

# SILICON ATOMS AS INTERMEDIATES IN THE NONLINEAR PHOTOCHEMISTRY OF $\text{Si}(\text{CH}_3)_{4-n}\text{Cl}_n$ ( $n = 0, 1, 2, 3, 4$ ) COMPOUNDS

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The resonance enhanced multiphoton ionization (REMPI) of  $\text{Si}(\text{CH}_3)_{4-n}\text{Cl}_n$  compounds (with  $n = 0, 1, 2, 3, 4$ ) was measured in the 400–360 nm range. The resonances observed were attributed to a silicon atom formed in the  $^1\text{D}_2$  excited state. This indicates that the first step in the photochemical process is the dissociation of the molecule which is followed by the ionization of the silicon atom.

## INTRODUCTION

The detection of silicon atoms in processes such as chemical vapor deposition<sup>1–4</sup> and vapor-phase processing of ceramic particles<sup>5–6</sup> is of great importance. Various experimental methods have been employed for this purpose, of which laser induced fluorescence (LIF)<sup>1,2</sup> is the most common. This method, however, has some drawbacks, especially in particle-forming flows.<sup>3</sup> An alternative to the LIF technique is resonance-enhanced multiphoton ionization (REMPI).

This irradiation of molecules by an intense laser pulse leads to two general types of nonlinear photochemistry. The first, called class A, involves ionization followed by fragmentation and is common for most of the organic molecules undergoing nonlinear photochemistry.<sup>7</sup> Class B, on the other hand, involves fragmentation followed by ionization and encompasses inorganic and organometallic systems.<sup>7</sup> The adherence to a class B behavior is universal for the organometallic carbonyl compounds.<sup>7,10</sup> Regarding the metal-alkyl complexes,  $\text{Hg}(\text{CH}_3)_2$ ,<sup>11</sup> and  $\text{B}(\text{C}_2\text{H}_5)_3$  (Ref. 12) prefer a class A behavior, while  $\text{Sn}(\text{CH}_3)_4$ ,<sup>7</sup>  $\text{Al}_2(\text{CH}_3)_6$ ,<sup>12,13</sup>  $\text{Ga}(\text{CH}_3)_3$ ,<sup>12</sup>  $\text{In}(\text{CH}_3)_3$  (Ref. 12) and  $\text{Si}(\text{CH}_3)_4$ ,<sup>7</sup> fragment prior to ionization of the bare atoms (class B).

Three papers over the past decade have reported the REMPI of silicon atoms in the gas phase as an intermediate fragment in photochemical processes.<sup>7–9</sup> The first presented the ionization spectra of  $\text{SiCl}_4$  and  $\text{Si}(\text{CH}_3)_4$  in a parallel plate cell.<sup>7</sup> Sharp, atomic-like peaks were observed for both molecules, although a few of the lines in the two spectra did not coincide. In the second study, Brewer<sup>8</sup> explored the two-photon LIF and REMPI of  $\text{Si}(\text{CH}_3)_4$  in the 400–460 nm region. The dissociation of the parent molecule yielded silicon atoms in their ground states  $^3\text{P}_J$  ( $J = 0, 1, 2$ )

and first singlet  $^1D_2$  state. In a third paper,<sup>9</sup> silane was added to the  $H_2$  stream of a hydrogen/oxygen/argon flame. The silicon atoms were detected by a 2 + 1 REMPI process in which two photons at 408 nm excite ground state atoms to the  $4p\ ^3P$  state.

In the current study, we have measured the REMPI of a series of 5 silicon compounds  $Si(CH_3)_{4-n}Cl_n$  where  $n = 0, 1, 2, 3, 4$ . The measurements were carried out over a wavelength range of 400–360 nm. If a class B mechanism governs the photochemistry of these silicon-containing molecules, then the ionization spectrum of the silicon atom should be independent of the nature of the parent molecule. We have also checked the previous spectra of  $SiCl_4$  and  $Si(CH_3)_4$  which indicated some differences in peak positions and appearances. Finally, for a better understanding of the first photochemical event in the photodissociating process we also measured the one-photon absorption spectrum of  $Si(CH_3)_2Cl_2$  and  $Si(CH_3)Cl_3$  in the vacuum ultraviolet (VUV). These spectra, which are broad and structureless, indicate the formation of intermediate silicon atoms in the gas phase following the absorption of the first few photons.

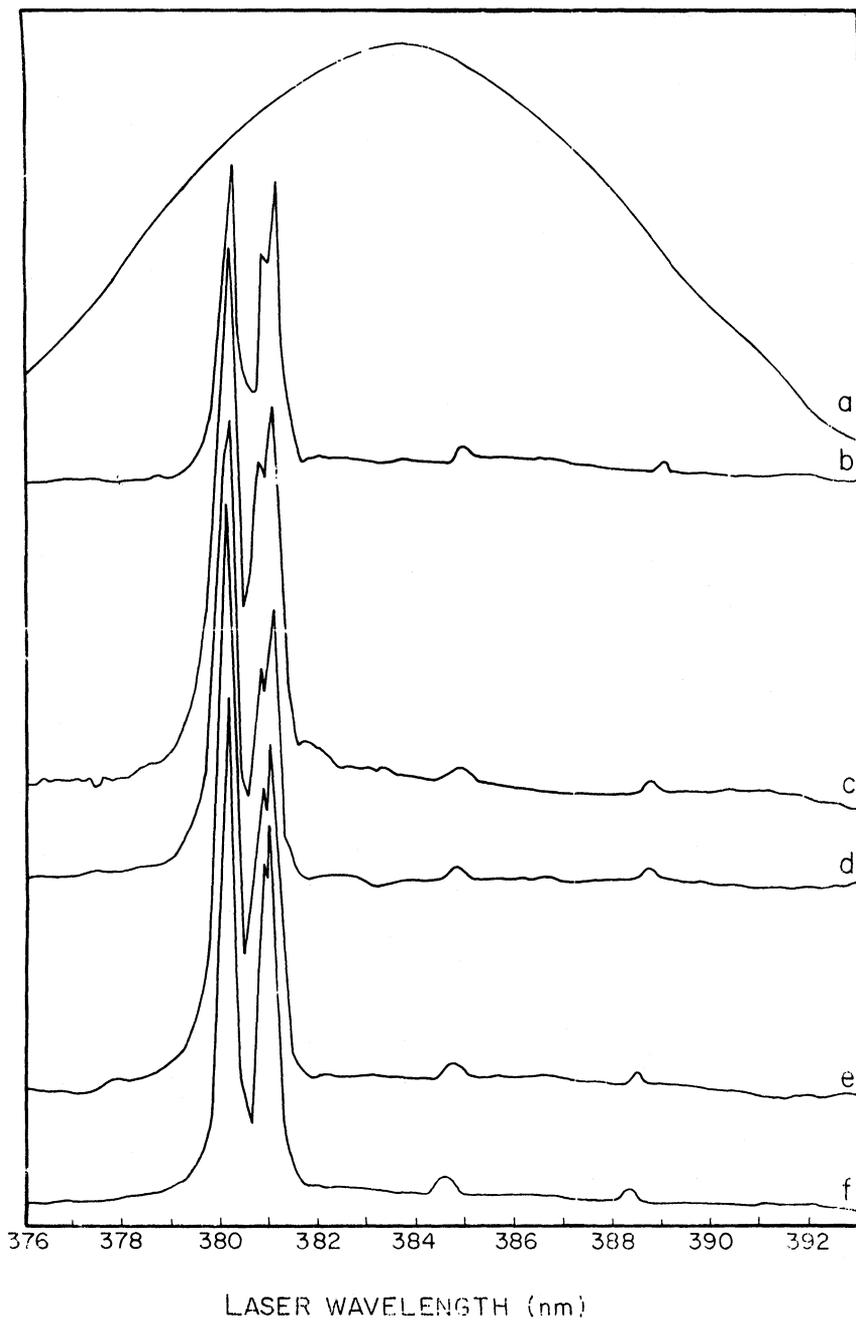
## EXPERIMENTAL

The output of an excimer laser (Lambda Physik, EMG 102, 308 nm) was used to drive a dye laser (Lambda Physik, FL 2000) operating with the dyes BBQ, PBD, DMQ and PTP. The ionizing light was focused into the ionization cell with a 15 cm quartz lens. A bias of a 100 V was applied across a gap formed by two tungsten electrodes separated by 2 cm. The current was amplified using a Keithley 642 current amplifier. The starting methylsilyl chlorides were purchased from Aldrich and were used without further purification. The pressure introduced into the ionization cell was  $\sim 10$  torr. The VUV absorption measurements were carried out using a McPherson 225 monochromator. The vapor pressure of the compounds was measured by a Wallace and Tiernan absolute pressure gauge. The results are reported with the full slit width (2 mm). However, no changes in the spectra were observed by employing narrower slits (800  $\mu m$ ). The samples were measured in an 11 cm cell.

## RESULTS

The REMPI of the 5 aforementioned methylsilyl chlorides are depicted in Figure 1. Although this figure presents only the peaks that were obtained in the BBQ dye region (375–392 nm), identical spectra were also measured for the five silicon compounds using other dyes. This led to an immediate assignment of the peaks as originating from resonances of the silicon atom. The atomic transitions of the silicon atom involve a 2 + 1 excitation in which the silicon atom is formed in the  $^1D_2$  level. This level, which lies  $6299\text{ cm}^{-1}$  above the ground state, belongs to the ground state configuration,  $3s^23p^2$ , and is one of 5 ground state levels composing this manifold.

The summary of all the observed peaks and their assignment is presented in Table I. The selection rules that determine the two-photon transitions in atoms,  $\Delta J \leq 2$ ,



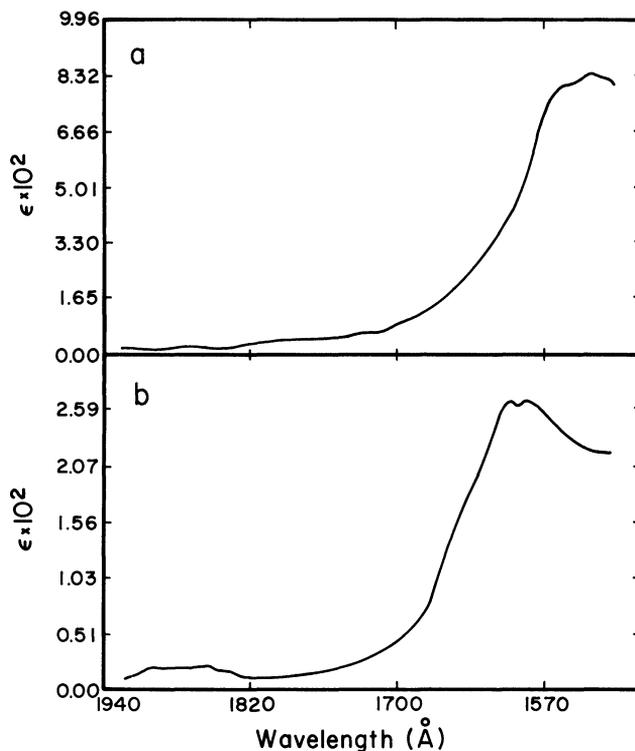
**Figure 1** The REMPI spectra of silicon atoms from the dissociation of: (b)  $\text{Si}(\text{CH}_3)_4$ ; (c)  $\text{Si}(\text{CH}_3)_3\text{Cl}$ ; (d)  $\text{Si}(\text{CH}_3)_2\text{Cl}_2$ ; (e)  $\text{Si}(\text{CH}_3)\text{Cl}_3$ ; and (f)  $\text{SiCl}_4$ .

**Table 1** Assignment of two-photon transitions of silicon atom formed in the photodissociation of  $\text{Si}(\text{CH}_3)_{4-n}\text{Cl}_n$  molecules ( $n = 0, 1, 2, 3, 4$ )

Wavelength of one-photon (nm)	Energy of two-photons ( $\text{cm}^{-1}$ )	Transition
388.36	51498	$^1\text{D}_2 \rightarrow ^1\text{D}_2$
384.53	52012	$^1\text{D}_2 \rightarrow ^1\text{S}_0$
381.14	52475	$^1\text{D}_2 \rightarrow ^1\text{F}_3$
380.96	52500	$^1\text{D}_2 \rightarrow ^1\text{P}_1^0$
380.26	52596	$^1\text{D}_2 \rightarrow ^1\text{F}_3^0$
363.65	54998	$^1\text{D}_2 \rightarrow ^1\text{D}_2$
363.62	55002	$^1\text{D}_2 \rightarrow ^1\text{P}_1$
362.75	55134	$^1\text{D}_2 \rightarrow ^1\text{F}_3^0$
362.09	55235	0
361.75	55287	
359.83	55582	$^1\text{D}_2 \rightarrow ^1\text{P}_1^0$
358.05	55857	$^1\text{D}_2 \rightarrow ^1\text{D}_2^0$

$\Delta S = 0$ , and that  $J = 0 \leftrightarrow J = 1$  is forbidden for all polarizations,<sup>14</sup> are kept for all the proposed transitions. The transitions all start at the  $^1\text{D}_2$  ( $3s^23p^2$ ) excited state and terminate at high Rydberg states. According to the selection rule governing the multiplicity changes in two-photon absorption,  $\Delta S = 0$ , the final states should all be singlets. The lines at 55235 and 55287  $\text{cm}^{-1}$  closely match transition to higher triplet states. We have resisted the temptation, however, to assign these lines as singlet to triplet transitions, since the  $\Delta S = 0$  selection rule is almost universally obeyed. Perforce, we attribute the unassigned peaks to resonances of  $\text{Si}_2$ , although the absorption spectra of  $\text{Si}_2$  is not known in this region. However, the intensity of these peaks was time dependent and increased the longer the compounds stayed in the cell. The results of the REMPI spectra of the silicon compounds clearly illustrate a class B photochemistry, in which dissociation precedes ionization. We turn now to the more fundamental question alluded to above: why do the alkyl complexes of Si, Sn, Al, Ga and In react via class B photochemistry, while class A behavior is the rule for the Hg and B analogs? A priori, one might attempt to correlate the classification of the metal-alkyl compounds with bond energy. This approach fails, however, because the Hg–C bond, which is the weakest among the methyl-alkyl compounds (121 kJ/mol),<sup>16</sup> is not broken when the light is focused on dimethyl mercury. On the other hand, the Si–C bond (311 kJ/mol),<sup>15</sup> one of the strongest among the metal alkyl compounds, is easily broken, leaving a silicon atom to further ionize.

A more plausible explanation for these differences focuses in on the initiating photochemical event which is carried out by the absorption of the first two photons. Whether this absorption leads to a bound or a repulsive state determines the classification of the molecules as class A or B. In those molecules where the absorption of the two photons terminates in a repulsive state, the dissociation of the molecules takes place first and leads to the formation of the naked atom which is subsequently



**Figure 2** Absorption spectra of (a)  $\text{Si}(\text{CH}_3)\text{Cl}_3$ ; (b)  $\text{Si}(\text{CH}_3)_2\text{Cl}_2$  in the gas phase. Spectral resolution is 16 Å.

ionized. When, on the other hand, the absorption leads to a bound state, the parent molecule is excited to this bound state and is then ionized by absorbing a few more photons. This is reflected in the one-photon absorption where the molecules belonging to class B show a structureless, broad one-photon absorption, while the molecules of class A reveal a rich vibrational structure characteristic of a bound state. This long-lived bound state leads to the ionization of the parent molecules. To check these assumptions we measured the as yet unreported VUV one-photon absorption of  $\text{Si}(\text{CH}_3)_2\text{Cl}_2$  and  $\text{Si}(\text{CH}_3)\text{Cl}_3$ . The results (depicted in Figure 2) show a broad structureless spectra demonstrating that in both molecules the first two  $\sim 360$  nm photons would reach a dissociative excited state ultimately leading to a bare silicon atom.

## CONCLUSION

The REMPI of methylsilyl chlorides reveal atomic resonances attributed to the formation of a silicon atom. This class B behavior is related to the one-photon

absorption of these molecules which is diffuse and broad. For other alkyl-metal complexes, which exhibit a vibrational structure in their one-photon absorption, a class A is predicted. We therefore expect that dimethyl zinc and dimethyl cadmium<sup>16</sup> will belong to class A and their REMPI spectrum will show molecular peaks associated with excited states of the parent molecule.

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