Application of Laser Dispersion Method in Apparatus Combining H Atom Rydberg Tagging Time-of-Flight Technique with Vacuum Ultraviolet Free Electron Laser

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Photodissociation of H\textsubscript{2}S in the VUV region plays an important role in the atmospheric chemistry and interstellar chemistry. To date, however, few studies have been focused on this topic. In this article, we have described a laser dispersion method applied in the apparatus combining the high-\textit{n} H atom Rydberg tagging time-of-flight technique with the vacuum ultraviolet free electron laser (VUV FEL). The Lyman-\alpha laser beam (121.6 nm) used in the H-atom detection was generated by the difference frequency four-wave mixing schemes in a Kr/Ar gas cell. After passing through an off-axis biconvex LiF lens, the 121.6 nm beam was dispersed from the 212.6 nm and 845 nm beams due to the different deflection angles experienced by these laser beams at the surfaces of the biconvex lens. This method can eliminate the background signal from the 212.6 nm photolysis. Combined with the VUV FEL, photodissociation of H\textsubscript{2}S at 122.95 nm was studied successfully. The TOF spectrum was measured and the derived total kinetic energy release spectrum was displayed. The results suggest that the experimental setup is a powerful tool for investigating photodissociation dynamics of molecules in the VUV region which involves the H-atom elimination processes.

Key words: Photodissociation, Vacuum ultraviolet, Free electron laser

I. INTRODUCTION

As an engine of atmospheric and interstellar chemical processes, molecular photodissociation is of great importance for atmospheric and interstellar science \cite{1,2}. Photodissociation induced by the absorption of single photon permits the detailed study of molecular dynamics such as the breaking of bonds, internal energy transfer and radiationless transitions. Over the last decades, the availability of powerful lasers operated over a wide frequency range \cite{3–6} has stimulated rapid development of new experimental techniques \cite{7–10} which make it possible to study photodissociation processes in unprecedented detail. At the same time, theorists have developed powerful methods to treat these fundamental processes, at least for small polyatomic molecules, in an essentially exact quantum mechanical way. The confluence of theory and experiment has greatly advanced understanding of molecular motion in excited electronic states.

In the recent decades, due to the development of the intense ultraviolet (UV) light sources using nonlinear crystals such as KDP and BBO, great advances have been obtained in molecular photodissociation in the UV region (200–400 nm). However, the vacuum ultraviolet (VUV) photodissociation studies are only focused on the wavelengths of 193 nm and 157.6 nm, which are generated by the commercial excimer lasers. Later, the development of Four-Wave Mixing (FWM) techniques provided an opportunity to study the molecular photodissociation in a wide VUV region. Noble gases (Xe \cite{6}, Kr \cite{4,11}, Ar \cite{12}, and Ne \cite{13}) are frequently employed as the nonlinear media, as they have appropriate...
energy-level structures and are more convenient to use than mercury (Hg) vapor [14–16]. Meanwhile, VUV generation by resonant third-order difference frequency FWM ($\omega_{\text{VUV}}=2\omega_{\text{R}}-\omega_{\text{T}}$) in Kr has been investigated with flying colors. The frequency $\omega_{\text{R}}$ (212.6 nm) is resonant with the Kr two-photon transition 4p$^2$P$_{1/2}$ → 5p$^2$P$_{1/2}$, for which $\omega_T$ = 5p$^2$P$_{3/2}$ → 6s$^2$S$_{1/2}$ at 212.6 nm. By tuning $\omega_T$ in the range of 220–860 nm, it is possible to generate $\omega_{\text{VUV}}$ in the wavelength range 121–190 nm [17]. As to the VUV region below 120 nm, resonance-enhanced sum-frequency FWM ($\omega_{\text{VUV}}=2\omega_{\text{R}}+\omega_{\text{T}}$) needs to be employed [18, 19]. For the specific Lyman-α wavelength (121.6 nm), by adding three times volume Ar into Kr, the phase matching makes it possible to use higher gas pressures and significantly enhances conversion efficiency, facilitating the production of $\sim 10^{12}$ photons/pulse [17]. However, such phase matching is not universal, which means that the light intensities of VUV beams at most wavelengths produced by FWM are relatively weak. This causes some difficulty for investigating the VUV molecular photodissociation in which the photoabsorption cross section of molecules are quite small. Another intense VUV source is a third generation synchrotron, which provides $\sim 10^{16}$ photons/s with an energy resolution, $\Delta E/E$, of $\sim 1\%$ [20]. The quasi-continuous nature of synchrotron radiation generally prohibits some applications, such as photodissociation, in which the high peak VUV powers are required. Recently, the development of VUV free electron laser (FEL) at the Dalian Coherent Light Source (DCLS) has provided an extremely powerful VUV source, the pulsed energy of which is many orders of magnitude higher than other VUV sources used thus far. Photodissociation dynamics of H$_2$O at 111.5 nm [21] and 115.2 nm [22] have been investigated successfully by using this VUV source combined with the H atom Rydberg tagging time of flight technique (HRTOF).

The HRTOF technique, providing the extremely high translational energy resolution, has been widely applied in the study of the H-elimination process in molecular photodissociation [23–25] and chemical reactions [26, 27]. The key point in the HRTOF technique is the efficient excitation of the H atom, which involves absorbing one Lyman-α photon (121.6 nm) to excite the H atom from $n=1$ to $n=2$ level. The Lyman-α photon was usually generated by difference FWM schemes of 212.6 nm and 845 nm in a Kr/Ar mixing gas cell [17]. However, for some molecules, like H$_2$S [28] and NH$_3$ [29, 30] which have strong absorption cross sections at 212.6 nm, the background signals from 212.6 nm photolysis are extremely large. For some other molecules, like CH$_4$ [31] and C$_2$H$_6$, though they have very weak absorption cross sections at 212.6 nm, their primary dissociation products [32, 33] can be photodissociated by absorbing one 212.6 nm photon immediately. Thus, photodissociation dynamics of such molecules in the VUV region are quite difficult due to the 212.6 nm signal contamination. In this work, we designed a laser dispersion scheme [34, 35] applied in our new apparatus which has combined the HRTOF technique with the VUV FEL laser. Photodissociation dynamics of H$_2$S molecule in the VUV region were investigated by using this setup successfully, and the preliminary result at 122.95 nm photolysis has been presented here.

II. METHODOLOGY

The VUV FEL laser [8] and HRTOF technique [7, 36] have been described in detail previously, here is a brief description. The HRTOF technique used here was developed in the early 1990s by Welge et al. [36]. The central scheme of this technique is the sequential two-step excitation of the H atom. The first step involves the resonant excitation of the H atom from the $n=1$ to $n=2$ state at 121.6 nm. The second step concerns the UV laser excitation (365 nm) of the H atom from the $n=2$ state to a high-$n$ ($n=30–80$) Rydberg state, lying slightly below the ionization threshold. Any charged species can be extracted away from the TOF axis by adding a weak electric field ($\sim 2000$ V/cm) applied between the front plate of the Z-stack MCP detector [24] and the grounded fine metal grid. The signal detected by the MCP was then amplified by a fast pre-amplifier (ORTECVT120) and counted by a multichannel scaler (P7888).

The horizontal cutaway view of the experimental apparatus is shown in FIG. 2. The main vacuum chamber is a large stainless steel cube, evacuated by a 2000 L/s turbo-molecular pump (BOC EDWARDS STP-A2203C) and a 1600 L/s turbo-molecular-pump (BOC EDWARDS STP-A1603C) backed by a pump station (Hicube 80 Eco, 35 L/s). The source chamber is separated from the main chamber by a stainless steel cover, which is pumped by another 2000 L/s turbo-molecular pump backed by the same pump station used in the main chamber. The pressure of the main chamber and the source chamber is typically $10^{-8}$ and $10^{-9}$ torr respectively ($10^{-7}$ and $10^{-5}$ torr during the molecular beam operation). Meanwhile, for the purpose of decreasing the H atom background in the chamber, a cryo-pump (OXFORD, 350A) is employed in the main chamber.

FIG. 2 also displays the arrangement of the laser systems for generating the H atom detection laser beams (121.6 and 365 nm). Coherent light source at 121.6 nm was generated by difference FWM of two 212.6 nm photons and one 845 nm photon in a clean stainless steel cell filled with 3:1 ratio Ar/Kr gas mixture. The mixing cell was sealed at both ends with a quartz window at
the entrance and an LiF window at the light exit. Laser light at 212.6 nm was produced by doubling the output of a 355 nm (Nd:YAG laser, Spectra Physics Pro-290, 30 Hz) pumped dye laser (Sirah, PESC-G-24) operating at ~425 nm. A half of the 532 nm output of the same Nd:YAG laser was used to pump another dye laser (Continuum ND6000) operated at ~845 nm. These two beams were then focused into a cell by an achromatic lens (f=200 mm) to generate 121.6 nm using the difference FWM technique. To make sure the focus spots of these two beams spatially overlap, the 845 nm light was pre-focused by another lens (f=1500 mm). By adjusting the pressure of the mixing gas, the optimal VUV radiation at 121.6 nm was generated in the same direction with the fundamental beams of 212.6 nm and 845 nm. For some molecular systems, the 212.6 nm light will cause large background signals when it crosses the photodissociation region. Thus, the three beams then intersected an off-axis biconvex LiF lens (f=160 mm at 121.6 nm), where the VUV beam was dispersed from the UV beam. The biconvex lens was mounted on an aluminum flange, which allows the lens to slide off axis under vacuum conditions. By adjusting the position of the off-axis biconvex lens, the deflection angle and thus the direction of the VUV beam can be varied. The 365 nm laser light, exciting the H atom from the \( n=2 \) state to a high Rydberg state (\( n=30–80 \)), was generated by doubling the output of a third dye laser (Radiant Dye Laser-Jaguar, D90MA) operating at ~730 nm, pumped by the remaining of the 532 nm output of the Nd:YAG laser. The VUV FEL laser was used as the photodissociation laser, which was operated at 10 Hz and the maximum pulse energy was ~500 μJ/pulse (~3×10^{14} photons/pulse) with the wavelength continuously tuning between 50–150 nm. This light had horizontal polarization and went into the main chamber through the vacuum tube, which was perpendicular to the front side of the chamber and connected the port on the chamber. To avoid the multi-photon dissociation, the pulsed energy of the FEL laser was suppressed as low as possible. In this experiment, we fixed the FEL laser energy to be about 5 μJ/pulse. The crossing angle of the detection laser beams ((121.6+365) nm) and the VUV FEL light beam was around 7°. The MCP detector was rotated in the plane that was perpendicular to the VUV FEL beam, so that the signal with the detection axis parallel (0°) and perpendicular (90°) to the photolysis laser polarization can be both recorded by rotating the MCP detector. A molecular beam of H\(_2\)S was generated by expanding a mixing of H\(_2\)S and Ar at a stagnation pressure of 600–900 torr through a 0.5 mm diameter pulsed nozzle (General Valve) and was perpendicular to the VUV FEL propagating direction. To record the signal from the VUV FEL photodissociation, we can subtract the 121.6 nm background signal by turning the VUV FEL beam on and off. In this experiment, the signal ratio of 122.95 nm to 121.6 nm is controlled to be about 50/1.

III. RESULTS AND DISCUSSION

Photodissociation of H\(_2\)S in the VUV region has long served as the prototype system for molecular photodissociation because of its important role in atmospheric chemistry and interstellar chemistry. Many experimental [28, 36–47] and theoretical [48–51] studies have been performed on this system during the last few decades. Similar to H\(_2\)O [52], the adsorption spectrum of H\(_2\)S [28]...
displays a series of peaks. The first absorption band of H$_2$S peaks at ~195 nm with a progression of structures superimposed upon the broad continuum extending to ~270 nm. Previous studies showed that photodissociation of H$_2$S in this band provided an ideal model of the direct dissociation, yielding an H atom and a ground state SH($X^2\Pi$) with little internal excitation [44–46]. As the excitation energy increased, the SH($X$) product showed moderate vibrational excitation and cold rotational excitation.

From 160 nm to 118 nm, there are many strong absorption peaks which were assigned to several Rydberg series. In this region, only few studies were reported so far for the photodissociation of H$_2$S, which were conducted by Schieder et al. [36] and Cook et al. [37] at 121.6 nm, and by Liu et al. [47] at 157.6 nm. The SH($X$)+H channel was found to be the dominant dissociation process at 157.6 nm photolysis. The SH($X$) products were both vibrationally and rotationally excited. An intriguing bimodal rotational distribution in the lowest two vibrational states ($v=0$ and 1) has been clearly observed, indicating that there are two distinctive dissociation mechanisms involved in the photodissociation of H$_2$S at 157.6 nm excitation. At 121.6 nm photolysis, however, the dissociation dynamics are much more complicated. Experimental studies revealed that the electronically excited SH($A^2\Sigma^+$) is predominant products, and no ground state SH($X$) products are observed. The H atoms produced from the predissociation of SH($A$) [53] can also be detected in the experiments, this makes it more difficult to determine the internal state distribution of the SH product and the branching ratios of the fragmentation pathways. Even though, the experimental results [36, 37] demonstrated that most of the SH($A$) was in its vibrational ground state, with the rotational state distribution spanning almost all energetically available states (with the rotational level $N$ up to over 40). High SH($A$) vibrational states with $v$ up to 4 were also considerably populated.

Since the light 212.6 nm can also photodissociate H$_2$S, none of the experimental studies have been performed in the H$_2$S photodissociation with the tunable VUV source generated by difference FWM technique. Actually, in the H$_2$S photodissociation at 157.6 nm, the background signal from 212.6 nm photolysis has already been observed and partially overlapped with that from 157.6 nm. The relative low intensity of the tunable VUV source (the power of VUV light is two orders of magnitude lower than that of 212.6 nm) prevent us from obtaining the signals from subtracting the background signal. FIG. 3 displays a comparison of the product translational energy distributions ($E_T$) from the photodissociation of H$_2$S at 121.6 nm with and without the light 212.6 nm in the photodissociation region (without and with the light dispersion method). It is obviously observed that the signal intensity from 212.6 nm photolysis is a few times stronger than that from 121.6 nm.

![FIG. 3 The product translational energy distributions for H$_2$S photodissociation at 121.6 nm with the detection axis parallel to photolysis laser polarization. The black line was recorded without the laser dispersion and the red line was recorded with the laser dispersion.](image)

The severe overlap prevents us extracting the signal from 121.6 nm photolysis. With the dispersion method, however, the signal from 212.6 nm photolysis totally disappears. We can easily get the results from the VUV photolysis with high signal to noise ratio. The results from the 121.6 nm photolysis of H$_2$S are similar to that reported in the literatures, suggesting our dispersion method works very well.

Using the above mentioned methods, we have studied photodissociation dynamics of H$_2$S at many wavelengths in the range 121.6–155 nm by using VUV FEL laser combined with the HRTOF technique. These results are reserved for a further study. Here we only show the result at 122.95 nm. The TOF profiles of H products have been recorded with the detection axis both parallel and perpendicular to the polarization vector of the photolysis laser. The derived total product translational energy spectra are exhibited in the FIG. 4. It is clear that a wealth of resolved structures associated with the various internal energy states of SH ($A^2\Sigma^+$) has been observed, which is similar to that at 121.6 nm [37]. At 122.95 nm photolysis, there are four energetically allowed H elimination fragmentation pathways for H$_2$S [36, 37]:

- $H_2S + h\nu \rightarrow H(2S) + SH(X^2\Pi), \quad E_T \leq 49938 \text{ cm}^{-1}$
- $H_2S + h\nu \rightarrow H(2S) + SH(A^2\Sigma^+), \quad E_T \leq 18932 \text{ cm}^{-1}$
- $H_2S + h\nu \rightarrow 2H(2S) + S(3P), \quad E_T \leq 19569 \text{ cm}^{-1}$
- $H_2S + h\nu \rightarrow 2H(2S) + S(1D), \quad E_T \leq 10226 \text{ cm}^{-1}$

The threshold energies for each pathway are marked by arrows in the FIG. 4. The $E_T$ spectrum in the region of 20000 cm$^{-1}$–50000 cm$^{-1}$ corresponds to the dissociation channel H+SH($X$). A small intensity in this region suggests this channel is quite minor at 122.95 nm photolysis. The well-resolved structures below 20000 cm$^{-1}$ can be assigned to the ro-vibrational states of SH($A$) products. The combs in FIG. 4 show that the SH($A$)
FIG. 4 The product translational energy distributions for H$_2$S photodissociation at 122.95 nm with the detection axis parallel (a) and perpendicular (b) to the VUV FEL laser polarization. All of the energetically allowed H elimination channels are marked by arrows.

fragments are formed mostly in low $v$ levels but have rotational state distributions that extend to the highest $N$ levels supported by the SH(A) potential energy function. The underlying broad peaks at low $E_T$ may come from the three-body channels. The threshold energies for three-body channels $S(^{1}D)+2H$ and $S(^{3}P)+2H$ have been marked by downward pointing arrows.

According to the previous theoretical calculations [36], the topology of the $^1A_1$ ($^B^1A_1$) surface of H$_2$S, which correlates adiabatically with the SH(A)+H asymptote, is markedly more complex than its H$_2$O counterpart. Along the S–H bond direction with little change of bond angle, the direct dissociation on $^B^1A_1$ potential energy surface (PES) leads to the slightly vibrational SH($^A^2\Sigma^+$) products ($v=0$–3). With great change of bond angle, one part of H$_2$S molecules will dissociate on the $^B^1A_1$ PES producing extremely rotational SH($^A^2\Sigma^+$) products, while another part will cross to the ground state PES by conical intersection (CI) and dissociate on the ground state producing the H(2$S$)+SH(X$^2\Pi$) products. However, based on the experimental results, the probability of dissociation through CI is quite small, indicating that the two CIs between $^B^1A_1$ and $X^1A_1$ state is not important for dissociation dynamics of H$_2$S. The H–S–H bond angle in ground state H$_2$S is $\sim 92^\circ$, smaller than that for H$_2$O ($\sim 104^\circ$), and a deep well appears in the Franck-Condon region of the $^B$ state PES, all of these cause H$_2$S molecules to be hard to dissociate from the $X$ state PES through the CIs. In addition, the associated centrifugal forces could result in three body dissociation to H+H+SH($^{1}D$) products before the molecule had a chance to reach the linear configurations where nonadiabatic coupling to the lower surfaces (which correlate with H+SH(X) products) becomes effective. The detailed dissociation mechanism of H$_2$S still awaits further theoretical and experimental investigation. This experimental result suggests our setup is likely applicable to the tunable VUV photochemistry of many molecules that has significant H atom dissociation channels.

IV. CONCLUSION

A new experimental setup has been demonstrated for studying photochemistry using the high resolution time-of-flight Rydberg tagging technique, based on a laser dispersion method. By comparing the signal recorded with and without the laser dispersion, it is revealed that the laser dispersion is of great necessity for the study of H$_2$S photodissociation. Combining with the broadly tunable VUV FEL radiation source, photodissociation of H$_2$S was studied at 122.95 nm. Experimental results showed that the background signal from 212.6 nm has been eliminated, and the VUV photodissociation with high signal to noise ratio is clearly feasible. This technique is also likely applicable to the photochemistry of many other molecular systems (such as NH$_3$, CH$_4$, C$_2$H$_6$, etc.) in the VUV region that is important in the atmospheric and interstellar chemistry.

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