Lyα irradiation of solid-state formamide

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ABSTRACT

\textbf{Context.} Formamide (NH\textsubscript{2}CHO) has been proposed as a potential prebiotic precursor in the scientific discourse on the origin of life. It has been observed in different environments in space, including protostellar regions and comets. The abundance and stability of NH\textsubscript{2}CHO in the early stages of star formation can be better understood by incorporating the formation and destruction data in astrochemical models.

\textbf{Aims.} We carried out an experimental investigation to study the destruction of pure NH\textsubscript{2}CHO ice at 12 K as a result of the interaction with Ly\alpha (121.6 nm) photons.

\textbf{Methods.} We studied UV photo destruction of NH\textsubscript{2}CHO using Fourier-transform infrared spectroscopy.

\textbf{Results.} After UV processing, the intensity of NH\textsubscript{2}CHO IR bands decreases and new bands corresponding to HCN, CO, NH\textsubscript{3}, OCN\textsuperscript{−}, HNCO, and CO\textsubscript{2} appeared in the spectrum. We then derived the destruction and cumulative product formation cross-sections.

\textbf{Conclusions.} A comparison of destruction rates derived from the cross-section in a cold and dense molecular cloud for different energetic processing agents reveals that UV photons induce NH\textsubscript{2}CHO destruction at a level that is one order of magnitude greater than that affected by cosmic rays; however, it is three orders of magnitude lower than that of H atoms.

\textbf{Key words.} astrochemistry – methods: laboratory: solid state - techniques: spectroscopic - ISM: molecules - Ultraviolet: ISM

1. Introduction

Formamide (NH\textsubscript{2}CHO) is one of the simplest molecules to contain the four primary biogenic elements and an amide bond. It is considered a promising precursor molecule in the context of the origin of life on our planet (Saladino et al. 2012). Formamide chemistry in a controlled terrestrial environment allows for the formation of essential biological life components such as amino acids, nucleobases, sugars, and carboxylic acids (Saladino et al. 2012; Ferus et al. 2015; Botta et al. 2018). Moreover, it has been observed in many astrophysical environments such as galactic centres, star-forming regions, and comets (e.g. Blake et al. 1986; Turner 1991; Bisschop et al. 2007; Méndez et al. 2014; López-Sepulcre et al. 2015; Bockelée-Morvan et al. 2000; Biver et al. 2014; Goesmann et al. 2015). In fact, the mass spectrometric analysis by COMetary Sampling And Composition (COSAC), aboard Rosetta’s Philae lander on comet 67P/Churyumov–Gerasimenko, revealed that NH\textsubscript{2}CHO (1.8% with respect to water) is the second-most abundant molecule after H\textsubscript{2}O (Goesmann et al. 2015; Altwegg et al. 2017). Solid-state NH\textsubscript{2}CHO has also been identified tentatively in the interstellar medium by the Infrared Space Observatory towards NGC 7538 IRS9 and W33A (Raunier et al. 2004a; Gibb et al. 2004).

Based on experimental and theoretical studies, it has been proposed that NH\textsubscript{2}CHO was formed in space by a series of ion-molecule and neutral-neutral reaction channels in the gas phase, whereas solid NH\textsubscript{2}CHO could be formed via a processing of interstellar ices on dust grain surface by electrons, ions, ultraviolet (UV) photons, heat, and H atoms (López-Sepulcre et al. 2019, and references therein). Once formed, NH\textsubscript{2}CHO can undergo further processing both in the gas or solid phase to form simple and complex organic molecules. As a result, the abundance of NH\textsubscript{2}CHO in a certain space environment will depend both on the formation and destruction channels. Therefore, understanding the destruction channels of NH\textsubscript{2}CHO under energetic and non-energetic processing has been the subject of numerous studies.

Quantum mechanical calculations on the thermal decomposition of NH\textsubscript{2}CHO revealed three main reaction channels (Nguyen et al. 2011). In decreasing order of kinetically favoured pathways, these are: dehydration [H\textsubscript{2}O loss to hydrogen cyanide (HCN)], decarbonylation [carbon monoxide (CO) loss to ammonia (NH\textsubscript{3})], and dehydrogenation [hydrogen (H\textsubscript{2}) loss to isocyanic acid (HNC\textsubscript{O})]. A high-energy laser spark induces the decomposition of NH\textsubscript{2}CHO gas to HCN, CO, NH\textsubscript{3}, carbon dioxide (CO\textsubscript{2}), nitrous oxide (N\textsubscript{2}O), hydroxylamine (HONH\textsubscript{2}), and methanol (CH\textsubscript{3}OH), which was identified by infrared (IR) spectroscopy (Ferus et al. 2011). The NH\textsubscript{2}CHO decomposition in matrices also leads to similar products as observed in the gas-phase reactions (Lundell et al. 1998; Maier & Endres 2000; Durney et al. 2005). A limited number of studies have been dedicated to investigate the destruction of NH\textsubscript{2}CHO in the condensed phase. Ion irradiation experiments with 200 keV H\textsuperscript{+} were performed on NH\textsubscript{2}CHO films deposited on inert silicon and olivine substrate (Brucato et al. 2006b,a). An IR analysis showed the formation of CO, CO\textsubscript{2}, NH\textsubscript{3}, N\textsubscript{2}O, HCN, cyanide ion (CN\textsuperscript{−}), ammonium ion (NH\textsubscript{4}\textsuperscript{+}), isocyanate ion (OCN\textsuperscript{−}), and isocyanic acid (HNCO) on silicon whereas all the other products except CN\textsuperscript{−} and NH\textsubscript{3} were formed on the olivine surface. In a different set of experiments, pure NH\textsubscript{2}CHO films show no significant degradation upon processing by UV-enhanced xenon lamp, whereas oxide minerals titanium dioxide (TiO\textsubscript{2}) and spinel (MgAl\textsubscript{2}O\textsubscript{4}) used...
as substrates induce a gradual but minimal degradation (Corazzi et al. 2020). On the other hand, Lyman (Lyα) photons and 1 keV electrons bombardment of amorphous or crystalline NH₂CHO film deposited on silica (SiO₂) nanopowder at 70 K revealed only OCN⁻ and CO (Dawley et al. 2014a).

More recently, two independent investigations were made to study the reaction of H atoms on NH₂CHO ice (Haupa et al. 2019; Suhasarisa & Mennella 2020). Haupa et al. (2019) showed that HNCO was formed through H-abstraction reactions via a H₂NCO radical intermediate when NH₂CHO was subject to H atoms in the para-hydrogen quantum-solid matrix host. Furthermore, Suhasarisa & Mennella (2020) studied the effect of H atom exposure on NH₂CHO at 12 K to estimate the effective destruction cross-section. This quantity was used to evaluate the destruction rate of NH₂CHO by H atoms in space and was then compared with the destructive effects of cosmic rays and UV photons. However, the absence of destruction cross-section for NH₂CHO under Lyα (10.2 eV) photons only allowed the estimation of an upper limit for the destruction rate under interstellar medium conditions. The present study reports the results of the interaction of Lyα with pure NH₂CHO ice film at 12 K. The NH₂CHO destruction and new products formed after UV irradiation have been studied by Fourier-transform infrared (FTIR) spectroscopy. The destruction cross-section for NH₂CHO and the cumulative formation cross-section for the formed new species have been obtained. The determination of the destruction cross-section has then allowed us to compare the destructive effects of H atoms, cosmic rays, and UV photons on pure solid NH₂CHO in dense interstellar cloud conditions.

2. Experimental methods

Experiments were performed in a high vacuum chamber, which is described in detail in previous works (Mennella et al. 2006; Suhasarisa & Mennella 2020). The salient features of the set-up relevant to this work are briefly described here. The main chamber, with a base pressure better than 10⁻⁸ mbar, is equipped with a closed-cycle helium cryostat and a dosing unit. A caesium iodide (CsI) substrate was mounted on the cold finger of the cryostat such that the substrate can be cooled down to 12 K. Experiments were performed in a high vacuum chamber, which is described in detail in previous works (Mennella et al. 2006; Brucato et al. 2006a). The NH₂CHO ice film thickness was derived separately from the column density of combined symmetric and antisymmetric NH, C-H, and C=O stretching IR modes using the band strengths values listed in Table 1. The average value, expressed in units of monolayer (1 ML = 10¹⁸ molecules cm⁻²), is 29.5 ML which is equivalent to 0.03 μm. For the thickness determination, we took into account the cosine of the angle between the IR beam and the normal to the surface plane and the NH₂CHO ice density 0.937 g cm⁻³ derived by Brucato et al. (2006a). The NH₂CHO ice thickness was found to be below the UV penetration depth since the mean free path of UV photons, d_UV, through the NH₂CHO films has been estimated to be 0.04 μm. The mean free path of UV photons was derived using the relation, d_UV = 1/β = 1/σn, where β is the absorption coefficient, σ is the UV photo-absorption cross-section of NH₂CHO, and n is the number of NH₂CHO molecules per unit volume. In the absence of direct measurements of the UV absorption cross-section for NH₂CHO ice, the gas phase value of ca. 2 × 10⁻¹⁷ cm² (Gingell et al. 1997) acquired at 10.2 eV photons is taken into the calculation.

3. Results and discussion

3.1. Ice growth

The IR spectrum of pure solid NH₂CHO at 12 K is displayed in Fig. 1 and the corresponding fundamental vibration modes reported in Table 1 are in good agreement with the previous results (Brucato et al. 2006a; Suhasarisa & Mennella 2020). The NH₂CHO ice film thickness was derived separately from the column density of combined symmetric and antisymmetric NH, C-H, and C=O stretching IR modes using the band strengths values listed in Table 1. The average value, expressed in units of monolayer (1 ML = 10¹⁸ molecules cm⁻²), is 29.5 ML which is equivalent to 0.03 μm. For the thickness determination, we took into account the cosine of the angle between the IR beam and the normal to the surface plane and the NH₂CHO ice density 0.937 g cm⁻³ derived by Brucato et al. (2006a). The NH₂CHO ice thickness was found to be below the UV penetration depth since the mean free path of UV photons, d_UV, through the NH₂CHO films has been estimated to be 0.04 μm. The mean free path of UV photons was derived using the relation, d_UV = 1/β = 1/σn, where β is the absorption coefficient, σ is the UV photo-absorption cross-section of NH₂CHO, and n is the number of NH₂CHO molecules per unit volume. In the absence of direct measurements of the UV absorption cross-section for NH₂CHO ice, the gas phase value of ca. 2 × 10⁻¹⁷ cm² (Gingell et al. 1997) acquired at 10.2 eV photons is taken into the calculation.

3.2. UV irradiation of NH₂CHO

Figure 1 also presents the IR spectrum of NH₂CHO ice after exposure to UV photon fluence of 6.5×10¹⁸ photons cm⁻². The intensity decrease of the NH₂CHO IR bands indicates that the NH₂CHO ice was depleted. At the same time, several new bands appear in the spectrum. The most intense band at 2341 cm⁻¹
band is due to the asymmetric stretch mode of CO$_2$. The second most intense band at 2163 cm$^{-1}$ shows a good agreement with the expected frequency of the N=C=O asymmetric stretching mode of OCN$^-$ (Gerakines et al. 2004). The counter ion NH$_3^+$ was clearly identified from the very broad N-H IR bending mode feature around 1483 cm$^{-1}$ (Raunier et al. 2004a). Further evidence for the presence of NH$_3^+$ ion comes from the broad features at 3210 and 3065 cm$^{-1}$ overlapping with formamide N-H stretching modes. These peaks are in close agreement with the NH$_3^+$ peaks at 3206 and 3074 cm$^{-1}$ assigned previously by Brucato et al. (2006a).

At 2138 cm$^{-1}$, there is the symmetric stretch feature of CO which appears as a shoulder to the OCN$^-$ peak. The band observed at 2259 cm$^{-1}$ and a shoulder peak at the lower wavenumber side, centred around 2240 cm$^{-1}$, was assigned to the N=C=O asymmetric stretching mode of HNCO (Raunier et al. 2004b). The shoulder peak at 2240 cm$^{-1}$ could also be associated with the N=N stretching mode of N$_2$O (Brucato et al. 2006a). Furthermore, a shoulder peak at the higher wavenumber side of the 2259 cm$^{-1}$ band, centred around 2277 cm$^{-1}$, is attributed to $^{13}$CO$_2$ (Modica & Palumbo 2010). Within the errors, the natural abundance ratio of $^{13}$C:$^{12}$C = 0.011 is in agreement with the band area ratio of $^{13}$CO$_2$:12CO$_2$ = 0.015. A peak around 2100 cm$^{-1}$ has been assigned previously to the C=N stretching mode of HCN (Brucato et al. 2006a). The 2100 cm$^{-1}$ band is the second strongest IR band of pure solid HCN ice after 3115 cm$^{-1}$ (Couturier-Tamburelli et al. 2018), which has not been identified in the present experiment but could be obscured by the broad stretching band of N-H in NH$_2$CHO. Also, NH$_3$ has been tentatively identified after UV irradiation from the band present at 3375 cm$^{-1}$ due to N-H stretching based on the assignment by Brucato et al. (2006a). The band positions of the newly formed species are reported in Table 1. A control experiment was also performed where a bare substrate was subjected to the same UV photon fluences as NH$_2$CHO ice. In this case, a stretching mode for CO$_2$ was observed. At the maximum fluence, its intensity accounts for 12.5% of the CO$_2$ band observed in the formamide irradiation (see Fig. 1).

Figure 2 shows the evolution of normalised column densities, $\tau(t)$, of N-H, C-H, and C=O stretching modes of NH$_2$CHO as a function of UV photon fluence, $F_{UV}$. The experimental data was fitted following first order kinetic relation:

$$\tau(t) = [1 - a_1(1 - e^{-\sigma d t_F F_{UV}})],$$

The equation refers to the destruction with the boundary condition that considers a residual reactant for $F_{UV} = \infty$. Fits to the experimental data in Fig. 2 allowed us to estimate the cross-sections and asymptotic values for the NH$_2$CHO destruction ($\sigma d, a_1$). The destruction cross-section estimated from the three stretch modes are equal within the errors, suggesting that there is no difference in the chemical bond cleavage of corresponding functional groups upon irradiation by UV photons. This result differs from what we have found during H atoms exposure to NH$_2$CHO, where the C=H bonds are cleaved by H atom abstraction before the N-H bonds of the NH$_2$ group (Suhasaria & Mennella 2020). The estimated destruction cross-section was in agreement with the preliminary values obtained for formamide destruction by Ly$\alpha$ photons in an entirely different set-up (A. J. Escobar & A. Ciaravella, 2022, priv. comm.). The average of the three estimated asymptotic fit parameters $a_{N=H}, a_{CH}_1$, and $a_{CH}_2$ is 0.77 that corresponds to the destruction of 22.7 ML of the initial NH$_2$CHO ice. In the Ly$\alpha$ irradiation experiments of NH$_2$CHO deposited on a SiO$_2$ nanoparticles, after a UV photon fluence of 7x10$^{19}$ photons cm$^{-2}$, ca. 29% of the initial NH$_2$CHO ice was destroyed (Dawley et al. 2014b). On the other hand, ion irradiation of NH$_2$CHO leads to the destruction of 64 and 78% of the initial NH$_2$CHO molecules at fluences of 6.8x10$^{14}$ and 1.4x10$^{15}$ ions cm$^{-2}$, respectively (Brucato et al. 2006a).

The evolution of the column density of newly formed photo products normalised to the initial column density of NH$_2$CHO ice film as a function of UV fluence is shown in Fig. 3.

### Table 1. IR absorption band positions of pure NH$_2$CHO ice and the new species formed after the UV irradiation of NH$_2$CHO. Only the band strengths of those modes are reported when the respective column densities were evaluated.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Band position cm$^{-1}$</th>
<th>Vibrational mode</th>
<th>Band strength cm$^{-1}$ molecule$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$CHO</td>
<td>3355 ν$_s$ (N-H)</td>
<td>1.4 × 10$^{-16a}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3170 ν$_s$ (N-H)</td>
<td>4.7 × 10$^{-18}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2878 ν (C-H)</td>
<td>6.5 × 10$^{-17}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1690 ν (C=O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1631 δ (N-H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1386 δ$_s$ (C-H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1324 ν (CN)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>3375 ν (N-H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>3210 ν (N-H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3065 ν (N-H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1483 δ (N-H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2341 ν$_s$ (C-O)</td>
<td>7.6 × 10$^{-17b}$</td>
<td></td>
</tr>
<tr>
<td>$^{13}$CO$_2$</td>
<td>2277 ν$_s$ (C-O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNCO</td>
<td>2259 ν$_s$ (N=C=O)</td>
<td>7.2 × 10$^{-17c}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2240 ν$_s$ (N=C=O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCN$^-$</td>
<td>2163 ν$_s$ (N=C=O)</td>
<td>1.3 × 10$^{-16c}$</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2138 ν (C≡O)</td>
<td>1.1 × 10$^{-17d}$</td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>2100 ν (C≡N)</td>
<td>1.1 × 10$^{-17e}$</td>
<td></td>
</tr>
</tbody>
</table>

Notes. (a) The band strength corresponds to (ν$_s$ + ν$_v$). All the band strength values are taken from Brucato et al. (2006a). (b) Yamada & Person (1964) (c) Van Broekhuizen et al. (2004) (d) Jiang et al. (1975) (e) Gerakines et al. (2022)
band strength values used in the calculation of the individual column densities of the photo products are also listed in Table 1. Some photo products display similar behaviours while others vary drastically with the increasing $F_{\text{UV}}$. CO, OCN$^-$, and HNCO after UV irradiation of deposited NH$_2$CHO, followed by a decrease in their intensity at the highest fluence is also clearly visible in the difference IR spectra in Fig. 4. On the other hand, HCN shows a delayed formation with respect to CO, OCN$^-$, and HNCO, while HCN appears only after UV photon fluence of $1.9 \times 10^{18}$ photons cm$^{-2}$. CO, OCN$^-$ starts to increase rapidly. We can clearly see in Fig. 4 that CO$_2$ intensity at the highest UV fluence increases with respect to that at $1.9 \times 10^{18}$ photons cm$^{-2}$.

It is difficult to fit the abundance evolution of individual products over the entire UV fluence range by a single kinetic equation, due to the simultaneous formation and depletion behaviour. Therefore, following Chuang et al. (2021) a single first order kinetic relation was fitted to the cumulative abundance of all the photo products ($\chi(t)$):

$$\chi(t) = a_2(1 - e^{-\sigma t F_{\text{UV}}}),$$

where $\sigma_f$ is the formation cross-section and $a_2$ is the asymptotic formation. Fits to the experimental data allowed us to estimate the effective formation cross-section, $\sigma_f = 7.8 \pm 0.6 \times 10^{-19}$ cm$^2$, and the asymptotic value, $a_2 = 0.76 \pm 0.02$, for the product formation. The asymptotic value of total product formation with respect to the initial formamide column density exactly matches the average formamide destruction of 0.77. Of course, there could be other minor species produced in the irradiation experiment that have not clearly been identified by IR spectroscopy.

In the Ly$\alpha$ processing reactions of pure NH$_2$CHO ice deposited on SiO$_2$ nanopowder, cross-sections $\sigma_{\text{CO}} = 3.9 \times 10^{-20}$ and $\sigma_{\text{OCN}} = 3.6 \times 10^{-20}$ cm$^2$ were estimated for the formation of CO and OCN$^-$, respectively (Dawley et al. 2014a). Furthermore, in our previous study (Suhasaria & Mennella 2020) we
estimated the effective formation cross-section of HNCO due to H atoms exposure of formamide to be \( \sigma_{f,\text{HNCO}} = 4.4 \times 10^{-17} \) cm\(^2\). Therefore, for the sake of comparison, we tried to fit only the individual growth curves of CO, OCN\(^-\), and HNCO up to the UV fluence of 3.7\times10\(^{18}\) photons cm\(^{-2}\) using the same exponential equation as used for the cumulative growth. We derived the formation cross-sections of \( \sigma_{f,\text{CO}} = 1.5 \pm 0.1 \times 10^{-18} \), \( \sigma_{f,\text{OCN}^-} = 1 \pm 0.1 \times 10^{-18} \), and \( \sigma_{f,\text{HNCO}} = 4.2 \pm 0.5 \times 10^{-18} \) cm\(^2\) for CO, OCN\(^-\), and HNCO, respectively. The CO and OCN\(^-\) formation cross-sections are two orders of magnitude higher than those estimated by Dawley et al. (2014a). The above two experiments differ in surface temperature and the surface type that impacts the formation cross-section. Out of the two, the primary impact would be of the surface temperature since there is an increase in the radical recombination efficiency with temperature as radicals diffuse faster within the ice. This would result in lower formation of CO and OCN\(^-\) from NH\(_2\)CHO at a higher surface temperature. On the other hand, the impact of SiO\(_2\) nanoparticle surface could be less relevant since 600 ML thick ice was deposited on top of the surface for UV irradiation experiment. The HNCO formation cross-section that we derived in this experiment is an order of magnitude lower than that obtained previously by the exposure of H atoms on formamide (Suhasaria & Mennella 2020). The lower value of the HNCO formation cross-section can be taken as an indirect measure of the lesser stability of formamide under H atoms exposure compared to UV photons.

In Fig. 3, we see that the growth curves of all the photo products, apart from CO\(_2\), resemble a first-order kinetic behaviour, except for the very high fluences, which indicates that they must be formed directly from NH\(_2\)CHO. Furthermore, CO\(_2\) could have been formed by the effect of UV photons on CO and H\(_2\)O molecules formed in the reaction network (Watanabe & Kouchi 2002). This may explain why CO\(_2\) formation rate is low at the initial fluence and increases only when more CO is produced in the ice mixture. At the highest UV fluence, there is not only a small decrease in the intensity of NH\(_2\)CHO but also of all the newly formed photo products except CO\(_2\) and HCN. This suggests that in addition to NH\(_2\)CHO, there is a processing of those species produced in the ice mixture at the highest fluence, hinting that there is a complex reaction network at play. It is beyond the scope of the present work to decipher such a complex re-

**Fig. 3.** Evolution of normalised column density of different photo products with increasing UV photon fluence. The normalisation factor is the column density of NH\(_2\)CHO before UV irradiation. The IR absorption area is obtained by Gaussian fitting, with one standard deviation used as an error bar. When the error bar is not visible, the error is within the size of the symbol. The best fit to the cumulative abundance growth of the total product (solid black line) is also shown. The estimated formation cross-section \((\sigma_f)\) and asymptotic formation \((a_2)\) are also reported. Similarly, the best fit to the growth curves (till \(F_{UV} = 3.7\times10^{18}\) photons cm\(^{-2}\)) of CO, OCN\(^-\), and HNCO is also shown.
Three specific routes have been suggested for the formation of OCN\(^-\) in the condensed phase from the UV irradiation of NH$_3$CHO ice (Dawley et al. 2014a). The first is the direct photodissociation followed by ionisation reaction, the second is direct ionisation followed by ion-electron recombination and electron capture, and the third is a direct dissociative electron attachment (preceded by a direct excitation in formamide, indicated by an asterix):

\[
\text{NH}_3\text{CHO} \xrightarrow{\text{hv}} \text{OCN}^- + \text{H}_2 + \text{H}^+ ,
\]

\[
\text{NH}_3\text{CHO} \xrightarrow{\text{hv}} \text{NH}_2\text{CHO}^+ \rightarrow \text{OCN}^- + \text{H}_2 ,
\]

\[
e^- + \text{NH}_2\text{CHO} \rightarrow (\text{HNCHOH})^+ \rightarrow \text{OCN}^- + \text{H}_2 + \text{H} .
\]

Since we cannot rule out any possibilities, any of the three, or even all three, reactions could potentially yield OCN\(^-\) in our study.

4. Astrophysical implications

Solid-state abundances of NH$_3$CHO molecule can be predicted from gas-grain chemical models only when a complete picture of its formation and destruction under different conditions are taken into account. A knowledge of the corresponding rates related to the cross-sections is therefore necessary. Formamide ice could most likely be present in the dense interstellar cloud conditions not in a pure form but mixed with water or other interstellar ice components. However, formamide is more refractory than water or other volatiles, which means that small quantities of pure formamide ice could exist in elevated grain temperatures. In addition, to determine the extent of destruction under various energetic processing agents and to compare their effects, here we have considered a pure ice as done in previous studies. Dawley et al. (2014a) showed that H$_2$O plays a catalytic role by increasing the product formation when H$_2$O mixed NH$_3$CHO ice is exposed to Ly\(\alpha\) photons. However, the impact of other volatiles is still unknown and would require dedicated experiments to gain further insight.

In fact, in an earlier study, we derived the effective destruction cross-section, \(\sigma_{d,\text{eff}} = 3.0 \pm 0.6 \times 10^{-17}\text{ cm}^2\) for pure NH$_3$CHO due to thermal H atom exposure. This was found to be an order of magnitude lower than that derived for the destruction of formamide by 200 keV H\(^+\), simulating the effects of cosmic rays. Under the approximation of monoenergetic 1 MeV protons, a value of \(\sigma_{d,\text{eff}} = 3.7 \pm 0.4 \times 10^{-16}\text{ cm}^2\), was derived (G. A. Baratta & M. E. Palumbo, 2020, priv. comm.). Furthermore, due to the lack of experimentally derived NH$_3$CHO destruction cross-section under Ly\(\alpha\) (10.2 eV) photons, we made
the decision to derive only an upper limit value of the destruction cross-section, $\sigma_{UV} = 7.5 \times 10^{-16}$ cm$^2$. We argued that high energy protons would induce multiple bond breaking in the molecules along the “hot track” compared to a single photolysis step by Ly6 photons and therefore the UV destruction cross-section should be lower than that for energetic protons. In agreement with the above argument, we found that the UV destruction cross-section of formamide, $\sigma_{d,UV} = 1.9 \pm 0.2 \times 10^{-18}$ cm$^2$, estimated in the present work, is two orders of magnitude lower than that obtained for energetic protons. Moreover, $\sigma_{d,UV}$ is about ten times lower than $\sigma_{d,H}$, the destruction cross-section by H atoms (see Table 2).

The derivation of the cross-section further allowed us to evaluate the NH$_2$CHO destruction rate under UV photons in dense clouds and to compare it with the destruction rates induced by H atoms and cosmic rays. In the dense cloud cores, formamide ice should be shielded from the external UV radiation but there are locally produced UV rays resulting from cosmic-ray induced ionisation of hydrogen. The energy of the UV photons that impinge on the interior of dense clouds resembles the Ly6. Taking into account the UV photons flux of $4.8 \times 10^3$ cm$^{-2}$ s$^{-1}$ (Mennella et al. 2003) in those environments, the destruction rate of R$_6 = 9.1 \times 10^{-15}$ s$^{-1}$ was obtained. Although this rate was found to be an order of magnitude higher than the cosmic rays, the rate was still three orders of magnitude lower than that induced by H atoms. This means that H atoms induce the higher destruction efficiency in formamide compared to UV photons or cosmic rays in those environments. The destruction rates for formamide under different energetic processing are also given in Table 2.

5. Conclusions
This experimental study of Ly6 irradiation of NH$_2$CHO ice at 12 K under high vacuum conditions is intended to improve our understanding of its photo stability under dense cloud conditions. The UV photolysis results in the formation of new products: CO, NH$_3$, OCN$^-$, HCN, HNCO, and CO$_2$, which were identified by FTIR spectroscopy. The formation mechanism of other photo products is also discussed in this work. The destruction of N-H, C-H, and C=O functional groups in NH$_2$CHO occurred in a single step, unlike the case of H atom bombardment, as examined in our previous study. For the first time, the Ly6 destruction cross-section of NH$_2$CHO and the cumulative formation cross-section of different photo products have been estimated. The comparison of the destruction rate of NH$_2$CHO in dense clouds obtained in the present work with those induced by other processes indicates that interaction among H atoms remains the driving mechanism leading to the destruction of this molecule in those environments.

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References

1 The path of the swift ions through the ice film which gets locally heated from the energy of the ions.