



**HAL**  
open science

## Quantifying the photoionization cross section of the hydroxyl radical

O. Harper, M. Hassenfratz, J.-C. Loison, G. Garcia, N. de Oliveira, H.R. Hrodmarsson, S. Pratt, S. Boyé-Péronne, B. Gans

► **To cite this version:**

O. Harper, M. Hassenfratz, J.-C. Loison, G. Garcia, N. de Oliveira, et al.. Quantifying the photoionization cross section of the hydroxyl radical. *The Journal of Chemical Physics*, 2019, 150 (14), pp.141103. 10.1063/1.5091966 . hal-02354964

**HAL Id: hal-02354964**

**<https://hal.science/hal-02354964v1>**

Submitted on 5 Nov 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Quantifying the photoionization cross section of the hydroxyl radical

O. J. Harper,<sup>1</sup> M. Hassenfratz,<sup>1</sup> J.-C. Loison,<sup>2</sup> G. A. Garcia,<sup>3</sup> N. de Oliveira,<sup>3</sup> H.R. Hrodmarsson,<sup>3</sup> S. T. Pratt,<sup>4</sup> S. Boyé-Péronne,<sup>1</sup> and B. Gans<sup>1, a)</sup><sup>1</sup>*Institut des Sciences Moléculaires d'Orsay (ISMO), UMR 8214 CNRS, Univ. Paris-Sud, Université Paris-Saclay, F-911405 Orsay Cedex, France*<sup>2</sup>*Institut des Sciences Moléculaires, UMR 5255 CNRS - Université de Bordeaux, Bt.A12, 351 cours de la Libération, F-33405 Talence Cedex, France*<sup>3</sup>*Synchrotron SOLEIL, L'Orme des merisiers, Saint Aubin BP48, F-91192 Gif sur Yvette Cedex, France*<sup>4</sup>*Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois 60439, USA*

(Dated: 25 February 2019)

The hydroxyl free radical, OH, is one of the most important radicals in atmospheric and interstellar chemistry, and its cation plays a role in the reactions leading to H<sub>2</sub>O formation. Knowledge of the photoionization efficiency of the OH radical is crucial to properly model the water photochemical cycle of atmospheres and astrophysical objects. Using a gas-phase radical source based on a single H-abstraction reaction combined with a photoelectron/photoion imaging coincidence spectrometer coupled with synchrotron radiation, we recorded the OH<sup>+</sup> photoion yield over the 12.6 -15 eV energy range, and we set it to an absolute cross section scale using an absolute point measurement performed at 13.8 eV:  $\sigma_{\text{OH}}^{\text{ion}} = 9.0 \pm 2.7$  Mb. The resulting cross section values differ by approximately a factor 2 from the recent measurement of Dodson *et al.* performed with a different radical source (L. G. Dodson, J. D. Savee, S. Gozem, L. Shen, A. I. Krylov, C. A. Taatjes, D. L. Osborn, and M. Okumura, *The Journal of Chemical Physics* **148**, 184302 (2018)), which is somewhat greater than the combined uncertainties of the measurements. This finding underlines the need for further investigations of this cross section.

The hydroxyl radical, OH, is one of the most important free radicals in atmospheric and astrophysical chemistry. It is involved in atmospheric cycles, *e.g.* as an oxidizing "detergent" on Earth,<sup>1,2</sup> but also in complex photophysical processes in a wide variety of astrophysical media (planetary atmospheres,<sup>3-5</sup> comets,<sup>6</sup> interstellar clouds,<sup>7,8</sup> etc.). In these media, OH plays a key role in the water photochemical cycle. The OH + H<sub>2</sub> → H<sub>2</sub>O + H reaction is endothermic,<sup>9</sup> thus most of the reactions involving OH at low temperature occur with O, N, and C atoms and lead to O<sub>2</sub>, NO, and CO compounds rather than H<sub>2</sub>O. On the other hand, the cationic form OH<sup>+</sup> reacts fast with H<sub>2</sub>,<sup>10</sup> to produce H<sub>2</sub>O<sup>+</sup> which in turn reacts with H<sub>2</sub> to generate H<sub>3</sub>O<sup>+</sup>. H<sub>2</sub>O can then be formed through dissociative recombination of H<sub>3</sub>O<sup>+</sup>.<sup>11</sup>

Several theoretical<sup>12</sup> and experimental<sup>13-17</sup> studies have been carried out on the lowest electronic states of neutral OH. However, absorption studies in the Vacuum UltraViolet (VUV) range ( $\lambda < 200$  nm) are scarce and absolute measurements in this region are even more so.<sup>18,19</sup> For the ionization process, only three experimental works have reported the relative photoionization yield (or constant-ionic-state spectra) of the hydroxyl radical in the VUV range, to our knowledge.<sup>20-23</sup> Dehmer's work covered the photon energy range between 13.0 and 16.5 eV ( $\approx 95 - 75$  nm), at a resolution of 1 - 3 meV (0.007 - 0.023 nm).<sup>20</sup> Autoionization features were observed in the ion yield and were assigned to a Rydberg

series converging to the  $a^{+1}\Delta$  state of the OH<sup>+</sup> ion (located 2.16 eV above the cationic ground state). Later, Cutler *et al.* carried on Dehmer's work and studied the photoionization of both OH and OD isotopologues between 13.1 and 18.2 eV (94.64 - 68.12 nm) at a resolution of 1 meV (0.007 nm).<sup>21</sup> They assigned two new Rydberg series converging to the OH<sup>+</sup>  $b^{+1}\Sigma^{+}$  and  $A^{+3}\Pi$  ionic states. In 2018, Dodson *et al.* published the first experimental measurement of the absolute photoionization cross section for OH, where they deduced the cross section from the analysis of time-resolved radical-kinetics measurements of a multi-reaction network in which OH is produced in the reaction of O(<sup>1</sup>D) with H<sub>2</sub>O. The absolute cross section of OH was determined relative to that of O(<sup>3</sup>P). Their work was supported by new theoretical calculations of the OH cross section using equation-of-motion coupled-cluster Dyson orbitals and a Coulomb photoelectron wave function.<sup>24</sup>

The absolute photoionization cross section of the OH radical is important for reliably describing the abundances of OH and OH<sup>+</sup> and their involvement in the photochemical networks of interstellar media. However, before the work of Dodson *et al.*, modelers could only use the results from theoretical calculations,<sup>12,25,26</sup> or ignore the cross section completely. For instance, the photoionization of OH is not present in the Leiden Database<sup>27</sup> or the Meudon PDR code.<sup>28</sup> The new value is expected to find considerable applications in the modeling of atmospheric and interstellar chemistry. Given the importance of this cross section, a complementary experimental determination would also be valuable.

We have recently determined the absolute photoion-

<sup>a)</sup>corresponding author; Electronic mail: berenger.gans@u-psud.fr

ization cross section of OH by a different method that appears to be considerably simpler than the approach of Doss *et al.*<sup>24</sup> The experiments were carried out at the French SOLEIL synchrotron facility, on the DESIRS beamline.<sup>29</sup> The DELICIOUS III spectrometer was used to record the OH<sup>+</sup> ion yield and to measure the corresponding absolute photoionization cross section. The experimental setup for the production of radicals and their analysis by mass spectroscopy has been described in previous works,<sup>30</sup> and here only the specificities of the OH experiment are discussed. The OH radical was produced *via* H abstraction of H<sub>2</sub>O by F atoms (H<sub>2</sub>O + F → HO + HF). These F atoms were generated in a microwave discharge applied to F<sub>2</sub> diluted in He. H<sub>2</sub>O vapor, also diluted in He, was injected in the flowtube reactor and then combined with the F atoms to produce OH. We adjusted the experimental conditions to optimize the single H abstraction while keeping parasitic reactions, such as double H abstraction or F addition, negligible. The products of this reaction were then skimmed twice before arriving inside the double imaging photoelectron / photoion spectrometer DELICIOUS III.<sup>31</sup> The ion detector was checked to give a linear response to the number of ion counts. This point is of great importance, since the H<sub>2</sub>O signal is up to 10 times and 100 times higher than that of OH and O, respectively. At the centre of this spectrometer, the radicals were photoionized by the monochromatized synchrotron radiation at a right angle with a photon resolution of 4 meV. The absolute calibration of the photon energy was performed using the well-known ionization threshold of H<sub>2</sub>O, OH, and O, and the argon absorption lines generated by the gas filter of the beamline. The photon-energy accuracy is found to be about 4 meV for the ion yield spectrum but only 10 meV for the absolute measurement performed at fixed energy (13.8 eV = 89.84 nm, see below). Both the resulting ions and electrons were collected in coincidence with an extraction field of 115 V · cm<sup>-1</sup>.

We chose to perform the absolute measurement at a photon energy of 13.8 eV. This energy was a good compromise to be out of a narrow resonance in the OH<sup>+</sup> ion yield (*i.e.* in a region where the intensity does not depend on the resolution), and above the Franck-Condon (FC) region for the ionizing transition of both OH and H<sub>2</sub>O. In general, the ion yield can be strongly affected, especially near the ionization energy threshold, by the temperature of the neutral species, especially when the FC factors are spread out over many vibrational levels as for the ionizing transition towards  $\tilde{A}^+$  state of H<sub>2</sub>O<sup>+</sup>.<sup>32</sup> The chosen energy of 13.8 eV is between the two lowest electronic states of OH<sup>+</sup> and H<sub>2</sub>O<sup>+</sup> and above the ionizing transition towards the highest excited vibrational states of the electronic ground state of these cations with significant intensity.<sup>30</sup>

In Figures 1 a) and 1 b), the mass spectra recorded at 13.8 eV are depicted for the microwave discharge off and on, respectively. When the discharge is turned off (Figure 1 a)), there is no F atom production, hence no

OH radicals are generated, and only the H<sub>2</sub>O<sup>+</sup> signal is observed at  $m/q = 18$ . When the discharge is turned on (Figure 1 b)), mass 17 (OH<sup>+</sup>) appears and a small, albeit observable, signal at  $m/q = 16$  shows up due to atomic oxygen produced by secondary H abstraction: HO + F → O + HF. In panel c) of Figure 1, the difference spectrum ("c) = b) - a)") is plotted. It directly correlates with the produced and consumed species in the radical source.

In a recent theoretical work, Li *et al.* found that the H<sub>2</sub>O + F → HO + HF reaction leads to strong vibrational excitation in HF while OH remains vibrationally cold.<sup>33</sup> The OH + F → O(<sup>3</sup>P) + HF and OH + F → O(<sup>1</sup>D) + HF reactions being exothermic and endothermic, respectively, we can conclude that the oxygen atoms are produced in their <sup>3</sup>P ground state.

In mass spectrometry, the temporal integration of an ion signal ( $S_{A^+}$ ) for a given ion A<sup>+</sup> is proportional to the number of irradiated A species ( $n_A$ ) and to its photoionization cross section ( $\sigma_A^{\text{ion}}$ ) at the corresponding photon energy:  $S_{A^+} \propto n_A \cdot \sigma_A^{\text{ion}}$ . For two ions with close  $m/q$  values in a mass spectrum, one can assume that the coefficient of proportionality is constant (same mass discrimination factor for close masses, same photon flux,...). Due to the principle of matter conservation, the quantity of consumed H<sub>2</sub>O when switching on the discharge ( $\Delta n_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}^{\text{OFF}} - n_{\text{H}_2\text{O}}^{\text{ON}}$ ) is equal to the quantity of free radicals formed:  $\Delta n_{\text{H}_2\text{O}} = n_{\text{OH}}^{\text{ON}} + n_{\text{O}}^{\text{ON}}$ .

We can thus write the following equation :

$$\frac{\Delta(S_{\text{H}_2\text{O}^+})}{\sigma_{\text{H}_2\text{O}}^{\text{ion}}} = \frac{S_{\text{OH}^+}}{\sigma_{\text{OH}}^{\text{ion}}} + \frac{S_{\text{O}^+}}{\sigma_{\text{O}}^{\text{ion}}} \quad (1)$$

where  $\Delta(S_{\text{H}_2\text{O}^+}) = S_{\text{H}_2\text{O}^+}^{\text{OFF}} - S_{\text{H}_2\text{O}^+}^{\text{ON}}$ ,  $S_{\text{OH}^+} = S_{\text{OH}^+}^{\text{ON}}$  and,  $S_{\text{O}^+} = S_{\text{O}^+}^{\text{ON}}$ .

From Eq. 1, we can deduce the photoionization cross section of the OH radical if the cross sections of H<sub>2</sub>O and O are known.

The photoionization cross section of water has been published by Fillion *et al.*<sup>34</sup> In their study, they measured the absolute absorption cross section and the ionization quantum yield which allowed us to derive the photoionization cross section. The absorption cross section is structured in the 12.6 – 14 eV region because of a Rydberg series converging to the  $\tilde{A}^+ 2A_1$  state of H<sub>2</sub>O<sup>+</sup> at 13.84 eV.<sup>35</sup> The same structures are observed in the photoionization cross section through autoionization. The absolute values of the cross sections can thus depend strongly on the photon resolution. As the measurement of Fillion *et al.*<sup>34</sup> was performed with a photon resolution of 25 meV, we had to measure the absorption cross section of H<sub>2</sub>O at the same photon resolution as our absolute measurement (4 meV). This measurement has been performed using the VUV Fourier Transform spectrometer of the DESIRS beamline of the SOLEIL synchrotron.<sup>36,37</sup> This measurement, not reported here, allowed us to check that all the structures were already resolved in the work of Fillion *et al.* and that we could use their absolute photoionization cross section ( $\sigma_{\text{H}_2\text{O}}^{\text{ion}} =$

8.7 ± 0.8 Mb at 13.8 eV) albeit not measured at the same resolution. It is important to note that the photoionization cross section derived from the work of Fillion *et al.* is in very good agreement with those reported by Watanabe *et al.*<sup>38</sup> and Katayama *et al.*<sup>39</sup> Our measurement of the H<sub>2</sub>O ion yield between 13 and 15 eV scaled with the work of Fillion *et al.* is reported in the upper panel of Fig. 2.

The ion signal of atomic oxygen is flat in the region of the 13.8 eV energy. This means that the photon resolution does not affect the absolute value of the cross section and thus we used  $\sigma_{\text{O}^{\text{ion}}}^{\text{ion}} = 3.08 \pm 0.25$  Mb at 13.8 eV by interpolating the data of Angel *et al.*,<sup>40</sup> which are assumed to be the most correct for the atomic oxygen photoionization cross section.<sup>41</sup> Our measurement of the atomic O<sup>+</sup> ion yield between 13 and 15 eV scaled with the work of Angel *et al.* is depicted in the lower panel of Fig. 2.

Combining 10 sets of measurements recorded at 13.8 eV under various experimental conditions producing radicals in more or less abundance, the H<sub>2</sub>O and O photoionization cross sections, and Eq.(1), we obtained  $\sigma_{\text{OH}}^{\text{ion}} = 9.0 \pm 2.7$  Mb ( $2\sigma$  confidence interval assuming that the uncertainties of the H<sub>2</sub>O and O photoionization cross sections correspond to  $2\sigma$  confidence intervals). The uncertainties of this value have been derived from the distribution that was built using a Monte Carlo uncertainty propagation on Eq.(1). The correction of the cross section value by the atomic oxygen signal appeared to be quite significant. Indeed, using the same procedure and omitting the atomic oxygen production, we obtained a photoionization cross section of 7.1 Mb which is about 2 Mb below the corrected value (9.0 Mb). To make sure that the detected photoionized atomic oxygen resulted from the reactivity of water with the fluorine atoms, we have checked that  $S_{\text{O}^+}$  recorded under different experimental conditions was correlated with  $\Delta(S_{\text{H}_2\text{O}^+})$ .

In Figure 3, our relative OH ion yield is depicted and compared with the ones measured by Dehmer<sup>20</sup> and Cutler *et al.*<sup>21</sup> Unlike Cutler *et al.*'s spectrum, which represents the original data points, note that Dehmer's spectrum has been digitized and thus does not correspond to the real data points, which degrades the resolution. The resolution of our spectrum (4 meV) is close to that of Dehmer (3.5 meV) and Cutler *et al.* (1 meV) in their original papers. The three spectra are in very good agreement apart from a few structure intensity differences which might be attributed to slightly different resolutions. Dehmer and Cutler *et al.* produced OH *via* the reaction of  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ , rather than *via* the present H abstraction from H<sub>2</sub>O. The similarity of the three spectra suggests that the OH temperature is comparable in all three experiments.

Using our absolute measurement described above and our relative measurement displayed in the lower panel of Figure 3, we derived the photoionization cross section of the OH radical over a large energy range (from the ion-

ization threshold (13.01698(25) eV)<sup>42</sup> to 15.0 eV). This cross section is reported in Figure 4. The corresponding data are available in the Supplemental Material.

In Figure 4, one can clearly see that the cross section measured in this work is higher than the two values previously reported by Dodson *et al.*<sup>24</sup> although the trend of both dataset is consistent. Stephens and McKoy calculated the non-resonant continuum background of the photoionization cross section of the OH radical over a broad energy range (from the ionization threshold up to 50 eV) using multiplet-specific Hartree-Fock potentials and numerical photoelectron continuum orbitals.<sup>12</sup> They presented two results (for dipole length form and for dipole velocity form) which lead to a cross section at 14 eV of 3.3 Mb and near 5 Mb, respectively. These results are also below our measurement and the first one agrees with the measurements and the computed values of Dodson *et al.*<sup>24</sup> Veseth and Kelly have used many body perturbation theory to calculate the OH photoionization cross section as well.<sup>25</sup> Their value for the direct photoionization cross section is considerably larger, corresponding to  $\approx 12$  Mb near 14 eV, in better agreement with the present results. It appears, however, that their calculation is actually the photoabsorption cross section, and that they have assumed an ionization quantum yield of one above the ionization threshold. Dodson *et al.* proposed that a considerable component of the calculated cross section of Veseth and Kelly may not lead to ionization, and that this is what leads to the larger cross section in their calculation. However, the photoabsorption cross section must always be higher than the photoionization cross section, and at somewhat higher energies, Figure 2 of Ref. 25 shows that the absorption cross section of Veseth and Kelly is well below the ionization cross section of Stephens and McKoy. This observation reinforces the need for higher level calculations of the cross section, as well as for calculations that include resonant excitation processes.

We have attempted to identify potential issues that could result in our finding a cross section that was higher than the correct value. If we assume that the photoionization cross section of O and H<sub>2</sub>O are correct, Eq. 1 implies that an overestimation of the OH cross section could result from either a too small value of  $\Delta(S_{\text{H}_2\text{O}^+})$ , a too high value of  $S_{\text{O}^+}$ , or a too high value of  $S_{\text{OH}^+}$ . It appears, however, that the most likely issues that we can identify would push one or more of these values ( $\Delta(S_{\text{H}_2\text{O}^+})$ ,  $S_{\text{O}^+}$ , and  $S_{\text{OH}^+}$ ) in the opposite direction, and result in an even higher value for the OH cross section. The considerations leading to this conclusion are discussed in the Supplemental Material.

Assuming the error bars of Dodson *et al.* and the present study are realistic, we do not have an explanation for the discrepancy between the results at this time. Nevertheless, it should be noted that both results rely on different absolute photoionization cross sections from the literature and thus on the accuracy of those values.

Although the two sets of experimental measurements

of the OH photoionization cross section (this work and that of Dodson *et al.*) provide a good estimate, in particular for the description of the OH radical photoionization in astrophysical models, new investigations are needed to enlighten the disagreement between the two different experimental approaches. Photoionization cross section measurements are challenging in particular for free radicals and therefore are often missing, or are found in the literature within a wide range of values.

## ACKNOWLEDGMENTS

This work was performed on the DESIRS beamline under Proposal No. 20170808. The authors thank SOLEIL for provision of synchrotron radiation beamtime and the DESIRS beamline team for their assistance. The authors acknowledge Dr. J. N. Cutler and Prof. J.-H. Fillion for sharing the original data of Ref. 21 and Ref. 34, respectively. This work was supported by the French Agence Nationale de la Recherche (ANR) under Grant No. ANR-12-BS08-0020-02 (project SYNCHROKIN) and by the CNRS program Physique et Chimie du Milieu Interstellaire (PCMI) co-funded by the Centre National d'Etudes Spatiales (CNES). This material is based on work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences respectively under contract No. DE-AC02-06CH11357 (STP).

- <sup>1</sup>F. J. Comes, "Recycling in the Earth's atmosphere: the OH radical - its importance for the chemistry of the atmosphere and the determination of its concentration," *Angewandte Chemie International Edition in English* **33**, 1816–1826 (1994).
- <sup>2</sup>T. McGee and T. McIlrath, "Absolute OH absorption cross sections (for lidar measurements)," *Journal of Quantitative Spectroscopy and Radiative Transfer* **32**, 179–184 (1984).
- <sup>3</sup>G. Piccioni, P. Drossart, L. Zasova, A. Migliorini, J.-C. Gérard, F. P. Mills, A. Shakun, A. García Muñoz, N. Ignatiev, D. Grassi, V. Cottini, F. W. Taylor, and S. Erard, "First detection of hydroxyl in the atmosphere of Venus," *Astronomy & Astrophysics* **483**, L29–L33 (2008), arXiv:arXiv:0801.3609v1.
- <sup>4</sup>Atreya, S. K. and Z. G. Gu, "Stability of the Martian atmosphere: Is heterogeneous catalysis essential?" *Journal of Geophysical Research: Planets* **99**, 13133–13145 (1994).
- <sup>5</sup>R. Todd Clancy, B. J. Sandor, A. García-Muñoz, F. Lefèvre, M. D. Smith, M. J. Wolff, F. Montmessin, S. L. Murchie, and H. Nair, "First detection of Mars atmospheric hydroxyl: CRISM near-IR measurement versus LMD GCM simulation of OH Meinel band emission in the Mars polar winter atmosphere," *Icarus* **226**, 272–281 (2013).
- <sup>6</sup>F. Biraud, G. Bourgois, J. Crovisier, R. Fillit, E. Gerard, and I. Kazes, "OH observation of comet Kohoutek (1973f) at 18 cm wavelength," *Astronomy & Astrophysics* **34**, 163 (1974).
- <sup>7</sup>J. Dickey, J. Crovisier, and I. Kazes, "Emission-absorption observations of OH in diffuse interstellar clouds," *Astronomy & Astrophysics* **98**, 271–285 (1981).
- <sup>8</sup>A. Dalgarno and J. H. Black, "Molecule formation in the interstellar gas," *Reports on Progress in Physics* **39**, 573–612 (1976).
- <sup>9</sup>M. Agúndez, E. Roueff, F. Le Petit, and J. Le Bourlot, "The chemistry of disks around T Tauri and Herbig Ae/Be stars," *Astronomy & Astrophysics* **616**, A19 (2018).
- <sup>10</sup>V. G. Anicich, "An index of the literature for bimolecular gas phase cation-molecule reaction kinetics," *Jet Propulsion Laboratory Publication* **19** (2003).
- <sup>11</sup>A. E. Ketvirtis and J. Simons, "Dissociative Recombination of  $\text{H}_3\text{O}^+$ ," *The Journal of Physical Chemistry A* **103**, 6552–6563 (1999).
- <sup>12</sup>J. A. Stephens and V. McKoy, "Photoionization of the valence orbitals of OH," *The Journal of Chemical Physics* **88**, 1737–1742 (1988).
- <sup>13</sup>A. E. Douglas, "Absorption of OH in the 1200 Å region," *Canadian Journal of Physics* **52**, 318–323 (1974).
- <sup>14</sup>J. C. Viney, "Preliminary identification of hydroxyl bands at < 1200 Å," *Journal of Molecular Spectroscopy* **83**, 465–468 (1980).
- <sup>15</sup>H. van Lonkhuyzen and C. A. de Lange, "U.V. photoelectron spectroscopy of OH and OD radicals," *Molecular Physics* **51**, 551–568 (1984).
- <sup>16</sup>S. Katsumata and D. Lloyd, "The photoelectron spectra of the OH and OD radicals," *Chemical Physics Letters* **45**, 519–522 (1977).
- <sup>17</sup>A. J. Merer, D. N. Malm, R. W. Martin, M. Horani, and J. Rostas, "The ultraviolet emission spectra of  $\text{OH}^+$  and  $\text{OD}^+$ . Rotational structure and perturbations in the  $\text{A}^3\Pi_i \leftarrow \text{X}^3\Sigma^-$  transition," *Canadian Journal of Physics* **53**, 251–283 (1975).
- <sup>18</sup>J. B. Nee and L. C. Lee, "Photoabsorption cross sections of OH at 115 - 183 nm," *The Journal of Chemical Physics* **81**, 31–36 (1984).
- <sup>19</sup>A. Heays, N. de Oliveira, B. Gans, K. Ito, S. Boyé-Péronne, S. Douin, K. Hickson, L. Nahon, and J. Loison, "High-resolution one-photon absorption spectroscopy of the  $\text{D}^2\Sigma^- \leftarrow \text{X}^2\Pi$  system of radical OH and OD," *Journal of Quantitative Spectroscopy and Radiative Transfer* **204** (2018), 10.1016/j.jqsrt.2017.08.021.
- <sup>20</sup>P. Dehmer, "Photoionization of OH in the region 750 - 950 Å," *Chemical Physics Letters* **110**, 79–84 (1984).
- <sup>21</sup>J. N. Cutler, Z. X. He, and J. A. R. Samson, "Relative photoionization cross section study of OH and OD from 68 nm to 95 nm," *Journal of Physics B: Atomic, Molecular and Optical Physics* **28**, 4577 (1995).
- <sup>22</sup>J. D. Barr, A. D. Fanis, J. M. Dyke, S. D. Gamblin, N. Hooper, A. Morris, S. Stranges, J. B. West, and T. G. Wright, "Study of the OH and OD radicals with photoelectron spectroscopy using synchrotron radiation," *The Journal of Chemical Physics* **110**, 345–354 (1999).
- <sup>23</sup>F. Innocenti, L. Zuin, M. L. Costa, A. A. Dias, A. Morris, A. C. S. Paiva, S. Stranges, J. B. West, and J. M. Dyke, "Photoionization studies of the atmospherically important species N and OH at the Elettra synchrotron radiation source," *Journal of Electron Spectroscopy and Related Phenomena* **142**, 241–252 (2005).
- <sup>24</sup>L. G. Dodson, J. D. Savee, S. Gozem, L. Shen, A. I. Krylov, C. A. Taatjes, D. L. Osborn, and M. Okumura, "Vacuum ultraviolet photoionization cross section of the hydroxyl radical," *The Journal of Chemical Physics* **148**, 184302 (2018).
- <sup>25</sup>L. Veseth and H. P. Kelly, "Polarizabilities and photoionization cross sections of OH and HF," *Phys. Rev. A* **45**, 4621–4630 (1992).
- <sup>26</sup>R. Riahi, P. Teulet, Y. Cressault, A. Gleizes, and Z. Ben Lakhdar, "Calculation of radiative transition probabilities and radiative recombination rate coefficients for  $\text{H}_2$ , OH,  $\text{H}_2^+$  and  $\text{OH}^+$  molecules," *Eur. Phys. J. D* **49**, 185–192 (2008).
- <sup>27</sup>A. N. Heays, A. D. Bosman, and E. F. van Dishoeck, "Photodissociation and photoionisation of atoms and molecules of astrophysical interest," *Astronomy & Astrophysics* **602**, A105 (2017).
- <sup>28</sup>F. L. Petit, C. Nehmé, J. L. Bourlot, and E. Roueff, "A Model for Atomic and Molecular Interstellar Gas: The Meudon PDR Code," *The Astrophysical Journal Supplement Series* **164**, 506 (2006).
- <sup>29</sup>L. Nahon, N. de Oliveira, G. A. Garcia, J.-F. Gil, B. Pilette, O. Marcouillé, B. Lagarde, and F. Polack, "DESIRS: a state-of-the-art VUV beamline featuring high resolution and variable polarization for spectroscopy and dichroism at SOLEIL," *Journal of Synchrotron Radiation* **19**, 508–520 (2012).
- <sup>30</sup>G. A. Garcia, X. Tang, J.-F. Gil, L. Nahon, M. Ward, S. Batut,

- C. Pittchen, C. A. Taatjes, D. L. Osborn, and J.-C. Loison, "Synchrotron-based double imaging photoelectron/photoion coincidence spectroscopy of radicals produced in a flow tube: OH and Cl," *The Journal of Chemical Physics* **142**, 164201 (2015).
- <sup>31</sup>G. A. Garcia, B. K. Cunha de Miranda, M. Tia, S. Daly, and L. Nahon, "DELICIOUS III: a multipurpose double imaging particle coincidence spectrometer for gas phase vacuum ultraviolet photodynamics studies," *Review of Scientific Instruments* **84**, 053112 (2013).
- <sup>32</sup>C. R. Brundle, D. W. Turner, and W. C. Price, "High resolution molecular photoelectron spectroscopy II. Water and deuterium oxide," *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **307**, 27–36 (1968).
- <sup>33</sup>J. Li, B. Jiang, H. Song, J. Ma, B. Zhao, R. Dawes, and H. Guo, "From ab Initio Potential Energy Surfaces to State-Resolved Reactivities:  $X + H_2O \leftrightarrow HX + OH$  [ $X = F, Cl, \text{ and } O(^3P)$ ] Reactions," *The Journal of Physical Chemistry A* **119**, 4667–4687 (2015).
- <sup>34</sup>J.-H. Fillion, F. Dulieu, S. Baouche, J.-L. Lemaire, H. W. Jochims, and S. Leach, "Ionization yield and absorption spectra reveal superexcited Rydberg state relaxation processes in  $H_2O$  and  $D_2O$ ," *Journal of Physics B: Atomic, Molecular and Optical Physics* **36**, 2767–2776 (2003).
- <sup>35</sup>S. Pratt, J. Dehmer, and P. Dehmer, "Photoelectron spectroscopy of the linear ( $\tilde{A}^2 A_1$ ) $3p_b2$   $^1B_2$  Rydberg state of water," *Chemical Physics Letters* **196**, 469–474 (1992).
- <sup>36</sup>N. de Oliveira, D. Joyeux, D. Phalippou, J. C. Rodier, F. Polack, M. Vervloet, and L. Nahon, "A Fourier transform spectrometer without a beam splitter for the vacuum ultraviolet range: from the optical design to the first UV spectrum," *Review of Scientific Instruments* **80**, 043101 (2009).
- <sup>37</sup>N. de Oliveira, M. Roudjane, D. Joyeux, D. Phalippou, J.-C. Rodier, and L. Nahon, "High-resolution broad-bandwidth Fourier-transform absorption spectroscopy in the VUV range down to 40nm," *Nature Photonics* **5**, 149–153 (2011).
- <sup>38</sup>K. Watanabe and A. S. Jursa, "Absorption and photoionization cross sections of  $H_2O$  and  $H_2S$ ," *The Journal of Chemical Physics* **41**, 1650–1653 (1964).
- <sup>39</sup>D. H. Katayama, R. E. Huffman, and C. L. O'Bryan, "Absorption and photoionization cross sections for  $H_2O$  and  $D_2O$  in the vacuum ultraviolet," *The Journal of Chemical Physics* **59**, 4309–4319 (1973).
- <sup>40</sup>G. C. Angel and J. A. R. Samson, "Total photoionization cross sections of atomic oxygen from threshold to 44.3Å," *Physical Review A* **38**, 5578–5585 (1988).
- <sup>41</sup>J. Berkowitz, "Absolute photoionization cross sections of atomic oxygen," *Journal of Physics B: Atomic, Molecular and Optical Physics* **30**, 583 (1997).
- <sup>42</sup>R. T. Wiedmann, R. G. Tonkyn, M. G. White, K. Wang, and V. McKoy, "Rotationally resolved threshold photoelectron spectra of OH and OD," *The Journal of Chemical Physics* **97**, 768–772 (1992).

FIG. 1. Mass spectra recorded at a photon energy of 13.8 eV with the microwave discharge turned off (panel a)), turned on (panel b)). The difference spectrum (spectrum of panel b)) - spectrum of panel a)) is plotted in panel c). The same arbitrary unit is used for all 3 panels.

FIG. 2. Measured ion yields of  $\text{H}_2\text{O}^+$  (upper panel) and  $\text{O}^+$  (lower panel) adjusted to an absolute photoionization cross section scale (in black) with the work of Fillion *et al.* (blue line)<sup>34</sup> and Angel *et al.* (blue dots),<sup>40</sup> respectively. For the oxygen ion yield, the vertical scale is cut hence the two autoionization structures around 14.1 eV are not fully displayed. The red vertical dashed line indicates the photon energy chosen to perform the absolute cross section measurement in this work.

FIG. 3.  $\text{OH}^+$  ion yields from Cutler *et al.* (upper panel),<sup>21</sup> Dehmer (middle panel),<sup>20</sup> and this work (lower panel) as a function of the incident photon energy. The arbitrary vertical unit varies for each spectrum.

FIG. 4. Absolute photoionization cross-section of OH (black curve) as a function of the incident photon energy; the blue-shaded area defines the  $2\sigma$  uncertainties. The red triangle at  $13.800 \pm 0.004$  eV corresponds to the absolute measurement used to scale the entire ion yield displayed in the lower panel of Figure 3. The green dots are the absolute measurements of Dodson *et al.*<sup>24</sup>

ACCEPTED MANUSCRIPT









