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Tunable VUV photochemistry using vacuum ultraviolet free electron laser combined with H-atom Rydberg tagging time-of-flight spectroscopy

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In this article, we describe an experimental setup for studying tunable vacuum ultraviolet photochemistry using the H-atom Rydberg tagging time-of-flight technique. In this apparatus, two vacuum ultraviolet laser beams were used: one is generated by using a nonlinear four-wave mixing scheme in a Kr gas cell and fixed at 121.6 nm wavelength to probe the H-atom product through the Lyman α transition and the other beam, produced by a seeded free electron laser facility, can be continuously tunable for photodissociating molecules in the wavelength range of 50-150 nm with extremely high brightness. Preliminary results on the H₂O photodissociation in the 4*d* (000) Rydberg state are reported here. These results suggest that the experimental setup is a powerful tool for investigating photodissociation dynamics in the vacuum ultraviolet region for molecules involving H-atom elimination processes. *Published by AIP Publishing*. https://doi.org/10.1063/1.5017757

I. INTRODUCTION

The field of molecular photochemistry and photodissociation dynamics has grown tremendously in the past few decades.^{1–3} It now pervades many subfields in physical chemistry from atmospheric chemistry, interstellar chemistry, environmental chemistry to quantum chemistry. With the developments in laser and molecular beam techniques, many sophisticated spectroscopic techniques have been developed. One of the useful techniques is translational energy spectroscopy with sufficiently high resolution, in which product internal state distributions over a wide energy range for state-selected photodissociation can be obtained based on the principle of energy conservation. State-resolved translational energy spectroscopy, which is converted from high-resolution time-of-flight (TOF) spectroscopy, has provided rigorous tests for first principle theoretical calculations. Traditional TOF measurements are usually made by using an electron impact ionization mass spectrometer.⁴ Due to relatively low energy resolution achieved in electron impact ionization, it suffers from the lack of product state resolution. This shortcoming can be overcome by the application of the resonance-enhanced multiphoton ionization technique (REMPI) or the H atom Rydberg tagging time-of-flight technique (HRTOF).^{5–7} Both of these techniques are based on laser excitation, and a small laser spot size at the photodissociation region can minimize the uncertainty of the TOF path length. However, the space charge broadening in TOF ion imaging measurements by REMPI limits the energy resolution. The HRTOF, which involves TOF measurements of neutral atoms in excited high-n Rydberg states, is not subject to the space charge effect, making it an ideal method for TOF measurements of photo-fragments formed in photodissociation. The HRTOF technique was first introduced in the early 1990s and now has been applied successfully to the studies of many important unimolecular dissociation processes, such as H_2O ,^{8–10} CH₄,^{11,12} C₂H₂,^{13,14} HNCO,^{15–17} and NH₃.^{18,19}

Great advances have been made in molecular photodissociation in the UV region (200-400 nm) during the past 30 years or so; this is largely due to the development of the intense UV light sources using nonlinear crystals such as KDP and BBO. However, since commercial birefringent crystals are not capable of transmitting wavelengths shorter than 155 nm,²⁰ coherent light sources in the vacuum ultraviolet (VUV) below 150 nm employ gases rather than solids for nonlinear frequency conversion. Unfortunately, due to the low densities and small nonlinear susceptibilities of gases, conversion efficiencies producing VUV light are typically much less than 1%. Since the first experiments by Ward and New^{21,22} and Young *et al.*,²³ much effort has been devoted

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to develop mixing schemes with both increased conversion efficiency and greater wavelength tuning range. The most commonly used frequency-mixing schemes in the VUV region are those based on four-wave mixing (FWM) in a gas cell. Noble gases (Xe, Kr, Ar, and Ne) are frequently employed as the nonlinear media as they have appropriate energy-level structures and are also convenient to use. Recently, VUV generation by resonant third-order difference frequency FWM $(\omega_{VUV} = 2\omega_R - \omega_T)$ in Kr has been investigated. The frequency ω_R ($\lambda_R = 212.55$ nm) was resonant with the Kr twophoton transition 4p-5p[1/2,0]. By tuning ω_T in the range $\lambda_T = 220-860$ nm, it was possible to generate ω_{VUV} in the wavelength range $\lambda_{VUV} = 121-190$ nm.²⁴ For generation of the VUV pulse below 120 nm, resonance-enhanced sum frequency FWM ($\omega_{VUV} = 2\omega_R + \omega_T$) is employed.^{25,26} For specific VUV wavelengths, for example, at 121.6 nm, phase matching by the addition of gases such as Ar or Xe makes it possible to use higher gas pressures and significantly enhance conversion efficiency, facilitating the production of $\sim 10^{12}$ photons/pulse.²⁴ However, such phase matching is not always possible, which means that the light intensities of VUV beams produced by FWM are relatively low. Recently, Davis and co-workers²⁷ reported the method to produce unprecedented intensities of VUV radiation at specific vacuum ultraviolet wavelengths (around 130.2 nm or 125 nm) by resonance-enhanced FWM of unfocused laser beams in mercury (Hg) vapor. Another intense VUV beam source is a third generation synchrotron, which provides $\sim 10^{16}$ photons/s with an energy resolution, $\Delta E/E$, of $\sim 1\%$.^{28,29} 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 Dalian Coherent Light Source (DCLS), which is a seeded free electron laser (FEL) facility with a continuously tunable wavelength of 50-150 nm and extremely high brightness, makes the studies of various atomic and molecular processes possible.³⁰ In this report, we would like to describe a scheme to use the VUV-FEL beam combined with the HRTOF method to study the photodissociation dynamics of molecules in the VUV region. Preliminary results of the photodissociation study of the H₂O molecule in the 4*d* (000) Rydberg state using this method have been presented.

II. METHODOLOGY

With the advent of the intense, pulsed VUV-FEL beam in DCLS, China, translational energy spectroscopy of H atoms from photodissociation has become feasible for wavelengths below 120 nm using HRTOF with the supersonic expansion beam. The schematic of the VUV-FEL beam line has been shown in Fig. 1. The detailed description can be found elsewhere,³⁰ and here is the brief description. The VUV-FEL facility operates in the high gain harmonic generation (HGHG) mode,³¹ in which the seed laser is injected to interact with the electron beam in the modulator. The seeding pulse at 240-360 nm with the energy $\sim 170 \ \mu J$ is generated by a Ti:sapphire laser. The electron beam generated from a photocathode RF gun is accelerated to the beam energy of ~300 MeV by 7 S-band accelerator structures, with a bunch charge of 500 pC. The micro-bunched beam is sent through the radiator, which is tuned to the *n*th harmonic of the seed wavelength, and coherent FEL radiation at λ/n is emitted. With proper optimization of the LINAC (linear accelerator), a high quality



FIG. 1. Schematic of the VUV-FEL beam line (a) and the arrangement of laser systems for the VUV-FEL HRTOF experimental setup (b).

beam with the emittance down to ~ 1.5 mm mrad, a projected energy spread of $\sim 1\%$, and a pulse duration of ~ 1.5 ps can be obtained. The VUV-FEL pulse presently operates at 20 Hz and can tune up to 50 Hz, and the maximum pulse energy is ~500 μ J/pulse (~3 × 10¹⁴ photons/pulse) with the wavelength continuously tuning between 50 and 150 nm. For recording the pulse spectral characteristic, an online VUV spectrometer is presented to monitor each single FEL pulse. This instrument is a grazing incidence spectrometer with a toroidal mirror and a variable-line-spacing plane grating.³² In this facility, the incidence angle of grating is 87.5° , and about 1%-5% of the total flux is diffracted for on-line FEL spectral characteristic diagnosing, and more than 90% of the radiation is redirected to the following beam lines. Because the price of the CCD used in the VUV wavelength range is very expensive, a 5 mm thick YAG crystal is used to convert the incoming radiation to visible wavelengths. The incoming radiation is focused onto the YAG crystal and imaged by a CCD detector. For the FEL laser pulse wavelength calibration, we use the absorption lines of noble gases for comparison.

The VUV-FEL light pulse has horizontal polarization and goes into the photodissociation chamber through the vacuum tube, which is perpendicular to the front side of the chamber and connects the port on the chamber. The typical spectrum of the VUV-FEL pulse has been shown in Fig. 2(a). The frequency bandwidth of the VUV-FEL pulse at 121.567 nm is around 0.076 nm (\sim 51.5 cm⁻¹). The tuning spectra of VUV-FEL pulses between 106 and 118 nm, which are used in water photodissociation experiments, are shown in Fig. 2(b). The water molecules are excited to several high Rydberg states by absorbing photons at these wavelengths.



FIG. 2. (a) The typical spectrum of the VUV-FEL pulse at the center wavelength of 121.567 nm. The bandwidth of the VUV pulse is around 0.076 nm. (b) The tuning spectra of VUV-FEL pulses between 106 and 118 nm, which are used in water photodissociation experiments.

The detection system used here is the HRTOF technique, which was developed in the early 1990s by Welge *et al.*⁶ A detailed description of this technique used for studying molecular photodissociation can also be found in Ref. 6. The central scheme of this technique is the sequential two-color VUV-UV excitation of the H atom. The first step involves the VUV laser excitation of the H atom from the n = 1 ground state to the n = 2 state at 121.6 nm, which has the absorption cross section of ~3 × 10⁻¹³ cm².^{6,33} The second step concerns the UV laser excitation (365 nm) of the H atom to a high-n (n = 30-80) Rydberg state from the n = 2 state.

The laser system for the two-step excitation and for the generation of the 121.6 nm VUV radiation was arranged as in Fig. 1. A coherent light source at 121.6 nm was generated by difference FWM of two 212.55 nm photons and one 845 nm photon in a stainless steel cell filled with a 3:1 ratio Ar/Kr mixture (for non-phase matching cases, pure Kr gas is employed). The mixing cell is sealed at both ends with a quartz window at the entrance and an MgF2 lens at the light exit. Laser light at 212.55 nm (\sim 1.0 mJ/pulse and \sim 0.1 cm⁻¹ bandwidth) was produced by doubling the output of a 355 nm (Nd:YAG laser, Spectra Physics Pro-290, 30 Hz, 8-10 ns) pumped dye laser (Sirah, PESC-G-24) operating at ~425 nm. A portion of the 532 nm output of the same Nd:YAG laser was used to pump another dye laser (Continuum ND6000) which operates at ~845 nm (~5.0 mJ/pulse and ~0.1 cm⁻¹ bandwidth). These two beams are then focused into a cell with Ar/Kr gas to generate 121.6 nm $(10^{11}-10^{12} \text{ photons/pulse}^{25})$ using the difference FWM technique. The remaining 532 nm power from the YAG laser was used to pump a third dye laser (Radiant Dye Laser-Jaguar, D90MA), operating around 555 nm. The output from this dye laser was mixed with the fundamental output of the YAG (1064 nm) to generate light at about 365 nm, which was used to excite the H atom from the n = 2 level to a Rydberg state of high principal quantum number (n = 30-80), lying slightly below the ionization threshold. Any charged species formed in the tagging region by multi-photon excitation are extracted away from the TOF axis by a small electric field (~30 V/cm) placed across the interaction region. The neutral Rydberg H atoms then fly a certain TOF distance (~280 mm) to reach a rotatable microchannel plate (MCP) Z-stack detector with a fine metal grid (grounded) in the front. After passing through the grid, the Rydberg atoms are then immediately field-ionized by the electric field (~2000 V/cm) applied between the front plate of the Z-stack MCP detector and the fine metal grid. The signal detected by the MCP is then amplified by a fast pre-amplifier and counted by a multichannel scaler.

The experimental apparatus used to study the H_2O photodissociation is depicted by the schematic shown in Fig. 3. A molecular beam of H_2O was generated by expanding a mixing of H_2O and Ar at a stagnation pressure of 600-900 Torr through a 0.5 mm diameter pulsed nozzle (General Valve) and propagated along the Z axis. The mixture of H_2O and Ar was made by bubbling Ar through the water sample at room temperature. The VUV-FEL light beam direction was along the Y axis, and the VUV-FWM beam direction was 7° crossed with the Y axis. The H atom product from the photodissociation process is excited to a high-n Rydberg state in nearly unity efficiency by the VUV-UV excitation scheme. Since the polarization of



FIG. 3. The experimental setup for the photodissociation of H_2O by using the VUV-FEL laser beam.

the VUV-FEL light pulse is fixed in the horizontal direction, the parallel and perpendicular photodissociated signals were obtained by rotating the MCP detector in the XZ plane. The VUV-FEL pulse and VUV-FWM pulse were synchronized by the electronic signals from the seed laser, and the delay time between the VUV-FEL and the VUV-FWM was controlled by one digital delay generator (DG645). Since the detection beam of 121.6 nm light would generate photodissociation signals for most molecules, it is necessary to subtract the 121.6 nm background signal by turning the photodissociating beam on and off.

It is noted that there is another laser system labeled as (*), which is shown in Fig. 1. The dye laser (Jaguar, D90MA) pumped by the Nd:YAG laser (Spectra Physics Pro-290, 8–10 ns) could be tuned in a spectral range from 205 to 800 nm (λ_T) using different dyes and also with doubling crystals. This tunable laser beam was focused into the same FWM cell to produce tunable VUV radiation from 121 to 190 nm (λ_{VUV}) with narrow bandwidth (~0.3 cm⁻¹) when the on-line experiments are not available. This tunable VUV radiation from FWM is employed as a photolysis laser beam for off-line photodissociation experiments, which has been introduced in our previous paper.³⁴

III. PRELIMINARY RESULTS

Photochemistry of H_2O in the vacuum ultraviolet region has long served as the prototype system for molecular photodissociation since it is an important process in atmospheric chemistry and interstellar chemistry. Extensive experimental and theoretical studies have been performed on this system during the last few decades.^{35–39} Excitation between 150 and 200 nm to the lowest excited electronic state (\tilde{A}^1B_1) leads to a direct dissociation that produces an H atom plus OH($X^2\Pi$) with little internal excitation.⁴⁰ Dynamics of the $\tilde{B}(^{1}A_{1})$ -state photodissociation have been investigated at the Lyman- α wavelength (121.6 nm). This dissociation proceeds via two main pathways: one leading to the $OH(A^2\Sigma^+) + H$ products when the dissociation energy is above the threshold for this channel and the other leading to $OH(X^2\Pi)$ + H through two conical intersections between the \tilde{B} -state and the ground state (\tilde{X}^1A_1) at the linear H–O–H and O–H–H geometries. In both cases, the OH product is highly rotationally excited but with limited vibrational excitation. Interesting quantum interference between the two conical intersection pathways has been observed.^{41–43} In addition, H₂O photodissociation in the deep VUV region has been studied using tunable synchrotron radiation. However, only the OH(A) product channel was detected through the ensuing $A \rightarrow X$ fluorescence.^{44,45} Most recently, the use of a tunable VUV laser has facilitated the single photon excitation of H₂O near 124 nm to individual rotational levels of the long-lived $\tilde{C}({}^{1}B_{1})$ -state, and the total translational energy spectra indicate a dramatic variation in the OH product distribution.^{46–48} This state decays via Coriolis coupling to the \tilde{B} -state, followed by the steps mentioned earlier yielding highly rotationally inverted $OH(X^2\Pi)$ and some $OH(A^2\Sigma^+)$ products or through a newly discovered vibronic coupling to the $\tilde{A}(^{1}B_{1})$ -state yielding highly vibrationally inverted OH($X^2\Pi$). Recently, Wu *et al.* reported the vibrational excitation effects on the predissociation dynamics of the \tilde{C} state using the time-resolved photoelectron imaging method.⁴⁹ An accidental resonance mediated predissociation pathway for the $\tilde{C}(010)$ state of H₂O has been revealed. The absorption band arising from the \tilde{D}^1A_1 state with its electronic origin around 122 nm shows no rotational structure.⁵⁰ A strong interaction with the \tilde{B} state due to avoiding crossing at bent geometries can explain this feature. The photodissociation dynamics show that dissociation from the \hat{D}^1A_1 state leads to a fast homogeneous, purely electronic predissociation to the \tilde{B} state.⁵¹ The next part of the electronic spectrum (98-118 nm) is dominated by the $nd \leftarrow 1b_1$ series.⁵² Theoretical approaches have been devoted to the corresponding high lying Rydberg states. So far, however, few experimental studies have focused in this region. The experimental scheme described here allows us to probe the photodissociation dynamics of H₂O via these high lying Rydberg states.

The first experiment has been performed for the photodissociation of H₂O at 121.56 nm by using a VUV-FEL light pulse (~10 μ J). Figure 4 shows TOF spectra of the H atom product from the photodissociation of H₂O at 121.56 nm with the detection axis parallel to the photolysis laser polarization. The VUV light pulse generated by FWM is fixed at 121.6 nm. It is noted that the VUV pulse at 121.56 nm for photodissociating molecules also can be used as the detection laser, which pumps the H atom with Lyman α transition. It is clear that the signal intensity from VUV-FEL light photolysis (VUV-FEL light and VUV-FWM light both were tuned on) is more than 5 times larger than that from VUV-FWM or VUV-FEL light tuned on only. This is reasonable since the H atom detection efficiency by using the VUV-FEL light pulse is relatively low due to the broad bandwidth of its spectrum ($\sim 50 \text{ cm}^{-1}$), while the pulse energy of VUV-FWM light is relatively low due to low frequency conversion efficiency in the FWM process.



FIG. 4. Time-of-Flight spectra of the H atom product from the photodissociation of H₂O at 121.56 nm with the detection axis parallel to the photolysis laser polarization. The pulse energy of the VUV-FEL beam at 121.56 nm is ~10 μ J. The spectra show that the H atom intensity from VUV-FEL light photodissociation (VUV-FEL light and VUV-FWM light both were tuned on) is 5 times larger than that from VUV-FWM or VUV-FEL light tuning on only.

When the VUV-FEL light pulse acts as the photolysis laser and VUV-FWM light pulse acts as the detection laser, the maximum signal can be reached. Compared with previous results at 121.6 nm photodissociation of H₂O, the resolution of the TOF spectrum is satisfactory, though the bandwidth of the photolysis laser (VUV-FEL pulse) is much broader than that previously used.⁹ All sharp peaks can be clearly resolved, which has been assigned to the high rotationally excited state of OH(X, v = 0) products. The peak intensity oscillation due to quantum interference through two conical intersections has also been observed in the spectrum. This suggests that the experimental setup provides high intensity and high resolution of the H atom TOF spectrum for H₂O photodissociation dynamics. By tuning the wavelength of the VUV-FEL light pulse, photodissociation dynamics of H₂O via high lying Rydberg states can be studied.

It is necessary to point out that there is some subtle difference among the 121.56 nm H atom TOF spectra by FWM only, FEL only, and FEL + FWM (Fig. 4). The reason is that the polarization of the VUV-FWM pulse has the vertical direction, which is different from that of the VUV-FEL pulse. Thus the perpendicular signal is recorded by FWM only, while parallel signals are recorded by FEL only and FEL + FWM. In addition, the different laser spot sizes ($\sim 1 \times 3 \text{ mm}^2$ for FEL pulse and $\sim 1 \times 1 \text{ mm}^2$ for FWM) and different pulse durations (~ 1.5 ps for FEL pulse and 5-8 ns for FWM pulse) may be responsible for the subtle difference among the H atom TOF spectra by FEL only and FEL + FWM.

Preliminary experiment has been carried out for photodissociation of H₂O at 105.734 nm, which is assigned as 4*d* (000) \leftarrow 1b₁ band.⁵² Figure 5 shows the translational energy spectra of the H atom product from the photodissociation of H₂O at 105.734 nm with the detection axis parallel and perpendicular to the VUV-FEL laser polarization. Due to large available energy [$E_{avail} = hv - D_0(HO-H) = 53\ 426 \pm 50\ cm^{-1}$], four dissociation channels producing H atoms can be observed: OH($X^2\Pi$) + H, OH($A^2\Sigma^+$) + H, O(³P) + 2H, and O(¹D) + 2H. The underlying broad peaks with the center at around

FIG. 5. The experimental translational energy spectra for the photodissociation of H_2O at 105.734 nm with the detection axis parallel and perpendicular to the VUV-FEL laser polarization. The threshold energies for three-body channels $O(^1D)$ + 2H and $O(^3P)$ + 2H have been marked by downward pointing arrows.

1000 cm⁻¹ and 15 000 cm⁻¹ should come from the threebody channels. The threshold energies for three-body channels $O(^{1}D) + 2H$ and $O(^{3}P) + 2H$ have been marked by downward pointing arrows. The sharp features around 20 000 cm⁻¹ can be clearly assigned to the highly excited rotational states of OH(X, v = 0) products, while the small sharp peaks around 10 000 cm⁻¹ can be assigned to the ro-vibrational states of OH(A) products. The possible dissociation mechanism would be non-adiabatic coupling from the Rydberg state 4d (000) to the \tilde{B} state and then dissociates on the \tilde{B} state surface to produce OH(A) products or through B-X conical intersections at H-O-H and O-H-H geometries to produce OH(X) products. From this figure, it is now clearly possible to study the photodissociation of H₂O in the entire VUV region in a continuously tunable fashion. This experimental setup is also likely applicable to the tunable VUV photochemistry of many other molecules that has significant H atom dissociation channels.

IV. SUMMARY

We have demonstrated a new experimental setup in our laboratory for studying photochemistry using the high resolution time-of-flight Rydberg tagging technique combined with a broadly tunable VUV-FEL radiation source. Experimental results for the photodissociation of H₂O on the 4*d* (000) state show that high-resolution photodissociation dynamics investigation using this technique is clearly feasible. This technique is also likely applicable to the photochemistry of many other molecular systems in the entire VUV region that is important in the atmospheric and interstellar chemistry.

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