Imaging the Dissociation Dynamics of Si$_2^{+}$ via Two-Photon Excitation at 193 nm

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In the one-color experiment at 193 nm, we studied the photodissociation of Si$_2^{+}$ ions prepared by two-photon ionization using the time-sliced ion velocity map imaging method. The Si$^+$ imaging study shows that Si$_2^{+}$ dissociation results in two distinct channels: Si($^3P_g$)+Si$^+$ ($^2P_u$) and Si($^1D_2$)+Si$^+$ ($^2P_u$). The main channel Si($^3P_g$)+Si$^+$ ($^2P_u$) is produced by the dissociation of the Si$_2^{+}$ ions in more than one energetically available excited electronic state, which are from the ionization of Si$_2$ ($v=0$–5). Particularly, the dissociation from the vibrationally excited Si$_2$ ($v=1$) shows the strongest signal. In contrast, the minor Si($^1D_2$)+Si$^+$ ($^2P_u$) channel is due to an avoided crossing between the two $^2$II$_g$ states in the same symmetry. It has also been observed the one-photon dissociation of Si$_2^{+}$ ($X^4\Sigma_g^+$) into Si($^1D_2$)+Si$^+$ ($^2P_u$) products with a large kinetic energy release.

Key words: Slice imaging, Photodissociation, Silicon dimmer Si$_2$, 193 nm

I. INTRODUCTION

Silicon is abundant in interstellar space and silicon materials are important to semiconductor industry. Over the past four decades, the properties of small silicon clusters have received a great deal of interest in order to understand how their structure and properties evolve with size [1]. As a first step in understanding the nature of electronic states in large clusters, there have been numerous experimental and theoretical studies reported on the spectroscopic and electronic states of the simple yet important Si$_2$ dimers [2–18]. In these studies, most focused on the potential energy surfaces on the neutral Si$_2$ molecules, and there were only a few studies on the electronic structure of Si$_2^{+}$.

Combined with theoretical and experimental studies, the ground state of neutral Si$_2$ is $X^3\Sigma_g^−(\sigma^2\pi^2\sigma^2)$, and the lowest excited $1^3\Pi_u(\pi^2\pi^2\sigma^2)$ state is located at $T_c$=669 cm$^{-1}$ [7, 19]. Considering both $X^3\Sigma_g^−$ and $1^3\Pi_u$ of Si$_2$, which have nearly equal minimal energies, the ground states of the neutral and ionic species are related by a direct $\sigma_g$ or $\pi_u$ ionization in Si$_2$. Specifically, the ground state of the Si$_2^{+}$ is $X^4\Sigma_g^−(\sigma^2\pi^2\sigma^2)$ and the first excited $1^2\Pi_u(\pi^2\pi^2\sigma^2)$ state lies at $T_c$=4194 cm$^{-1}$ (0.52 eV) [10, 15]. Dixon and coworkers studied the role of excited states of Si$_2$ in photoionization [15]. Marijnissen and ter Meulen used the N $^3\Sigma_g^−$ state at 46763 cm$^{-1}$ (5.80 eV) as the intermediate state in the two-photon ionization process of Si$_2$ and measured its ionization potential at 63884 cm$^{-1}$ (7.92 eV) [20]. Sefyani and Schaeps calculated the lowest-lying Rydberg state of Si$_2$ in the range of 35000–55000 cm$^{-1}$ (4.34–6.82 eV) [15]. For the electronic states of Si$_2^{+}$ ions, Bruna and co-workers predicted series of potential curves of the electron configurations which dissociate into Si($^3P_g$)+Si$^+$ ($^2P_u$) through large-scale $ab$ initio CI calculations [10]. Liu et al. performed $ab$ initio all-electron relativistic calculations of the low-lying excited states of Si$_2^{+}$ with and without consideration of spin-orbit interaction on Si$_2^{+}$ [21].

The previous experimental and theoretical studies have provided details on the spectroscopy and thermodynamics properties of Si$_2$ dimers. However, to the best of our knowledge, we found no experiments on the photodissociation dynamics of silicon dimers. In this work, the photodissociation of Si$_2^{+}$ molecule prepared by two-photon ionization at 193 nm was studied by using timesliced ion velocity map imaging method. Two types of ionic photodissociation channels Si($^3P_g$)+Si$^+$ ($^2P_u$) and Si($^1D_2$)+Si$^+$ ($^2P_u$) were observed and more details on the related dissociation mechanisms are given below.

II. EXPERIMENTS

The photodissociation experiment of Si$_2^{+}$ at 193 nm was performed in self-designed crossed-molecular beam...
III. RESULTS AND DISCUSSION

The raw slice image of Si\(^+\) ions from one color experiment at 193 nm is shown in FIG. 1. The Si\(^+\) ions lying near the center and having a speed of almost zero are ionized Si monomers generated by laser ablation of Si rod, and the Si\(^+\) ions having a recoil speed are produced from the dissociation process. As the Si\(^+\) speed increases in FIG. 1, four distinct dissociation channels appear, marking regions A, B, C and D, respectively. The linear polarization direction of the laser is shown in FIG. 1. We define \(\theta\) as the angle between the polarization vector of the photolysis laser and the recoil velocity vector of the product. By integrating the signal over the \(\theta=0^\circ\sim 360^\circ\) angular range, the corresponding speed distribution is present in FIG. 2(a). In order to obtain better speed resolution, the integrated speed distribution in the small angular range of \(\theta=0^\circ\sim 5^\circ\) is shown in FIG. 2(b), and clear vibrational structures are resolved in regions B and C. The species observed in the molecular beam are mainly Si\(^+\) and Si\(_2^+\), and trace amounts of SiO\(^+\). The Si\(^+\) ions in the region A are related to the dissociation of SiO, and when the carrier gas of argon is changed to O\(_2\), the dissociation channel of SiO in region A becomes stronger. The dissociation dynamics of silicon oxide will be discussed in detail in the next paper and will therefore not be discussed in this work. The sharp rings of Si\(^+\) with large recoil velocity in regions B, C and D are related with the dissociation dynamics of silicon dimmer, which is the focus of this paper. The similar ring structure in regions B and C reflects the vibrational excitation of the parent molecule, i.e., silicon dimmer.

According to the recoil momentum conservation in Si\(_2\)/Si\(_2^+\) photodissociation, the speed distribution of Si\(^+\) is converted to the total kinetic energy release (TKER) distribution of Si\(^+\)+Si, as shown in FIG. 3. The TKER interval between adjacent peaks in regions B and C respectively is approximately 500 cm\(^{-1}\), which is consistent with the experimental obtained vibrational frequency (511 cm\(^{-1}\)) of the Si\(_2^+\)(\(X^3\Sigma^+\)) molecule [25]. The first excited electronic state of Si\(_2\)(\(D^3\Pi_2\)) of the low energy level (\(T_e=669\) cm\(^{-1}\)) can also be involved in photon excitation, where the vibrational frequency \(\nu_e=536\) cm\(^{-1}\) and the equilibrium inter-nuclear distance \(R_e=2.12\) Å (comparatively, 2.25 Å for \(X^3\Sigma^-\)) [7]. The first peak in region C has a total kinetic energy release of 10030 cm\(^{-1}\) which is about 6000 cm\(^{-1}\) higher than the first peak at 4030 cm\(^{-1}\) in region B. The energy analysis shows that the signals in regions B

FIG. 1. Raw slice image of Si\(^+\) ions from the one-color experiment at 193 nm. As the radius of the ring increases, four distinct dissociation pathways are divided into four regions.

FIG. 2 Speed distributions of Si\(^+\) ions obtained by integrating the signals over (a) the whole angular range (0\(^\circ\)–360\(^\circ\)) and (b) a small angular range (0\(^\circ\)–5\(^\circ\)), where the integration of a small angle gives a better speed resolution.
the two-photon absorption are

\[ E_{\text{TKER}}(\text{Si}^+ + \text{Si}) = E_{\text{int}}(\text{Si}^+ + \text{Si}) + E_{\text{KER}}(e^- + \text{Si}^+ + \text{Si}) \]

where the two-photon excitation energy \(2h\nu=103627 \text{ cm}^{-1} (12.85 \text{ eV})\), \(E_{\text{int}}(\text{Si}_2)\) is the internal energy of \(\text{Si}_2\), \(E_{\text{int}}(\text{Si}_2)\) is the ionization energy of \(\text{Si}_2\), \(v=0\), \(63884 \text{ cm}^{-1} (7.92 \text{ eV})\) [20], \(D_0(\text{Si}^+_2)\) is the ground state dissociation energy of \(\text{Si}^+_2\), \(3.57 \text{ eV}\) [21], \(E_{\text{int}}(\text{Si}^+ + \text{Si})\) is the electronic energy of \(\text{Si}^+ + \text{Si}\) products, \(6298.85 \text{ cm}^{-1}\) for \(\text{Si}^+(2\text{P}_u) + \text{Si}^+(1\text{D}_2)\) channel, and \(E_{\text{KER}}(e^- + \text{Si}^+ + \text{Si})\) is the translational energy distributed in the \(\text{Si}^+ + \text{Si}\) and electrons. The internal energy difference between the \(\text{Si}^+(2\text{P}_u) + \text{Si}^+(1\text{D}_2)\) and \(\text{Si}^+(2\text{P}_u) + \text{Si}^+(1\text{D}_2)\) channels is \(6298.85 \text{ cm}^{-1}\) which is consistent with the observation of the TKER difference between the two channels for \(\text{Si}_2(X^3\Sigma_g^-, \nu=0)\).

As shown in FIG. 3, the channel of \(\text{Si}^+(2\text{P}_u) + \text{Si}^+(1\text{D}_2)\) from the excitation of \(\text{Si}_2(X^3\Sigma_g^-, \nu=0)\) has the TKER of \(10030 \text{ cm}^{-1}\), and corresponds to the electron recoil energy about \(886 \text{ cm}^{-1}\) according to Eq.(3). Hence the energy analysis indicates that, according to the Franck-Condon factors, one or even more than one repulsive state of \(\text{Si}_2^+\) with \(T_c\approx38857 \text{ cm}^{-1} (4.82 \text{ eV})\) is involved

The peak in region D has a total kinetic energy release of \(16000 \text{ cm}^{-1}\). The energy analysis shows that the \(\text{Si}^+\) ions in region D are from the one-photon dissociation of \(\text{Si}_2^+(X^4\Sigma_g^-)\), which is produced by two-photon ionization of \(\text{Si}_2(X^3\Sigma_g^-)\). The process is:

\[ \text{Si}_2(X^3\Sigma_g^-) \xrightarrow{2h\nu} \text{Si}_2^+(X^4\Sigma_g^-) + e^- \]

\[ \text{Si}_2^+(X^4\Sigma_g^-) \xrightarrow{h\nu} \text{Si}_2^+(1\text{D}_2) + \text{Si}^+(2\text{P}_u) \]

Based on energy conservation, the TKER of \(\text{Si}_2^+(1\text{D}_2) + \text{Si}^+(2\text{P}_u)\) fragments will be simplified as

\[ E_{\text{TKER}}(\text{Si}^+ + \text{Si}) = h\nu - D_0(\text{Si}^+_2) - E_{\text{int}}(\text{Si}^+ + \text{Si}) \]

where \(E_{\text{TKER}}(\text{Si}^+ + \text{Si})\) is the total kinetic energy in the \(\text{Si}_2^+(1\text{D}_2) + \text{Si}^+(2\text{P}_u)\) products, \(h\nu \approx 51813.5 \text{ cm}^{-1}\), \(D_0(\text{Si}^+_2)\) is the ground state dissociation energy of \(\text{Si}^+_2\), \(3.57 \text{ eV}\), and \(E_{\text{int}}(\text{Si}^+ + \text{Si})\) is the internal energy of \(\text{Si}_2(1\text{D}_2) + \text{Si}^+(2\text{P}_u)\) products, \(6298.85 \text{ cm}^{-1}\) \((0.78 \text{ eV})\). Then the total kinetic energy \(E_{\text{TKER}}\) for the \(\text{Si}_2(1\text{D}_2) + \text{Si}^+(2\text{P}_u)\) products is predicted to be approximately \(16688 \text{ cm}^{-1}\), which is consistent with the measured TKER of \(16440 \text{ cm}^{-1}\). The slight energy difference of \(250 \text{ cm}^{-1}\) can be attributed to the excitation of the spin-orbit coupling state of \(\text{Si}^+(2\text{P}_{3/2})\) \((287.24 \text{ cm}^{-1})\) above the \(2\text{P}_{1/2}\) state. Considering that the channel in region D requires more photons in the associated dissociation dynamics than the channels in regions B and C, it is reasonable to observe a relatively weak signal in this region.

According to the two theoretical calculations by Bruna et al. [10] and Liu et al. [21], more than one
of the excited potential curves of ionic state can be involved in the ionic dissociation into Si\(3^3\)P\(_g\)+Si\(^+\)\(2^2\)P\(_u\)). According to the information of the excited electronic state obtained above, that is, \(T_v=38857\) cm\(^{-1}\) (4.82 eV) at the bond length of \(R=2.25\) Å, compared with the potential energy curves of Liu et al. [21], the repulsive doublet \(2^2\Sigma_u^+\) state and the quartet \(2^4\Sigma_u^+\) and \(1^4\Pi_u\) states can be involved in the ionic dissociation. In the work of Bruna et al. [10], in addition to the contributions of quartet \(2^4\Sigma_u^-(T_v=4.94\) eV at \(R=2.33\) Å) and doublet \(2^2\Sigma_u^-\) \((T_v=4.56\) eV at \(R=2.33\) Å) states, the doublet \(2^2\Pi_g\) state \((T_v=3.94\) eV at \(R=2.33\) Å) can also contribute to the dissociation of \(Si(3^3\)P\(_g\)+Si\(^+\)\(2^2\)P\(_g\)). Bruna et al. predicted that the energy of \(2^2\Pi_g\) state decreases suddenly at large distance due to the avoided crossing with the \(3^2\Pi_g\) state, which is decomposed into Si\(1^1\)D\(_2\)+Si\(^+\)\(2^2\)P\(_u\)). The role of \(2^2\Pi_g\) state helps to explain the Si\(1^1\)D\(_2\)+Si\(^+\)\(2^2\)P\(_u\)) channel. For clarity, FIG. 4 shows the associated channels for the formation of Si\(^+\) ions from Si\(^2+\) \((v=1)\) and \(Si(1^1\)D\(_2\)+Si\(^+\)\(2^2\)P\(_u\)) are from the vibrationally excited Si\(^2+\) \((v=3)\) state.

The angular distributions of Si\(^+\) ions in regions B and C are shown in FIG. 5 and FIG. 6, respectively. The angular distribution of photofragment produced from the two-photon photolysis of unaligned molecules with a linearly polarized laser can be expressed as [26]

\[
I(\theta) = I_0 \left[ 1 + \sum_{n} \beta_{2n} P_{2n}(\cos \theta) \right]
\]

(7)

where \(n\) is the number of photons involved in photolysis, and \(n=2\) in regions B and C, and \(\beta_{2n}\) is a coefficient that weights contributions from various order \(P_{2n}\) Legendre polynomials. The parameters \(\beta_2\) and \(\beta_4\) are fitted by

FIG. 5 The angular distributions of the peaks observed in region B of FIG. 2(b). The solid lines represent fits to the measured angular distributions using Eq. (7).

FIG. 6 The angular distributions of the peaks observed in region C of FIG. 2(b). The solid lines represent fits to the measured angular distributions using Eq. (7).
Eq. (7) and are shown in FIG. 5 and FIG. 6. It can be easily seen from the figures that the experimental data are well fitted. The small anisotropy parameters obtained for the regions B and C can be explained if we consider that more than one potential energy surface is involved in the parent ion dissociation that leads to the production of this channel, but also if the dissociation to the channel is slow compared to the rotational period of the parent ion.

IV. CONCLUSION

Two types of the ionic dissociation after the two-photon ionization of \( \text{Si}_2^{+} \) molecules at 193 nm were observed by using time-sliced velocity map imaging technique. One leads to \( \text{Si}(3P_g^1)+\text{Si}^+(2P_u^1) \), and the other is \( \text{Si}(1D_2^1)+\text{Si}^+(2P_u^1) \). More than one excited electronic state of \( \text{Si}_2^{+} \) obtained by two-photon ionization can directly produce \( \text{Si}(3P_g^1)+\text{Si}^+(2P_u^1) \) channel. The avoided crossing between two excited electronic states in the same symmetry was contributed to the \( \text{Si}(1D_2^1)+\text{Si}^+(2P_u^1) \) channel. In order to better understand the dissociation dynamics of \( \text{Si}_2/\text{Si}_2^{+} \) molecules, more studies on \( \text{Si}_2/\text{Si}_2^{+} \) photodissociation in the ultraviolet region will be reported.

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