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ABSTRACT

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_2O 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^+ 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: $\sigma_{OH}^{ion} = 9.0 \pm 2.7$ Mb. The resulting cross section values differ by approximately a factor 2 from the recent measurement of Dodson *et al.* [J. Chem. Phys. **148**, 184302 (2018)] performed with a different radical source, which is somewhat greater than the combined uncertainties of the measurements. This finding underlines the need for further investigations of this cross section.

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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,[1,2] but also in complex photophysical processes in a wide variety of astrophysical media (planetary atmospheres,[3–5] comets,[6] interstellar clouds,[7,8] etc.). In these media, OH plays a key role in the water photochemical cycle. The $OH + H_2 \rightarrow H_2O + H$ reaction is endothermic;[9] thus, most of the reactions involving OH at low temperature occur with O, N, and C atoms and lead to O_2, NO, and CO compounds rather than H_2O. On the other hand, the cationic form OH^+ reacts quickly with H_2[10] to produce H_2O^+ which in turn reacts with H_2 to generate H_3O^+. H_2O can then be formed through dissociative recombination of H_3O^+.[11]

Several theoretical[12] and experimental[13–17] 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.[18,19] For the ionization process, only three experimental studies have reported the relative photoionization yield (or constant-ionic-state spectra) of the hydroxyl radical in the VUV range, to our knowledge.[20–23] Dehmer's work covered the photon energy range between 13.0 and 16.5 eV (≈95–75 nm) at a resolution of 1–3 meV (0.007–0.023 nm).[20] 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^+ 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).[21] They assigned two new Rydberg series converging to the $OH^+\ b^+\ {}^1\Sigma^+$ 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

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from the analysis of time-resolved radical-kinetics measurements of a multi-reaction network in which OH is produced in the reaction of $O(^1D)$ with H_2O. The absolute cross section of OH was determined relative to that of $O(^3P)$. 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.[24]

The absolute photoionization cross section of the OH radical is important for reliably describing the abundances of OH and OH^+ 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[12,25,26] or ignore the cross section completely. For instance, the photoionization of OH is not present in the Leiden Database[27] or the Meudon PDR (Photon-Dominated-Region) code.[28] 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 photoionization cross section of OH by a different method that appears to be considerably simpler than the approach of Dodson *et al.*[24] The experiments were carried out at the French SOLEIL synchrotron facility, on the DESIRS (Dichroïsme Et Spectroscopie par Interaction avec le Rayonnement Synchrotron) beamline.[29] The DELICIOUS III spectrometer was used to record the OH^+ ion yield and to measure the corresponding absolute photoionization cross section. The experimental setup for the production of radicals and their analysis by mass spectrometry has been described in previous studies,[30] and here, only the specificities of the OH experiment are discussed. The OH radical was produced via H abstraction of H_2O by F atoms (H_2O + F → HO + HF). These F atoms were generated in a microwave discharge applied to F_2 diluted in He. H_2O 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.[31] 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_2O signal is up to 10 times and 100 times higher than that of OH and O, respectively. At the center 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_2O, 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^{-1}.

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^+ 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_2O. 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 toward $\tilde{A}^+$ state of H_2O^+.[32] The chosen energy of 13.8 eV is between the two lowest electronic states of OH^+ and H_2O^+ and above the ionizing transition toward the highest excited vibrational states of the electronic ground state of these cations with significant intensity.[30]

In Figs. 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 [Fig. 1(a)], there is no F atom production, and hence, no OH radicals are generated, and only the H_2O^+ signal is observed at m/q = 18. When the discharge is turned on [Fig. 1(b)], mass 17 (OH^+) 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 Fig. 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_2O + F → HO + HF reaction leads to strong vibrational excitation in HF, while OH remains vibrationally cold.[33] The OH + F → $O(^3P)$ + HF and OH + F → $O(^1D)$ + HF reactions are exothermic and endothermic, respectively; hence, we can conclude that the oxygen atoms are produced in their ^3P ground state.

In mass spectrometry, the temporal integration of an ion signal (S_{A^+}) for a given ion A^+ is proportional to the number of irradiated A species (n_A) and to its photoionization cross section (σ_A^{ion}) at the corresponding photon energy $S_{A^+} \propto n_A.\sigma_A^{ion}$. For two ions with close m/q values in a mass spectrum, one can assume that the coefficient

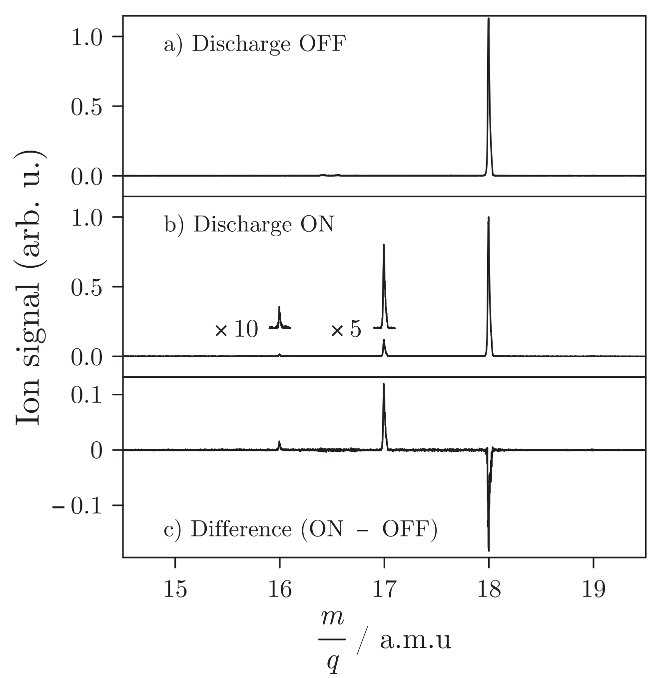

FIG. 1. Mass spectra recorded at a photon energy of 13.8 eV with the microwave discharge turned off [panel (a)], and turned on [panel (b)]. The difference spectrum [spectrum of panel (b) − spectrum of panel (a)] is plotted in panel (c). The same arbitrary unit is used for all 3 panels.

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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_2O when switching on the discharge ($\Delta n_{H_2O} = n^{OFF}_{H_2O} - n^{ON}_{H_2O}$) is equal to the quantity of free radicals formed $\Delta n_{H_2O} = n^{ON}_{OH} + n^{ON}_{O}$.

We can thus write the following equation:

$$\frac{\Delta(S_{H_2O^+})}{\sigma^{ion}_{H_2O}} = \frac{S_{OH^+}}{\sigma^{ion}_{OH}} + \frac{S_{O^+}}{\sigma^{ion}_{O}}, \quad (1)$$

where $\Delta(S_{H_2O^+}) = S^{OFF}_{H_2O^+} - S^{ON}_{H_2O^+}$, $S_{OH^+} = S^{ON}_{OH^+}$, and, $S_{O^+} = S^{ON}_{O^+}$.

From Eq. (1), we can deduce the photoionization cross section of the OH radical if the cross sections of H_2O and O are known.

The photoionization cross section of water has been published by Fillion *et al.*[34] 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 $\tilde{A}^{+\,2}A_1$ state of H_2O^+ at 13.84 eV.[35] 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.*[34] was performed with a photon resolution of 25 meV, we had to measure the absorption cross section of H_2O 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.[36,37] 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 ($\sigma^{ion}_{H_2O} = 8.7 \pm 0.8$ 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 and Jursa[38] and Katayama *et al.*[39] Our measurement of the H_2O ion yield between 13 and 15 eV scaled with the work of Fillion *et al.* is shown 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 $\sigma^{ion}_{O} = 3.08 \pm 0.25$ Mb at 13.8 eV by interpolating the data of Angel and Samson,[40] which are assumed to be the most correct for the atomic oxygen photoionization cross section.[41] Our measurement of the atomic O^+ ion yield between 13 and 15 eV scaled with the work of Angel and Samson is shown 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_2O and O photoionization cross sections, and Eq. (1), we obtained $\sigma^{ion}_{OH} = 9.0 \pm 2.7$ Mb (2σ confidence interval assuming that the uncertainties of the H_2O and O photoionization cross sections correspond to 2σ confidence intervals). The uncertainty 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_{O^+} recorded under different experimental conditions was correlated with $\Delta(S_{H_2O^+})$.

In Fig. 3, our relative OH ion yield is depicted and compared with the ones measured by Dehmer[20] and Cutler *et al.*[21] 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

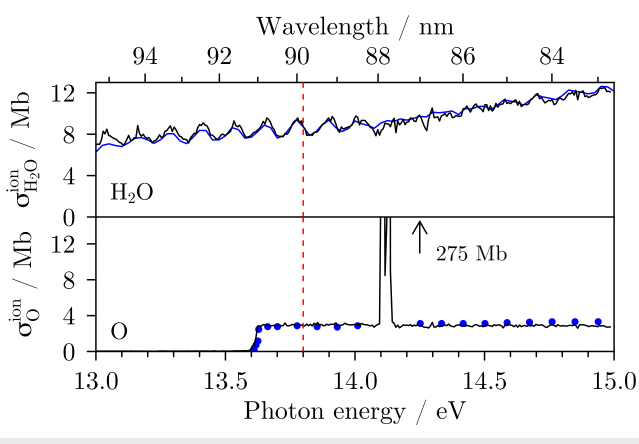

FIG. 2. Measured ion yields of H_2O^+ (upper panel) and O^+ (lower panel) adjusted to an absolute photoionization cross section scale (in black) with the work of Fillion *et al.* (blue line)[34] and Angel and Samson (blue dots),[40] respectively. For the oxygen ion yield, the vertical scale is cut; hence, 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.

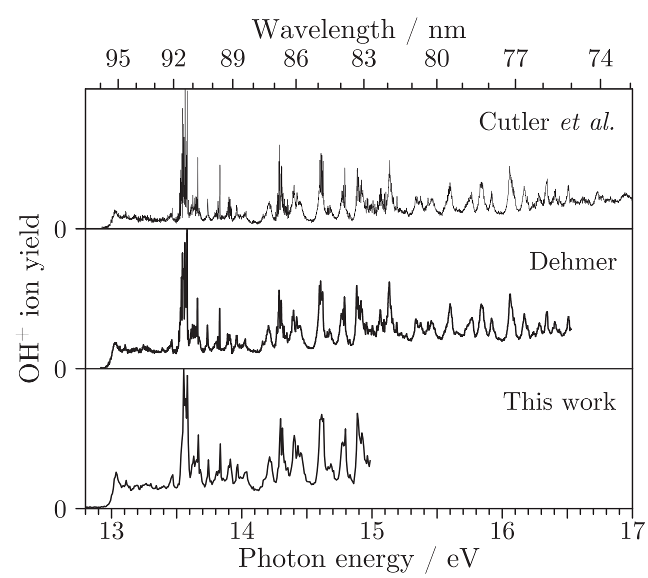

FIG. 3. OH^+ ion yields from Cutler *et al.* (upper panel),[21] Dehmer (middle panel),[20] and this work (lower panel) as a function of the incident photon energy. The arbitrary vertical unit varies for each spectrum.

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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 H + $NO_2 \rightarrow$ OH + NO, rather than via the present H abstraction from H_2O. 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 Fig. 3, we derived the photoionization cross section of the OH radical over a large energy range {from the ionization threshold [13.01698(25) eV][42] to 15.0 eV}. This cross section is reported in Fig. 4. The corresponding data are available in the supplementary material.

In Fig. 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.*[24] although the trend of both datasets 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.[12] 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.*[24] Veseth and Kelly have used many body perturbation theory to calculate the OH photoionization cross section as well.[25] Their value for the direct photoionization cross section is considerably larger, corresponding to ≈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, Fig. 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_2O are correct, Eq. (1) implies that an overestimation of the OH cross section could result from either too small a value of $\Delta(S_{H_2O^+})$, too high a value of S_{O^+}, or too high a value of S_{OH^+}. It appears, however, that the most likely issues that we can identify would push one or more of these values ($\Delta(S_{H_2O^+})$, S_{O^+}, and S_{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 supplementary 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

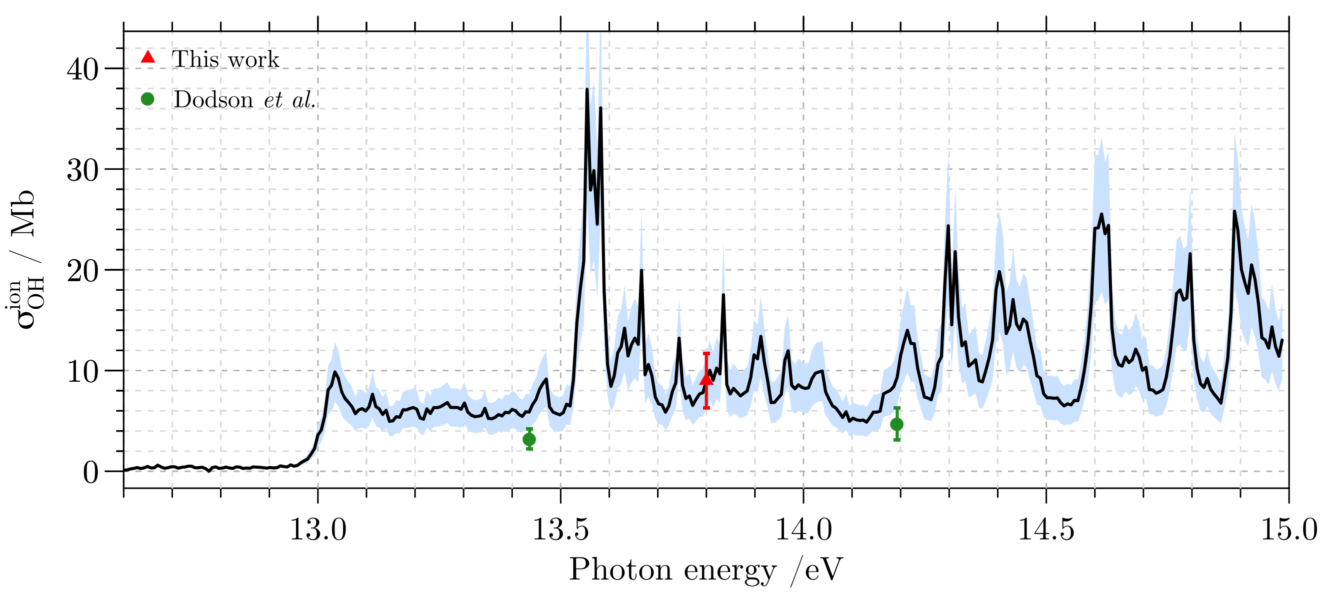

FIG. 4. Absolute photoionization cross section of OH (black curve) as a function of the incident photon energy; the blue-shaded area defines the 2σ uncertainties. The red triangle at 13.8 eV corresponds to the absolute measurement used to scale the entire ion yield displayed in the lower panel of Fig. 3. The green dots are the absolute measurements of Dodson *et al.*[24]

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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.

See supplementary material for a discussion about the potential sources of error in the photoionization cross-section measurement and for the absolute photoionization cross-section data of OH.

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