SF2A 2021
A. Siebert, K. Baillié, E. Lagadec, N. Lagarde, J. Malzac, J.-B. Marquette, M. N'Diaye, J. Richard, O. Venot (eds)

EXPERIMENTAL STUDY OF X-RAY PHOTON-INDUCED DESORPTION FROM METHANOL CONTAINING ICES AND ITS ASTROPHYSICAL IMPLICATIONS

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Abstract. Detections of gas phase methanol CH_3OH in the cold regions of protoplanetary disks are still poorly understood. The role of X-rays, emitted from the central young stellar object (YSO), to explain these observations is still an open question. X-ray photodesorption, which is the desorption of molecules from interstellar ices, induced by its X-ray irradiation, is a potential candidate to explain the observed CH_3OH abundances. We have experimentally studied this process in the soft X-ray range near the O K-edge ($\sim$ 560 eV) on CO or H_2O-rich ices containing methanol. The X-ray photodesorption spectra of the desorbing molecules are found to be well-correlated with the ice X-ray absorption spectrum. X-ray photodesorption yields, which represent the efficiency of a X-ray to desorb a given molecule, are found to be strongly dependent on the ice composition. X-ray photodesorption of CH_3OH is efficient (with a yield of $\sim 10^{-2}$ molecule/photon at 565 eV) when CH_3OH is embedded in CO-rich ices. When embedded in H_2O-rich ices, the X-ray photodesorption of CH_3OH is not detected. This was assumed to be due to the X-ray induced-chemistry. Consequently, X-ray photodesorption should participate into explaining the presence of gas phase CH_3OH only beyond the CO snowline of protoplanetary disks.

Keywords: X-ray photodesorption, laboratory astrophysics, interstellar ices, complex organic molecules, protoplanetary disks

1 Introduction

The recent gas phase detection of methanol CH_3OH in the cold regions of the TW Hya protoplanetary disk is not fully understood so far (Walsh et al. 2016). This molecule is expected to accrete and/or form on interstellar ices that populates these regions. These ices originate from the condensation of gas phase molecules and from catalytic formation on the surface of cold ($T<100$ K) dust grains. They are mainly composed of H_2O, CO and CO_2 (Boogert et al. 2015) but can also contain more complex molecules such as CH_3OH. Therefore, the presence of CH_3OH in the gas phase of these cold regions implies that a non-thermal process should eject it from the ices into the gas phase. It is expected that UV photons and/or cosmic rays coming from various sources could trigger the ejection of methanol from the icy dust grains into the gas phase and participate in the overall gas-to-ice ratio of these cold regions (Dartois et al. 2020; Öberg et al. 2009; Cruz-Diaz et al. 2016; Bertin et al. 2016). Recent studies have shown that X-rays, emitted from various sources, such as the central Young Stellar Object (YSO) in the case of protoplanetary disks, could also participate in the desorption of molecules from interstellar ices (Dupuy et al. 2018; Ciaravella et al. 2020), a process known as X-ray photodesorption. The efficiency and the significance of this process for methanol-containing ices is still an open question. We have recently studied X-ray photodesorption from methanol-containing ices in the 525-570 eV range by coupling the ultra-high vacuum SPICES set-up to the SEXTANTS beamline of the SOLEIL synchrotron facility in Paris-Saclay. Pure methanol ices and mixed $^{13}CO:CH_3OH$ and $H_2O:CH_3OH$ ices were formed on a rotatable copper substrate and irradiated at 15 K by X-rays while the photodesorbing neutral species were probed in the gas phase by mass spectrometry. This allowed to derive quantitative X-ray photodesorption yields (expressed in

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molecule desorbed by incident photon, displayed as molecule/photon in the following) that are representative of the efficiency of X-rays to desorb a given molecule. The copper substrate is also electrically insulated from its sample holder by a Kapton foil, which allows a measurement of the drain current generated by the escape of electrons from the ice surface after X-ray absorption, referred to as the Total Electron Yield (TEY) in the following. The critical influence of several parameters on the X-ray photodesorption yields, such as the ice composition (mainly the influence of CO and H_2O molecules) and the incident photon energy, allows to shed light on the chemical and physical mechanisms at play in these X-ray irradiated organic ices. The main results of these findings, from Basalgète et al. 2021a and Basalgète et al. 2021b, will be presented in the next sections.

2 Experimental results

2.1 *Photodesorption spectra*

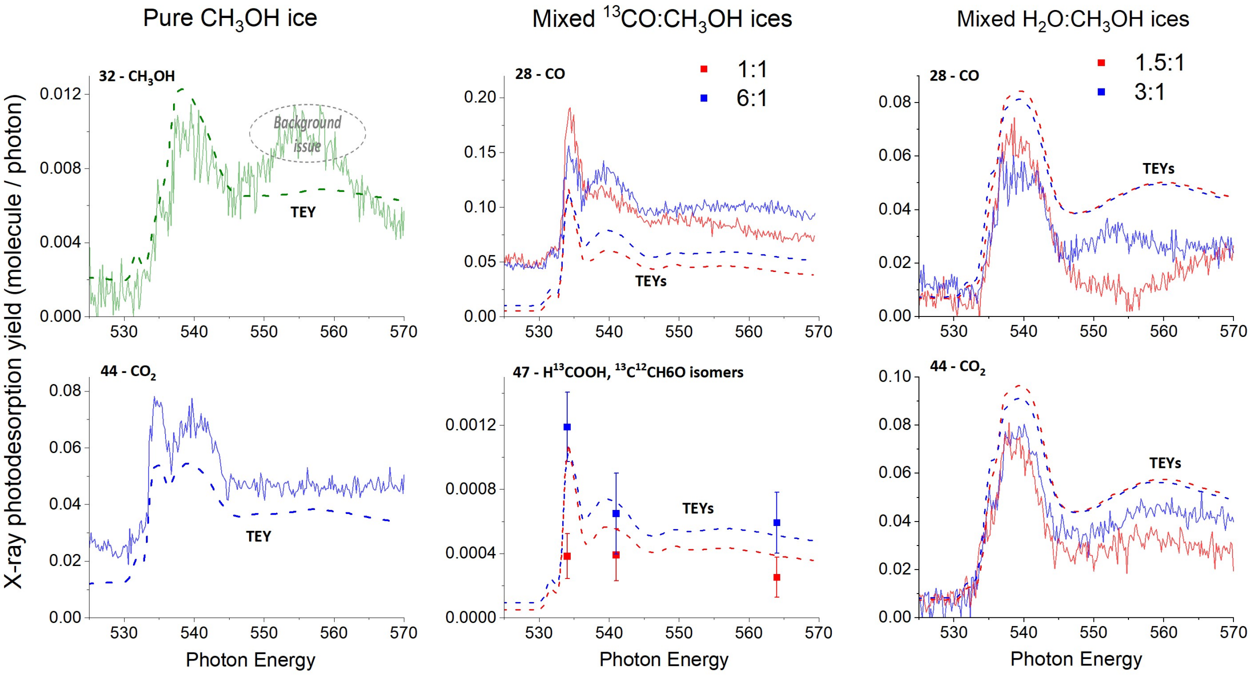

Fig. 1. X-ray photodesorption yields (solid noisy lines and squares with error bars) as a function of the incident photon energy, from pure methanol ice (left panels), mixed ^{13}CO:CH_3OH ices (middle panels) and mixed H_2O:CH_3OH ices (right panels). In dashed lines is also displayed the Total Electron Yield (TEY) measured simultaneously during the irradiations. These data are adapted from (Basalgète et al. 2021a,b)

In Figure 1, we present some examples, from Basalgète et al. 2021a and Basalgète et al. 2021b, of molecules detected as photodesorbing in the gas phase during the X-ray irradiation of the ices tested : pure methanol ices and mixed ^{13}CO:CH_3OH and H_2O:CH_3OH ices. We also displayed the Total Electron Yield (TEY) in dashed lines. The TEY is a direct measurement of the drain current escaping the ice after the X-ray absorption. It is due to the release of an Auger electron (~ 500 eV) in the ice after relaxation of the core excited states of oxygen-bearing molecules, which thermalizes within the ice, ionizing the surrounding molecules and creating secondary low energy electrons that escapes the ice surface. The TEY is proportional to the X-ray absorption cross section of the molecules present in the ice. Its energy features are typical of the X-ray absorption structure of the molecules studied and can be directly compared to X-ray spectroscopy studies (Püttner et al. 1999; Parent et al. 2002; Wilson et al. 2005; Laffon et al. 2006). As one can see in Figure 1, there is a good correlation between the TEYs and the photodesorption spectra of the molecules detected for each ice tested. This shows that the photodesorption process is well-correlated with the X-ray absorption profile of the ice and this implies that the X-ray photodesorption yields are strongly dependent on the ice composition and the incident photon energy.

2.2 X-ray photodesorption of methanol and ice composition

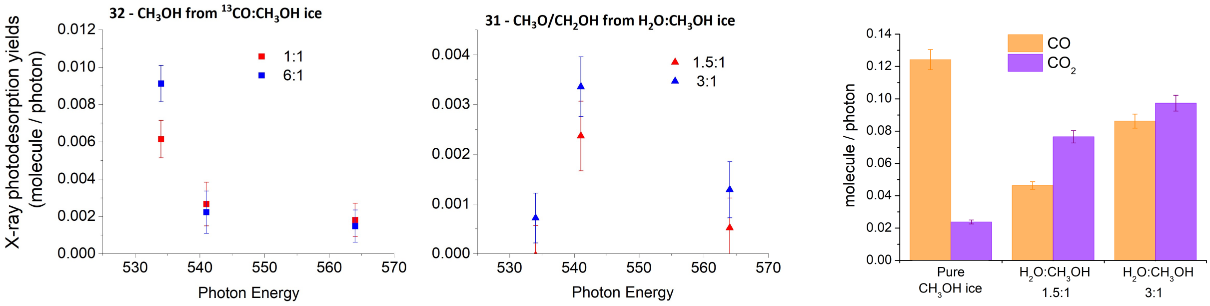

Fig. 2. X-ray photodesorption yield of CH_3OH (mass 32) from mixed ^{13}CO:CH_3OH ices (left panel) and of CH_2OH and/or CH_3O radical (mass 31) from mixed H_2O:CH_3OH ices (middle panel) as a function of the incident photon energy. Right panel: comparison of CO and CO_2 X-ray photodesorption yields at 565 eV from pure CH_3OH ice and mixed H_2O:CH_3OH ices. These results are taken from Basalgète et al. 2021b.

X-ray photodesorption of CH_3OH from mixed ^{13}CO:CH_3OH ices is detected in our experiments with a yield of the order of 10^{-2} molecule/photon (see left panel of Figure 2). However, when methanol is mixed in water ice, the X-ray photodesorption of CH_3OH is not detected anymore (with a detection upper limit of 5×10^{-4} molecule/photon) and we observe instead the photodesorption of radicals that could be attributed to either CH_3O or CH_2OH (see middle panel of Figure 2). These results can be nicely explained as a consequence of the chemistry induced by X-rays in the ice. This has been studied in the case of mixed methanol-water ices by Laffon et al. 2010. In their work, they observed the appearance and disappearance of NEXAFS peaks around the C K-edge in X-ray irradiated H_2O:CH_3OH ices and they deduced a corresponding chemical reaction network that can be summarized as followed and in which the radical OH is playing a major role:

$$H_2O \xrightarrow{(h\nu,e^-)} OH + H \tag{2.1}$$

$$CH_3OH + OH \longrightarrow CH_3O/CH_2OH + H_2O \tag{2.2}$$

$$CO + OH \longrightarrow CO_2 + H \tag{2.3}$$

When comparing this chemical network to our X-ray photodesorption yields, a good agreement can be found. In fact, we do not observe the X-ray photodesorption of CH_3OH when it is mixed in water ice, which can be explained by the fact that it is chemically destroyed by reacting with OH. Instead, we observe the photodesorption of the products of this reaction which can be attributed to either CH_3O or CH_2OH radical. Moreover, when comparing the X-ray photodesorption yields at 565 eV of CO and CO_2 between pure CH_3OH and mixed H_2O:CH_3OH ices (see right panel of Figure 2), we see that the X-ray photodesorption yield of CO_2 is higher than the one of CO in the case of mixed H_2O:CH_3OH ice. In the case of pure methanol ice, we observe the opposite. These observations could be explained by the last reaction of the chemical network presented above, in which CO is reacting with OH to form CO_2 only in the case of mixed H_2O:CH_3OH ice. X-ray photodesorption from methanol-containing ices is thus well correlated with the X-ray induced chemistry happening at the ice surface.

2.3 Implications for protoplanetary disks

YSOs (Class I, Class II, and Class III) have been shown to be X-ray emitters in the range of 0.1–10 keV (Imanishi et al. 2003; Ozawa et al. 2005; Giardino et al. 2007) with a typical luminosity of 10^{30} erg.s^{-1}. This X-ray radiation field can reach regions of protoplanetary disks that are shielded from VUV photons (Agundez et al. 2018; Walsh et al. 2015), and can originate from the central star and also from other surrounding young stars inside an YSO cluster, thus irradiating the disk out of its plane (Adams et al. 2012). Moreover, the stellar winds and the magnetic field structure produced by the YSO can reduce the cosmic-ray flux incident on the protoplanetary disk (Cleeves et al. 2013) such that, in some regions, the X-ray flux may be dominant over the other sources of irradiation. In that sense, our experimental results clearly show that X-ray photodesorption from interstellar ices in these regions should participate in the enrichment of the gas phase with molecules of astrochemical interest. As it has been demonstrated in the previous sections, this process is strongly dependent on the ice composition and should produce different outcomes depending on the region considered. In the regions where the surface temperature of the ices is below 20 K, regions in which the ices are expected to have an upper CO-rich phase with some traces of CH_3OH, X-rays should photodesorb COMs such as methanol, formic acid, dimethyl ether and/or ethanol in the gas phase. In the regions where the surface temperature of the ices is between 100 K and 20 K, regions in which the ices are expected to have an H_2O-rich phase with some traces of CH_3OH, X-ray photodesorption of the previous COMs is quenched and X-ray photodesorption of radicals such as CH_3O or CH_2OH should be observed.

3 Conclusions

X-ray photodesorption from methanol-containing ices is a process capable of explaining the presence of CH_3OH and other COMs (such as formic acid, dimethyl ether and/or ethanol) in the gas phase of the cold regions of protoplanetary disks, beyond CO snowlines. Experimentally, X-ray photodesorption of CH_3OH from H_2O-rich and CH_3OH-poor ices is not detected. Our results allows to better understand the presence of COMs such as CH_3OH in the gas phase of protoplanetary disks as a function of the ice composition and the incident X-ray energy. The experimental yields derived could also be incorporated in disk modeling.

This work was done with financial support from the Region Ile-de-France DIM-ACAV+ program and by the European Organization for Nuclear Research (CERN) under the collaboration Agreement No. KE3324/TE. We would like to acknowledge SOLEIL for provision of synchrotron radiation facilities under Project Nos. 20181140, and we thank N. Jaouen, H. Popescu and R. Gaudemer for their help on the SEXTANTS beam line. This work was supported by the Programme National “Physique et Chimie du Milieu Interstellaire” (PCMI) of CNRS/INSU with INC/INP co-funded by CEA and CNES. Financial support from the LabEx MiChem, part of the French state funds managed by the ANR within the investissements d’avenir program under Reference No. ANR-11-10EX-0004-02, is gratefully acknowledged. We also acknowledge support from the ANR PIXyES project, grant ANR-20-CE30-0018 of the French ”Agence Nationale de la Recherche”.

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