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UV laser multiphoton ionization–dissociation of phenylsilane and its homogeneous dimers

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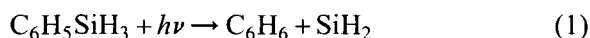
Abstract

Homogeneous dimers of phenylsilane, formed in a rare-gas seeded supersonic expansion have been studied by laser resonant two-photon ionization combined with a time-of-flight mass spectrometer. The resonant intermediate states are the S_1 (270 nm) and S_2 (210 nm) ones. The ionization of phenylsilane monomer is inefficient at 210 nm whereas phenylsilane homo-dimers are resonantly ionized with high efficiency at this wavelength region. The wavelength dependence of the dimer at $S_1 \leftarrow S_0$ origin region implies the existence of at least two, almost isoenergetic, dimer conformers in the molecular beam. Photoionization of phenylsilane dimer induces chemical reactions within the dimer. The detected dissociation channels have to do with $-\text{SiH}_3$ and $-\text{C}_6\text{H}_6$ loss and proton-transfer. Van der Waals fragmentation (evaporation of a neutral phenylsilane) is also taking place. © 1998 Elsevier Science B.V.

Keywords: Phenylsilane; Clusters; Ionization; Fragmentation; Intracuster reactions

1. Introduction

Phenylsilane ($\text{C}_6\text{H}_5\text{SiH}_3$), is the simplest aromatic silicon compound and has received much attention, because it is a good precursor for silicon film formation by chemical vapor deposition [1–3]. Laser induced dissociation in the IR and UV regions has been studied by means of gas chromatography [4] and laser-induced fluorescence (LIF) [5–7]. Silylene (SiH_2) and silyldiyne (SiH) are the major products of the photolysis of phenylsilane and analysis of the products at 193 nm laser irradiation has led to the conclusion that there are two primary dissociation channels [4]:

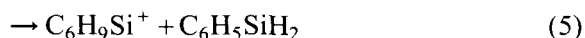
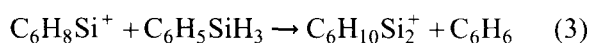


where the latter is found to be six times more efficient than reaction (1). Excitation at 193 nm brings the molecule to the third singlet S_3 electronic state which corresponds to the E_{1u} state of benzene [8]. The corresponding $S_3 \leftarrow S_0$ absorption band is broad and structureless, indicative of rapid radiationless transitions. Ishikawa and Kajimoto [7] compared the LIF spectrum of the fragmentation products induced at 248 nm ($S_1 \leftarrow S_0$ transition) with that at 193 nm and they concluded that the dissociation mechanism is the same at both wavelengths. They suggested that the molecule at the excited electronic state (S_1 or S_3) undergoes rapid internal conversion to the ground state followed by dissociation. Thermal decomposition studies support this conclusion [9].

More recently, Oujja et al. [10] have reported

LIF measurements where the photofragmentation was performed via the second S_2 excited electronic state (the analogue of the B_{1u} state of benzene) at 212.5 nm. The comparison with the LIF induced at 193 nm has shown some interesting differences.

The gas-phase ion/molecule chemistry of phenylsilane, investigated by Fourier transform ion cyclotron resonance (FT-ICR) spectrometry, has been of fundamental interest because of the reactivities and structural isomerism of the parent and fragment ions [11,12]. Unlike the toluene radical cation, the phenylsilane radical cation is reactive with the neutral parent. Three reaction channels have been observed:



To the best of our knowledge, studies on the multiphoton ionization–dissociation processes of phenylsilane by means of a time-of-flight (TOF) mass spectrometer have not been reported. Moreover, despite the efforts to understand the fragmentation processes of the neutral molecule, no work has been done concerning the clusters formed by this molecule. Dimers of benzene, toluene and fluorobenzene show resonant two-photon ionization (R2PI) features at the red side of the $S_1 \leftarrow S_0$ origin transition of the monomer [13–15]. It is well known [16,17] that Van der Waals clusters, besides the interest they have in their own right, offer the opportunity to observe new phenomena or reveal mechanisms which have very low probabilities of taking place in the monomer itself. As an example relevant to the present work, the unexpected abundance of benzene ions observed in supersonic beam experiments at 210 nm, is attributed to the ionization–dissociation processes of benzene clusters (mainly dimers) [18,19]. Moreover, an intracuster ion/molecule reaction has been observed after ArF excitation (but not with KrF): the initially formed $C_6H_6^+$ attacks a

neighboring benzene unit of the cluster and $C_7H_7^+$ is formed while the C_5H_5 radical is expelled from the cluster [20].

In this work the UV laser-induced multiphoton ionization–dissociation of phenylsilane and its dimer have been studied over the range of 207–275 nm using a linear TOF mass spectrometer. One photon absorption at this region causes molecular excitation to S_2 and S_1 electronic states. The ionization energy (IE) of $C_6H_5SiH_3$ is 9.14 eV [21], thus two-photon absorption leads to ionization. Aromatic homo-dimers have lower IE than the corresponding monomer by about 0.6 eV. Molecular dissociation can take place through the above mentioned excited electronic states and/or after molecular ionization (above ionization–dissociation). From the observed mass peaks, the possible photodissociation routes of phenylsilane monomer and phenylsilane dimer ions are discussed with respect to the excitation photon energy.

2. Experimental

Phenylsilane (Ventron GMBH, 99.8% purity) seeded in He, Ar or N_2 was expanded into a vacuum chamber through a pulsed valve (General Valve Corporation, Iota One). The pulse duration of the valve (800 μm orifice diameter) was 200 μs . The temperature of the sample reservoir and the pulse valve could be varied (0–30°C). The total stagnation pressure of the carrier gas could be regulated in the range of 0–4 atm. Moreover, the dimer signal was maximized by changing the delay between valve and laser pulse. The vacuum chamber was evacuated by a rotary-backed Varian VHS-6 diffusion pump and a liquid nitrogen trap was used to ensure an oil free chamber. The resulting supersonic molecular beam was crossed by the pulsed laser beam at about 4 cm downstream from the orifice. A dye laser (Lambda Physik, LPD3000) was pumped by a XeCl excimer laser (Questec 2320) and the dye laser output

(approximately 10 ns duration) was frequency-doubled in a BBO-I or a BBO-II (at shorter wavelengths) crystal. The laser system produced light at wavelengths necessary for R2PI via either the first singlet S_1 ($\lambda = 270$ nm) or the second singlet S_2 ($\lambda = 210$ nm) state of the neutral molecule. The UV laser light was focused by a +50 cm quartz lens and the pulse energy was monitored continuously behind the vacuum chamber by a Joulemeter (OPHIR, Nova). The values of laser power given in the text refer to the interaction position.

The time-of-flight (TOF) mass spectrometer used is of the conventional linear Wiley–McLaren design. Ions formed by R2PI process were accelerated up to ca. 1700 eV and then introduced into a field-free region ($L = 1.10$ m). An einzel lens in conjunction with two pairs of parallel plates placed normal to each other increased the ion transmission. The ions were detected by a dual microchannel plate (Comstock, CP602). The mass resolution was typically 250 at 100 Da.

TOF mass spectra were accumulated by taking the output of a fast preamplifier (SR440), connected with the detector, to a digitizing storage oscilloscope (Hewlett–Packart 54210A), where the signals were averaged over 256 laser shots. The laser was operated at 7 Hz. The number of the averaged shots could be increased using a PC connected to the oscilloscope but the mass spectra in this work have been averaged over 256 laser shots only. For the wavelength-dependent measurements, the signal corresponding to different masses was processed by two gated integrators (SRS 250) connected to a PC via a computer interface module (SRS 245).

3. Results and discussion

3.1. Phenylsilane monomer. Mass spectra by $S_1 \leftarrow S_0$ R2PI

The origin of the $S_1 \leftarrow S_0$ transition of $C_6H_5SiH_3$ is at $\lambda = 268.9$ nm (4.61 eV) [21–23]

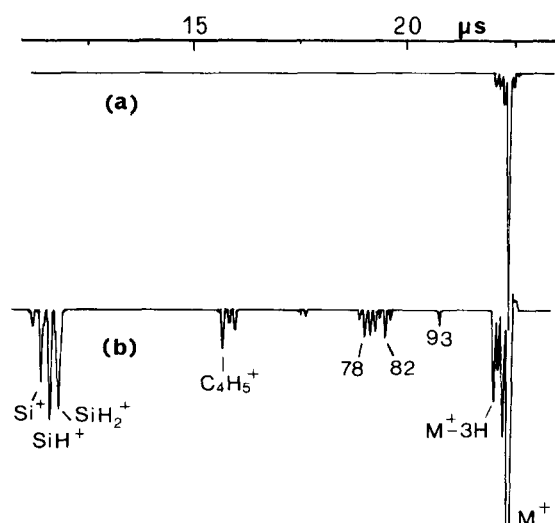


Fig. 1. TOF mass spectrum produced after resonance-enhanced two-photon ionization of phenylsilane seeded in Ar. The excitation wavelength, $\lambda = 268.9$ nm, corresponds to the $S_1 \leftarrow S_0$ origin of the monomer: (a) laser energy 11 μ J; (b) laser energy 70 μ J. M^+ stands for $C_6H_5SiH_3^+$ ($m/z = 108$). Other ions are: $C_2H_5^+$ ($x = 3, 4$); $C_4H_x^+$ ($x = 5, 6, 7$); $C_6H_x^+$ ($x = 6, 7, 8$); $C_4H_5Si^+$, $C_5H_5Si^+$ and $C_6H_5Si^+$ ($x = 5, 6, 7$).

and the mass spectrum induced at this resonance wavelength (1 color — R2PI) is shown in Fig. 1. At laser intensities below 5 μ J/pulse only the parent ion $C_6H_5SiH_3^+$ ($m/z = 108$) is present. Ions with $m/z = 107$, 106 and 105 appear clearly at 11 μ J/pulse (Fig. 1a). With 35 μ J/pulse, lighter masses show up, while Fig. 1b has been recorded with 70 μ J/pulse. The abundance of the ion peaks is increasing with laser intensity, especially for those corresponding to lighter masses, which is indicative of sequential fragmentation of the daughter fragments after further photon absorption. As mentioned in the Introduction, dissociation can take place from excited states of the neutral molecule. Dissociation through reaction (1) has been proposed to take place via highly excited vibrational states of the ground electronic state where the molecules are lead from the S_1 state through fast radiationless processes (internal conversion). Therefore it is expected that, at least some of the molecules dissociate according to reaction (1) and it is possible that the released fragments are ionized after further photon

absorption from the same laser pulse. This scheme could probably explain the generation of $C_6H_6^+$ and of SiH_x^+ ($x = 2, 1, 0$), but cannot be used for the interpretation of the heavier mass ion peaks ($m/z > 78$) in the mass spectrum. Furthermore our results (Fig. 1) show soft ionization at low laser powers (where only the parent ion is observed), while, by increasing the laser power, lighter masses appear too. It is obvious therefore, that reaction (1) is not the only fragmentation mechanism of phenylsilane at this wavelength. Up-pumping through the energy levels of the parent molecular ion with the subsequent decomposition to smaller ionic fragments seems thus to be the main dissociation mechanism (i.e. ionization–dissociation route, ladder-switching model [24,25]). Moreover, this is in agreement with Electron Impact (EI) dissociation experiments, where heavy ion peaks have been recorded [11,12]. The $m/z = 107$ ($C_6H_7Si^+$) ion peak we observe has been studied using FT-ICR after EI ionization of phenylsilane and has been found that it is formed in two isomeric forms, noninterconverting at room temperature. There are controversial suggestions about the structure of these isomers [11,12]. Nevertheless, it has been found that this ion and the $m/z = 105, 106$ ions are produced in EI experiments by increasing electron energies and at least one of them has been suggested to be produced through the dissociation of the parent ion [11,12]. These ions have been recorded in the present experiment too, and this is further evidence that the ionization–dissociation mechanism is involved in the dissociation of phenylsilane.

3.2. Phenylsilane dimer

3.2.1. $S_1 \leftarrow S_0$ region 270 nm

It is well known that formation of clusters is possible in supersonic jet expansions. $S_1 \leftarrow S_0$ resonant two-photon ionization (R2PI) of benzene, toluene and fluorobenzene homo-dimers have been studied [13–15] and the origin of the first absorption band has been found to be close



Fig. 2. One-color R2PI mass selected spectrum of $(\text{phenylsilane})_2$ monitoring the photoion signal in the $m/z = 216$ TOF channel (top curve). In the same run the $m/z = 185$ ion signal has been monitored (middle curve). The lowest curve has been obtained by monitoring the $m/z = 138$ ion signal. The sensitivity of the vertical axis (ionization current) is not the same for the three signals; the relative intensity is 5:2:1 for the $m/z = 216, 185, 138$ ion signals. The phenylsilane monomer absorbs strongly at 269 nm and therefore an experimental artifact is observed as a deep at this region (see text).

to the electronic origin of the respective monomer. By monitoring the $m/z = 216$ ion signal of $(\text{phenylsilane})_2$ versus laser wavelength, the mass selected R2PI spectrum has been recorded and presented in Fig. 2 (upper curve). Contrary to the sharp origin of the monomer in the R2PI spectrum [21,23], the dimer displays a broad one, about 400 cm^{-1} wide, and the spectrum has a double-hump structure. The signal dip at 269 nm in Fig. 2 is due to the signal overloading and the inertia of the microchannel plates to record ions heavier than $m/z = 108$, because at this wavelength the $S_1 \leftarrow S_0$ origin of the monomer exists which strongly absorbs. In Fig. 2, the wavelength dependence of two other strong ion signals ($m/z = 185, 138$) has been included. The precursor of these ions is the phenylsilane dimer. The identity and the production mechanism of these ions will be discussed in Section 3.2.2. The $S_1 \leftarrow S_0$ R2PI origin spectrum of $(\text{phenylsilane})_2$ is similar to those of $(\text{toluene})_2$ [14] and $(\text{fluorobenzene})_2$ [15]. Furthermore, by changing the expansion conditions, the absorption envelope does not retain its shape. The same effect has been observed by Rademann et al. [15] for $(\text{fluorobenzene})_2$. The broadening of

the spectral features for the $S_1 \leftarrow S_0$ transition of dimers can be attributed to the following reasons [15]:

1. the existence of nearly isoenergetic conformers which are produced in the beam in different ratios depending on the expansion conditions;
2. photofragmentation from higher clusters, since a one color R2PI scheme is used; in the case of (toluene)₂ [14], where a two-color experiment is involved, the width of the absorption is about half that of (fluorobenzene)₂ or (phenylsilane)₂;
3. vibrational structure due to the excitation of intermolecular motion in the S_1 state; and
4. excitation from thermally occupied vibrational levels of the ground electronic state which are expected to have frequencies between 10 and 50 cm⁻¹.

Theoretical calculations and analysis of experimental data of benzene homo-dimers [14,19,26–28] suggest that four different conformations are plausible: the perpendicular or ‘T’, the parallel stacked, the parallel side by side, and parallel displaced and tilted arrangements (for the C₆H₅CH₃ homo-dimers see Refs. [14] and [28]), while no information about the possible structures of the C₆H₅SiH₃ dimer exist in the literature.

In Fig. 3a the mass spectrum at $\lambda = 270.5$ nm and 25 μ J/pulse is presented. The $m/z = 216$ is not the only heavy ion peak detected in the R2PI of (phenylsilane)₂. Cations with $m/z = 185$, 138, 109, 108, 107, 106 and 105 are present, as well as lighter masses. The lighter masses, not shown in Fig. 3, are analogous to those of Fig. 1. The wavelength dependence of the $m/z = 185$ and 138 ion are presented in Fig. 2 and it is clear that the $m/z = 185$ and 138 ion signals follow the absorption of (phenylsilane)₂. Furthermore, the mass selected R2PI $S_1 \leftarrow S_0$ spectrum of the phenylsilane monomer obtained by monitoring the $m/z = 108$ mass channel, is the same as the spectra in Refs [21,23] and has an underlying

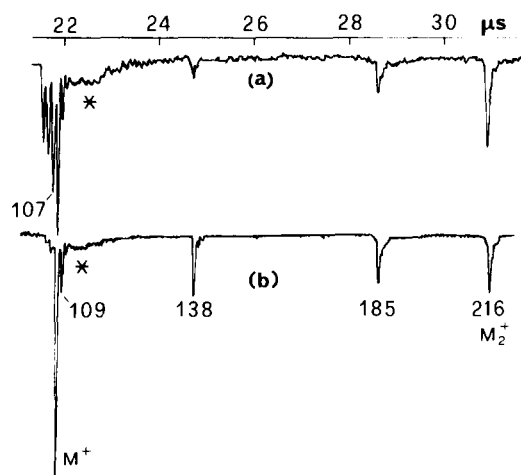


Fig. 3. TOF mass spectrum produced after resonance-enhanced two-photon ionization of (phenylsilane)₂: (a) the excitation wavelength ($\lambda = 270.5$ nm, 25 μ J) corresponds to the $S_1 \leftarrow S_0$ dimer transition; (b) the excitation wavelength ($\lambda = 210$ nm, 7 μ J) corresponds to the $S_2 \leftarrow S_0$ dimer transition. The ion signal scale in spectrum (a) is more sensitive than in (b). M^+ stands for C₆H₅SiH₃⁺ ($m/z = 108$).

background that mimics the structure of Fig. 2. This underlying background disappears when the vapor pressure of the sample is reduced (temperature of the sample 0°C) and the pressure of the carrier gas is below 2.5 atm. Under such conditions the concentration of the dimer is very low. All these observations lead to the conclusion that the phenylsilane dimer ion is the precursor of the $m/z = 185$, 138, 109 and 108 ions. Cluster ions produced by the ionization of neutral clusters are usually energy-rich with a broad distribution of internal energies. The dimer may cool by evaporation of a neutral phenylsilane molecule and this mechanism explains the $m/z = 108$ ion peak in the wavelengths where the monomer molecule does not absorb. In order to gain more information about the mechanisms for the appearance of the heavy ions, experiments in the 210 nm region have been carried out. In this region the dimer is expected to absorb strongly ($S_2 \leftarrow S_0$ transition) as in the case of benzene [18,19].

3.2.2. $S_2 \leftarrow S_0$, region 210 nm

Fig. 3b shows the mass spectrum ($m/z > 105$) recorded at $\lambda = 210$ nm and low laser intensity

(7 μJ). This wavelength region corresponds to the $S_2 \leftarrow S_0$ transition of $\text{C}_6\text{H}_5\text{SiH}_3$. As can be seen, the $m/z = 108, 109, 138, 185$ and 216 signals are strong while the $m/z = 105, 106$ and 107 ions are almost absent. These later ions, as well as the lighter masses (analogous to those of Fig. 1) show up at higher laser intensities (30 μJ) with a noticeable exception compared to that of Fig. 1: the appearance of the SiH_3^+ peak, which is stronger than the SiH_2^+ peak. This observation can be understood by taking into consideration the photoelectron spectrum of phenylsilane [29]: a broad band with maximum at 11.0 eV has been assigned to ionization from a σ bonding orbital involving silicon. The energy of two photons at $\lambda = 210$ nm is 11.81 eV, while at $\lambda = 270$ nm it is 9.18 eV. Ionization at $\lambda = 270$ nm is attributed to excitation from a π -MO which is spread all over the aromatic ring and therefore causes a small weakening of all bonds. On the contrary, when laser light at $\lambda = 210$ nm is used, excitation from σ bonding silicon orbital is possible leading to a weakening of the C–SiH₃ bond and facilitating the –SiH₃ loss from the molecule. In this picture, the relatively strong appearance of SiH_3^+ in the mass spectrum could be interpreted as evidence for direct dissociation from the excited ionic state.

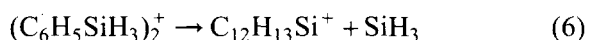
Fig. 3 shows that the $m/z = 185$ and 138 ion peaks are much stronger than those obtained by $\lambda = 270.5$ nm excitation and the $m/z = 138$ peak gains more intensity than the 185 peak.

An observation worthy of some discussion is the unexpected abundance of phenylsilane ions recorded at $\lambda = 210$ nm. At this wavelength the ionization of the monomer could take place after a two-photon absorption excitation. However, it is known that in benzene and its derivatives the intermediate S_2 state has a lifetime shorter than several picoseconds [30,31]. A lifetime of this order is also expected for phenylsilane, as can be deduced from the one-photon absorption spectrum, where the corresponding $S_2 \leftarrow S_0$ transition is very broad [8]. Therefore, with nanosecond laser pulses, molecular deactivation and/or

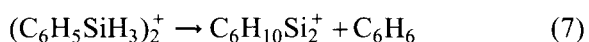
dissociation occurs prior to ionization. In the absence of clusters, the ionization at these wavelengths (in the 210 nm region) could be explained in a way similar to that proposed for benzene [32], i.e. the excitation to S_2 is followed by fast internal conversion leading the molecule to very high excited vibrational levels of the ground electronic state and the absorption of another photon at this stage causes molecular ionization. On the other hand, when clusters are present, the production of the parent ion can be attributed to fragmentation processes from cluster ions (evaporation process). It has been proved for the benzene case that the majority of the intensity of the monomer molecular ion peak comes from the evaporative dissociation of cluster ions [18]. Moreover, it has been shown [18,19] (and references therein) that the S_2 state stabilizes largely upon dimerization owing to the formation of a deeply bound excimer state which is more tightly bound than the lowest excimer state arising from the S_1 electronic state of the monomer. The existence of this dimer bound state increases the probability for a (1 + 1) photon ionization process for the cluster. The easily produced dimer ions at these photon energies are the precursors of the monomer ions via an evaporative dissociation. In the case of phenylsilane there are no theoretical predictions, but it is reasonable to assume a similar procedure for the monomer ion generation, $m/z = 108$, at these wavelengths.

The mechanisms for the production of the $m/z = 185, 138$ and 109 ion peaks are proposed to be intracluster ion/molecule reactions according to the following schemes.

The cation at $m/z = 185$ is produced by a SiH_3 loss channel in the dimer ion



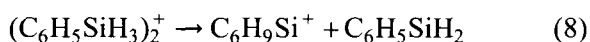
while for the generation of the $m/z = 138$ ion peak a benzene molecule is expelled from the dimer ion



Most probably, the cation in the right-hand side

of Eq. (7) is the phenyldisilane ion, $(\text{C}_6\text{H}_5\text{Si}_2\text{H}_5)^+$.

As far as the appearance of the $m/z = 109$ ion is concerned, it can be attributed to a proton-transfer reaction:



For benzene and its derivatives no such channel fragmentation has been reported. Molecules that most often undergo a proton-transfer reaction in the ionization threshold region are polar molecules, particularly those intermolecularly bound by hydrogen bonds.

A further comment can be made for the $m/z = 109$ ion peak. Silicon has three isotopes with $A = 28, 29$ and 30 in a respective abundance of 92.2:4.7:3.1. The intensity ratio for the $m/z = 108, 109$ and 110 ion peaks has been measured to be 92:18:4. The isotopomer contribution of $\text{C}_6\text{H}_8\text{Si}^+$ to the $m/z = 110$ ion signal is as expected, but it does not explain the measured intensity of the 109 peak, therefore reaction (8) can be invoked.

The above mentioned dissociation channels of homo-phenylsilane dimers (intracluster ion/molecule reactions 6, 7 and 8) are in impressive agreement with the products of the gas-phase reactions of $\text{C}_6\text{H}_5\text{SiH}_3^+$ with neutral phenylsilane examined by FT-ICR spectrometry (reactions 3, 4 and 5) [11,12].

The quadratic signal dependence on laser intensity at both wavelengths (270 and 210 nm) implies that the $(\text{phenylsilane})_2$ ionization is a two-photon process. In such a case the dimer ions will have enough excess energy upon 210 nm excitation and this could be the reason for the enhancement of the $m/z = 185$ and 138 ion signals in Fig. 3b, as compared to the same signals in Fig. 3a, since processes (6) and (7) are expected to be assisted by the excess energy of the dimer ions. Furthermore, the phenylsilane cation may also be electronically excited in the 210 nm experiments.

An interesting spectral feature of Fig. 3 is the hump, marked by an asterisk, near the parent ion

peak. This hump is attributed to $\text{C}_6\text{H}_5\text{SiH}_3^+$ ions produced from the dissociation of cluster ions in the acceleration region of the TOF system. It is known that cluster ions with large internal energy dissociate ‘instantaneously’ in the focus of the ionizing laser by ejecting neutral molecules (‘prompt dissociation’) [33]. A part of the less hot ions dissociate while traveling in the acceleration region. For benzene clusters, this delayed dissociation takes place on the time scale of 10^{-7} – 10^{-6} s, resulting in a flight time asymmetry of the ion signals on the mass spectrum, when a reflectron is used. By simulating the ion flight trajectories for our system, the decay time for this delayed dissociation has been calculated to be about 600 ns for the $\text{C}_6\text{H}_5\text{SiH}_3$ case. The calculation of such a decay time is based on an arrival time corresponding to the maximum intensity of the hump and on the assumption that the hump is due to $\text{C}_6\text{H}_5\text{SiH}_3^+$ generated upon evaporation of dimer ions in the acceleration area. The broad shape of the hump is due to the dissociation of dimers in all directions, with those fragments in the direction of the TOF axis arriving at shorter times.

Si production by phenylsilane photolysis is of particular interest. Si neutral atoms from dissociation of phenylsilane have been reported extensively. The SiH_2 radical has been suggested to be the precursor of the Si atoms [3]. In most of the cases the generation of Si atoms were verified by means of LIF [7,10]. Neutral Si fragments of $\text{C}_6\text{H}_5\text{SiH}_3$ have also been observed in our lab using the MPI technique in a static cell [8,34]. In the present work it was impossible to detect any resonant enhancement for the Si^+ ion signal at the wavelengths which correspond to Si transitions from the ground atomic state. Such a lack of resonances cannot be attributed to low transition probabilities for the ionization of Si atoms, since they were easily recorded in the $\text{C}_6\text{H}_5\text{SiH}_3$ MPI spectrum in a static cell at the same wavelength regions and with lower laser intensities. Probably the precursor of Si has either a much longer dissociative lifetime than the laser pulse width or the

dissociative state does not produce Si in the ground state. The detection of Si atoms in the ground state by MPI experiments in the static cell could then be attributed to faster collisional deactivation of the precursor or/and the released Si excited atoms prior to ionization.

4. Conclusions

The multiphoton ionization–dissociation of $C_6H_5SiH_3$ in supersonic beams has been studied in the wavelength range of 207–275 nm by means of a TOF system. For the interpretation of the observed features an above-ionization–dissociation mechanism has been invoked.

Homo-dimers of phenylsilane can be easily produced in a supersonic jet beam and their photophysical and photochemical properties have been studied by R2PI using a TOF system. The resonance states are the S_1 (270 nm) and S_2 (210 nm). The (1 + 1) ionization spectrum of the dimer corresponding to the $S_1 \leftarrow S_0$ origin region has been recorded and found to be red shifted with respect to that of the monomer. Its broad shape and dependence on the carrier gas suggest the existence of almost isoenergetic conformers in the molecular beam. Unfortunately, no theoretical predictions for the plausible structures of $C_6H_5SiH_3$ clusters are available in the literature.

The (1 + 1) ionization of the dimer at the $S_2 \leftarrow S_0$ region has been found to be very efficient. Simultaneously with their ionization process, the ionized dimers disperse their excess energy by evaporation of a neutral parent molecule. A delayed evaporation is also taking place. Furthermore, the phenylsilane homo-dimers behave as natural ‘test tubes’ and intracluster ion/molecule reactions yield the $C_{12}H_{13}Si^+$, $C_6H_{10}Si_2^+$ and $C_6H_9Si^+$ ions. The efficiency of these reactions increases (and the $C_6H_{10}Si_2^+$ ion peak gains more intensity than the $C_{12}H_{13}Si^+$ peak) as the R2PI switches from the $S_1 \leftarrow S_0$ weak dimer transition to the strong $S_2 \leftarrow S_0$ transition.

Finally, despite our efforts, no resonant MPI

signal from Si ground state atoms has been recorded in the jet beam experiment.

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