SOFT X-RAY IRRADIATION OF METHANOL ICE: IMPLICATION FOR H$_2$CO FORMATION IN INTERSTELLAR REGIONS

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ABSTRACT

We performed 0.3 keV soft X-ray irradiation of a methanol ice at 8 K under ultra-high vacuum conditions. To the best of our knowledge, this is the first time that soft X-rays are used to study photolysis of ice analogs. Despite the low irradiation dose of 10^{-6} photons molecule^{-1}, the formation of formaldehyde has been observed. The results of our experiments suggest that X-rays may be a promising candidate to the formation of complex molecules in regions where UV radiation is severely inhibited.

Key words: ISM: molecules – methods: laboratory – X-rays: ISM

1. INTRODUCTION

Organic molecules of considerable complexity have been found in dark interstellar clouds and in localized regions in hot cores, protoplanetary nebulae and disks, and circumstellar envelopes (Dalgarno 2006, and references therein). In particular, there exist substantial column densities of large partly hydrogen-saturated molecules, many of them being of pre-biotic interest (Snyder 2006). These species challenge the completeness of the standard ion–neutral scheme in interstellar chemistry, suggesting that reactions on dust grains are involved in their formation. Unfortunately, reaction pathways leading to the formation of such complex molecules are largely unknown. Surface migration on icy grains involves the overcoming of large diffusion barriers, making this process inefficient at temperatures in the 10–20 K range for species other than hydrogen. Therefore, diffusion-limited mechanisms on grain surfaces may hardly lead to the formation of complex organic molecules (Leitch-Devlin & Williams 1984). However, dust icy mantles within dense molecular clouds may be subject to irradiation by UV photons as well as cosmic rays. Such an ionizing radiation field might chemically modify the pristine ices as condensed onto interstellar grains, producing a significant increase in the complexity of the photolyzed mixtures, as it has been shown in laboratory experiments (e.g., Muñoz Caro et al. 2002; Bernstein et al. 2002).

Extremely detailed computational models by Herbst, Garrod, and their collaborators (e.g., Garrod et al. 2008) simulating the chemistry that may arise from the production of mobile radicals within interstellar ices predict that a rich and relatively complex chemistry can slowly arise in the low temperature ices. Then, when the ices are evaporated in the very dense and warm gas in the vicinity of a newly forming star, these complex molecules are released to the gas phase. Thus, both the cold early stages of star formation and the following warm-up to the final hot-core phase are involved (Herbst & van Dishoeck 2009).

However, during the phase in which the cloud core collapses and the star is still deeply embedded, the UV radiation density in the gas is drastically reduced, and the dominant ionizing source is X-rays. Indeed, unless a low-density region allows UV radiation to escape from the innermost region of the envelope, its influence on the chemistry is restricted to a small volume surrounding the star (e.g., Stäuber et al. 2004). In addition, in young stars, X-rays may dominate the high-energy emission. In the case of a solar-type star of 100 Myr old, the X-ray flux is larger than the extreme UV, and it remains within a factor of two up to 1 Gyr old (Ribas et al. 2005). Such a copious hard emission must affect the chemistry of interstellar material.

A first molecular generation of limited complexity may be achieved in the interstellar medium on cold dust surfaces, e.g., methanol via surface hydrogenation of accreted carbon monoxide. CH$_3$OH is regarded as an important starting point in the formation of more complex species (Öberg et al. 2009). In this Letter, we present the results of soft X-ray irradiation of a methanol ice. The experiments have been performed at the Interstellar Astrochemistry Chamber (ISAC) and analysis of the products has been obtained by in situ infrared and quadrupole mass spectroscopy. According to our results, soft X-rays appear to be effective in the production of H$_2$CO.

Absorption of X-rays by an icy mixture involves the excitation of core electrons and ionization continua, leading to multiple ionizations. The net resulting quantum yields for photon-induced chemical reactions are expected to be high. We perform the experiments using a low-intensity X-ray source to obtain more realistic astrophysical conditions. We use radiation of 0.3 keV, the energy at which the quiet X-ray emission of the Sun peaks. In Section 2 we describe the experimental setup, and in Section 3 we present the results. The discussion of results is presented in Section 4. In Section 5, we discuss the astrophysical implications.

2. EXPERIMENT

The irradiation experiments are carried out with ISAC, which is designed for the characterization of ices in interstellar and circumstellar environments, and the study of their evolution due to vacuum–UV, cosmic-ray irradiation, or thermal processing. ISAC is an ultra-high vacuum setup with pressure down to $(2.5–4.0) \times 10^{-11}$ mbar, where an ice layer made by the deposition of a gas mixture onto an IR-transparent CsI window mounted on a cold finger at 8 K, achieved by means
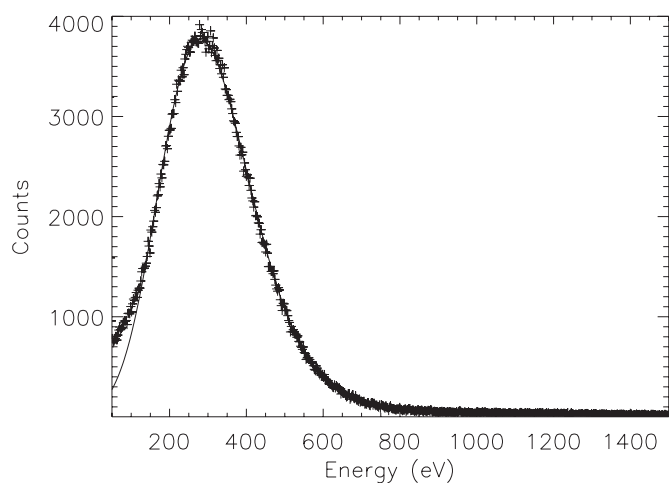
Figure 1. X-ray spectrum of the C anode used for the irradiation of the sample. The crosses are the experimental data, while the solid curve is the two components' fit corresponding to the C Kα 0.283 keV emission line and the bremsstrahlung continuum, respectively.

of a closed-cycle helium cryostat, can be UV irradiated. The chamber is equipped with a transmittance Fourier Transform Infrared (FTIR) spectrometer and a Quadrupole Mass Spectrometer (QMS) providing monitoring of the sample during the experiments and an H I Lyα vacuum UV source (see Muñoz Caro et al. 2010 for a detailed description of the setup). X-ray radiation is obtained with a Manson 2 (Austin Instruments Inc.) source mounted onto one of the chamber's port. The source produces X-rays by focusing an electron beam emitted by a hot ($\sim$3000 K) tungsten filament onto an anode. The anode used for the experiment is made of high purity carbon. Figure 1 shows the spectrum emitted by the source during the experiments (crosses) and is given by the sum of two components, the C Kα line and the bremsstrahlung continuum above the absorption edge. The small discrepancy between model and data at low energies is due to a non-optimal modeling of the continuum component. Since the spectrum is largely dominated by the C Kα component, this small discrepancy is non-significant in the estimate of the actual X-ray dose in our experiments. The spectrum in Figure 1 is measured with a Gas Flow Proportional Counter in 812 s and has 5×10^5 counts. The total flux at the ice sample was 4.8×10^7 photons cm^{-2}s^{-1}.

Methanol (Panreac Química S.A. with an HPLC-gradient grade higher than 99.9%) is deposited onto a CsI window, of 1.3 cm diameter and 2 mm thick, kept at a temperature of 8 K during the experiments. The deposition is done at a rate of 0.3 monolayers s^{-1} for 92 minutes, assuming that a monolayer corresponds to a column density of 1.0×10^{15} molecules cm^{-2}. Thus, a column density of 1.6×10^{18} molecules cm^{-2} results from the ratio of the integrated optical depth on the CH$_3$OH infrared absorption band at 1026 cm^{-1} and the CH$_3$OH band strength value of 1.8×10^{-17} molecules cm^{-1} (D'Hendecourt & Allamandola 1986).

The CH$_3$OH ice is irradiated with X-rays for 62,340 s. During the irradiation a total number of 3.9×10^{12} photons are deposited on the ice. Low-energy photons are more likely to be absorbed by the ice than high-energy ones. Indeed more than 90% of photons with energy near the absorption edges of carbon (283 eV) and oxygen (531 eV) atoms are absorbed by the CH$_3$OH ice, while only 10% of, e.g., 1.5 keV photons hitting the ice would be absorbed. As a consequence, taking into account the spectrum energy profile (cf. Figure 1), only $\sim$57% of the total number

of photons derived above is absorbed by the CH$_3$OH ice, i.e., 2.2×10^{12} photons or 1.7×10^{12} photons cm^{-2}.

After irradiation, ice evaporation is induced by heating at a constant rate of 1 K minute^{-1}. The evolution of ice structure is monitored by FTIR spectroscopy taking spectra before and after the irradiation, as well as during warm-up. In the latter case, IR spectra are collected every 10 K from 10 K to 150 K, and every 5 K from 150 K to 170 K. The desorbed gas molecules are continuously monitored inside the chamber by the QMS. The QMS is set for the detection of all mass-to-charge (m/z) values up to 62.

For comparison few more experiments are performed on a CH$_3$OH ice obtained with the same procedure as described above: blank, i.e., with no radiation, and others in which the ice is irradiated with a UV H I Lyα lamp.

In the blank experiments, before starting the warming-up procedure, the CH$_3$OH is kept inside the ISAC at a constant temperature of 8 K for the same time as the duration of the X-ray irradiation experiment.

In the UV experiment, the CH$_3$OH ice is irradiated for 5, 15, 30, and 60 s with an H I Lyα lamp emitting a flux at the sample of 2.5×10^{14} photons cm^{-2}s^{-1} (Muñoz Caro et al. 2010). The total number of UV photons impinging onto the ice is in the range 1.7×10^{15}–2.0×10^{16} photons corresponding to doses of 2.3×10^{-2}–2.8×10^{-1} eV molecule^{-1} for the top ≈ 500 monolayers of the ice where penetration is expected and assuming UV photons of 9.2 eV average energy emitted by the lamp. This is between 70 and 900 times higher than the dose in the X-ray experiment.

3. RESULTS

Mass spectrometry is used for the determination of the elemental composition of a molecule and can serve to elucidate its chemical structure. Molecules in the gas phase are ionized by the filament of the QMS and can generate molecule fragments characterized by their m/z ratios. As an example, the mass spectrum of methanol contains $m/z = 32$ (molecular ion), but also fragments with $m/z = 15, 28, 29, 30,$ and 31 (NIST database http://webbook.nist.gov/chemistry/, and references therein). Therefore, two different molecules can present mass spectra with some overlapping m/z values. To distinguish between two such molecules based on their mass spectra, fragments with the same m/z should be avoided when possible for the interpretation of the data. If that is not possible, other physical properties of the molecules can be of help, e.g., CH$_3$OH and H$_2$CO have both $m/z = 30$ in their mass spectrum, but if $m/z = 30$ is detected during ice desorption at 35 K, it can only be due to H$_2$CO since CH$_3$OH desorbs at much higher temperatures. Following this line of thought, it may occur that the molecular ion m/z value, e.g., $m/z = 28$ for CO, may not always be the most useful to trace the molecule, since it may also be present in the mass spectrum of another molecule or molecule fragment, e.g., N$_2$ has $m/z = 28$. Finally, to follow the interpretation of the experimental results provided below, we note that natural isotopes also contribute to the detected m/z values. For instance, ^{13}CO, which molecular ion has $m/z = 29$, is about 1% in abundance relative to ^{12}CO. During the desorption of CO, a relatively small peak with $m/z = 29$ due to ^{13}CO is detected.

Figure 2 shows the ion current corresponding to $m/z = 28$ (dashed), 29 (dotted), and 30 (solid) as measured by the QMS during the warm-up phase for the irradiated (top panel) and the blank (bottom panel) experiments. The $m/z = 28, 29,$ and
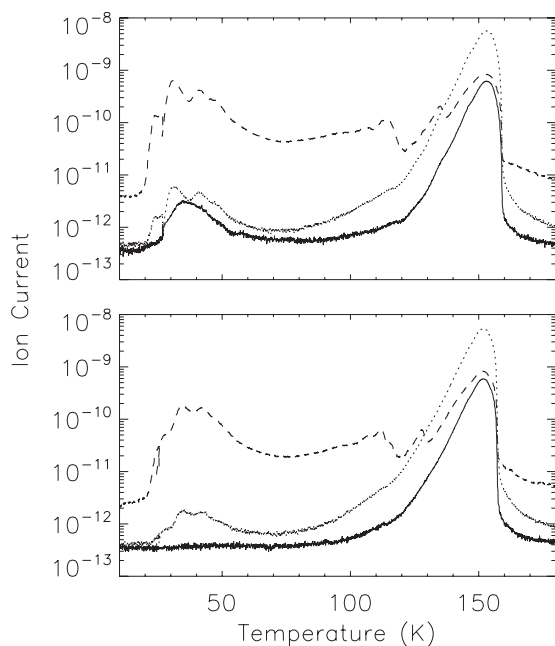
Figure 2. Ion current vs. temperature of the CH$_3$OH sample as detected by the QMS during the warm-up, for the X-ray irradiation (top panel) and blank (bottom panel) experiments. The continuum, dashed, and dotted lines correspond to mass 30 (solid), 29 (dotted), and 28 (dashed), respectively.

30 are fragments of CH$_3$OH, although they could correspond to H$_2$CO as well. The broad peak around 35 K for $m/z = 30$ in the irradiated ice is attributed to H$_2$CO. It agrees with the sublimation temperature of this species and is not present in the blank experiments without X-ray irradiation. Other observable mass fragments of H$_2$CO at $m/z = 28$ and 29 overlap with masses due to the CO and N$_2$ background gases present in the chamber at very low abundances. Therefore, only $m/z = 30$ is free from overlap with other components in the gas phase. In addition to H$_2$CO, other simple species could contribute to $m/z = 30$, in particular CH$_3$OH and ethane (C$_2$H$_6$). However, CH$_3$OH desorbs at much higher temperature (around 150 K), as evidenced by the main desorption peak in the bottom panel of Figure 2, corresponding to the blank experiment. Ethane is also discarded because no $m/z = 27$ is detected and the intensity of this mass fragment for ethane should be comparable to $m/z = 30$ in our QMS data.

The H$_2$CO assignment based on QMS data could not be confirmed by infrared spectroscopy. No changes were observed in the infrared spectra of the irradiated ice. The main H$_2$CO band in the mid-infrared falls near 1720 cm^{-1} (5.81 μm, C=O stretching) and is not detected. This is expected because the sensitivity of our FTIR detector is much lower than that of the QMS spectrometer, and the relatively low flux of the X-ray source cannot induce formation of sufficient products after almost one day of irradiation to allow their detection in the infrared. An upper limit on the production of H$_2$CO is obtained from integration of the spectral region where the 1720 cm^{-1} H$_2$CO band falls: using a band strength of 9.6×10^{-18} cm molecule^{-1} (Schutte 1996) we obtained an H$_2$CO ice column density value of N(H$_2$CO) $< 1 \times 10^{15}$ molecules cm^{-2}, corresponding to about one monolayer. However, given the low X-ray dose in our experiments, the real production of H$_2$CO should be much lower than this estimated upper limit. For the experiments involving UV-irradiation of CH$_3$OH ice, no desorption is observed around 35 K. Compared to the X-ray results, UV-
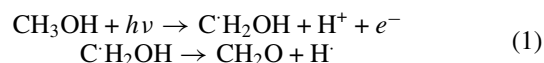
irradiation of CH$_3$OH led to a more complex photochemistry and several products were detected, in agreement with recent results by Öberg et al. (2009). In our UV experiments, the 1720 cm^{-1} band of H$_2$CO is clearly visible above the noise level after 60 s of irradiation; for that irradiation time, the column density of H$_2$CO ice formed is N(H$_2$CO) 1.8×10^{16} molecules cm^{-2} or about 18 monolayers. On average 3.4×10^{14} molecules cm^{-2} are formed in 1 s with a UV energy of 2.3×10^{15} eV cm^{-2}. Thus, the formation of one H$_2$CO molecule requires 7.7 eV.

Assuming an efficiency of X-rays the same as UV photons, the 1.7×10^{12} X-ray photons cm^{-2} absorbed in the ice would induce formation of 6.6×10^{13} H$_2$CO molecules cm^{-2}. A value well below the upper limit derived above from infrared spectroscopy.
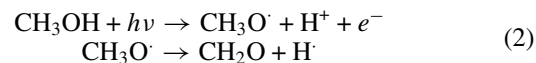
4. DISCUSSION

As a result of the soft X-ray irradiation of CH$_3$OH ice we detect the formation of H$_2$CO, by observing its characteristic desorption peak at about 35 K for $m/z = 30$. Given the low flux used in the experiments, we expect weak chemical changes in the sample, as opposite to standard irradiation experiments performed at lower energy, UV and EUV, with much more powerful sources (Öberg et al. 2009; Wu et al. 2002). The lack of the 1720 cm^{-1} H$_2$CO feature in the IR spectra provides the upper limit of 1×10^{15} molecules cm^{-2} in the H$_2$CO column density.

Photo-electric cross sections of H, C, and O are quite similar at 300 eV. Thus, the interaction of the ionizing X-ray flux occurs mainly with hydrogen, that is four times more abundant. H$_2$CO is synthesized in the icy matrix by dehydrogenation of CH$_3$OH via ionization of bounded hydrogen atoms, directly by X-rays or electron impact by secondary cascade. The process is followed by the detachment of a second H atom, during the stabilization of the activated complex, according to the oxidation driven by radiation

$$\begin{aligned} CH_3OH + h\nu &\rightarrow C^\cdot H_2OH + H^+ + e^- \\ C^\cdot H_2OH &\rightarrow CH_2O + H^\cdot \end{aligned} \quad (1)$$

or through the similar but less probable route:

$$\begin{aligned} CH_3OH + h\nu &\rightarrow CH_3O^\cdot + H^+ + e^- \\ CH_3O^\cdot &\rightarrow CH_2O + H^\cdot \end{aligned} \quad (2)$$

in which a neutral excited hydrogen, a proton, and a primary photo-electron are ejected in the matrix. Secondary electron impacts provide similar formation routes. Therefore, the average energy required to form a H$_2$CO molecule is the ionization energy of the hydrogen atom, i.e., 13.6 eV. Thus, the number of molecules formed during the irradiation can be estimated through the ratio $5.1 \times 10^{14}/13.6 \cong 4 \times 10^{13}$ molecules cm^{-2}, where 5.1×10^{14} eV cm^{-2} is the total X-ray energy per cm^{-2} assuming that all the photons are of 300 eV. The estimate is similar to the value derived from the UV experiments assuming the same efficiency for X-rays as for UV.

A comparison with the UV irradiation experiment is not straightforward as both flux and mechanism of interaction are quite different from the X-ray irradiation. In particular, the level of flux in the UV irradiation is more than five orders of magnitude higher than that found in most astrophysical environments, while the X-ray flux is not far from that emitted by the Sun today at the same energy as in our experiments.

In this respect, the X-ray experiment presented here resembles more realistic astrophysical conditions.

5. ASTROPHYSICAL IMPLICATIONS

The higher penetrability of X-rays into the hydrogen-rich interstellar gas suggests that their role in inducing chemical evolution both on ices (as suggested by this work) and in the gas phase need to be taken into account in modeling and interpretation of observational data (e.g., Bruderer et al. 2009). If low-energy X-ray photons, such as those used in this work, are absorbed within a hydrogen column density of 10^{21} cm^{-2}, higher energy photons, e.g., 1 keV, can easily reach up to $\sim 10^{24}$ cm^{-2} (Cecchi-Pestellini et al. 2009), $A_V \sim 500$ mag, the extension of a hot molecular core. Given the low flux X-ray source used in our experiments, the exposure time was chosen long enough to obtain effects on the ice. The energy absorbed by the ice sample is similar to that deposited at 1 AU by the Sun during its quiet phase. The same amount of energy, if deposited at 0.05 pc, roughly the distance of a hot core from a source, would require about 10^5 yr, the lifetime of a hot core. This time would be significantly reduced in the case of a young solar-type star whose X-ray emission is few orders of magnitude brighter than the Sun today.

The detection of glycolaldehyde, reported by Beltrán et al. (2009), in the hot molecular core G31.41+0.31 in a region within 10^4 AU from the star, has been interpreted as the manifestation of a multi-step heterogeneous chemistry in which eventually H$_2$CO combines with HCO and H. Previously, Charnley & Rodgers (2005) suggested that such reactions might proceed with reactant in close proximity via the hot secondary electron generated by the passage of a cosmic ray through the ice, or via photoprocessing of grain mantles by UV starlight which create a high concentration of radicals in the bulk interior of mantles. Grain–grain collisions then provide excess heat causing radical–radical reactions to occur and form large organic molecules. In this work, we show that H$_2$CO (and possibly CH$_3$OH radicals) can be produced by X-ray induced one-step photo-chemistry in situ, providing both reactants and close proximity for the synthesis to proceed. In order to provide IR analysis of the photolyzed products, further studies in which a more powerful X-ray source is exploited are on going.

The results of our experiments suggest that X-rays may be a promising candidate to the formation of H$_2$CO and therefore a possible route to the formation of more complex molecules, e.g., glycolaldehyde, in interstellar regions where UV radiation is severely inhibited.

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