Photodesorption of Acetonitrile CH$_3$CN in UV-irradiated Regions of the Interstellar Medium: Experimental Evidence

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Abstract

Pure acetonitrile (CH$_3$CN) and mixed CO:CH$_3$CN and H$_2$O:CH$_3$CN ices have been irradiated at 15 K with vacuum ultraviolet (VUV) photons in the 7–13.6 eV range using synchrotron radiation. VUV photodesorption yields of CH$_3$CN and of photoproducts have been derived as a function of the incident photon energy. The coadsorption of CH$_3$CN with CO and H$_2$O molecules, which are expected to be among the main constituents of interstellar ices, is found to have no significant influence on the VUV photodesorption spectra of CH$_3$CN, CHCN$,^+$, HCN, CN$,^+$, and CH$_3$. Contrary to what has generally been evidenced for most of the condensed molecules, these findings point toward a desorption process for which the CH$_3$CN molecule that absorbs the VUV photon is the one desorbing. It can be ejected in the gas phase as intact CH$_3$CN or in the form of its photodissociation fragments. Astrophysical VUV photodesorption yields, applicable to different locations, are derived and can be incorporated into astrochemical modeling. They vary from $0.67(\pm 0.33) \times 10^{-3}$ to $2.0(\pm 1.0) \times 10^{-3}$ molecule photon$^{-1}$ for CH$_3$CN depending on the region considered, which is high compared to other organic molecules such as methanol. These results could explain the multiple detections of gas-phase CH$_3$CN in different regions of the interstellar medium and are well correlated to astrophysical observations of the Horsehead nebula and of protoplanetary disks (such as TW Hya and HD 163296).

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Interstellar dust processes (838); Interstellar molecules (849); Interstellar medium (847); Dense interstellar clouds (371)

1. Introduction

Acetonitrile (CH$_3$CN) is a complex organic molecule (COM) regularly detected in several regions of the interstellar medium (ISM) at different stages of star formation (Purcell et al. 2006; Bergner et al. 2018; Calcutt et al. 2018; Liszt et al. 2018; Zeng et al. 2018). In the ISM, acetonitrile can be formed both by gas-phase reactions and by grain surface chemistry in icy mantles. In protoplanetary disks, pure gas-phase chemistry fails to explain the observed abundances of CH$_3$CN (Öberg et al. 2015; Loomis et al. 2018), indicating that its detection is intimately linked to processes associated with ices. In these disks, CH$_3$CN detection extends far from the central young stellar object (YSO), in regions where the temperature of the icy mantles is expected to be low enough ($T < 100$ K) so that gas-phase CH$_3$CN should accrete on the surface of the icy dust grains. The presence of CH$_3$CN in the gas phase therefore implies that a nonthermal process should maintain a sufficient amount of gas-phase CH$_3$CN via desorption from the surface of ice mantles. UV photodesorption of CH$_3$CN from ices, which is the desorption induced by the UV irradiation of ices, is so far the most important nonthermal process taken into account in disk modeling. In the case of the Horsehead nebula, for which the separation between the UV-illuminated photo-dominated region (PDR) and the UV-shielded dense core is easily made (Gratier et al. 2013; Guzmán et al. 2014), observations show that CH$_3$CN gas abundance is 30 times higher in the PDR region than in the dense core. As pure gas-phase reactions also fail to explain these abundances, UV photodesorption of CH$_3$CN from icy mantles is expected to play a major role in PDRs.

Recent experimental investigations on CH$_3$CN vacuum UV (VUV) photodesorption were conducted using an indirect method in the 7–10.2 eV range (Bulak et al. 2020). UV photodesorption of CH$_3$CN from pure CH$_3$CN ice was estimated to be $< 7.4 \times 10^{-4}$ molecule desorbed by incident photon. This study is so far the only constraint on the UV photodesorption of CH$_3$CN from pure CH$_3$CN ices. Several experimental studies regarding UV photodesorption of simple molecules such as CO, CO$_3$, N$_2$, or CH$_4$ (Bertin et al. 2013; Fillion et al. 2014; Carrascosa et al. 2019; Dupuy et al. 2017) and more complex molecules such as CH$_3$OH and H$_2$CO (Bertin et al. 2016; Martín-Domènech et al. 2016; Féraud et al. 2019) have shown that UV photodesorption yields are strongly dependent on the ice composition: e.g., when diluted in CO-dominated ices, CH$_3$OH UV photodesorption is quenched, whereas H$_2$CO UV photodesorption is enhanced, compared to the case of pure CH$_3$OH and H$_2$CO ice, respectively. This indicates that the UV photodesorption of complex molecules should be systematically studied as a function of the ice composition. This is even more relevant when considering that pure ices of organics are not likely to be found in the ISM. However, the exact role played by the ice composition is still difficult to predict a priori. We thus propose to provide absolute photodesorption yields in composite ices where the molecule to study is embedded in a CO or H$_2$O icy matrix. Those two kinds of ices can serve as models of the realistic icy mantles that could be found in the ISM, mainly composed of water, but which can also present a CO-rich phase in denser regions beyond the CO snowlines (Pontoppidan et al. 2003; Boogert et al. 2015).
In the present study, we quantify the VUV photodesorption, in the 7–13.6 eV range, of CH$_3$CN from pure CH$_3$CN ice and from CH$_3$CN mixed with or on top of CO and H$_2$O ices. VUV photodesorption yields of photoproducts are also derived. The yields are obtained as a function of the incident VUV photon energy, which allows us to discuss the physical mechanisms at play. Absolute VUV photodesorption yields applicable to astronomically relevant environments are also provided in order to be incorporated into astrochemical modeling. In Section 2, the experimental procedure is presented. In Section 3, the results and their astrophysical implications are discussed.

2. Methods

Experiments are conducted at the DESIRS beamline of the SOLEIL synchrotron facility (Nahon et al. 2012). The setting used on this beamline provides VUV photons in the energy range of 7–14 eV with a ∼1 eV bandwidth. The photon flux, measured with a calibrated silicon photodiode, depends on the photon energy. It varies from $6.3 \times 10^{14}$ photon s$^{-1}$ at 7 eV to $6.4 \times 10^{13}$ photon s$^{-1}$ at 14 eV. The beamline is equipped with a rare gas filter to suppress higher-energy harmonics from the undulator. The Surface Processes and ICES (SPICES) setup is connected to the synchrotron beamline to run the experiments. It consists of an ultrahigh vacuum chamber (base pressure $\sim 10^{-10}$ mbar) within which a rotatable copper substrate (polycrystalline oxygen-free high-conductivity copper) can be cooled down to 7–15 K by a closed-cycle helium cryostat. A tube positioned a few millimeters away from the substrate allows to inject a partial pressure of gas-phase molecules that will stick on the cold substrate, thus forming the molecular ices. During this process, the base pressure of the chamber is not significantly modified. The gaseous molecules used during these experiments were acetonitrile (CH$_3$CN; 99.8% purity, Sigma-Aldrich), carbon monoxide (CO; Air Liquide, 99.9%), and water (H$_2$O; liquid chromatography standard, Fluka). Liquid products (H$_2$O and CH$_3$CN) were further purified using several freeze–pump–thaw cycles. To form the mixed ices (CO:CH$_3$CN and H$_2$O:CH$_3$CN), the corresponding gaseous mixture is prepared in a gas-introduction system equipped with a capacitive pressure gauge before introduction into the experiment.

The ice thickness is expressed in monolayer (ML), roughly equivalent to a molecule surface density of $10^{13}$ molecules cm$^{-2}$. Prior to the synchrotron experiments, the temperature-programmed desorption (TPD) technique is used to calibrate the ice thickness. This calibration allows us to control the number of ML deposited onto the substrate with a relative precision of about 10% (Bertin et al. 2017). Pure CH$_3$CN ices (~60 ML) and mixed CO:CH$_3$CN (~100 ML) ices were formed at 15 K. Mixed H$_2$O:CH$_3$CN ices (~100 ML) were formed at 100 K and cooled down to 15 K before irradiation to ensure that the resulting water ice is in its compact amorphous phase. This phase is commonly referred to as compact amorphous solid water (c-ASW). 1 ML of CH$_3$CN was also deposited on pure CO ice (~30 ML) at 15 K and on pure H$_2$O ice (~30 ML) at 100 K, followed by a cooling down to 15 K.

The VUV beam is sent at a 45° incidence on the ice surface on a spot of $\sim 1$ cm$^2$. While the ices are irradiated, the photodesorption of neutral species is monitored by recording the desorbed molecules in the gas phase using a quadrupolar mass spectrometer (QMS) equipped with an electron-impact ionization chamber at 70 eV. Each gas-phase species is probed by monitoring the mass signal of its corresponding intact cation. Typical desorption signals (raw data) are shown in Appendix A. At the end of the irradiation procedure, TPD experiments (from 15 to 200 K with a ramp of 12 K min$^{-1}$) are performed to evaporate all molecules from the substrate before a new ice is formed. These TPD experiments have also been used to investigate any photochemistry (see Appendix B). The photodesorption yields presented in this article (in molecule desorbed per incident photon, displayed as molecule photon$^{-1}$ for more simplicity in the following) are derived from the raw desorption signals given by the QMS on the considered mass channel. A detailed explanation is provided in Appendix A. The mixture ratios used for the mixed ices were chosen to progressively study the impact of the dilution of CH$_3$CN in CO or H$_2$O ices on the photodesorption yields but may not be representative of the interstellar ice analogs that could be found in the ISM.

3. Results and Discussion

3.1. Pure Acetonitrile Ice

In Figure 1, we present the VUV photodesorption spectra derived from our experiments on pure CH$_3$CN ices and we also compare these spectra with the VUV absorption spectrum (in the 7–11.2 eV range) of pure CH$_3$CN ice at 10 K from Sivaraman et al. (2016). The attribution of photoproducts to the mass channels is discussed in the following. The VUV photodesorption of masses 15 and 26 is attributed to CH$_3$ and CN$^-$, respectively, which are expected to be direct UV photodissociation products of CH$_3$CN. This is consistent with the UV photodissociation of gas-phase acetonitrile for which C–C bond breaking is observed (Moriyama et al. 1998; Kanda et al. 1999). HCN and CH$_4$ are observed as major photoproducts in VUV photolysis experiments of pure CH$_3$CN ice at 20 K (Bulak et al. 2021) and 12 K (Hudson & Moore 2004). Accordingly, we attributed masses 16 and 27 to CH$_4$ and HCN photodesorption, respectively. HCN was also proposed as a possible direct UV photodissociation product of CH$_3$CN in gas phase by Schwell et al. (2008). We assumed that mass 39 corresponds to CHCN$^+$ photodesorption. Based on gas-phase experiments for which H-loss reaction is assumed to occur for the UV photodissociation of CH$_3$CN (Moriyama et al. 1998; Schwell et al. 2008), the detection of CHCN$^+$ in our experiment could be expected to come from dehydrogenation of CH$_3$CN induced by VUV photoabsorption. A raw photo-desorption signal was detected on mass 40, which could correspond to the desorption of CH$_2$CN$.^+$. However, when considering the fragmentation of mass 41 (CH$_3$CN) into mass 40 (CH$_2$CN$^+$) in the ionization chamber of our QMS, the corrected signal on mass 40 falls below our detection limit so that we can only provide an upper limit of $\sim 1 \times 10^{-6}$ molecule photon$^{-1}$ for the VUV photodesorption yield of CH$_2$CN$^+$ from pure acetonitrile ices (this is also the case for the binary mixed ices in Section 3.2).

Additionally, Hudson & Moore (2004) have observed the isomerization of CH$_3$CN into CH$_2$NC during VUV irradiation (with a hydrogen lamp) of pure CH$_3$CN ice at 12 K. This isomerization was detected by infrared via the $\sim$N=C stretching mode at 2170 cm$^{-1}$. From Hudson & Moore (2004), we could expect to have only a few percent of CH$_3$CN isomerization during our irradiation experiments and we did not observe the $\sim$N=C stretching mode by infrared on pure
CH$_3$CN ices (this is also the case for the binary mixed ices in Section 3.2). Therefore, we made the assumption that the VUV photodesorption of mass 41 in our experiments is dominated by CH$_3$CN desorption rather than CH$_3$NC. The isomerization of HCN into HNC was not observed by Hudson & Moore (2004), and accordingly, we estimated that the VUV photodesorption of mass 27 in our experiments is dominated by HCN desorption and not its isomer HNC.

Mass 30 was attributed to C$_2$H$_6$ desorption, assumed to originate from radical–radical reaction between CH$_3$• molecules, based on low-energy electron irradiation experiments of pure CH$_3$CN ices (Ipolyi et al. 2007; Bass et al. 2012). Mass 28 is the most desorbing one in our experiments. It could be attributed to N$_2$, H$_2$CN, and/or C$_2$H$_4$ VUV photodesorption. Post-irradiation TPD experiments have also revealed a mass 28 desorption feature that peaks below 40 K, the intensity of which increases with the total irradiation fluence, and is not observed on nonirradiated ices (see Appendix B). This indicates that the irradiation also implies the accumulation of the associated species onto the ice during irradiation. Among all the possible candidates at the origin of the mass 28 channel, the low desorption temperatures points toward its association with N$_2$ (sub)monolayer desorption (Collings et al. 2004; Smith et al. 2016). Accordingly, we assumed that the photodesorption of mass 28 from pure CH$_3$CN ice was dominated by N$_2$. The formation of N$_2$ might result from photochemistry involving CN•, which is left in electronically excited states (A $^2\Pi$, $^2\Sigma^+$) after dissociation of CH$_3$CN according to gas-phase experiments (Schwell et al. 2008).

The VUV photodesorption spectra of the species presented in Figure 1 have the same dependence in energy: the photodesorption efficiency is increasing from 7 to 10–10.5 eV and seems to be constant above 10.5 eV. The small variations above this energy are significantly lower than the error bars, and cannot be confidently considered as a “real” modification of the photodesorption yields. In Figure 1, we can also see that there is a good correlation between the VUV absorption spectrum of CH$_3$CN ice and the VUV photodesorption spectra of the different molecules presented. The similarities between these spectra indicate that the photodesorption of these species originates from the same phenomena, which is the VUV absorption of CH$_3$CN in the condensed phase. Concerning the photodesorption efficiencies, they range from $\sim 1.2 \times 10^{-5}$ molecule photon$^{-1}$ for CHCN• to $\sim 1.6 \times 10^{-3}$ molecule photon$^{-1}$ for N$_2$, around 10.5 eV. Finally, the VUV photodesorption yield of intact CH$_3$CN is $\sim 2.5 \times 10^{-5}$ molecule

Figure 1. VUV photodesorption spectra (squares with error bars), as a function of the incident photon energy, of CH$_3$CN (mass 41), CHCN (mass 39), C$_2$H$_6$ (mass 30), N$_2$ (mass 28), HCN (mass 27), CN (mass 26), CH$_4$ (mass 16), and CH$_3$ (mass 15) from pure CH$_3$CN ice at 15 K. Each mass channel is corrected from the cracking of higher-mass fragmentation in the mass spectrometer. The attribution of species to the mass channels is discussed in Section 3.1. In each panel, we also displayed in red dashed lines the VUV absorption spectrum of CH$_3$CN ice at 10 K (in arbitrary units) from Sivaraman et al. (2016).
photon$^{-1}$ at 10.5 eV. Our results compare very well to the recent study of Bulak et al. (2020), who could not measure directly the photodesorption yield of CH$_3$CN from pure CH$_3$CN ice but provided an upper limit of 7.4 x 10$^{-4}$ molecule photon$^{-1}$, compatible with our measurements.

### 3.2. Binary Ices

In Figure 2, we summed up our results on CH$_3$CN, HCN, and CN$^+$ photodesorption from the binary ices tested: mixed CH$_3$CN:CO ice, mixed CH$_3$CN:H$_2$O ice, and layered ices (~1 ML of CH$_3$CN on top of pure CO and on top of pure H$_2$O ice). For the specific case of CH$_3$CN photodesorption from a mixed CH$_3$CN:CO (1:7) ice, the yields above 10.5 eV are not shown for more visibility because of the large error bars. In addition to the presented molecules in Figure 2, we searched for the desorption of masses 42, 43, 45, and 52 that could correspond to CNO$^+$, HCON, NH$_2$CHO (formamide), and C$_2$N$_2$, respectively. However, the signals on these channels were too noisy to derive a photodesorption yield and we can only provide an upper limit of 5 x 10$^{-6}$ molecule photon$^{-1}$ for these masses. The photodesorption data for masses 30, 28, and 16 in the case of the mixed ices are displayed in Appendix C. The desorption signals for masses 30 and 28 are significantly higher in the case of mixed CH$_3$CN:CO ices compared to the case of mixed CH$_3$CN:H$_2$O ice. This is due to a contribution of CO photodesorption for the mass signal 28 and most probably H$_2$CO and/or NO photodesorption for the mass signal 30 in the case of mixed CH$_3$CN:CO ices. The desorption signal on mass 16 is not significantly dependent on the presence of CO or H$_2$O molecules in the ice, but a possible contribution of atomic O photodesorption to this mass signal prevents us from precisely quantifying a possible VUV photodesorption of CH$_4$ from the mixed ices.

We do not observe a significant influence of the presence of H$_2$O and CO molecules on the shape of the VUV photodesorption spectra for the presented molecules in Figure 2 (CH$_3$CN, HCN, and CN$^+$). A similar behavior is observed for masses 15 and 39 that can be unambiguously attributed to CH$_3$ and CHCN$^+$ (see Appendix C). In similar experiments, indirect desorption mechanisms have been observed in the case of simpler molecules such as N$_2$ or CH$_4$ deposited on top of pure CO ice (Bertin et al. 2013; Dupuy et al. 2017), “pre-irradiated” pure CO$_2$ ice (Fillion et al. 2014), or N$_2$, CO, Kr, and Ar on top of pure water c-ASW ice (Dupuy et al. 2021). In these cases, the desorption of one molecule is induced by the UV photoabsorption of another one whose excited state relaxation induces an energy transfer to the desorbing molecule. Experimentally, this

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**Figure 2.** VUV photodesorption spectra, as a function of the incident photon energy, of CH$_3$CN (mass 41) from mixed CH$_3$CN:CO and mixed CH$_3$CN:H$_2$O ices (top left panel) and from 1 ML of CH$_3$CN on top of CO and on top of H$_2$O ice (top right panel). VUV photodesorption of HCN (mass 27) and CN (mass 26) from mixed CH$_3$CN:CO and CH$_3$CN:H$_2$O ices are presented in the bottom panels. These yields were derived for ices at 15 K.
results in similarities between the VUV photodesorption spectrum of the molecule considered and the VUV absorption spectrum of CO or H$_2$O in condensed phase. In the case of more complex molecules, such as CH$_3$OH, this indirect mechanism was not observed (Bertin et al. 2016). In our CH$_3$CN experiments, the VUV photodesorption spectra of CH$_3$CN, CHCN*, HCN, CH$_3$*, and CN* from the mixed and layered ices do not show any similarities with the UV absorption profile of CO or H$_2$O molecules in condensed phase. These data are compared for the case of CH$_3$CN UV photodesorption from the layered ices in Figure 3. It is however surprising to observe that the VUV photodesorption yields of CH$_3$CN from CO-dominated ices are similar (when considering the error bars) between the 1:2 and 1:7 ratios (see Figure 2, upper left panel). As CH$_3$CN is more diluted in the CH$_3$CN:CO—1:7 ices, we would have expected to obtain a lower yield compared to the case of the CH$_3$CN:CO—1:2 ice. The fact that there is no clear signature of the CO UV absorption spectrum between 7.5 and 9.5 eV in the photodesorption spectrum of CH$_3$CN from CH$_3$CN (1 ML) on top of CO ice (see Figure 3) seems to exclude the possibility of a significant indirect desorption mechanism induced by CO molecules when the CH$_3$CN surface concentration is high.

However, for higher dilution of CH$_3$CN in a CO environment, a desorption of CH$_3$CN triggered by the excitation of the CO matrix cannot be totally ruled out. The similarities of the photodesorption yields of CH$_3$CN from CO-dominated ices for the 1:2 and the 1:7 ratios could also be explained by less bounded CH$_3$CN molecules in CO-dominated ices but this point would need additional experiments in lower concentration regimes to conclude. Finally, an indirect desorption mechanism induced by CO or H$_2$O molecules does not seem to be at play or significant in our set of experiments for the desorption of the molecules cited above (CH$_3$CN, CHCN*, HCN, CH$_3$*, and CN*) from CH$_3$CN-containing ices.

The absolute values of the VUV photodesorption yields of CH$_3$CN, CHCN*, HCN, CH$_3$*, and CN* from the binary mixed ices are slightly diminished compared to the case of pure CH$_3$CN ice, but this effect is not significant when considering the error bars and could be explained by a lower number of CH$_3$CN molecules available for desorption at the ice surface, inducing a lower desorption flux in the case of mixed ices. The deposition technique (mixed ices or layered ices) does not have a significant influence on the VUV photodesorption of these molecules either. The photodesorption yields of CH$_3$CN from 1 ML of CH$_3$CN on top of CO or H$_2$O ice are about half of that from pure CH$_3$CN ice, which could be due to the fact that several CH$_3$CN-containing layers are involved in the desorption of CH$_3$CN from pure CH$_3$CN ice. It is more likely that the VUV photodesorption of CH$_3$CN, CHCN*, HCN, CH$_3$*, and CN* from the ices tested (pure, mixed, and layered ices) occurs via a process for which the CH$_3$CN molecule that absorbs the VUV photon is the one desorbing. It can be ejected as intact CH$_3$CN or in the form of its photodissociation fragments. The desorption of CH$_3$CN may involve dissociation and exothermic recombination of the excited molecule. According to our results, this process seems to be independent of the presence of CO or H$_2$O molecules surrounding the VUV absorbing CH$_3$CN molecule in the ice.

### 3.3. Astrophysical Implications

By integrating our experimental photodesorption spectra with UV spectra that are representative of the UV fields found in different regions of the ISM, we are able to provide photodesorption yields that are suitable for astrophysical environments. The UV fields used were the UV emission spectra of a classical T Tauri star representative of protoplanetary disks (France et al. 2014), the UV field produced by cosmic-ray secondary electrons representative of dense interstellar clouds (Gredel et al. 1987), and the UV interstellar radiation field (ISRF) from Mathis et al. (1983). The resulting yields are presented in Table 1 and can be incorporated in astrochemical modeling. As discussed previously, we found that the VUV photodesorption of CH$_3$CN and what is associated with its photofragments (CHCN*, HCN, CN*, and CH$_3$*) does not strongly depend on the presence of CO or H$_2$O molecules in the ice, which are expected to be among the main constituents of ices in the ISM (Boogert et al. 2015). Accordingly, we took the photodesorption spectra from pure CH$_3$CN ice (Figure 1) to derive the yields presented in Table 1, which are thus assumed to be applicable to any CO- or H$_2$O-dominated ices containing CH$_3$CN molecules. The yields corresponding to protoplanetary disks and dense interstellar clouds are found to be identical within the error bars and are approximately equal to the experimental yields at the Lyman $\alpha$
around 10.2 eV (Figure 1), as it is the energy that dominates the UV field in these regions. The yields corresponding to the ISRF are found to be lower due to a higher contribution of the UV field at low energy (<10 eV) where photodesorption is less efficient. Interestingly, the desorption of CH3CN and its photofragments are found in the same order of magnitude in the region considered. The desorption of masses 30, 28, and 16 from the mixed ices will not be discussed in this section as it is not possible to clearly attribute species to these mass channels (see Section 3.2). Moreover, the formation of the associated species (N2, C2H4, and CH4) has more likely involved the absorption of at least two UV photons, in a limited time and spatial interval for the resulting radicals to react. This makes their possible experimental desorption not astrophysically relevant when considering the very low UV flux observed in the discussed regions of the ISM compared to our experimental UV flux.

As stated in the 1, the astrophysical observations of gas-phase acetonitrile (CH3CN) and of gas-phase methanol (CH3OH) in the Horsehead UV-illuminated PDR and UV-shielded dense core region show that UV photodesorption of these molecules from icy grains should play a significant role (Gratier et al. 2013; Guzmán et al. 2014). A quantitative comparison of CH3OH and CH3CN abundances in this region is to be put in contrast with our experimental results. According to Gratier et al. (2013) and Guzmán et al. (2014), CH3CN abundances are found to be similar between the PDR and the dense core region, whereas CH3CN is 30 times more abundant in the PDR than in the dense core region. In the PDR, CH3OH is found to be less abundant than CH3CN by approximately one order of magnitude. Among the possible mechanisms that could explain these observations, our experiments clearly point toward a higher quantitative role of CH3CN VUV photodesorption compared to the case of CH3OH VUV photodesorption. In fact, we found that VUV photodesorption of CH3CN is not significantly dependent on the ice composition and is above 10^-5 molecule photon^-1, whereas, in similar experiments (Bertin et al. 2016), CH3OH VUV photodesorption is not detected when methanol is mixed with CO ice (only an upper limit of 10^-6 molecule photon^-1 has been derived).

The higher VUV absorption cross section of CH3CN compared to CH3OH (based on gas-phase absorption cross sections; Cheng et al. 2002; Schwell et al. 2008) along with the resilience of nitriles to UV photolysis, which has been demonstrated in the case of acetonitrile versus acetic acid in pure ices at 15 K (Bernstein et al. 2004), could be an interesting route to explain these experimental results.

Our experimental results may also explain the astrophysical observations of gas-phase CH3CN and CH3OH in protoplanetary disks. In the case of the protoplanetary disk around the T Tauri star TW Hya, gas-phase abundances of CH3CN and CH3OH are found to be similar (Walsh et al. 2016; Loomis et al. 2018), whereas in the case of the disk around the Herbig Ae star HD 163296, CH3CN is strongly detected and CH3OH emission lines are below the detection limits (Bergner et al. 2018; Carney et al. 2019). As suggested in Bergner et al. (2018), Herbig Ae stars are expected to be stronger UV emitters than T Tauri stars. Therefore, the role of VUV photodesorption of CH3CN and CH3OH from interstellar ices has been raised by Bergner et al. (2018) as a possible candidate to explain these differences in the observations of these COMs in protoplanetary disks. Our experimental results, which show a higher VUV photodesorption efficiency of CH3CN from interstellar ice analogs, by at least one order of magnitude, compared to that of CH3OH, clearly support the assumption of Bergner et al. (2018). However, the VUV photodesorption yields of COMs used in disk modeling are often higher than the experimental ones (e.g., Loomis et al. 2018 considered a CH3CN VUV photodesorption yield of 10^-3 molecule photon^-1 in their modeling of the TW Hya disk), and other processes may be of importance to explain the detection of gaseous COMs in these regions (Dupuy et al. 2018; Dartois et al. 2019; Ciavarella et al. 2020; Basalgête et al. 2021a, 2021b).

In this experimental study, we derived a CH3CN VUV photodesorption yield of ~2.5 x 10^-5 molecule photon^-1 at 10.5 eV. This photodesorption was observed to be independent of the presence of CO and H2O molecules in the ice, which are expected to be among the main constituents of interstellar ices. Interestingly, CH3CN VUV photodesorption is found to be more efficient than CH3OH VUV photodesorption (Bertin et al. 2016) by at least one order of magnitude. This shows that the VUV photodesorption of organics from interstellar ices cannot be so far extrapolated from the specific case of one organic molecule. The results obtained from our experiments could participate in explaining the multiple detections of CH3CN in UV-irradiated regions of the ISM, especially in the case of protoplanetary disks (Bergner et al. 2018; Loomis et al. 2018) and in the case of the Horsehead nebulae (Gratier et al. 2013; Guzmán et al. 2014).

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### Appendix A

**Derivation of the VUV Photodesorption Yields and Determination of the Error Bars**

The photodesorption yields presented in this article (in molecule desorbed per incident photon, displayed as molecule photon^-1 for greater simplicity) are derived from the raw desorption signals given by the QMS on the considered mass

| Photodesorbed Species | ISRF (a) | Dense Clouds and Disks (b) |
|-----------------------|----------|---------------------------|
| CH3CN                 | 0.67 ± 0.33 | 2.0 ± 1.0 |
| CHCN                  | 0.34 ± 0.17 | 1.0 ± 0.5 |
| HCN                   | 1.1 ± 0.6 | 3.3 ± 1.7 |
| CN                    | 0.60 ± 0.30 | 1.7 ± 0.9 |
| CH3                   | 2.1 ± 1.0 | 6.5 ± 3.3 |

*Note. (a) UV field from Mathis et al. (1983). (b) UV field from Gredel et al. (1987). (c) UV field from France et al. (2014).*
channel, using the following formula:

\[ \Gamma_X(E) = k_X \times \frac{I_X(E)}{\phi(E)}, \tag{A1} \]

where \( X \) is the neutral species associated with the mass channel considered, \( E \) is the photon energy, \( \Gamma_X(E) \) is the photodesorption yield of \( X \) at \( E \), \( I_X(E) \) is the current given by the QMS for the considered mass channel during the irradiation at \( E \), \( \phi(E) \) is the photon flux at \( E \), and \( k_X \) is a proportionality factor between the molecular desorption flux and the QMS signal. The ices studied in this article were sequentially irradiated during a few seconds at several fixed energies while the desorbing masses are continuously recorded by the QMS. Examples of typical signals obtained from the QMS are shown in Figure 4 where the sudden increase and decrease of the mass signals are associated with the opening (irradiation) and closing (background) of the beamline shutter, respectively. For each photon energy and each species, \( I_X(E) \) is derived by computing the height of the mass signal with respect to the background level for the irradiation step considered. For molecules that could originate from the cracking of their desorbing parent molecules in the ionization chamber of the QMS, \( I_X \) is corrected accordingly by using the cracking patterns available on the National Institute of Standards and Technology (NIST) chemistry Webbook.

The proportionality factor \( k_X \) in Equation (A1) is first calibrated using the photodesorption of CO (\( k_{CO} \)): a VUV photodesorption spectrum of CO from pure CO ice is obtained by irradiating a pure CO ice (30 ML) previously grown at 15 K in the experiment and it is compared to a reference VUV photodesorption spectrum obtained at higher spectral resolution (Fayolle et al. 2011). \( k_{CO} \) is deduced by matching the two spectra after taking into account the \( \sim 1 \) eV width of the photon energy profile used in the present study. The proportionality factors corresponding to neutral species other than CO are then computed by taking into account the differences in electron-impact ionization cross sections and apparatus functions of the mass filter, resulting in the following formula:

\[ k_X = \frac{\sigma(\text{CO}^+/\text{CO})}{\sigma(\text{X}^+/\text{X})} \times \frac{AF(X)}{AF(\text{CO})} \times k_{CO}, \tag{A2} \]

where \( AF(X) \) is the apparatus function of our QMS for the given species \( X \) and \( \sigma(\text{X}^+/\text{X}) \) is the nondissociative electron-impact ionization cross section for the \( X \) neutral species. These cross sections are taken at 70 eV and are available in the literature for CH\(_3\)CN (Zhou et al. 2019), C\(_2\)H\(_6\) (Chatham et al. 1984), N\(_2\) (Straub et al. 1996), HCN and CN (Pandya et al. 2012), CH\(_4\) (Tian & Vidal 1998), and CH\(_3\) (Tarrovsky et al. 1996). Due to the absence of available data, the nondissociative electron-impact ionization cross section of radical CHCN,
σ(CHCN+/CHCN), was assumed to be equal to the one of CH3CN, σ(CH3CN+/CH3CN). The apparatus function \(AF(X)\) describes the transmission of the quadrupolar mass filter in the QMS for a fragment with a given mass \(m\), and thus participates, together with the ionization cross section, to the detection efficiency of a given species. For our instrument, the apparatus function has been measured and follows a power law: \(AF(X) = (m/28)^{1.77}\).

The uncertainty associated with \(I_X(E)\), \(\delta I_X(E)\), depends on the signal-to-noise ratio and is estimated as the sum of the half-height of the signal noise in the background, and on the top of each peak for the corresponding irradiation step (see Figure 4).

The error bars associated with the photodesorption yields for each energy and each species, \(\delta \Gamma_X(E)\), and displayed in Figures 1, 2, and 3 are derived from the following equation:

\[
\delta \Gamma_X(E) = k_X \times \frac{\delta I_X(E)}{\phi(E)}
\]  

Equation (A3) results in experimental error bars that depend on the photon energy. Consequently, these error bars are usually larger at high energy due to a lower photon flux. Finally, these error bars only reflect the quality of the recorded signals and do not take into account the uncertainty associated with the calibration of \(k_X\), which is systemic. This uncertainty is not impacting the shape of the UV photodesorption spectra but only the uncertainty on the absolute values of the photodesorption yields. It mainly depends on the uncertainties associated with the apparatus function of the QMS and on the ionization cross sections \(\sigma(X^{+}/X)\). We estimate this uncertainty to be in the order of magnitude of 50% relative to the measured photodesorption yields.

**Appendix B**

**Attribution of the Desorbing Mass 28 Channel Using TPD**

As stated in the main text, each studied ices, after one or several irradiations, i.e., energy scans between 7 and 14 eV, were further probed using the temperature-programmed desorption (TPD) technique. To this end, the ices were warmed up using a constant heating rate of 12 K minute\(^{-1}\), and the desorbed species were detected concomitantly using mass spectrometry. TPD has been in particular used in order to identify the origin of mass channel 28 detected during photodesorption. Figure 5 presents several TPD curves associated with mass channel 28 performed from irradiated CH3CN ices. As one can see from these curves, the majority of the desorption occurs below 40 K, with an onset of desorption at around 25–27 K. Such a low-temperature desorption is usually characteristic of the desorption of very volatile species, and matches very well the thermal desorption of a small quantity of N\(_2\) deposited onto metallic substrates or water ice substrates (see, e.g., work from Collings et al. 2004 and Smith et al. 2016). The other feature observed at higher temperature is in fact associated with the desorption of N\(_2\) trapped into the CH3CN bulk, which is suddenly released when the ice is sublimated.

Since the mass 28 signal desorption rises with the irradiation fluence, we attributed this TPD feature to the accumulation of N\(_2\) onto or into the ice during the irradiation. And thus we believe that the photodesorbed mass 28 signal should also be due to some N\(_2\) desorption subsequent to its formation. It should be noted, however, that TPD is not in itself sufficient to be categorical on this attribution, since, for instance, C\(_2\)H\(_4\) could also contribute to this mass 28 signal, even if it should be observed at slightly higher temperature. Finally, any possible uncontrolled pollution by another species, such as CO, has been ruled out by (i) blank experiments, (ii) the correlation with the photon fluence, and (iii) the fact that no CO vibration could have been detected using in situ infrared spectroscopy on the irradiated samples. Mass signal 14 was not monitored during the TPD experiments, which prevents us from definitively concluding on the origin of mass 28 thanks to a possible fragmentation of N\(_2\) into N. Mass signal 14 was, however, detected during photodesorption experiments, but it was high...
enough so that the possible fragmentation of \( \text{N}_2 \) into \( \text{N} \) in the ionization chamber of our QMS has no significant impact on its amplitude, which also prevents us from definitively concluding. The photodesorption of this mass 14 is therefore due to either \( \text{CH}_2 \) radical or atomic \( \text{N} \) photodesorption.

Appendix C

UV Photodesorption Yields of Masses 39, 30, 28, 16, and 15 from Binary Ices at 15 K

In Figure 6, we display the VUV photodesorption yields of \( \text{CHCN}^* \) and \( \text{CH}_3^* \) from the mixed \( \text{CH}_3\text{CN}:\text{CO} \) and \( \text{CH}_3\text{CN}:\text{H}_2\text{O} \) ices tested. In Figure 7, we display the VUV photodesorption yields of the masses 30, 28 and 16 from the mixed \( \text{CH}_3\text{CN}:\text{CO} \) and \( \text{CH}_3\text{CN}:\text{H}_2\text{O} \) ices tested. These yields are discussed in the Section 3.2.

Figure 6. VUV photodesorption spectra, as a function of the incident photon energy, of \( \text{CHCN}^* \) (mass 39) and \( \text{CH}_3^* \) (mass 15) from mixed \( \text{CH}_3\text{CN}:\text{CO} \) and mixed \( \text{CH}_3\text{CN}:\text{H}_2\text{O} \) ices.

Figure 7. VUV photodesorption spectra, as a function of the incident photon energy, of masses 30, 28, and 16 from mixed \( \text{CH}_3\text{CN}:\text{CO} \) and mixed \( \text{CH}_3\text{CN}:\text{H}_2\text{O} \) ices. The attribution of species to these mass channels is not possible. This is discussed in Section 3.2.
