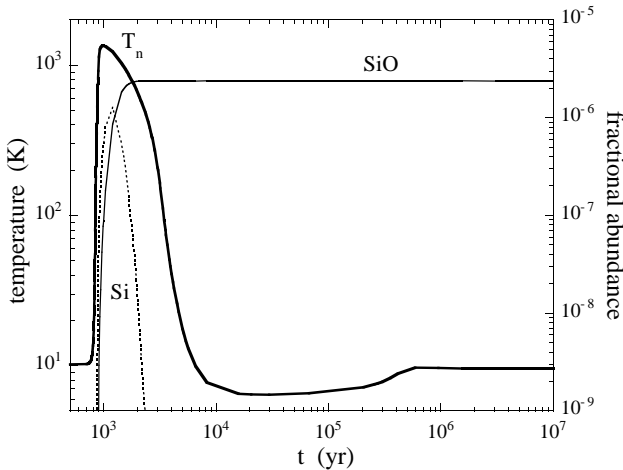


Fig. 5. Same model as in Fig. 4 where a rate constant of $2.54 \times 10^{-12} (T/300 \text{ K})^{0.78} \exp(-613 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (4) have been used (Zachariah & Tsang 1995).

4.3. Photodissociation regions (PDRs)

There is also evidence that photodesorption, through UV radiation from nearby stars, brings silicon back into the gas phase. The observations of the Orion Bar represent an interesting test case. Jansen et al. (1995) deduced from their observations in Orion Bar an upper limit on the SiO abundance of $[\text{SiO}]/[\text{H}]$ less than 10^{-10} , which corresponds to less than 3×10^{-6} of the solar abundance of silicon. However, in recent observations of the Orion Bar (Schilke et al. 2001), SiO has been detected with the IRAM 30-m telescope at levels consistent with the previous upper limits. The Si⁺ fine structure line at $35 \mu\text{m}$ wavelength has also been detected in several PDRs, including Orion Bar (Haas et al. 1986). It appears to be fairly certain that this line is emitted from a partially ionized (neutral) layer and not from the adjacent ionized gas. Schilke et al. (2001) estimate that the observed column density of SiO is roughly five orders of magnitude less than Si⁺; which makes it difficult to reconcile the SiO measurements with the column density inferred from the fine structure line.

Walmsley et al. (1999) computed a PDR model and concluded that the data could be consistent with silicon being photodesorbed (with a small photodesorption yield) for FUV photons incident on silicate dust grains. To illustrate the chemistry of Si-bearing species in a PDR, we present in Fig. 6 a model, for the conditions of the Orion Bar, showing the fractional abundances of Si⁺, Si and SiO as a function of depth (parameterized in terms of the visual extinction A_v). We assume the incident radiation field to be a factor of $\chi = 5 \times 10^4$ times the

standard interstellar UV field, and the hydrogen density n_{H} to be $5 \times 10^4 \text{ cm}^{-3}$ (see Walmsley et al. 1999, for more details on the parameters of the model). In contrast to the case of shocks, sputtering is expected to play no role in a PDR. Instead, we consider the case that silicon is ejected into the gas phase in atomic form, due to photodesorption from a refractory grain surface component, and using a photodesorption yield which has been deduced from the observations of Turner (1998). The importance of the reaction of Si with OH has the consequence that the silicon chemistry in a PDR is also sensitive to the OH abundance, formed at high temperature through the reaction $\text{O} + \text{H}_2$, and consequently to the kinetic temperature variation with depth. In this case, the region where OH is abundant ($A_v \sim 7$) is sufficiently close to the ionization front ($A_v = 0$) that Si photoionization is a competitive process. It should be noted that the SiO + OH reaction discussed in Sect. 4.2 plays no role in PDRs models as the destruction of SiO is dominated by photodissociation. The SiO abundance is of the order of 10^{-10} and is thus similar to the limit of Jansen et al. (1995) and a few times larger than the recent measured value of Schilke et al. (2001). The main conclusion is that the Si⁺ fine structure emission observed in many PDRs is likely to be a consequence of photo-erosion of grain mantles at depths corresponding to a few magnitudes of visual extinction. A small photodesorption yield, together with the assumption that silicon comes off in atomic form, suffice to explain the weakness of the emission from SiO in the Orion Bar and to account for the observed Si⁺. Modest amounts of atomic Si (typically 0.001 of the ionized Si) are predicted by such models.

5. Concluding remarks

In cold gas phase chemistry, SiO appears to be the main form of silicon and is formed through the reaction $\text{Si}(\text{}^3\text{P}) + \text{O}_2 \rightarrow \text{SiO} + \text{O}$, but SiO remains undetected in dark clouds. In addition to this reaction, the key reactions are $\text{Si}(\text{}^3\text{P}) + \text{OH} \rightarrow \text{SiO} + \text{H}$ which can dominate the formation of SiO in the hot gas, and SiO + OH forming SiO₂ which is “invisible” and could be, partly, the reservoir of silicon-bearing species in the cold gas. It would then be interesting to measure the rate coefficients of these two reactions at low temperature in the laboratory. This is presently, however, a difficult task, as when studying radical-radical reactions, one of the reactants has to be produced in large, well-known, and variable amounts. Furthermore, not only is the silicon sputtered from the silicate grains in the shock regions, but also Fe and Mg, which have not been detected in a molecular form. The study of oxidation of these two species by laboratory work and theoretical studies would also be very valuable. Another crucial parameter for oxidation to occur in molecular clouds is the O₂ fractional abundance. We note that recent results from the SWAS satellite (Goldsmith et al. 2000) suggest upper limits to the $[\text{O}_2]/[\text{H}]$ abundance ratio of 10^{-6} .

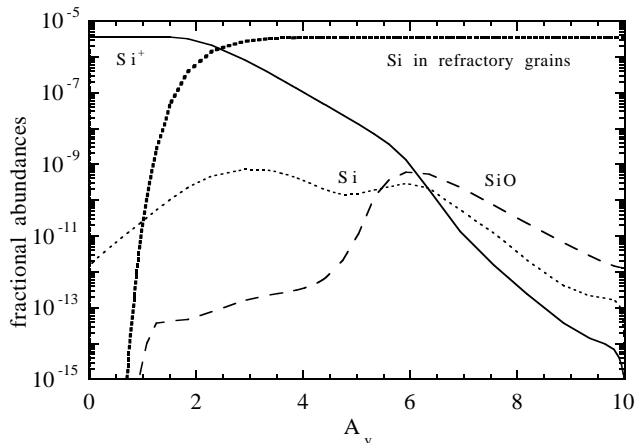


Fig. 6. Abundances of Si-containing species as functions of depth for the temperature profile ($T = 1000/(1 + 2 A_v)$ K). Calculations were carried out for a constant photodesorption yield of 5×10^{-7} . Bold dots show the variation of the abundance of Si in “refractory form”, whereas the dashed lines and the full curve show the variation of gaseous SiO and Si⁺, respectively; the light dots indicate atomic silicon.

A key role in understanding the balance between solid and gaseous phases in the interstellar medium is played by interstellar silicon, which is known to be depleted both in diffuse and dense interstellar clouds. The computed sputtering yields using the TRIM code (May et al. 2000) are a first step but laboratory studies of low energy sputtering yields for ions incident upon different silicate materials containing Fe, Mg and Si are also needed. Finally, another key problem which remains to be studied is how Si (and other refractory species) gets onto grains in molecular clouds and, more specifically, how Si reaches sites of high binding energy.

Acknowledgements. We wish to thank the Programme National “Physique Chimie du Milieu Interstellaire” and the European community under the Training and Mobility of Researchers programme (Astrophysical Chemistry network) for funding this work and also our colleagues from the University of Birmingham for having kindly lent us their 15 K nozzle. We are also grateful to Prof. Brian Mitchell for his comments on this manuscript.

References

- Chastaing, D., Le Picard, S. D., & Sims, I. R. 2000, *J. Chem. Phys.*, 112, 8466
- Chastaing, D., Le Picard, S. D., Sims, I. R., & Smith, I. W. M. 2001, *A&A*, 365, 241
- Field, D., May, P. W., Pineau des Forêts, G., & Flower, D. R. 1997, *MNRAS*, 285, 839
- Fitzpatrick, E. L. 1996, *ApJ* 473, L55
- Goldsmith, P. F., Melnick, G. J., Bergin, E. A., et al. 2000, *ApJS*, 539, L123
- Graff, M. M. 1989, *ApJ*, 339, 239
- Greaves, J. S., Ohishi, M., & Nyman, L. A. 1996, *A&A*, 307, 898
- Gry, C., Boulanger, F., Falgarone, E., Pineau des Forêts, G., & Lequeux J. 1997, *A&A*, 331, 1070
- Gry, C., Pineau des Forêts, G., & Walmsley, C. M. 1999, *A&A*, 348, 227
- Gueth, F., Guilloteau, S., & Bachiller, R. 1998, *A&A*, 333, 287
- Haas, M. R., Hollenbach, D. J., & Erickson, E. F. 1986, *ApJ*, 301, L57
- Herbst, E., Millar, T. J., Wlodek, S., & Bohme, D. K. 1989, *A&A*, 222, 205
- Husain, D., & Norris, P. E. 1978, *J. Chem. Soc. Faraday Trans. II*, 74, 93
- Jansen, D. J., Spaans, M., Hogerheijde, M. R., & van Dishoeck, E. F. 1995, *A&A*, 303, 541
- Jones, A. P., Tielens, A. G. G. M., Hollenbach, D. J., & McKee, C. F. 1994, *ApJ*, 433, 797
- Langer, W. D., & Glassgold, A. E. 1990, *ApJ*, 352, 123
- Le Picard, S. D., Canosa, A., Travers, D., et al. 1997, *J. Phys. Chem.*, 131, 529
- MacKay, D. D. S. 1995, *MNRAS*, 274, 694
- MacKay, D. D. S. 1996, *MNRAS*, 278, 62
- Martin-Pintado, J., Bachiller, R., & Fuente, A. 1992, *A&A*, 254, 315
- May, P. W., Pineau des Forêts, G., Flower, et al. 2000, *MNRAS*, 318, 809
- Pineau des Forêts, G., & Flower, D. R. 1997, *Molecules in Astrophys.: Probes and Proce.; Int. Astr. Union, Symposium No. 178*, 113 (Kluwer Academic.)
- Schilke, P., Walmsley, C. M., Pineau des Forêts, G., & Flower, D. R. 1997, *A&A*, 321, 293
- Schilke, P., Pineau des Forêts, G., Walmsley, C. M., & Martin-Pintado, J. 2000, *A&A*, in press
- Sims, I. R., Queffelec, J. L., Defrance, A., et al. 1994, *J. Chem. Phys.*, 100, 4229
- Smith, I. W. M., & Rowe, B. R. 2000, *Acc. Chem. Res.*, 33, 261
- Sofia, U. J., Savage, B. D., & Cardelli, J. A. 1993, *ApJ*, 423, 251
- Sofia, U. J., Cardelli, J. A., & Savage, B. D. 1994, *ApJ*, 430, 650
- Swearengen, P. M., Davis, S. J., & Niemczyk T. M. 1978, *Chem. Phys. Lett.*, 55, 274
- Turner, B. E. 1998, *ApJ*, 495, 804
- van Dishoeck, E. F., Jansen, D. J., & Phillips, T. G. 1993, *A&A*, 279, 541
- Walmsley, C. M., Pineau des Forêts, G., & Flower, D. R. 1999, *A&A*, 342, 542
- Zachariah, M. R., & Tsang W. 1995, *J. Phys. Chem.*, 99, 5308
- Ziurys, L. M., Friberg, P., & Irvine, W. M. 1989, *ApJ*, 343, 201