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Photodissociation of water molecule at short photon wavelengths: Dynamical studies

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In our last study [J. Phys. B At. Mol. Opt. Phys. 54, 125,102 (2021).], we reported the *ab initio* calculation of the full-dimensional potential energy surfaces of water molecule including 9 A′ and 9 A″ states in Cs symmetry. In this study, we performed additional non-adiabatic semi-classical studies based on the potential energy surfaces. Our simulation successfully repeated the near picosecond lifetime of the $\boldsymbol{\tilde{F}^1A'}$ state measured by time resolved photo-electron spectra experiment [Chinese J. Chem. Phys. **32**, 53 (2019)]. We also determined the dissociation branching ratio including H + OH(X, A), H + H + O and H_2+O channels. In addition, the reaction path corresponding to H_2+O (^{1}S) channel is clearly marked out, which is found in recent free-electron laser experiment [Nat. Commun. **12**, 6,303 (2021)].

KEYWORDS

photodissociation, semi-classical, surface-hopping, potential energy surface, non-adiabatic dynamics

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1 Introduction

With the development of vacuum ultra-violet free electron laser (VUV-FEL) light sources combined with time-sliced velocity-map imaging (TSVMI) [1] and time-resolved photo-electron spectroscopy (TRPES) technique [2], dynamical studies for the photo-chemistry process in molecules from highly excited electronic states have been performing for several years before [1, 3, 4]. Among small molecules, water had been extensively studied as an ideal polyatomic system. Interesting phenomena have been found for the photodissociation dynamics of highly-excited states of water, including the hot rotation of OH fragments in ground and excited states at special incident photon wavelengths [4, 5] the long-lived lifetime of $\tilde{F}$ and $\tilde{F}'$ states [6] and the high yield of the three-body H + H + O channel [7] at short wavelengths.

Despite the extensive experimental studies of the photodissociation of water molecule in highly-excited states, corresponding theoretical studies are relatively scarce due to the lack of the corresponding potential energy surfaces (PES). On the other hand, most theoretical studies focus on specific fragment quantum distributions such as the rovibronic [8] or the fine structures of OH radical [9], and few studies consist of all three channels of H + OH, H_2+O and H + H + O. In our latest work [10], we obtained the full dimensional potential energy surfaces with the combined multi configurational self-consistent field and multi reference single and double excitation configuration interaction method (MCSCF + MRDCI), nearly 99,000 geometries are considered which include all the three mentioned channels.

If we do not aim at studying quantum effects such as interference, energy resonant, or geometric phase, a semi-classical simulation of the nuclear motions is good enough to describe the reaction behavior with a lower computational cost. In this paper, based on our full-dimensional PESs, the photodissociation of water molecule with respect to the photon energy of 9–12 eV are studied with a semi-classical method, and the non-adiabatic transition is included using a Landau-Zener type approach near conical-intersections or avoid-crossings. It should be noted that, in the present study, only the states of $^1A'$ symmetry are taken into consideration because the ones with $^1A''$ symmetry are either long-lived [2, 6](second or higher $^1A''$) or lower than the energy range of interest ($\tilde{A}^1A'$, less than 8eV).

2 Theoretical method

The semi-classical simulation is performed by solving the Newton equations with the Verlet algorithm:

$$q(t+\Delta t) = 2q(t) - q(t-\Delta t) + \ddot{q}(t)\Delta t^2 \tag{1}$$

Here, q is the coordinate of an atom. The acceleration $\ddot{q}$ is determined from a finite difference on the PES with a multi-dimensional B-spline interpolation. Non-adiabatic process is considered using two main approximations—surface hopping and the Landau–Zener model [11, 12], which has been analyzed and tested in several conical intersection problems [13–15]. When the potential energy gap comes minimal along the classical trajectory, a non-adiabatic transition may occur. Considering a classical trajectory associated with the ith adiabatic surface, if at a critical time t_c, the energy gap function $Z_{ij}(q_c)$ between the ith and jth surfaces at the coordinate $\{q_c\}$ reaches a minimum, a transition from surface i to j can take place. The transition probability can be described by a Landau-Zener formula [11]:

$$P_{LZ} = exp\left(\frac{-\pi}{2\hbar}\sqrt{\frac{Z_{ij}(q_c)^3}{\frac{d^2}{dt^2}Z_{ij}(q(t))\mid_{t=t_c}}}\right) \tag{2}$$

During the simulation, such probability is compared with a pseudorandom number ξ within a uniform interval of [0,1]. If $\xi > P_{LZ}$ the trajectory stays on the current surface i. If $\xi < P_{LZ}$, the trajectory hops from the current surface i to the surface j, and the velocities are rescaled as:

$$\sum\nolimits_\alpha \frac{1}{2}m_\alpha|\dot{q}_\alpha(t)|^2 + U_i(q_c) = \sum\nolimits_\alpha \frac{1}{2}m_\alpha|\dot{q}_\alpha^{rs}(t)|^2 + U_j(q_c) \tag{3}$$

to ensure the energy conservation. The summation is over all nuclear with mass m_α. In our approach, only $j = i \pm 1$ are taken into consideration i.e. only the hopping between the adjacent surfaces are considered.

The initial geometry samplings are based on a Wigner distribution [16, 17] near the equilibrium geometry of the ground state $\tilde{X}^1A'$ at the ground vibrational state.

3 Results and discussion

3.1 The lifetime of state $\tilde{D}^1A'$ and $\tilde{F}^1A'$

We obtain the lifetime of state $\tilde{D}^1A'$ and $\tilde{F}^1A'$ by applying the simulation from each specific adiabatic surface. Thousands of trajectories are performed with different initial condition and then we can collect the numbers of undissociated trajectories at each time t as $N(t)$. Finally, the lifetime τ is obtained through an exponential fitting on $N(t)$ *versus* t as: $N(t) = N_0\,exp\,(-t/\tau)$.

The state $\tilde{D}^1A'$ is believed to be unstable due to the strong non-adiabatic coupling with the lower state of $\tilde{B}^1A'$ at the bending geometry. Several experimental studies have reported slightly diverging results. Steinkellner etal [18] obtained a value of 60 ± 50 fs with a large uncertainty using an ultrafast two-photon experiment in 2004. Then Yuan etal [19] estimated the lifetime of $\tilde{D}^1A'$ to be 13.5 fs from the bandwidth value of a two-photon spectrum. In the present study, as shown by Figure 1A, the dissociation lifetime for $\tilde{D}^1A'$ state is determined to be near 124 fs. The relatively short lifetime of 13.5 fs by Yuan etal [19] is within the lower limit of 60 ± 50 fs by Steinkellner etal [18] while the present value of 124 fs is near the upper limit of that. Present study may slightly overestimate the lifetime of $\tilde{D}^1A'$ state because other non-adiabatic processes (e.g. Coriolis couplings) may also lead to the dissociation thus reduce the dissociation lifetime. More theoretical and experimental works are required to accurately determine the lifetime of $\tilde{D}^1A'$ state. It should be noticed that, at the first 50 femtoseconds, the counts in Figure 1A is flat. This is caused by our simulation algorism: in first tens of femto-seconds, most trajectories cannot reach the defined dissociation conditions (e.g. OH bond length larger than a threshold value), so they are not regarded as ‘dissociated’.

The lifetime of $\tilde{F}^1A'$ state had been determined by Yang etal [6] to be as long as 1000 ± 300 fs using the time-resolved photo-electron spectroscopy (TRPES). They suggested a weak non-adiabatic traisition from $\tilde{F}^1A'$ to $\tilde{D}^1A'$, followed by dissociation from the $\tilde{D}^1A'$ surface as discussed above. However, in our last study [10], we suggested that the long lifetime should come from the long-time for symmetry-breaking process by analysing the PESs corresponding to such process. As shown in Figure 1B, the lifetime of $\tilde{F}^1A'$ is determined to be about 770 fs with our semi-classical simulation which is in good agreement with the TRPES results of Yang etal [6]. So our initial suggestions are well supported by the present simulation.

3.2 The channel ratio with respect to the incident photon energy

In previous theoretical studies, researchers mainly focus on part of the dissociation channels. e.g., for H + OH dissociation channel, Jiang etal [20] studied the rotational and vibrational distributions of the OH fragment, Zhou etal [8] studied the effect of spin-orbit couplings on the rotational distributions of OH fragment. For H_2+O channel, the only theoretical study was performed by van Harrevelt etal [21], in which the rotational and vibrational distributions of H_2 were obtained, a 10% ratio for the H_2+O channel was found which

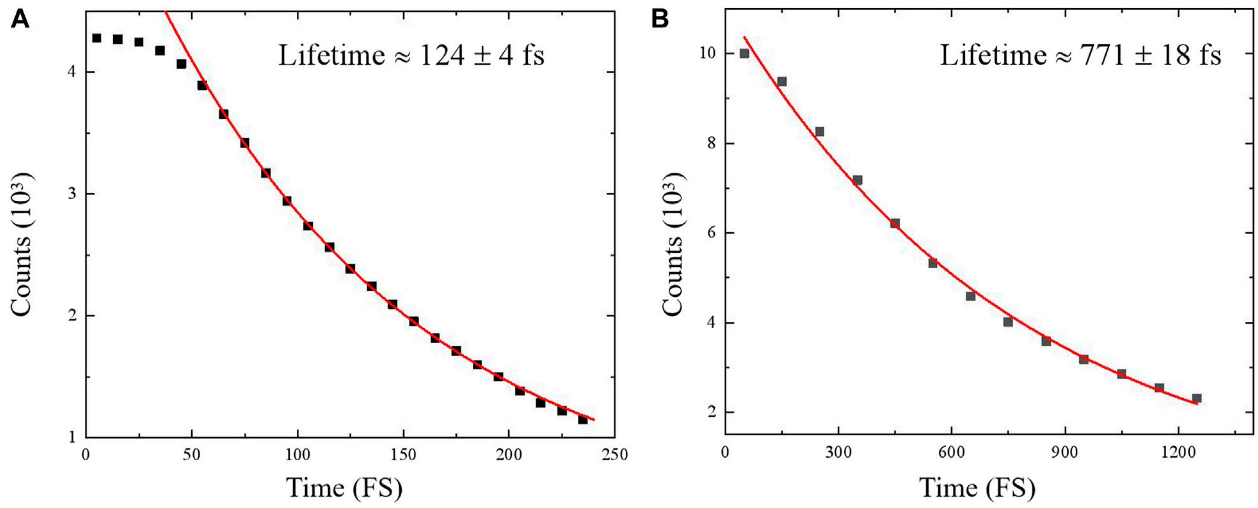

FIGURE 1
Number of undissociated trajectories *versus* simulation time of state $\tilde{D}^1A'$ (panel **(A)**) and $\tilde{F}^1A'$ (panel **(B)**). The lifetimes are obtained through a fitting procedure with an exponential function. Points are the simulated values and lines are the fitted curves. The uncertainties are due to the fitting procedure.

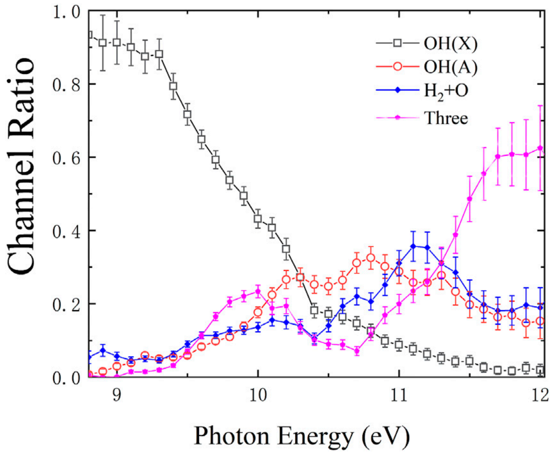

FIGURE 2
Branching ratio *versus* photon energy. OH(X) and OH(A) correspond to the H + OH channel with the OH fragment on ground and first excited states, respectively. "Three" correspond to the H + H + O channel. The error bars are determined from the statistical error of the number of the trajectories of each channel.

was in good accordance with earlier experimental results t [22]. For the three body channels, no specific theoretical studies are published. In a recent study, Chang etal [7] found a quite large ratio of the three-body channel at short wavelengths (near 100 nm, 12.34 eV).

Here we perform a simulation containing all three channels with the full-dimensional PESs obtained in our last work [10]. A key point is the determination of the initial surface. In the present study, we perform the simulation from all the excited $^1A'$ states and the numbers of the trajectories from each surface are determined as:

$$N_i \propto |D_{1i}(R_e)|^2 \big/ \omega_{1i}^2. \tag{4}$$

Here N_i is the number of the trajectories from the ith ($i > 1$) $^1A'$ surface, and $D_{1i}(R_e)$ and ω_{1i} are the transition dipole moments and vertical excitation energy at the equilibrium geometry from $^1A'$ to i^1A'. Such approximation is based on a vertical excitation from the ground state to the ith excitation state. Then the photon energy of each trajectory is determined as:

$$E_p = U_i(q(t=0)) + \sum\nolimits_{\alpha} \frac{1}{2} m_\alpha \left|\dot{q}_\alpha(t=0)\right|^2 - E_0 \tag{5}$$

E_p and E_0 are the photon energy and the zero-point energy of ground state, respectively. U_i is the PES of the ith surface. $q(t=0)$ and $\dot{q}_\alpha(t=0)$ correspond to the initial coordinates and velocities of each atom. Totally, hundreds of thousands of trajectories are performed, and the channel ratios are obtained and shown in Figure 2.

As shown in Figure 2, at low photon energy (near 9 eV), most trajectories lead to the H + OH(X) channel. As the photon energy increases the ratio of H + OH(X) channel reduces rapidly and the ratios of other channels rise. H + OH(A) channel corresponds to the dissociation on B^1A' surface: as the photon energy increases, the ratio of H + OH(A) channel rises to the maximum at near 10.7 eV. This may due to the fact that at higher photon energy, competition between three-body and H_2+O channel can take place. The H_2+O channel also rises with the photon energy increases from 9 eV and reaches the maximum at about 11.2 eV. It should be noted that, at about 10.2 eV, the H_2+O channel ratio is close to 10%, this is in good agreement with the ones presented by the theoretical results of van Harrevelt etal [21] and the experimental ones of Slanger etal [22]. The three-body dissociation of water molecule is an important way to generate the oxygen atom, and was discovered by both dissociative electron attachment [23] and photodissociation [7] experiments, but the mechanisms are different because the PESs of H_2O molecule and its anion are quite different. In present result, the ratio of three-body channel reaches the first maximum of about

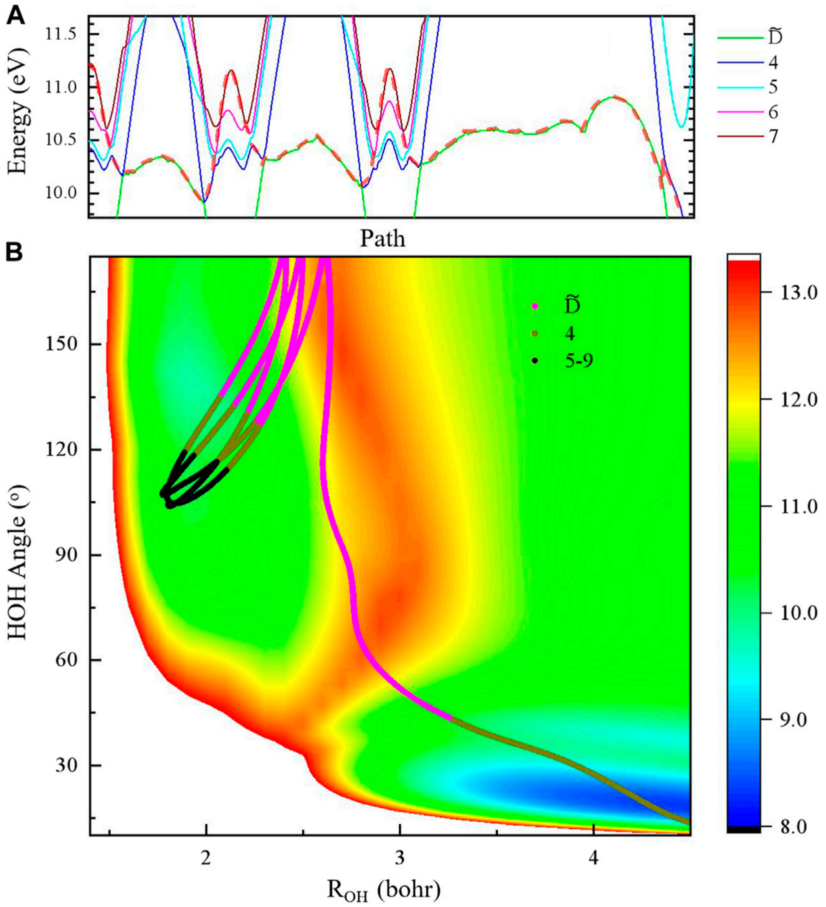

FIGURE 3
Reaction path corresponding to H_2+O (^{1}S) channel. In panel **(A)**, the adiabatic potential energies within the $^1A'$ symmetry along the reaction path is shown, the values corresponding to the trajectory is shown as a dashed line. In panel **(B)**, the symmetric ($R_{OH1} = R_{OH2}$) PES of $4^1A'$ in electron volts is shown, and the trajectory for the H_2+O (^{1}S) channel is shown in a multi-colored line, and each color correspond to an adiabatic surface shown by the legend. The color of the trajectory line depends on which adiabatic state the system is on during the reaction process. It should be noted that the horizonal axis correspond to the average length of the two OH bonds within this trajectory.

22% at near 10 eV, and reduces to below 10% at 10.6eV. Such reduction may come from the competition of the H + OH(A) and H_2+O channel. After that, the ratio of the three-body channel increases rapidly. A quite large value of 62% ± 12% of such channel is determined near 12 eV. In the recent experimental study by Chang etal [7], the ratios considering only H + OH and three-body channels are obtained, and a value of near 85% at 102 nm photon wavelength (12.15 eV) was presented. In present study, if we also exclude the H_2+O channel, the ratio of three-body channel can be determined as near 78% ± 15% at 12 eV. Such value is within the range of the experimental ones by Chang etal [7].

3.3 The H_2+O channel

In recent experimental work of Chang etal [3], the photo dissociation of water at wavelength ranging from 102.67 to 112.81 nm (10.99—12.08 eV), corresponding to the H_2+O channel, was studied. The H_2+O (^{1}S) channel was observed and the vibrationally excited H_2 molecule was mostly populated. This is surprising because the H_2+O (^{1}S) channels correspond to the fourth $1_{A'}$ surface at the asymptotic region and there exist a rather high energy barrier to overcome on this surface as shown in Figure 3B. In our last work [10] and the theoretical study in Chang etal [3], it was pointed out that the system can follow a non-adiabatic reaction path which corresponds to an avoid crossing zone between $\tilde{D}^1A'$ and 4th$^1A'$ (two OH bonds near 3.4 bohr and HOH angle near 45°), after such non-adiabatic transition, the system falls into a well which leads to the hot vibration of H_2 fragment. In present study, we also found few numbers of trajectories leading to the H_2+O (^{1}S) channel. A typical trajectory for the H_2+O (^{1}S) channel is shown in Figures 3A,B not only with the geometry movement but also the adiabatic state transition processes. Just as illustrated in our last study [10], the system oscillates for several cycles on the bending and symmetric stretching coordinates, but when the system transit to $\tilde{D}^1A'$ surface and the two OH bonds enlarge to near 2.6 bohr, at the HOH angle of 180°, the length of the two OH bonds will not shorten or elongate for a while and the system will keep staying at the $\tilde{D}^1A'$ surface. The main movement then is the contraction of HOH angle from 180 ° to near 60 °. Then the system moves to the avoid crossing between

$\tilde{D}^1A'$ and fourth $^1A'$ and transit to fourth $^1A'$ which leads to the H_2+O (^{1}S) channel.

4 Conclusion

By performing semi-classical simulation with Landau-Zener surface hopping approximation, the photo-dissociation dynamics of water molecule in high-lying states are studied. The lifetimes of $\tilde{D}^1A'$ and $\tilde{F}^1A'$ states are determined and found in good agreement with previous experiments. The dissociation channel ratio considering all three channels of H + OH, H_2+O and H + H + O within the photon energy from 9 to 12 eV are obtained. Good agreement is found between present ratio values and available experimental and theoretical ones. The H_2+O (^{1}S) channel is also found in the simulation and the corresponding reaction path is shown, which may help understanding such interesting reaction channel better. In future works, for deeper understanding of the dissociation mechanisms, more analysis of the reaction channels, and full-quantum mechanically studies including non-adiabatic coupling matrix elements and the wave-package propagation simulation should be performed.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

Conceptualization: YW, RL methodology: YP, NS investigation: YP, XH, visualization: YP, NS, XH supervision: YW, JW, RL writing—original draft: YP, NS writing—review and editing: YW, JW, RL.

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Conflict of interest

Publisher's note

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