Quantum state-selected photodissociation dynamics of H$_2$O: Two-photon dissociation via the $\tilde{C}$ electronic state

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The photodissociation dynamics of H$_2$O via the $\tilde{C}$ state by two-photon excitation has been investigated using the H atom Rydberg tagging time-of-flight technique. The rotational resolved action spectrum of the $\tilde{C} \rightarrow \tilde{X}$ transition band has been measured. The line widths show a pronounced dependence on the parent rotational excitation in the $\tilde{C}$ state. The quantum state resolved OH product translational energy distributions and angular distributions have also been obtained. By carefully simulating these distributions, quantum state distributions of the OH product as well as the state-resolved angular anisotropy parameters were determined. The experimental results confirm the variation of two competitive predissociation pathways. A heterogeneous predissociation channel is mediated by rotational coupling to the $\tilde{B} \, ^1A_1$ state associated with the $\alpha$-axis ($k_y'$), and a homogeneous pathway arises from purely electronic coupling to the $\tilde{A} \, ^1B_1$ state. We have also obtained the branching ratios of the OH($X$) and OH($A$) products, and related these to the $\tilde{C} \rightarrow A$ and $\tilde{C} \rightarrow \tilde{B}$ pathways. The branching ratios display a strong $k_y'$ dependence.

I. INTRODUCTION

The photodissociation of water molecules in the vacuum ultraviolet (VUV) has been the subject of extensive experimental and theoretical studies during the last 30 years. Because of its accessibility by various experimental techniques and high-level quantum chemical calculations, this system is a benchmark for the study of polyatomic photochemical dynamics. It is also an important process in atmospheric chemistry, astrochemistry, and astrophysics. Excitation in its long-wavelength ultraviolet absorption band around 150–200 nm leads to the first excited singlet state ($\tilde{A} \, ^1B_1$). The dissociation from this state has been studied at both 193 nm (Ref. 1) and 157 nm,$^{2-4}$ and was found to be a fast and direct process on a single potential energy surface, with a low internal excitation of the OH($X \, ^3Π$) product.

In contrast, the second excited singlet state ($\tilde{B} \, ^1A_1$) reached the second absorption continuum with its maximum at 128 nm, which leads to a more complex set of nonadiabatic dissociation pathways. The direct dissociation on this surface leads to an H atom and an excited electronic state of the OH partner ($\tilde{A} \, ^2Σ^+$). However, although OH($A \, ^2Σ^+$) molecules are produced, the dominant dissociation leads to an H atom plus a rovibrationally excited ground state OH($X$) molecule via nonadiabatic crossing from the $\tilde{B} \, ^1A_1$ state to the potential energy surfaces of either the $\tilde{A} \, ^1B_1$ state or the ground state of H$_2$O($\tilde{X} \, ^1A_1$). These perplexing photodissociation dynamics have been studied at the Lyman-α wavelength (121.6 nm).$^5-11$ Harich and co-workers$^5,6$ obtained the state-to-state dynamical picture by using the H atom Rydberg tagging technique, and observed striking even-odd intensity oscillations in the OH($X,v=0$) product rotational distribution. These oscillations had been attributed to the dynamical interference between the two conical intersection pathways. In addition, the photodissociation dynamics of H$_2$O in the VUV region from 125–133 nm has also been studied by using tunable synchrotron radiation or through two-photon excitation.$^{12-15}$ The OH($A$) rovibrational distributions have been measured by detecting the ensuing A $\rightarrow$ X fluorescence.

Excitation at wavelengths around 124 nm gives rise to the $\tilde{C} \, ^1B_1$ state of H$_2$O, which is bound adiabatically with fully resolved rotational structure. The predissociation mechanism for this state has been studied extensively using multiphoton ionization and spontaneous fluorescence detection methods.$^{16-21}$ Two-photon excitation of H$_2$O in the region of the $\tilde{C} \, ^1B_1$ state was first reported by Donovan and his co-workers$^{21}$ using untuned broadband KrF laser radiation. The approximate rotational distributions in the OH($A$) fragments were determined from the partially resolved fluorescence spectra. With the advent of the tunable, narrow-line KrF laser, Ashfold et al.$^{16,19}$ obtained the fully resolved photofragment fluorescence spectra. They suggested a homogeneous, rotation independent, and a heterogeneous, rotation dependent dissociation pathway with only the latter part giving rise to the excited OH($A$) fragments. Kuge et al.$^{17}$ investigated the predissociation of cold water molecules (17–75 K) in a supersonic free jet using 3+1 multiphoton ionization.
spectroscopy. The line-half widths and intensities in the rotationally resolved spectrum showed a pronounced dependence on parent rotational excitation in the \( \tilde{C} \) state. Recently, Steinkellner et al.\textsuperscript{22} studied the ultrafast predissociation dynamics of \( \text{H}_2\text{O} \) by using femtosecond pump-probe technique. For the heterogeneous predissociation out of the \( \tilde{C} \) state, the lifetime was determined to be \((0.5 \pm 0.1)\) ps.

More recently, the tunable, narrow-band VUV source combined with high resolution H atom translational spectroscopy has been developed in our laboratory.\textsuperscript{23} The previous paper\textsuperscript{24} described the first application of this scheme to study the rotational-state-specific dissociation dynamics of the \( \text{H}_2\text{O} \) in the \( \tilde{C} \) state at about 124 nm. The one-photon induced predissociation dynamics demonstrates dramatic variations in the OH product state distributions and its stereodynamics for \( \text{H}_2\text{O} \) dissociation in different rotational states. Photodissociation occurs exclusively through vibronic coupling to the \( \tilde{A} \tilde{A}_1 \) state for \( \text{H}_2\text{O} \) in rotational states with \( k_2'\geq0 \), leading to rotationally cold and vibrationally hot OH products. For \( \text{H}_2\text{O} \) in rotationally excited states with \( k_2' > 0 \), another pathway occurs through the Coriolis coupling to the \( \tilde{B} \tilde{B}_1 \) surface, which leads to the dramatic rotational variations of the dissociation dynamics via the \( \tilde{C} \) state. The two-photon induced predissociation dynamics has also been investigated and was briefly mentioned in the previous paper. The results by two-photon excitation, which extends the range of rotational quantum numbers, are also very interesting both from the striking alignment effects as well as the competition between two different predissociation pathways. Data analysis was difficult and has just been completed. In the present paper, we report the detailed results for the quantum state-selected two-photon photodissociation dynamics, which provides further insight into this interesting system.

II. EXPERIMENT

The high-\( n \) Rydberg H-atom time-of-flight technique utilized in this study has been described in details elsewhere,\textsuperscript{25,26} and only a brief description is presented here. A molecular beam of \( \text{H}_2\text{O} \) was generated by expanding a mixture of \( \text{H}_2\text{O} \) and Ar at a stagnation pressure of 600–900 Torr through a 0.5 mm diameter pulsed nozzle. The mixture of \( \text{H}_2\text{O}/\text{Ar} \) was made by bubbling Ar through the water sample at room temperature. Great efforts have been made on the optimization of the performance of the pulsed valve. A short beam pulse with a fast rise time \((\approx 80 \mu s)\) is very important to minimize water clusters in the molecular expansion. The rotational temperature of the water molecules in the molecular beam is about 10 K.\textsuperscript{27} The molecular beam is then crossed perpendicularly with the output of the photolysis laser, which consists of \( \text{Nd}:\text{YAG} \) (yttrium aluminum garnet) third harmonic pumped dye laser system. The second harmonic of the dye laser radiation \((\approx 248 \text{ nm}) \) is generated using an \( \beta \)-barium-borate crystal. The polarization of the photolysis laser can be changed by rotating a 248 nm zero-order half-waveplate. The H products from \( \text{H}_2\text{O} \) photodissociation are then excited to a high-\( n \) Rydberg level using a two-step excitation scheme: the coherent VUV excitation at the Lyman-\( \alpha \) wavelength \((121.6 \text{ nm}) \) followed by UV photon excitation at about 366 nm. The 121.6 nm VUV coherent radiation is generated by the four-wave mixing of two 212.5 nm photons and one 845 nm photon in a cell filled with a 3:1 ratio Ar/Kr mixture. Photons at 212.5 nm are generated by doubling the output of a tunable dye laser operating at about 425 nm, pumped by the third harmonic output of the second \( \text{Nd}:\text{YAG} \) laser. A portion of the 532 nm output of the second \( \text{YAG} \) is used to pump another dye laser operating at about 845 nm. These beams are then focused into a cell with Kr/Ar mixing gas where four-wave mixing at 121.6 nm is generated. The remainder of the 532 nm light is used to pump a third dye laser operating at 555 nm. The output from this dye laser was mixed with the fundamental output of the \( \text{YAG} \) \((1064 \text{ nm}) \) to generate light at about 366 nm, and used to excite the H atoms from the \( n=2 \) level to a Rydberg state with \( n=30–80 \) lying just below the ionization threshold. The charged species formed at the tagging region generated by the laser beams are extracted away from the time-of-flight (TOF) axis by a small electric field \((\approx 20 \text{ V/cm}) \) placed across the interaction region.

The neutral Rydberg H atoms then fly a well-defined distance \((\sim 74 \text{ cm}) \) to reach fixed micro-channel plate (MCP) detector located perpendicular to the molecular beam. The Rydberg tagged atoms are immediately field-ionized by the electric field 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 preamplifier and counted by a multichannel scaler.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Time-of-flight spectra and product translational energy distributions

The H atom action spectrum for the \( \tilde{C} \tilde{X} \) absorption band has been obtained by scanning the UV photolysis wavelength. Figure 1 shows this action spectrum of water in which six rotational lines between 247 and 248.5 nm \((2h\nu=80\, 458–80\, 947 \text{ cm}^{-1}) \) are easily resolved, and can be as-
signed as $J'_{KaK_a}(\tilde{C}(000))-J''_{KaK_a}(\tilde{X}(000))$ according to the two-photon selection rules. The line widths of the individual rotational transitions (Fig. 1) have been determined and mentioned in the previous paper. Among all the observed transitions, the $1_{11} \leftarrow 1_{10}$ rotational line has the narrowest line width, 4.26 cm$^{-1}$. While $2_{20} \leftarrow 1_{01}$, $2_{21} \leftarrow 0_{00}$, and $3_{22} \leftarrow 1_{01}$ rotational lines have the similar line widths, 7.20, 6.62, and 6.41 cm$^{-1}$, respectively. $3_{31} \leftarrow 1_{10}$ rotational line has the wider line width, 13.2 cm$^{-1}$. These widths show an increase that is approximately proportional to $k_a^2$ for the excited states, indicative of mediation by an $a$-axis Coriolis interaction, as observed in the resonance enhanced multiphoton ionization (REMPI) results. These widths also imply that the lifetime of the excited rotational states decreases as the rotational number increases. An estimated predissociation lifetime for the $3_{31}$ rotational state was determined to be 0.4 ps, which is similar to the value obtained by Steinkellner et al., $0.5 \pm 0.1$ ps.

We have also measured the TOF spectra of the H atom products for all the observed rotational lines using the experimental method described above. The spectra for each excitation wavelength were measured with the laser polarization direction perpendicular (90°) and parallel (0°) to the detection axis, as displayed in Fig. 2. The TOF spectra at the angles of 55° and 70° were also measured in order to determine the product spatial anisotropy. The TOF spectra have been converted into total translational energy (TE) distribution spectra using

$$\text{TE} = \frac{1}{2} m_H \left(1 + \frac{m_R}{m_H} \right) \left(\frac{1}{t} \right)^2,$$

where $m_H$ is the mass of the H atom, $m_R$ is the mass of the cofragment OH, $l$ is the path length from the interaction region to the detector, and $t$ is the H atom TOF measured over this distance. Figure 3 shows the product translational energy distributions in the perpendicular and parallel directions for the $2_{21} \leftarrow 0_{00}$ (80745 cm$^{-1}$) transition.

From the translational energy distributions obtained above, the OH product quantum state distributions and the quantum state specific anisotropy parameters can be determined. In a two-photon molecular photodissociation process, the center-of-mass differential cross section is given by

$$\sigma(\theta) = \frac{d^2 \sigma}{d \Omega} = \frac{4\pi}{k^5} \frac{\Delta E}{E} \frac{\Delta E}{E},$$

where $\theta$ is the angle between the incident laser polarization and the direction of the detected H atom, $k$ is the wave number of the laser, $\Delta E$ is the energy detuning, $E$ is the laser energy, and $\Delta E$ is the energy width of the TOF distribution.

FIG. 2. Time-of-flight spectra of the H atom product from the two-photon photodissociation of H$_2$O at (a) 247.316 nm(331 $\leftarrow$ 110), (b) 247.499 nm(322 $\leftarrow$ 101), (c) 247.618 nm(221 $\leftarrow$ 000), (d) 247.693 nm(220 $\leftarrow$ 101), (e) 247.871 nm(111 $\leftarrow$ 110), and (f) 248.018 nm(111 $\leftarrow$ 110) with different photolysis laser polarization.
A tum state of OH. The inner group of peaks relates to the levels of the excited $H_2O$ via these rotational lines, shown in Fig. 4. There are two nitional groups in each picture. The inner group corresponds to the photodissociation of $H_2O$. These sharp features all can be assigned to the excited OH(X) and OH(A) states, as displayed in Fig. 3(b).

For the $1_{11}→1_{10}$ transition, the two TOF spectra for the parallel and perpendicular directions are dramatically different from one another [Fig. 2(f)]. It is clear that the spectrum for the parallel direction has more sharp structures than that for the perpendicular direction. As illustrated in the one-photon dissociation, this feature suggests that the homogeneous predissociation pathway is predominant, i.e., the OH product is vibrationally excited for the parallel direction; while the heterogeneous predissociation pathway is prominent, i.e., the OH product is rotationally excited for the perpendicular direction. For the $2_{11}→1_{10}$ transition, the two TOF spectra are similar to that for the $1_{11}→1_{10}$ transition. The 3D product contour plots for these two transitions are shown in Figs. 4(e) and 4(f). It is obvious that the population of the OH(A) products relate to the inner group of peaks are much smaller than that for other four transitions.

For the other four transitions [Figs. 2(a)–2(d)], the TOF spectra for the parallel and perpendicular directions are all similar to that observed for direct excitation into the $B(1A_1)$ state. These imply that the heterogeneous predissociation pathway is significant in both parallel and perpendicular directions. The detailed analysis indicates that most of the OH(X) products have $v=0$ with extremely high rotational excitation, which is characteristic of dissociation via the $B→X$ conical intersection pathway. Compared to the one-photon dissociation, the TOF spectra from the Two-photon dissociation show that the OH products have more rotational excitation. This is reasonable since the quantum number $k_a$ of the excited state in the two-photon excitation is higher than that in the one-photon excitation.

In addition to the OH(X) and OH(A) products, two broad peaks have also been observed around 27 μs in the perpendicular direction (Fig. 2), which are similar to that observed from the $H_2O$ two-photon photodissociation via the $D$ state. However, these two peaks are not observed from the $H_2O$ one-photon photodissociation process. From the translational energy distributions, the difference of the threshold energy between the two peaks can be determined to be ~15 000 cm$^{-1}$. Since the experimental energetic values of O($^1D$) lies about 15 867 cm$^{-1}$ above the ground state of O($^3P$), these fast H-atom products should arise from the secondary photolysis of the OH(X) fragments at 248 nm to produce the O($^1D$) + H and O($^3P$) + H channels. The two broad peaks are far less evident in the parallel direction. This suggests that the angular anisotropy parameter of these fast H-atom products is about −1, which is also similar to the recent experimental values for OH photodissociation determined by Zhou et al. and Radenovic et al.

B. OH product quantum state distribution

Assignments have been made for almost all the peaks in the translational spectra using a knowledge of the complete set of bound states of OH(X) and OH(A). In total, 11 vibrational states ($v=0$–10) of OH(X) have been included in the fitting of the translational distributions. From the simulations, OH quantum state distributions can be determined, as

$$I(E_T, \theta_{cm}) = \sigma(E_T)(1 + \beta_2(E_T)P_2(\cos \theta_{cm}) + \beta_4(E_T)P_4(\cos \theta_{cm})).$$

FIG. 3. Experimental product translational energy distributions for the photodissociation of $H_2O$ at 247.618 nm($2_{31}→0_{00}$) with photolysis laser polarization parallel and perpendicular to the detection axis.

FIG. 4. The angular-dependent product translational energy distributions, relative to the polarization direction. The range of total translational energy shown is 0–25 000 cm$^{-1}$. Each sharp ring corresponds to a different quantum state of OH. The inner group of peaks relates to the levels of the excited $A→^2\Sigma^+$ state of OH, and the outer group to its ground $X→^2\Pi$ state.
in the previous works by Harich et al.\(^7\) Figure 5 shows the total rotational distributions of the OH(\(X^2\Pi, v=0\)) product by integrating distributions over different center-of-mass angles. Obviously, the rotational distributions at six rotational transitions are quite similar to that observed for direct excitation to the \(\tilde{B}(^1A_1)\) state.\(^7\) It is interesting that most of the OH(\(X, v=0\)) products are extremely rotationally excited with a peak at \(N=44\) or 45, corresponding to about 31 000 cm\(^{-1}\) rotational excitation. This means more than 70% of the available energy is deposited into purely rotational excitation. It is clear that the rotational distributions show some oscillations around \(N=40\). Such oscillations have been observed from the photodissociation of H\(_2\)O via the \(\tilde{B}(^1A_1)\) state and have been attributed to quantum interferences between the two conical \(\tilde{B}-\tilde{X}\) intersection pathways. Therefore, these OH(\(X, v=0\)) products are all populated from the \(\tilde{C} \rightarrow \tilde{B}\) heterogeneous predissociation pathway, mediated by \(a\)-axis Coriolis coupling (\(k_a\)). OH(\(X\)) products for \(v=1\)–10 have also been observed. However, the increasing density of rotational states leads to severe overlapping of the rotational manifolds for these higher vibrational levels.

Figure 6 shows the total rotational state distributions of the OH(\(A\)) product for \(v=0\)–2 at six rotational transitions. For \(v=0\) and 1, highly rotationally excited OH(\(A\)) products are as prominent as in the ground state, which indicates that the angular anisotropy of the potential energy surface is very important for dissociation via the \(\tilde{B}(^1A_1)\) state since OH(\(A\)) products only arise from direct dissociation on the \(\tilde{B}(^1A_1)\) surface. The rotational distribution of OH(\(A, v=2\)) is colder with some oscillations. These dynamics are still similar to those observed for direct excitation to the \(\tilde{B}(^1A_1)\) state, although subtle changes have also been observed for different rotational transitions.

The vibrational distributions have been obtained by integrating the rotational distributions for each vibrational level. Figure 7(a) shows the OH(\(X\)) vibrational distributions at six rotational transitions. It is clear that the OH(\(X, v=0\)) products are the most important single vibrational product channel; vibrationally excited OH products with \(v \geq 1\) comprise approximately half of the total OH(\(X\)) population for the transitions with rotational quantum numbers \(k_a > 1\) (for \(3_{31} \rightarrow 1_{10}, 3_{22} \rightarrow 1_{01}, 2_{31} \rightarrow 0_{00}\), and \(2_{20} \rightarrow 1_{01}\) transitions). For \(1_{11} \rightarrow 1_{10}\) and \(2_{11} \rightarrow 1_{10}\), however, the vibrationally excited OH(\(X\)) products are much more pronounced, with the peak at \(v=5\)–7. As illustrated in our previous paper,\(^24\) these vibrationally excited OH(\(X\)) products are generated via the \(\tilde{C} \rightarrow \tilde{A}\) homogeneous predissociation pathway. The distribution of the OH(\(X\)) products calculated by Dixon\(^24\) via this homogeneous pathway peaks at \(v=5\) and stretches to \(v=13\), which is consistent with our observations. The OH(\(A\)) product vibrational distributions have also been obtained for six transition lines [Fig. 7(b)]. It is apparent that the population for the OH(\(A\)) product decreases gradually as the vibrational energy increases at each rotational transition.

C. Angular distribution

In the present case, with an excited state lifetime much longer than the rotational period, the spatial anisotropy of the transient excited state varies with the rotational transition,

![FIG. 5. The total rotational state distributions of the OH(\(X, v=0\)) product from the photodissociation of H\(_2\)O at six rotational transitions.](image)

![FIG. 6. The total rotational state distributions of the OH(\(A, v=0,1,2\)) products from the photodissociation of H\(_2\)O at six rotational transitions.](image)
and therefore so does the space-fixed recoil anisotropy. By determining the values of the recoil anisotropy parameter for several transitions, it is possible to determine a more detailed picture of the dissociation in the molecular frame than with a short lived state. The dramatically changing of the spatial anisotropy for different rotational transitions has been mentioned in our one-photon experimental results. In this work, spatial anisotropy also changes significantly as rotational transitions change.

The distributions of the angular anisotropy parameter have been determined for the various quantum levels of the OH product by using Eq. (2). Figure 8 shows the anisotropy $\beta_2(N)$ distribution for the OH($X$) product in the $v=0$ state at six rotational transitions. These distributions show dramatic variations in the $\beta_2$ parameter over the observed range of $N$ values. For $N$ less than 40, the $\beta_2$ parameters are almost negative with the order of $-0.6$. While for $N$ between 40 and 45, the $\beta_2$ parameters alternate with negative $\beta_2$ for $2_{11} \leftarrow 1_{10}$ and $1_{11} \leftarrow 1_{10}$ transitions and positive $\beta_2$ for the other transitions. This variation can be clearly observed in the 3D contours (Fig. 4). The highly rotationally excited OH($X$) products populate predominantly in the perpendicular direction for $2_{11} \leftarrow 1_{10}$ and $1_{11} \leftarrow 1_{10}$ transitions, and change to the parallel direction for the others. Figure 9 shows the anisotropy $\beta_2(N)$ distributions for the OH($A$) product in the $v=0$–2 state at six rotational transitions. These distributions are quite different from each other. The $\beta_2$ parameter again varies strongly over the whole rotational range, rising and falling several times from low $N$ to high $N$.

Figure 10 shows $\beta_3(N)$ distribution for the OH($X$) product in the $v=0$ state. These parameters are almost all negative and oscillate strongly as the $N$ quantum number increases. However, there is no clear pattern to these

![Figure 7](image1.png)  
**FIG. 7.** The total vibrational state distributions of the OH($X$) (a) and OH($A$) (b) product from the photodissociation of H$_2$O at six rotational transitions.

![Figure 8](image2.png)  
**FIG. 8.** Rotational dependence of the anisotropy parameter $\beta_2$ for the OH($X$, $v=0$) products at six rotational transitions.
IV. DISCUSSION

The quantum state selected predissociation of H₂O from the \( \tilde{C} \) state have been served as a text book example of a fully state selected photodissociation dynamics system. Combined with previous experiments and calculations, two competitive predissociation pathways were observed in the \( \tilde{C} \) state dissociation. First, a heterogeneous predissociation pathway is mediated by rotational coupling to the \( \tilde{B}(^1A_1) \) state associated with the \( a \)-axis, the axis with the smallest moment of inertia. This channel yields extremely rotationally hot ground state OH(X, \( v=0 \)) products as a result of a large torque acting in the vicinity of the conical intersection at a collinear (H–O–H) geometry between \( \tilde{B} \) and \( \tilde{X} \) surfaces. The electronically excited OH(A) products also can be produced from direct dissociation on the \( \tilde{B} \) surface. Second, a homogeneous pathway arises from purely electronic coupling to the \( \tilde{A}(^1B_1) \) state. The outgoing wavepacket from the \( \tilde{C} \) state to the \( \tilde{A} \) state is then diverted by the rising potential on the diagonal toward the two low energy exit valleys, each leading to H+OH(X). The slalomlike oscillation across these exit valleys is very evident, indicating high vibrational excitation of the OH(X) products. The predissociation pathways involving four potential energy surfaces can be described as follows:

FIG. 9. Rotational dependence of the anisotropy parameter \( \beta_2 \) for the OH(A, \( v=0 \)) (a), OH(A, \( v=1 \)) (b), and OH(A, \( v=2 \)) (c) products at six rotational transitions.

FIG. 10. Rotational dependence of the anisotropy parameter \( \beta_4 \) for the OH(A, \( v=0 \)) (a), OH(A, \( v=1 \)) (b), and OH(A, \( v=2 \)) (c) products at six rotational transitions.

FIG. 11. Rotational dependence of the anisotropy parameter \( \beta_4 \) for the OH(A, \( v=0 \)) (a), OH(A, \( v=1 \)) (b), and OH(A, \( v=2 \)) (c) products at six rotational transitions.
TABLE I. Branching ratios of the OH(X) and OH(A) product channels and the $\tilde{C}\rightarrow \tilde{A}$ and $\tilde{C}\rightarrow \tilde{B}$ pathways. [The total branching of the OH(X) and OH(A) products, $f$(OH(X))+$f$(OH(A)), is equal to unity, and the sum of the branching ratios of the $\tilde{C}\rightarrow \tilde{A}$ and $\tilde{C}\rightarrow \tilde{B}$ pathways, $f$(C$\rightarrow \tilde{A}$)+$f$(C$\rightarrow \tilde{B}$) is also equal to unity.]

<table>
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<th>Pathway</th>
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<td>$f$(C$\rightarrow \tilde{B}$)</td>
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<tr>
<td>$2_{11}\leftarrow 1_{10}^a$</td>
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<td>0.071</td>
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<tr>
<td>$1_{10}\leftarrow 1_{10}$</td>
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<td>0.097</td>
</tr>
<tr>
<td>$2_{20}\leftarrow 1_{10}$</td>
<td>0.534</td>
<td>0.179</td>
</tr>
<tr>
<td>$3_{22}\leftarrow 1_{10}$</td>
<td>0.575</td>
<td>0.137</td>
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<tr>
<td>$3_{31}\leftarrow 1_{10}^a$</td>
<td>0.536</td>
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$^a$Reference 24.

The branching ratios of the OH products quantitatively describe the competition between different nonadiabatic dissociation pathways. Through careful simulations of the experimental results, we have determined the branching ratios for the OH(X) and OH(A) products, and related these to the $\tilde{C}\rightarrow \tilde{A}$ and $\tilde{C}\rightarrow \tilde{B}$ pathways. We assume that the high rotational states of OH(X,$v=0$) are all populated from the $\tilde{C}\rightarrow \tilde{B}$ pathway, as are the OH(A) products; whereas the vibrationally excited OH(X) products are from the $\tilde{C}\rightarrow \tilde{A}$ pathway (see Table I). Table I also includes the corresponding values from previous one-photon experiments. It is obvious that the branching ratios of the $\tilde{C}\rightarrow \tilde{A}$ and $\tilde{C}\rightarrow \tilde{B}$ pathways mainly depend on $k_\epsilon'$. For $k_\epsilon'=0$, only the homogeneous $\tilde{C}\rightarrow \tilde{A}$ pathway is active. For $k_\epsilon'=1$, an electronic Coriolis coupling around the $a$-axis mediates coupling between the $\tilde{C}$ and $\tilde{B}$ states. The measured branching ratios for the $\tilde{C}\rightarrow \tilde{B}$ pathway are around 0.3. For $k_\epsilon'=2$, the heterogeneous $\tilde{C}\rightarrow \tilde{B}$ pathway becomes more important, with the value of about 0.45. The simple theory suggested that the $\tilde{C}\rightarrow \tilde{B}$ rate has $(J_a^2)$ dependence, while the $\tilde{C}\rightarrow \tilde{A}$ rate is independent of rotation. This means the branching ratio ($\tilde{C}\rightarrow \tilde{B}$/$\tilde{C}\rightarrow \tilde{A}$) should scale with $(J_a^2)$, as do the line-widths. The branching ratio observed in our work does rise with $k_\epsilon'$, but more slowly than quadratic. This suggests that there is a second Coriolis coupling to increase the $\tilde{C}\rightarrow \tilde{A}$ rate. There are several instances where the branching ratios do seem sensitive to $k_\epsilon'$ in the Table I. For example, The branching ratios for the $\tilde{C}\rightarrow \tilde{A}$ pathway are determined to be 0.534, 0.546, and 0.575 for the rotational transitions $2_{20}\leftarrow 1_{10}$, $2_{21}\leftarrow 0_{00}$, and $3_{32}\leftarrow 1_{01}$, respectively. This means that the branching ratios for the $\tilde{C}\rightarrow \tilde{A}$ pathway increase as $k_\epsilon'$ increases, although they have the same value of $k_\epsilon'$. In addition, the branching ratios are also affected by the different quantum states of the ground electronic state of H$_2$O.

In Table I, the branching ratios for the transitions $2_{11}\leftarrow 1_{10}$ and $3_{31}\leftarrow 1_{10}$ are significantly different from the expected values. We also noted that the TOF spectra [Fig. 2(e)] for the $2_{11}\leftarrow 1_{10}$ can be considered to be a weighted sum of the TOF spectra with the quantum number $k_\epsilon'=0$ and $k_\epsilon'=1$. Therefore, the unexpected branching ratios are likely because state mixing occurs at these two wavelengths. Detailed theoretical investigations are still needed in order to understand fully this dynamical phenomenon. The results presented here illustrate the importance of molecular rotation in controlling the excited state dissociation dynamics as well as the branching between alternative electronic states and even the alternative product channels.

V. CONCLUSIONS

The two-photon photodissociation dynamics of H$_2$O via the $\tilde{C}$ state between 247 and 248.5 nm has been investigated using the high resolution H atom Rydberg tagging technique. The OH product translational energy distributions and angular distributions have been determined by measuring the H atom time-of-flight spectra. From these distributions, quantum state distributions of the OH product as well as the state-resolved angular anisotropy parameters were determined. Experimental results indicate dramatic differences in the OH product state distributions and its stereodynamics for different resonant states. Two competitive predissociation mecha-
nisms have been confirmed via the $\tilde{C}$ state: one homogeneous, rotation independent and one heterogeneous, rotation dependent dissociation pathway. As $k_4$, increases, this latter pathway becomes more and more important. Branching ratios have also been determined for the different product channels and compared with those obtained from one-photon experiments.

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