

# Photoionization Cross Section of the NH<sub>2</sub> Free Radical in the 11.1–15.7 eV Energy Range

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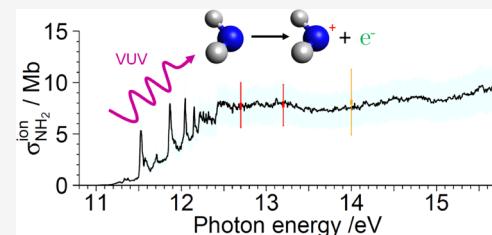
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**ABSTRACT:** The NH<sub>2</sub> radical is a key component in many astrophysical environments, both in its neutral and cationic forms, being involved in the formation of complex N-bearing species. To gain insight into the photochemical processes into which it operates and to model accurately the ensuing chemical networks, the knowledge of its photoionization efficiency is required, but no quantitative determination has been carried out so far. Combining a flow-tube H-abstraction radical source, a double imaging photoelectron-photoion spectrometer, and a vacuum-ultraviolet synchrotron excitation, the absolute photoionization cross section of the amino radical has been measured in the present work for the first time at two photon energies:  $\sigma_{\text{ion}}^{\text{NH}_2}(12.7 \text{ eV}) = 7.8 \pm 2.2 \text{ Mb}$  and  $\sigma_{\text{ion}}^{\text{NH}_2}(13.2 \text{ eV}) = 7.8 \pm 2.0 \text{ Mb}$ . These values have been employed to scale the total ion yield previously recorded by Gibson et al. (*J. Chem. Phys.* **1985**, *83*, 4319–4328). The resulting cross section curve spanning the 11.1–15.7 eV energy range will help in refining the current astrophysical models.



## INTRODUCTION

The amino or amidogen radical (NH<sub>2</sub>) is a molecule of great astrophysical interest. In a way similar to that of ammonia, it constitutes a building block from which more complex N-bearing species can derive (formamide NH<sub>2</sub>CHO, urea H<sub>2</sub>NCONH<sub>2</sub>, polycyclic nitrogen-containing hydrocarbons, amino acids, proteins, etc.).<sup>1,2</sup> Additional reactivity can be expected from neutral NH<sub>2</sub>, an open shell species, and even more from the NH<sub>2</sub><sup>+</sup> cation, which is a double radical isoelectronic to the methylene radical CH<sub>2</sub>. NH<sub>2</sub> is present in many astrophysical media in the gas phase,<sup>3–5</sup> within or in the close vicinity of solids (grains and ices),<sup>6,7</sup> and in particular comets, and it is implicated in chemical reactions therein.<sup>7,8</sup> Sandford et al.<sup>6</sup> reported, using laboratory experiments, the formation of pyrimidine (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>) in ices containing H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>3</sub>OH, and CH<sub>4</sub> following UV photolysis. They went on to expose the major role that neutral NH<sub>2</sub> then plays in reacting with pyrimidine to form cytosine, a nucleobase. In addition, NH<sub>2</sub> is one of the major fragments formed in the ultraviolet/vacuum-ultraviolet photodissociation of NH<sub>3</sub>, an important constituent of many astrophysical environments, including comets such as Churyumov–Gerasimenko.<sup>9</sup>

In terms of spectroscopy, neutral NH<sub>2</sub> has been widely studied since its first observation in 1952 by Herzberg et al.,<sup>10</sup> from pure rotational<sup>11,12</sup> to electronic studies.<sup>13–15</sup> There are fewer works however at higher energies, around the ionization potential (IP) and on the NH<sub>2</sub><sup>+</sup> cation itself. In 1980, Dunlavey et al.<sup>16</sup> performed the first photoelectron study on NH<sub>2</sub>,

employing a He lamp and an amidogen source based on the H-abstraction reaction: NH<sub>3</sub> + F → NH<sub>2</sub> + HF. They located the three lowest electronic states of the cation (X<sup>+</sup> <sup>3</sup>B<sub>1</sub>,  $\tilde{\alpha}^+ \text{ } ^1\text{A}_1$  and  $\tilde{\beta}^+ \text{ } ^1\text{B}_1$ ) and described their vibrational structure. High-lying bending modes of the two lowest electronic states of NH<sub>2</sub><sup>+</sup> were more recently investigated by Holzmeier et al.<sup>17</sup> via threshold-photoelectron spectroscopy, using an almost identical setup to that employed in the present work. The triplet–singlet splitting between these states was studied in more detail using pulsed-field-ionization zero-kinetic-energy spectroscopy.<sup>18,19</sup> These high-resolution studies yielded a full rotational description of the two lowest electronic states of the cation and the most precise determination to date of the ionization energy IE(NH<sub>2</sub>) = 90083.8(10) cm<sup>−1</sup> (=11.1689(1) eV). The photoionization of NH<sub>2</sub> has also been studied by accurate calculations.<sup>20,21</sup>

To our knowledge, no experimental determination of the absolute photoionization cross section of NH<sub>2</sub> has been published until now. Only its ion yield from threshold up to 16.6 eV has been measured by Gibson et al.<sup>22</sup> In their study, NH<sub>2</sub> was produced by H-addition onto N<sub>2</sub>H<sub>4</sub>, which initiated a

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set of reactions finally producing  $\text{NH}_2$ . Their paper provides a detailed discussion on the thermochemistry of the  $\text{NH}_x$  compounds (N–H bond energies and formation enthalpies) and a first determination of appearance energy of the  $\text{NH}_2$  dissociative ionization channel leading to  $\text{NH}^+$  (17.19 eV). A spectroscopic interpretation of the features present in the  $\text{NH}_2^+$  ion yield is also given.

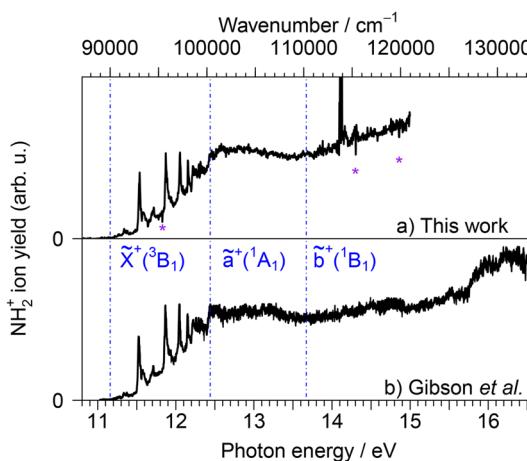
In the present paper, we report the first experimental measurement of the  $\text{NH}_2$  absolute photoionization cross section in the 11.1–15.7 eV energy range.

## ■ EXPERIMENTAL SECTION

The experiments were carried out on the DESIRS beamline<sup>23</sup> of the French synchrotron facility SOLEIL. The details of the experiment have been published previously,<sup>24</sup> and they include the specificities of this setup and the procedure for determining the radical cross section, as well as detailed descriptions of energy calibrations and energy resolution.<sup>25,26</sup> Briefly, F atoms created from the dissociation of  $\text{F}_2$  in a microwave discharge go on to react with helium-diluted  $\text{NH}_3$  in a flow-tube reactor. Experimental conditions are controlled via mass spectrometry to optimize the single-H abstraction of  $\text{NH}_3$  and to minimize all other side reactions (F addition, double-H abstraction, radical–radical reactions, etc.). After passing through two skimmers, the products from the reactor perpendicularly cross the monochromatized synchrotron radiation beam within the DELICIOUS III double imaging photoelectron/photoion spectrometer.<sup>27</sup> The resulting ionization produces ions and electrons that are simultaneously collected using a 177 V/cm extraction field, which ensures a 100% particle collection efficiency at the photon energies studied here. When recording ionization yield, the photon resolution was set to  $\delta E = 4$  meV over the whole scan range. For the absolute measurements, it was increased to  $\delta E = 10$  meV. This difference in photon energy resolution is not however important as the fixed energy measurements were purposefully carried out in spectral regions off-resonance with any structures, thus independent of the resolution. The beamline was equipped with a gas filter containing Ar, which removed any high harmonics stemming from the undulator in the final monochromatized radiation. The resulting Ar absorption lines present in the ion yield allowed the calibration of the photon energy to an accuracy of around 4 meV. The ion yield was recorded using 4 meV energy steps in two different measurements: one from 10.8 eV up to 14.3 eV and one from 13.4 eV up to 15.5 eV. The large overlap between the two scans enabled an unambiguous intensity scaling of the two measurements. A photodiode (AXUV, IRD) was used to correct the spectra from the incident VUV flux.

## ■ RESULTS AND DISCUSSION

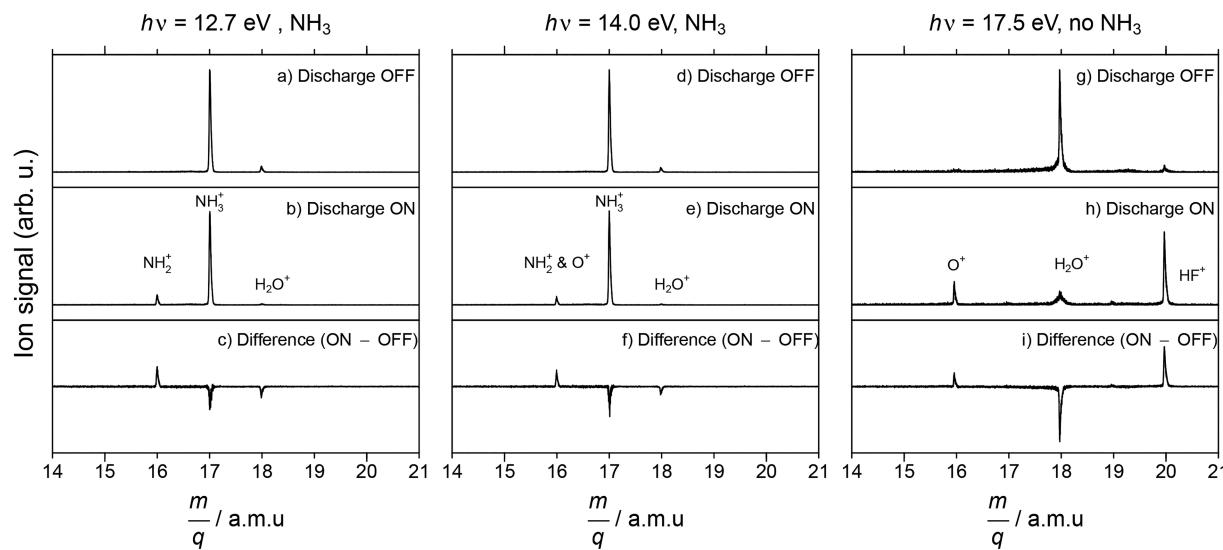
The ion yield from this work is compared to that of Gibson et al.<sup>22</sup> in Figure 1. The similarities between the two spectra are clear up to 13.6 eV and validate the measurements performed in the present work within this spectral range. Both spectra rise characteristically slowly from the first ionization potential at ~11.17 eV<sup>19</sup> to around 12.5 eV, i.e., the first excited state ( $\tilde{\alpha}^+(1\text{A}_1)$ ) of  $\text{NH}_2^+$ . During this increase, resonances punctuate the spectrum, which can be attributed to autoionizing Rydberg states converging to the  $\tilde{\alpha}^+(1\text{A}_1)$  state.<sup>16</sup> Above 12.5 eV, the ion yield is practically flat, but rises slightly at higher energies. In our spectrum, dominant resonances from atomic oxygen are present at around 14.1 eV. This observation shows that an  $\text{O}^+$



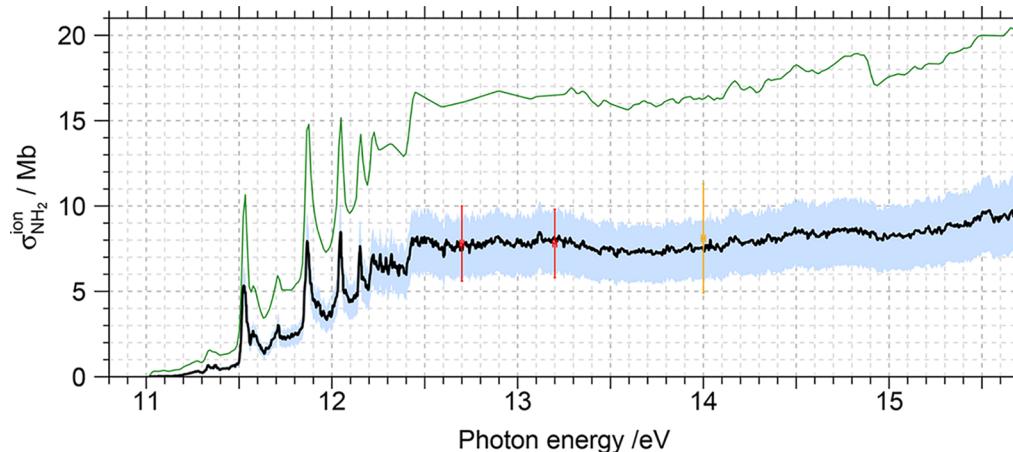
**Figure 1.** (a) Ion yield recorded in the present work for  $m/q = 16$  amu and attributed mainly to the  $\text{NH}_2^+$  cation. The off-scale sharp resonances at 14.1 eV correspond to the atomic oxygen autoionization resonances. Purple asterisks mark Ar absorption lines from the beamline gas filter. (b)  $\text{NH}_2^+$  ion yield measured by Gibson et al.<sup>22</sup> (unscanned data from the original paper). The blue dashed lines locate the three lowest electronic states of  $\text{NH}_2^+$ .<sup>16</sup>

signal issuing from  $\text{H}_2\text{O}$  (see below) contaminates the  $\text{NH}_2^+$  ion signal in our experiments, both cations being recorded in the same  $m/q = 16$  amu mass channel. This contamination must therefore be addressed and is discussed below. Note that the ion yield of Gibson et al. does not contain any  $\text{O}^+$  contamination. In their experiment, their radicals were produced using  $\text{H} + \text{N}_2\text{H}_4$  reaction. Their  $\text{NH}_2^+$  signal contains a contribution issuing from dissociative ionization of  $\text{N}_2\text{H}_4$  and  $\text{NH}_3$  (side-product) above 15.7 eV. They nevertheless succeeded in correcting the  $\text{NH}_2^+$  signal from the former process. Thus, their ion yield corresponds to ionization of neutral  $\text{NH}_2$  from the IP up to 15.7 eV.

Typical mass spectra are displayed in Figure 2. Panels a–c and panels d–f correspond to spectra recorded at 12.7 and 14.0 eV, respectively, and normalized to the  $\text{NH}_3^+$  signal obtained with the microwave discharge switched off. With the discharge turned on, the conditions were optimized to favor the production of  $\text{NH}_2$  from  $\text{NH}_3$  precursor while minimizing parasitic reactions. In particular, the absence of  $\text{NH}^+$  at  $m/q = 15$  amu in the 14.0 eV spectra (panels e and f) (i.e., above  $\text{IE}(\text{NH}) = 13.480$  eV<sup>24</sup>) shows that  $\text{NH}$  is not produced in the reactor via double-H abstraction.<sup>25</sup> As seen in panels a–f of Figure 2, water is present as an impurity in the experiment, and it is almost completely consumed when the F atom-producing discharge is turned on (panels b and e). It could lead to the formation of OH via the parasitic reaction  $\text{H}_2\text{O} + \text{F} \rightarrow \text{OH} + \text{HF}$ , which could then contaminate the  $\text{NH}_3^+$  signal at  $m/q = 17$  amu, rendering the exploitation of the mass spectra difficult if not impossible. For this reason, additional mass spectra were recorded, within the same conditions but without any  $\text{NH}_3$ , at a photon energy of 17.5 eV to be above the IP of any potentially produced fragments, including HF ( $\text{IE}(\text{HF}) = 16.03$  eV<sup>28</sup>) the byproduct of H abstractions by F. They are displayed in the right-hand panels of Figure 2, panels g–i. Note that in this case the mass signals have been normalized to that of  $\text{H}_2\text{O}^+$  recorded without discharge (panel g). This explains the amplified appearance of the water peak although the abundance of neutral water is the same as in the two left columns. Since the photoionization cross section of water at



**Figure 2.** (a–c) mass spectra recorded at 12.7 eV with  $\text{NH}_3$  in the source and the microwave discharge turned off (panel a) and on (panel b) and the resulting difference spectrum (panel c). (d–f) Same as panels a–c but for a photon energy of 14.0 eV. (g–i) Same as panels a–c but for a photon energy of 17.5 eV and without  $\text{NH}_3$  injected at the source. In each column, the signal has been normalized to the most intense peak of the upper panel. See text for details.



**Figure 3.**  $\text{NH}_2^+$  ion yield of Gibson et al.<sup>22</sup> scaled to an absolute photoionization cross section from threshold up to 15.7 eV. The absolute measurements undertaken in this work at 12.7, 13.2, and 14.0 eV are depicted as red and orange crosses along with their associated  $2\sigma$  error bars. The light blue area represents  $2\sigma$  error bars carried over the whole study range. The green curve recalls the cross section used in the Leiden astrophysical database.<sup>38</sup>

17.5 eV is about twice as large as at 14.0 eV,<sup>29</sup> the normalized signals observed in panels g and h, in particular at  $m/q = 16$  amu, are actually very weak compared to those of panels d and e. These ammonia-free spectra show that water is consumed by switching the discharge on (panels h and i), pointing toward a contamination upstream from the microwave discharge on the  $\text{F}_2$  gas line. The difference spectrum of panel i illustrates the consumption of  $\text{H}_2\text{O}$  and production of O and HF ( $\text{H}_2\text{O} + 2\text{F} \rightarrow \text{O} + 2\text{HF}$ ). In the presence of  $\text{NH}_3$ , atomic fluorine reacts mainly with  $\text{NH}_3$  giving  $\text{HF} + \text{NH}_2$  ( $k = 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$  at 298 K; see ref 30). As the reaction rates of  $\text{OH} + \text{NH}_3$  and  $\text{OH} + \text{NH}_2$  are low at room temperature ( $k = 1.6 \times 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}$  and  $\sim 10^{-12} \text{ cm}^3 \cdot \text{s}^{-1}$ , respectively),<sup>31</sup> OH will mainly react either with atomic fluorine to give O + HF or on the walls, but it will not react with  $\text{NH}_3$  or  $\text{NH}_2$ . Moreover, very little OH radical is left by the time the molecules enter the spectrometer and are ionized by the synchrotron radiation, likely because they are produced close to the discharge and undergo self-reactions

(producing O and  $\text{H}_2\text{O}$ ), reaction with O atoms (yielding  $\text{O}_2$ ) or reactions on the walls. The presence of OH in the experiment can only be detected at energies above the IP (13.0170 eV);<sup>32</sup> hence, it would have no consequences in the absolute values at 12.7 eV. In the present work, no OH is detected even above 13.0170 eV as shown by the identical curves in Figure 1. Oxygen atoms self-react producing  $\text{O}_2$ , and there also seems to be some reactivity with  $\text{N}_2$  impurity producing NO (both products identified via the recording of their ion yield).<sup>25</sup> The absence of  $m/q = 17$  amu in the spectra of panels h and i of Figure 2 further demonstrates that there is no contamination of the  $\text{NH}_3^+$  signal by that of  $\text{OH}^+$  in the experiment. The presence of O atoms in the experiment is however confirmed, which will induce a contamination of the  $\text{NH}_2^+$  signal at  $m/q = 16$  amu for photon energies above  $\text{IE}(\text{O}) = 13.61 \text{ eV}$ ,<sup>33</sup> and it will thus require that reliable absolute measurements be performed below 13.61 eV.

Absolute measurements of the  $\text{NH}_2$  photoionization cross section were thus undertaken at two energies, 12.7 and 13.2 eV located on a plateau (see Figure 1), to probe the  $\text{NH}_2$  cross section over a greater range, thus improving the precision. The procedure is the same as used in a previous work on the  $\text{OH}$  radical.<sup>25,34,35</sup> The difference between mass spectra recorded with the discharge on and mass spectra with the discharge off is a depletion of the  $m/q = 17$  amu signal in favor of  $m/q = 16$  amu. This change is the result of the consumption of  $\text{NH}_3$  by F atoms producing  $\text{NH}_2$ . Applying matter conservation to the number densities, we have  $\Delta(n_{\text{NH}_3}) = n_{\text{NH}_3}^{\text{off}} - n_{\text{NH}_3}^{\text{on}} = n_{\text{NH}_2}^{\text{on}}$ . As  $\text{NH}_2^+$  and  $\text{NH}_3^+$  are neighboring masses, we assume that their transmission and detection efficiencies are the same. We also neglect any wall loss of  $\text{NH}_2$ . In order to verify this, we measured the ratio of produced  $\text{NH}_2$  with respect to the quantity of consumed  $\text{NH}_3$  while varying the injector distance. We found this ratio to be independent of the injector distance which confirms that  $\text{NH}_2$  is not lost to the walls within our reaction times. The proportionality law between ion signal, number of irradiated species, and photoionization cross sections thus leads to

$$\sigma_{\text{NH}_2}^{\text{ion}} = \sigma_{\text{NH}_3}^{\text{ion}} \times \frac{S_{\text{NH}_2^+}}{\Delta(S_{\text{NH}_3^+})} \quad (1)$$

In eq 1,  $\Delta(S_{\text{NH}_3^+})$  and  $S_{\text{NH}_2^+}$  are measured experimentally from the mass spectra. The  $\text{NH}_3$  photoionization cross section is well-known.<sup>36,37</sup> We used the values of Samson et al.<sup>36</sup> of  $8.88 \pm 0.27$  and  $8.20 \pm 0.25$  Mb at 12.7 and 13.2 eV, respectively, and considered the stated accuracy on these values of 3% as being  $2\sigma$  accuracy. The  $\text{NH}_2$  photoionization cross section uncertainty was then derived via a Monte Carlo uncertainty propagation procedure applied on eq 1. We found:  $\sigma_{\text{ion}}^{\text{NH}_2}(12.7 \text{ eV}) = 7.8 \pm 2.2$  Mb and  $\sigma_{\text{ion}}^{\text{NH}_2}(13.2 \text{ eV}) = 7.8 \pm 2.0$  Mb.

These absolute measurements were further used to set the  $\text{NH}_2^+$  ion yield of Gibson et al.<sup>22</sup> to an absolute scale up to 15.7 eV. The resulting curve is displayed in Figure 3. Error bars were evaluated by taking the relative uncertainty at each of the two fixed energy measurements and propagating them over the whole scan range. The given final uncertainty, represented as light blue error bars in Figure 3, is the minimum relative uncertainty of the two. A third absolute measurement performed at 14 eV is reported on this curve without any attempt to correct it from the expected oxygen contamination:  $\sigma_{\text{ion}}^{m/q=16}(14.0 \text{ eV}) = 8.1 \pm 3.2$  Mb. It constitutes an upper estimate of the  $\text{NH}_2$  cross section (eq 1). The corresponding value lies within the estimated error bars and is still in excellent agreement with the scaled ion yield, indicating that the  $\text{O}^+$  contribution has a negligible impact on the cross section determination. Nevertheless, note that this point was not employed in the absolute scaling procedure.

## CONCLUDING REMARKS

The newly measured cross section values of this work can be compared to those available in databases dedicated to astrophysical models. For instance the Leiden database<sup>38</sup> proposes  $\text{NH}_2$  photoionization cross section values using the ion yield of Gibson et al.<sup>22</sup> that is arbitrarily set to 20 Mb at 15.5 eV to be in line with other molecules of their database. As shown in Figure 3 where the resulting curve is displayed in green, this scaling factor overestimates cross section values by about a factor of 2 and thus leads to an overestimation of the

$\text{NH}_2$  photoionization process in models relying on this database. The correction of this overestimation might lead to a greater predicted abundance of neutral  $\text{NH}_2$  in different regions, testifying to an increased importance of  $\text{NH}_2$  as a reactive intermediate in photodissociation regions as well as protoplanetary and protostellar envelopes where UV radiation and cosmic ray ionization is plentiful.<sup>39</sup> The present work illustrates the importance of an accurate determination of VUV photoionization cross sections of astrophysical species, especially of free radicals, in order to refine photochemical models.

Our measured values will be particularly useful in any laboratory experiments using mass-spectrometry coupled with single-photon ionization to derive quantitative data (e.g., branching ratio measurements of photodissociation channels following the experimental scheme of ref 40).

Finally, this first experimental measurement of the  $\text{NH}_2$  photoionization cross section opens new possibilities for deriving that of the  $\text{NH}$  radical, which has also been detected in comets,<sup>41</sup> in the sun,<sup>42</sup> or in the interstellar media.<sup>43</sup> The  $\text{NH}$  cross-section has yet to be reported, but it is achievable with this setup by tuning the flow-tube conditions to allow both a single- and a double-H abstraction. This operation mode is more challenging, but it will be attempted in a future experimental campaign.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c01876>

Photoionization cross section data of  $\text{NH}_2$  as a function of photon energy from 11.1 to 15.7 eV (TXT)

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### Notes

The authors declare no competing financial interest.

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