

Laser-induced fluorescence study of the hydrogen atom formation dynamics in the 248 nm gas-phase photodissociation of vibrational state selected water ($\text{H}_2\text{O}(|04^-|)$)

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Abstract—The vibrationally-mediated H_2O gas-phase photodissociation was studied at a photolysis wavelength of 248 nm. Single rotational states of the $|03^-|2\rangle$ and $|04^-|$ H_2O overtone vibrations were prepared by laser photoexcitation around 720 nm. H atoms formed in the photodissociation of the $\text{H}_2\text{O}(|04^-|J'_{K_a K_c} = 3_{13})$ were detected by Lyman- α laser-induced fluorescence spectroscopy with sub-Doppler resolution to determine their translational energy. The present result confirms that in the dissociation process the major part (*ca.* 93%) of the available energy is released as relative translational energy of the nascent H + OH photofragments, in agreement with earlier complementary measurements (R. L. Vander Wal, J. L. Scott and F. F. Crim, *J. Chem. Phys.* **94**, 1859 (1991)), where the internal excitation of the OH product radical was investigated at different photolysis wavelengths.

Keywords: Photolysis; fluorescence; photodissociation; vibrational state; water.

INTRODUCTION

The H_2O molecule has emerged to be a benchmark system for molecular photodissociation dynamics [1, 2]. Photoabsorption in the first ultraviolet (UV) absorption band of gas-phase H_2O exclusively yields OH and H photofragments in their electronic ground states by a fast and direct dissociation process *via* the $\text{H}_2\text{O}(\tilde{A}-\tilde{X})$ transition [1–4]. As the number of electrons is small, quite accurate *ab initio* cal-

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culations of the H₂O ground- and excited-state potential energy surfaces (PESs) are feasible [5]. This allows the treatment of the dissociation process by semiclassical as well as quantum mechanical methods [1, 5, 6].

In the pioneering vibrationally mediated photodissociation experiments of Andresen and his group H₂O was prepared in single rovibrational states of the asymmetric fundamental stretch mode by direct infrared excitation prior to the dissociation at a wavelength of 193 nm [2]. In these studies Λ -doublet and spin-orbit fine-structure state resolved rotational distributions of the OH ($v = 0$) photoproducts were analyzed showing that the distributions depend sensitively upon the initially prepared rotational state of the H₂O parent molecule [7, 8]. In subsequent experiments performed by Crim and co-workers, the effect of exciting different H₂O vibrational overtone states ($|04^-$; $|13^-$; $|03^-|2$), having similar total energies but very different distributions of excitation on the OH photoproduct vibrational and rotational state distribution was studied in detail at different UV photolysis wavelengths (218.5, 239.5 and 266 nm) [9–13]. These studies indicated that during dissociation the initial excitation in the undissociated bond is adiabatically conserved, suggesting that the undissociated O–H bond acts as a spectator, while the other O–H bond dissociates preferentially. In the local mode representation used above, the H₂O vibrational quantum numbers $|nm^-|k$ denote the antisymmetric combination of n and m quanta in the two stretching vibrations and k quanta in the bending excitation [13], where n and m roughly correspond to the quanta in the spectator and photolyzed OH bond, respectively. More recent studies by Nesbitt and co-workers, in which the 248 nm photolysis of lower H₂O overtone levels ($|12^\mp$; $|03^\mp$) was investigated, however, demonstrated that the relatively simple “undissociated OH bond spectator picture” does not hold for a “far off resonance” photodissociation process [14]. In the latter study, it could be shown both experimentally and in the framework of quantum mechanical model calculations that only vibrationally unexcited OH products are formed for both $|12^\mp$ and $|03^\mp$ initial excitation of the H₂O parent molecule, although different vibrational levels in the OH spectator bond were excited.

In a number of further experiments on the vibrationally-mediated photodissociation of HOD, it could be demonstrated that the bond excited in the stretching vibration is preferentially cleaved in the subsequent dissociation process [13, 15–18]. In these entire experiments laser-induced fluorescence (LIF) detection of either the OH($X^2\Pi$) or in case of the HOD photodissociation experiments the OH($X^2\Pi$) and OD($X^2\Pi$) photofragments were utilized. Complementary to this, in the work to be presented in the following an attempt has been made to detect the hydrogen atom counter-fragments *via* single-photon LIF excitation in the Lyman- α wavelength region. To the best of our knowledge UV photodissociation of highly vibrationally excited H₂O and HOD has not yet been combined with LIF detection of the lighter hydrogen atom photofragments. The present experiments were performed at a UV photolysis wavelength of 248 nm for which both experimental [9] and theoretical

[19] studies indicate that closeby there is a local maximum of the H₂O (ν_4^-) photoabsorption cross-section (see Fig. 8 of Ref. [9]).

EXPERIMENTAL

H₂O gas-phase laser photolysis studies were carried out in a flow reactor using the experimental arrangement described in detail elsewhere [20], which was complemented with an additional dye laser system for H₂O overtone excitation. All experiments were carried out at room temperature under flow conditions with H₂O degassed prior to use by several freeze–pump–thaw cycles. The gas flow rate in the reactor was set high enough to ensure fresh sample gases between successive laser shots at the laser repetition rate of 10 Hz. The H₂O pressure was typically 120–150 mTorr. In several experimental runs argon was added to a total pressure of 900–950 mTorr to allow for translational relaxation of the H atom products.

Single rovibrational states of the third overtone of the OH-stretching vibration of H₂O were excited in the wavelength region around 720 nm using a Nd:YAG pumped dye laser (65–70 mJ/pulse, $\Delta\nu_1 = 0.05 \text{ cm}^{-1}$, pulse duration 7 ns). The vibrationally excited H₂O was then photolyzed by 248 nm excimer laser radiation, which was counter propagating the overtone excitation laser beam. To ensure that the wavelength of this overtone excitation laser corresponded to a rovibrational transition of H₂O a small fraction of the beam was redirected into a photoacoustic cell (H₂O pressure approx. 15 Torr).

For H atom product LIF detection narrow-band vacuum ultraviolet (VUV) “probe” laser radiation ($\Delta\nu_3 \approx 0.3 \text{ cm}^{-1}$) tunable around the H and D atom Lyman- α transition (H, 82259 cm⁻¹; D, 82281.5 cm⁻¹) was generated by resonant third-order sum-difference frequency conversion of pulsed dye laser radiation (pulse duration 15–20 ns) in a phase-matched Kr/Ar mixture [21]. The probe laser beam was aligned to overlap the overtone excitation and photolysis laser beams at right angles in the viewing region of the VUV-LIF detector. Excitation and photolysis laser beams were slightly focussed ($f \approx 500 \text{ mm}$), with the focal points lying in the cross-over point with the probe laser. The delay time Δt_1 (see inset in Fig. 1) between the overtone vibration excitation and photolysis laser pulses was typically 20–30 ns during which relaxation of vibrationally excited H₂O can be neglected under the present experimental conditions [22]. In the experiments, Δt_2 , the delay time between the photolysis and probe laser pulse could be varied in the range from 160 ns to 4 μs . In the absence of the overtone excitation laser no H atoms were detectable from the 248 nm photolysis of ground-state H₂O due to its small absorption cross section at this wavelength. However, the Lyman- α probe radiation itself gives rise to a large H atom LIF background signal from VUV water photolysis [23]. To reduce this background signal an aperture (2 mm diameter) was installed in front of the LIF detector. In addition, the “VUV-self-photolysis-background” subtraction method described in Ref. [20] was adapted to obtain H atom signals (see, e.g., H

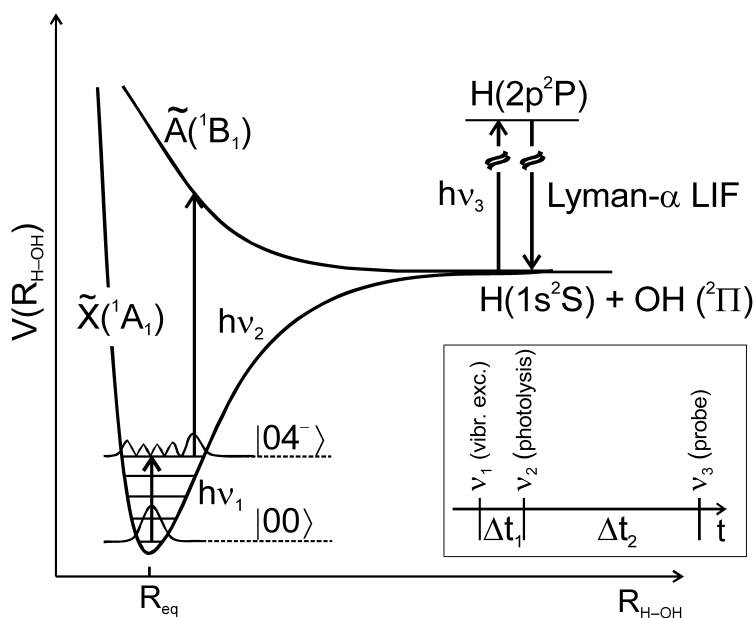


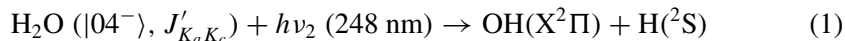
Figure 1. Schematic of the H₂O excitation/dissociation-H atom product probe sequence (adapted from Ref. [28]): H₂O is excited from the vibrational ground state |00⟩ to the third overtone of an OH stretching vibration |04⁻) (λ₁ ≈ 724 nm). The H₂O (|04⁻) molecules are then photolysed at λ₂ = 248 nm and the generated H atoms are probed *via* Lyman-α laser-induced fluorescence spectroscopy (λ₃ = 121.6 nm). The time sequence of the three laser pulses is shown on the right-hand side: after the overtone excitation the photolysis laser is fired (Δt₁), the generated H atom photofragments are then probed with a time delay of Δt₂.

atom action spectrum in the lower part of Fig. 2), which originate solely from the UV dissociation of vibrationally excited H₂O molecules.

RESULTS AND DISCUSSION

Vibrationally-mediated photodissociation of H₂O

The UV photolysis of rotational state-selected H₂O (|04⁻) can be represented by the following reaction equation:



In equation (1) J' is the total angular momentum quantum number, and K_a and K_c are its projections on the a - and c -axis in the prolate and oblate symmetric top limits, respectively [24]. In the present work, photoacoustic spectra were recorded (see, e.g., upper part of Fig. 2) to identify the H₂O rovibrational transitions by comparison with reference spectra, which were modeled using line position and intensity data listed in the HITRAN2000 database [25]. The photoacoustic spectrum

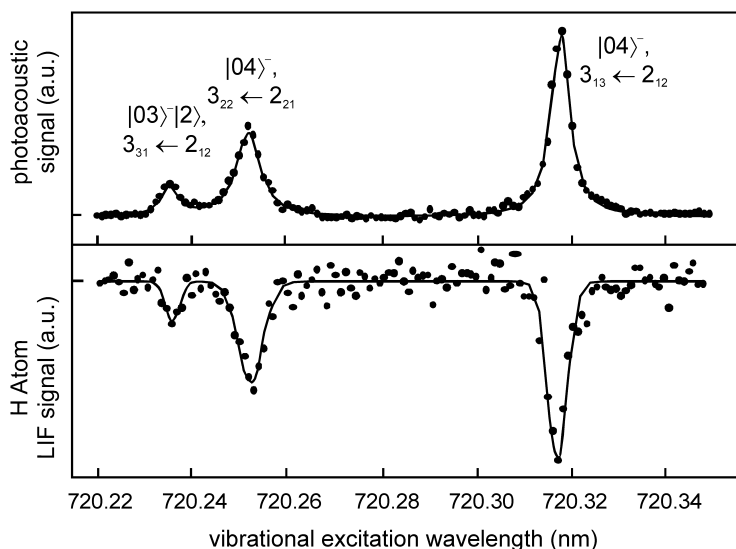


Figure 2. Comparison of simultaneously recorded photoacoustic (top part) and H atom photoproduct action spectra (bottom part) for H_2O $|03^- \rangle |2 \rangle$ and $|04^- \rangle$ vibrational states. For details see text.

depicted in Fig. 2 shows that in the excitation laser wavelength region 720.22–720.34 nm transitions which are associated with the $|04^- \rangle$ stretching vibration and with the $|03^- \rangle |2 \rangle$ combination of stretching and bending vibrations can be excited. In the latter case, the stretching vibration is excited with three quanta and, additionally, the bending vibration is energized with two quanta. The H atom photoproduct action spectrum, recorded simultaneously with the photoacoustic spectrum is depicted in the lower part of Fig. 2. The action spectrum was recorded by keeping the VUV probe laser frequency (ν_3) fixed at the center of the H atom Lyman- α transition ($82\,259\text{ cm}^{-1}$) while the overtone excitation laser frequency (ν_1) was scanned. H atom action spectra were recorded under translationally thermalized conditions, i.e., H atoms were detected in the presence of Ar buffer gas ($p_{Ar} = 800\text{ mTorr}$, $p_{H_2O} = 150\text{ mTorr}$) at a delay time of $\Delta t_2 = 4\ \mu\text{s}$.

At this point it is worth noting that in Fig. 2 the relative magnitudes of the integrated intensities of the lines in the H atom action spectrum closely resemble those of the photoacoustic spectrum, which reflects the known overtone absorption cross-sections [25]. A more quantitative evaluation based on a numerical least-squares fit modeling of the spectra of four independent measurements revealed that the 248 nm photolysis cross sections for H_2O ($|04^- \rangle$, 3_{13}), H_2O ($|04^- \rangle$, 3_{22}) and H_2O ($|03^- \rangle |2 \rangle$, 3_{31}) are equal within the experimental uncertainty: $\sigma^{248}(|04^- \rangle, 3_{13}) : \sigma^{248}(|04^- \rangle, 3_{22}) : \sigma^{248}(|03^- \rangle |2 \rangle, 3_{31}) = 1 : (1.0 \pm 0.1) : (1.1 \pm 0.2)$.

To determine the fraction of the available energy channeled into product translation ($f_{tr} = E_{tr,cm}/E_{av}$), Doppler profiles of H atoms formed in the 248 nm photolysis of H_2O ($|04^- \rangle$, 3_{13}) were recorded for different delay times (Δt_2) and total pressures $p = p_{Ar} + p_{H_2O}$ (see, e.g., Fig. 3). The available energy can be calculated

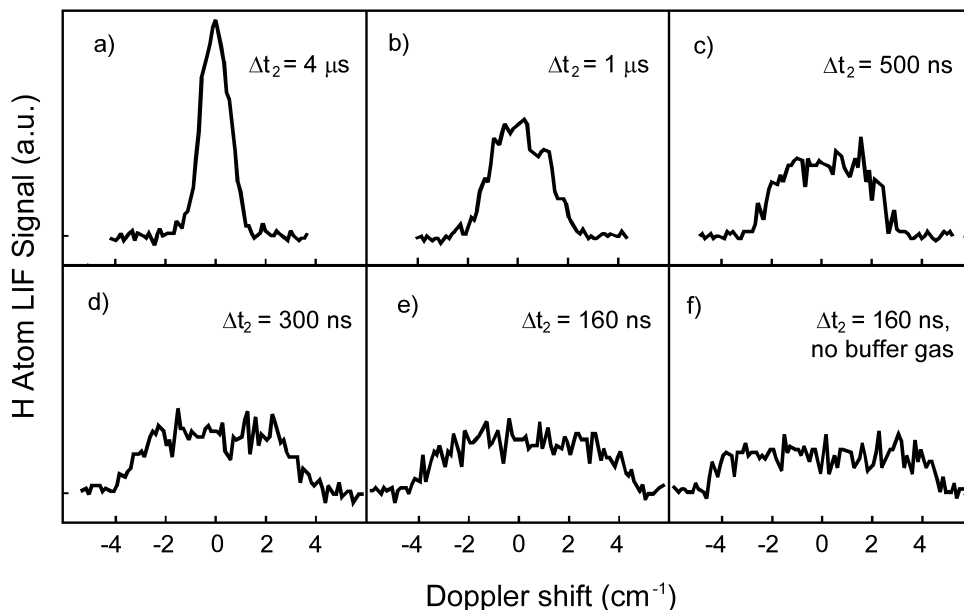


Figure 3. (a–e) H atom Doppler profiles measured at different photolysis/probe laser pulse delay times Δt_2 (values are given in the figure) after 248 nm photolysis of H_2O (104^- , 3_{13}) in a flowing mixture of 120 mTorr H_2O and 800 mTorr Ar buffer gas. (f) H atom Doppler profile obtained without Ar buffer gas at a H_2O pressure of 120 mTorr. The centers of the Doppler profiles correspond to the Lyman- α transition of the H atoms ($82\,259\text{ cm}^{-1}$).

according to $E_{av} = h\nu_1 + h\nu_2 + E_{\text{rot}}(\text{H}_2\text{O}) - D_0$ [26], where $E_{\text{rot}}(\text{H}_2\text{O})$ denotes the room-temperature rotational energy of the H_2O parent molecule and D_0 is the H–OH bond dissociation energy.

The measured H atom Doppler profiles were evaluated using a numerical least squares fit analysis of the line shape (for details, see Ref. [27]), to derive the corresponding value of the relative translational energy $E_{\text{tr,cm}}$ of the H atom fragments in the H–OH center-of-mass (cm) frame. f_{tr} values obtained from the Doppler profiles depicted in Fig. 3 are plotted in Fig. 4 against the product $p \times \Delta t_2$. The solid line represent a result of a numerical least-squares fit of the data points, which was used for extrapolation toward $p \times \Delta t_2$ equals zero to estimate the “collision-free” f_{tr} value of 0.93 ± 0.04 . The latter value demonstrates that the major part of the energy available to the products is channeled into the translational degree of freedom leaving only a fraction of about $1 - f_{\text{tr}} = 0.07 \pm 0.04 = f_{\text{rot}} + f_{\text{vib}}$ of the available energy to be distributed over the rotational and vibrational states of the OH photoproduct. This finding confirms the general results of Ref. [9], where OH fragments produced in the 239.5 nm photolysis of H_2O (104^-) were detected. In good agreement with theory [19], these studies showed that $(99 \pm 1)\%$ of the OH products are formed in the $\nu = 0$ state, with an $(1 \pm 1)\%$ population of OH ($\nu = 1$), which indicates negligible OH vibrational excitation ($f_{\text{vib}} \approx 0$). In the same study the nascent rotational state distribution of the OH ($\nu = 0$) fragments

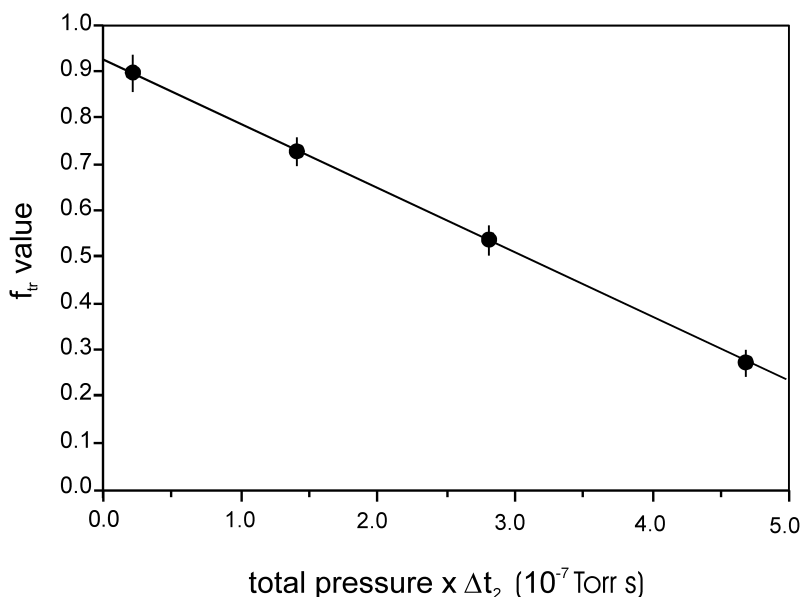
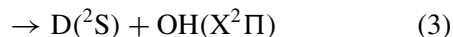
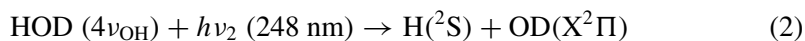


Figure 4. Plot of the fraction of the available energy channeled into H atom product translation energy ($f_{tr} = E_{tr,cm}/E_{av}$) against the product $p \times \Delta t_2$ (p = total pressure; Δt_2 = delay time between the photolysis and probe laser pulse). A linear least-squares-fit-based extrapolation toward $p \times \Delta t_2$ equals zero (solid line) was employed to estimate the “collision-free” f_{tr} value of 0.93 ± 0.04 .

was determined in the 239.5 nm photolysis of the H₂O ($|04^-$, 3_{13}) state. From the data reproduced in Fig. 4 of Ref. [9] a rotational temperature of *ca.* 400 K can be estimated, which corresponds to a value of $f_{rot} \approx 0.03$, and which is in agreement (within the limit of the experimental uncertainty) with the presents work result as well as with the theoretical predictions [8].

Vibrationally-mediated photodissociation of HOD

In further experiments the 248 nm photodissociation of HOD, selectively excited in the region of the $4\nu_{OH}$ transition in the wavelength region $\lambda_1 = 722\text{--}725$ nm, was investigated.



In these experiments the overtone excitation laser (λ_1) was tuned to the isolated HOD rovibrational transition marked in Fig. 5 by an * and the VUV probe laser (λ_3) was tuned over the wavelength region of the H and D atom Lyman- α transitions in an attempt to record Doppler profiles of H and D atom products formed *via* the dissociation channels (2) and (3), respectively, under translationally thermalized conditions. As can be seen in the lower part of Fig. 5, only H atoms could be observed (left side) while no D atom signal could be discerned (right

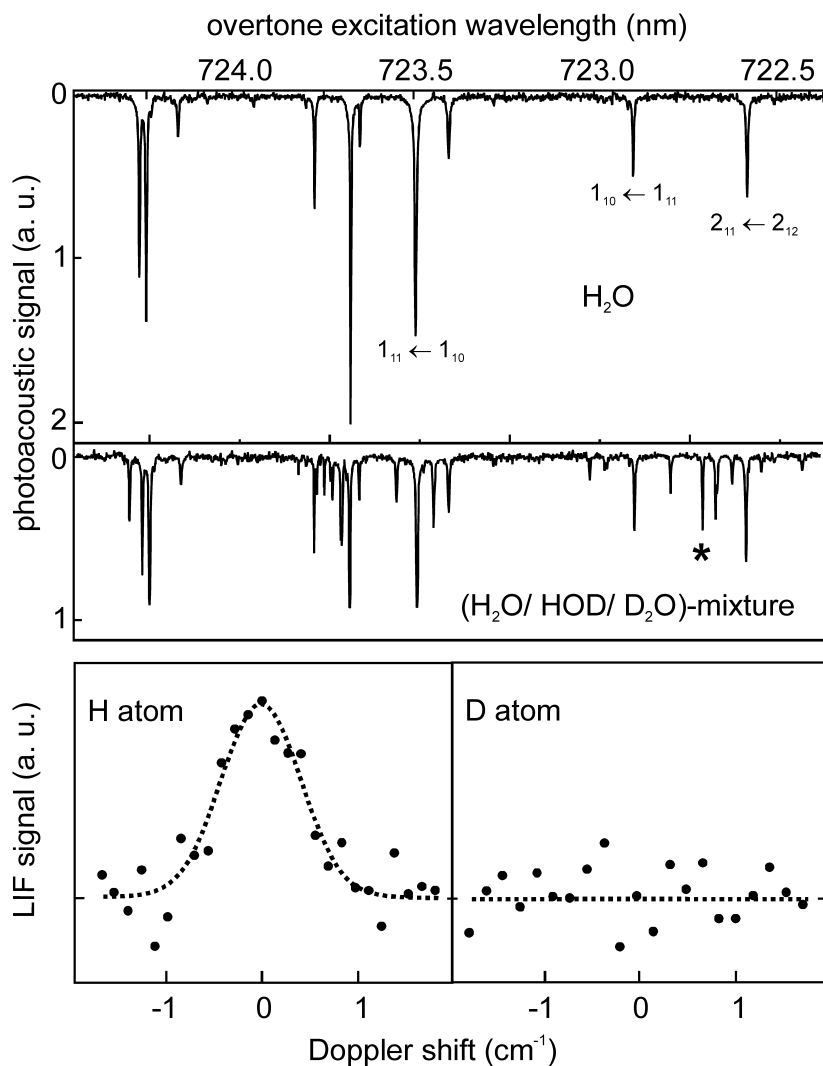


Figure 5. (Top) Photoacoustic spectra of H_2O and a 1:2:1 H_2O , HOD , D_2O mixture in the region of the $4\nu_{\text{OH}}$ transition. Features which appear in the H_2O , HOD , D_2O mixture but not in that of pure H_2O are from excitation of $4\nu_{\text{OH}}$ in the HOD molecule. (Bottom) Results of H atom (left side) and D atom (right side) Doppler profile measurements under thermalized conditions (150 mTorr of H_2O , HOD , D_2O mixture, 800 mTorr Ar, $\Delta t_2 = 4 \mu\text{s}$) in the 248 nm photolysis of HOD ($4\nu_{\text{OH}}$), which demonstrate the preferential formation of H atom photolysis products. The transition used for preparation of HOD ($4\nu_{\text{OH}}$) is marked in the photoacoustic spectrum by (*). For further details see text and Ref. [13].

side). This observation is in line with both the theoretical results of Schinke and the experimental results obtained by Crim and co-workers, who studied the photodissociation of HOD ($4\nu_{\text{OH}}$) at a photolysis wavelength of 239.5 nm using OD and OH LIF product detection [10]. In agreement with the present finding, these

experiments demonstrated that O–H stretching bond excitation in HOD leads to the preferential formation of OD product radicals *via* (2) with an estimated dissociation channel branching ratio of $\phi_{(2)}/\phi_{(3)} > 15$.

CONCLUSION

The 248 nm gas-phase laser photolysis of vibrationally excited H₂O and HOD could be successfully combined with Doppler-resolved single-photon hydrogen atom Lyman- α LIF detection. In agreement with complementary experimental studies (in which hydroxyl radical products were detected [9, 13]) and theoretical calculations [8] the present work demonstrates that in the UV dissociation of H₂O ($|04^-$, 3_{13}) the major part (*ca.* 93%) of the available energy is released as relative translational energy of the nascent H + OH fragments. The present studies also showed that the 248 nm photodissociation cross sections for rovibrational state selected water, H₂O ($|04^-$, 3_{13}), H₂O ($|04^-$, 3_{22}) and H₂O ($|03^-|2$, 3_{31}), are equal within the experimental uncertainty. Further vibrationally mediated photolysis studies of HOD confirmed the findings of previous experimental as well as theoretical studies, which indicated that upon excitation of the O–H stretch overtone this bond can be selectively photolyzed [10, 13].

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