Production of $\text{H}_3^+$ via photodissociation of organic molecules in interstellar clouds

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ABSTRACT

We present experimental results obtained from photoionization and photodissociation processes of abundant interstellar CH$_3$X type organic molecules like methanol (CH$_3$OH), methylamine (CH$_3$NH$_2$) and acetonitrile (CH$_3$CN) as alternative route for the production of $\text{H}_3^+$ in interstellar and star forming environments. The measurements were taken at the Brazilian Synchrotron Light Laboratory (LNLS), employing soft X-ray photons with energies between 200 and 310 eV and time of flight mass spectrometry. Mass spectra were obtained using the photoelectron-photoion coincidence techniques. Absolute averaged cross sections for $\text{H}_3^+$ production by soft X-rays were determined. We have found that, among the channels leading to molecular dissociation, the $\text{H}_3^+$ yield could reach values up to 0.7% for single photoionization process and up to 4% for process involving double photoionization. The $\text{H}_3^+$ photoproduction cross section due to the dissociation of the studied organic molecules by photons over the C1s edge (200-310 eV) were about $0.2\times10^{-15}$ cm$^2$. Adopting the typical X-ray luminosity $L_X \approx 10^{31}$ erg s$^{-1}$ which best fit the observational data for AFGL 2591 (Stäuber et al. 2005) we derive an estimative for the $\text{H}_3^+$ photoproduction rate due to methyl-compounds dissociation process. The highest value for the $\text{H}_3^+$ column density from methanol dissociation by soft X-rays, assuming a steady state scenario, was about $10^{13}$ cm$^{-2}$, which gives the fraction of the photoproduced $\text{H}_3^+$ of about 0.05%, as in the case of dense molecular cloud AFGL 2591. Despite the extreme small value, this represent a new and alternative source of $\text{H}_3^+$ into dense molecular clouds and it is not been considered as yet in interstellar chemistry models.

Key words: ISM: molecules - molecular process - molecular data - astrochemistry

1 INTRODUCTION

The $\text{H}_3^+$ ion plays an important role in diverse fields from chemistry to astronomy such as, the chains of reaction that lead to the production of many of complex molecular species observed in the interstellar medium (Hersbt & Klemperer 1973; Dalgarno & Black 1996; Suzuki 1979). The $\text{H}_3^+$ ion was discovered in molecular clouds (McCall et al. 1999; Geballe & Oka 1996) and in the diffuse interstellar medium (Oka et al. 2005; McCall et al. 1998) with column densities of $10^{15}$ cm$^{-2}$.

As point out by McCall & Oka (2000), observation of $\text{H}_3^+$ can be combined with those of other important molecules such as H$_2$ and CO to characterize the physical and chemical properties of the interstellar clouds. Moreover, the physics and chemistry from $\text{H}_3^+$ analysis, combined with low density and temperature of interstellar space, lead to interesting phenomena like the extraordinary deuterium fractionation, the bistability of chemical models and the radiative thermalization through forbidden rotational transitions. A detailed review about the $\text{H}_3^+$, the simplest stable interstellar polyatomic molecule, can be found in Oka (2006).

The main pathway formation of $\text{H}_3^+$ occurs via ionization of H$_2$ to H$_3^+$ by the ubiquitous cosmic ray or local X-ray, followed by the efficient Langevin reaction (Bowers et al. 1969):

$$\text{H}_2 + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \quad (1)$$

The main destruction pathway of $\text{H}_3^+$ occurs via proton-hop reaction:

$$\text{H}_3^+ + X \rightarrow \text{HX}^+ + \text{H}_2 \quad (2)$$
where $X = \text{CO, N}_2, \text{H}_2\text{O, NH}_3$, etc. These reaction have been studied by Burt et al. (1970) and all show Langvin-type behavior. As discussed by Oka (2004), the averaged $H^+_3$ number density in dense clouds is about $10^{4.7}$ cm$^{-3}$ where $X = \text{CO}$ is the main destroyer. In diffuse clouds, $X = e^-$ is the main destroyer and the averaged $H^+_3$ number density for these regions is about $10^{4.6}$ cm$^{-3}$. Despite the low rate coefficients, other formation reaction involving species like HeH$^+$, NH$^+$, HCO and CH$_3^+$ have also been proposed (McCall et al. 1999; Millar et al. 1999b).

Miller et al. (1992) have observed the $H^+_3$ emission in the infrared spectrum of the remnants of Supernova 1987A. Brittain & Rettig (2002) reported a detection of the $H^+_3$ emission from the Herbig Ae/Be star HD141569 and speculated that it is from a protoplanet in the preplanetary disk, however this detection remains controversial (Oka 2002). The $H^+_3$ emission has been found recently in other Herbig Be star LkHα 101 by Brittain et al. (2004) with a column density of about $2.2 \times 10^{14}$ cm$^{-2}$.

The observed ubiquity of $H^+_3$ in interstellar clouds suggests that it is also observable in many other objects where molecules and ionization abound. The intense $3.7 \mu m$ $H^+_3$ emission spectrum from Jupiter (Drossart et al. 1989; Oka & Geballe 1990; Connerney et al. 1993), Saturn (Geballe et al. 1993) and Uranus (Traffon et al. 1993) has become a general tool to study planetary ionospheres. It was even suggested that this emission might be detectable from Jupiter-like planets orbiting other stars (Connerney & Satoh 2000).

Planetary nebulae and proto-planetary nebulae are also interesting targets. As pointed by Oka (2004), due to the low metallicity, Magellanic clouds may also be interesting objects to try $H^+_3$.

The ionized triatomic hydrogen molecule is found as a primary fragment in the photoionization and electron impact mass spectra of several small molecules. Ruhl et al. (1990), have reported one of the first studies on the production of $H^+_3$ from methyl compounds, via two-body charge separation dissociation process due to the absorption of $40.8 \text{eV}$ photons from a toroidal grating monochromator. The authors have pointed out that the formation of double ionized methyl compound molecules requires excitation energies of the order of $30 \text{eV}$. Photon energies of this order of magnitude are not normally available within dense clouds because absorption by the abundant hydrogen species (and possibly by interstellar grains) in the other layers screens the high photons from penetrating deep into the cloud. However, it is recognized that stars can be buried within dense clouds and can act as local high energy sources (Charnley et al. 1988) promoting increase in chemistry complexity.

The $H^+_3$ peak, appearing at $m/q = 3$ in mass spectra, has also been observed in the dissociation of other methyl compound molecules, due to VUV photons and electrons, as the case of $C_2\text{H}_6, \text{CH}_3\text{CN, CH}_3\text{NCO, CH}_3\text{COOH, HCOOH}_2, \text{CH}_3\text{NH}_2, \text{cyclo-C}_6\text{H}_5, \text{n-C}_3\text{H}_7, \text{CH}_2\text{Cl, CH}_3\text{Br, CH}_3\text{I and others (Eland 1996; Thissen et al. 1994). The rates for rearrangement leading to $H^+_3$, $D^+_3$ and $HD^+_3$ have been studied by Furukawa et al. (2005) in an experiment on methanol and deuterated methanol (CD$_3$OH) under intense laser (800 nm) fields.}$

Recently, Sharma & Bapat (2006) have reported the production of $H^+_3$ ion by the ionization/dissociation of ethanol molecule by a $1.3 \text{keV}$ electron beam. The authors have pointed out the determination of active sites for $H$ atom rearrangement in the dissociation of single and double ionized ethanol (CH$_3$CH$_2$OH) and deuterated ethanol (CH$_3$CD$_2$OD). They also have found that $H^+_3$ is far more likely to be formed by of rearrangements of H atoms on the CH$_2$ and OH sites, rather than the CH$_3$ site.

In this work, we present a set of experimental results obtained from photoionization and photodissociation processes of abundant CH$_3$-X type interstellar organic molecules like, methanol (CH$_3$OH), methylamine (CH$_3$NH$_2$) and acetonitrile (CH$_3$CN), as another route for the production of $H^+_3$ ion in star-forming regions. In these environments the radiation field (UV and X-rays) can promote several photophysical and photochemical processes onto molecules, including the photodissociation. The products of organic molecules dissociation (ex. reactive ions and radicals) can also provide the formation of interstellar complex molecules like long carbon chain molecules and amino acids (ex. glycine).

In section 2 we present the experimental setup and the data analysis technique employed. The results are shown and described in section 3. Final remarks and conclusions are present in section 4.

2 EXPERIMENTAL

The measurements were taken at the Brazilian Synchrotron Light Laboratory (LNLS), in Campinas, São Paulo, Brazil. Briefly, soft X-rays photons (100-310 ev) from a toroidal grating monochromator (TGM) beamline (~ $10^{12}$ photons/s), perpendicularly intersect the gas sample inside a high vacuum chamber. The gas needle was kept at ground potential. The emergent photon beam flux was recorded by a light sensitive diode. The complete description of the experimental setup could be found elsewhere (Boechat-Roberty et al. 2005; Pilling et al. 2006).

Figure 1. Schematic diagram of the time of flight mass spectrometer inside the experimental vacuum chamber and the associated electronics.

Conventional time-of-flight mass spectra (TOF-MS) were obtained using the photoelectron and photon coincidence (PEPICO) technique. The ionized recoil fragments produced by the interaction with the photon beam were accelerated by a two-stage electric field and detected by two micro-channel plate detectors in a chevron configuration, after mass-to-charge ($m/q$) analysis by a time-of-flight mass spectrometer (297 mm long). They produced up to three stop signals to a time-to-digital converter (TDC) started by the signal from one of the electrons accelerated in the opposite direction and recorded without energy analysis by two micro-channel plate detectors. A schematic diagram of the time of flight spectrometer, mounted inside the experimental vacuum chamber, is shown in Fig. 1 where A1 and A2 are the pre-amplifiers and D1 and D2 are the

1 UMIST gas-phase chemical reaction network (www.ufda.net)
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the discriminators. The connection to the time-to-digital converter is also shown.

Besides PEPICO spectra, other two kinds of coincidence mass spectra were obtained simultaneously, PE2PICO spectra (photoelectron photoion coincidence) and PE3PICO spectra (photoelectron photoion photoion coincidence) (see details in Pilling 2006b; 2006c). These spectra have ions coming from double and triple ionization processes respectively, that arrive coincidentally with photoelectrons. Of all signals received by the detectors only about 10% come from PE2PICO and 1% from PE3PICO spectra, due to the limited detection efficiencies. This reflect that the majority contribution to data came from aborted double and triple coincidence events. Nonetheless, PEPICO, PE2PICO and PE3PICO signals were taken into account for normalization purposes. Negative ions may also be produced and detected, but the corresponding cross-sections are negligible.

The samples were bought commercially from Sigma-Aldrich with purity greater than 99.5%. No further purification was performed other than degassing the liquid sample by multiple freeze-pump-thaw cycles before admitting the vapor into the chamber.

The base pressure in the vacuum chamber was in the 10$^{-8}$ Torr range. During the experiment the chamber pressure was maintained below 10$^{-5}$ Torr. The pressure at the interaction region (volume defined by the gas beam and the photon beam intersection) was estimated to be $\sim$ 0.1-1 Torr ($10^{15}$ - $10^{16}$ molecules cm$^{-3}$). The measurements were made at room temperature.

The partial ion yield for $H_3^+$ (PIY$_{H_3^+}$) or relative intensities of $H_3^+$ produced due to the photodissociation of the studied organic molecules, was determined directly from PEPICO spectra by the expression

$$PIY_{H_3^+} = \frac{A_{H_3^+}}{A_i\times\sqrt{\frac{A_{H_3^+} + A_i \times ER}{100}}} \times 100\%$$ (3)

where $A_{H_3^+}$ is the area of a $H_3^+$ peak, the $A_i$ is the total area of the PEPICO spectrum. The $ER = 2-4\%$ is the estimated error factor due to the data acquisition and data treatment.

In a similar manner, for the PE2PICO spectra, we have determined the partial double coincidence yield for $H_3^+$ (PDCY$_{H_3^+}$), or the relative production of $H_3^+$ in coincidence with another ion $i$ from the dissociation of double ionized organic molecule, by

$$PDCY_{H_3^+} = \frac{A_{H_3^+}}{A_i\times\sqrt{\frac{A_{H_3^+} + A_i \times ER}{100}}} \times 100\%$$ (4)

where $A_{H_3^+}$ is the number of events in double coincidence of a given ion $i$ and $H_3^+$ pair and $A_i^{2+}$ is the total number of count of PE2PICO spectra.

The data treatment and analysis of PE2PICO spectra as well the determination of PDCY were performed using the program described elsewhere (Pilling 2006).

The complete results about the photoinitiation and photodissociation of methanol by soft X-rays could be found elsewhere (Pilling et al. 2006c; 2006d). The same experimental study for the other abundant CH$_3$-X type interstellar organic molecules like methylamine and acetonitrile are the subject of future publication.

3 RESULTS AND DISCUSSION

Figure 2 shows a detail of the mass spectrum of the fragments produced by single photoionization (PEPICO) of acetonitrile (Fig. 2a), methanol (Fig. 2b) and methylamine (Fig. 2c) recorded with photons at energies between 200 eV and 310 eV (over the C1s resonance, about $\sim$ 290 eV). The presence of the $H_3^+$ peak (m/q=3) and its relative intensity (PIY) are indicated in each figure. The other two lightest ions ($H^+$, $H_2^+$) are also seen. The insets in both figures represent the fully mass spectra of each molecule for comparison. Our data have shown that about 0.1%, 0.7% and 0.5% of the photodissociation channels of acetonitrile, methanol and methylamine, respectively, lead to the $H_3^+$ production.

In star-forming regions like Sgr B2, Orion KL and W51, the presence of widespread UV and X-ray fields could trigger the formation of photodissociation regions - PDRs (Tielens & Hollenbach 1985) and X-rays dominated regions - XDRs (Maloney, Hollenbach & Tielens 1996) where many molecules could be detected (ex. Ehrenfreund & Charnley 2000). As pointed out by Casanova et al. (1995), Koyama et al. (1996) and Imanishi et al. (2001), protostars are extremely efficient sources of X-ray photons that are capable of traversing large column densities of gas before being absorbed.
The X-ray-dominated regions (XDRs) in the interface between the  
ionized gas and the self-shielded neutral layers could influence the  
selective heating of the molecular gas. The complexity of these  
regions possibly allows a combination of different scenarios and  
excitation mechanisms to coexist (Goicoechea et al. 2004).  

In our previous works (Pilling 2006b; 2006c) we reported that  
the X-rays can penetrate deeper into the molecular clouds than,  
for example, UV photons and affect the gas-phase chemistry even  
at large distance from the source.

The averaged cross sections for H$_3^+$ production by soft X-rays  
photons in the energy range of 200 to 310 eV, were determined  
using the methodology describe elsewhere (Boechat-Roberty et al.  
2005; Pilling et al. 2006). The comparison between the partial  
double coincidence yield for H$_3^+$ ion (PDCY$_{H_3^+}$) recorded  
with VUV and soft X-ray photons is present in Table 1. Despite the  
small values on the H$_3^+$ photoproduction by soft X-rays compared  
with the VUV photons, inside molecular clouds the soft X-ray field  
could be higher than the VUV field.

Thissen (1993) have also reported the presence of H$_3^+$ (and  
also D$_3^+$, HD$_3^+$ and H$_2$D$_3^+$) on PE2PICO spectra of methylamine  
and deuterated-methylamine species recorded by 30-60 eV photons.  
Following the author, the production of H$_3^+$-like species from  
dissociation of single ionized methylamine-like molecules at these  
photon energies or lower is negligible.

### 3.1 H$_3^+$ photoproduction cross section and rate in soft X-ray field

As pointed by Stäuber et al. (2005), due to the low absorption cross  
section, X-rays can penetrate deeper into the molecular clouds than,  
for example, UV photons and affect the gas-phase chemistry even  
at large distance from the source.

The averaged cross sections for H$_3^+$ production by soft X-rays  
photons in the energy range of 200 to 310 eV, were determined  
using the methodology describe elsewhere (Boechat-Roberty et al.  
2005; Pilling et al. 2006a). Following the discussion of Chen et  
al. (1981) about the negligible fluorescence yield (due to the low  
carbon atomic number) and anionic fragments production in the  
present photon energy range, we adopted that all absorbed photon  
leads to cationic ionizing process. Therefore, in order to put our  
data on an absolute scale, after a subtraction of a linear background  
and false coincidences coming from aborted double and triple  
ionization, we have summed up all the contributions of all cationic  
fragments detected and normalized them to the absolute photoab-  
sorption cross section taken from literature. For acetonitrile and  
methanol, the absolute photoabsorption cross section wereobtained  
by Hitchcock et al. (1989) and by Ishii & Hitchcook (1988), respec-  
tively. In the case of methylamine, due to the lack of the absolute  
photoabsorption measurements on literature, we have used the values  
obtained for the methanol (Ishii & Hitchcook 1988) to gives an  
estimative of the averaged cross sections for H$_3^+$ production.

Briefly, the photoproduction cross section of H$_3^+$ by the dis-  
sociation of single ionized, $\sigma_3^+$, and from double ionized, $\sigma_3^{++}$,  
organic molecules are given by

$$\sigma_3^+ = \frac{PIY_{H_3^+}}{100} \quad \text{and} \quad \sigma_3^{++} = \frac{PDCY_{H_3^+}}{100}$$

Table 1. Comparison between the partial double coincidence yield for H$_3^+$  
ion (PDCY$_{H_3^+}$) recorded with VUV and soft X-ray photons.

| CH$_3$-X molecule | VUV$^a$ (40.8 ev) | Soft X-rays$^b$ (200-310 eV) |
|-------------------|------------------|-----------------------------|
| Acetonitrile      | 1.0              | 0.1 / 0.1$^c$               |
| Methanol          | 11.2             | 3.7 / 0.7$^c$               |
| Methylamine       | 13.0             | 3.9 / 0.5$^c$               |

$^a$ Eland (1996); $^b$ this work;  
$^c$ PIY (relatives intensities from single ionization)

recorded with VUV photons (Eland 1996) with soft X-ray photons  
from this work is present in Table 1. Despite the small values on the  
H$_3^+$ photoproduction by soft X-rays compared with the VUV pho-  
tons, inside molecular clouds the soft X-ray field could be higher  
than the VUV field.

![Figure 3](image)

**Figure 3.** Detail of the PE2PICO spectra obtained by the dissociation of  
double photoionized molecules a) acetonitrile, b) methanol c) methylamine.  
See details in text.
spectra as previously discussed. The estimated experimental error is considered to be lower than 30%.

In general, as discussed by Stäuber et al. (2005), primary X-ray ionization plays only a minor role in the chemistry since reaction are ~1000 times slower compared to the relevant chemical reactions and more than 10 times slower than electron impact ionization as the case of AFGL 2591 model parameters. However, in denser regions inside the molecular clouds, the X-ray ionization rate may exceed the cosmic-ray ionization and become a significative source of photoionization and photodissociation.

The $H_3^+$ photoproduction rate due to the dissociation of methyl-compound molecules by soft X-rays (200-310 eV) is given by the simple expression:

$$k_{ph} = \int \sigma_{H_3^+} \epsilon F(x) dx - \sigma_{H_3^+} F_{soft} \text{ [s}^{-1}]$$

where $\sigma_{H_3^+} = \sigma_{H_3^+}^{++} + \sigma_{H_3^+}^{+}$ and $F_{soft}$ is the averaged $H_3^+$ photoproduction cross section and photon flux over the soft X-ray energy (200-310 eV).

Table 2. Averaged $H_3^+$ photoproduction cross section and photoproduction rate for an X-ray luminosity of $L_x \geq 10^{31}$ erg/s (Stäuber et al. 2005), from the dissociation of methanol, methylamine and acetonitrile by soft X-rays photons over the C1s edge (200-310 eV). See details in text.

| CH$_3$-X molecule | $\sigma_{H_3^+}^{++}$ (x10$^{-19}$ cm$^2$) | $\sigma_{H_3^+}^{+}$ (x10$^{-19}$ cm$^2$) | $\sigma_{H_3^+} = \sigma_{H_3^+}^{++} + \sigma_{H_3^+}^{+}$ (x10$^{-18}$ cm$^2$) | $k_{ph}$ (x10$^{-15}$ s$^{-1}$) |
|-------------------|----------------------|----------------------|----------------------|----------------------|
| Acetonitrile      | 2.0                   | 0.2                   | ~0.2                 | 400; 0.05$^c$        |
| Methanol          | 12.0                  | 2.0                   | 1.4                  | 300; 0.4$^c$         |
| Methylamine$^a$   | 8.0                   | 3.0                   | 1.1                  | 200; 0.3$^c$         |

$^a$ Estimated value.

$^b$ At a distance $r \sim 200$ AU (2.5 x 10$^{15}$ cm) from the central source; $F_{soft} \geq 2 \times 10^5$ photons cm$^{-2}$ s$^{-1}$.

$^c$ $r \sim 5000$ AU (7 x 10$^{16}$ cm); $F_{soft} \geq 3 \times 10^5$ photons cm$^{-2}$ s$^{-1}$.

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3.2 Photoproduced $H_3^+$ abundance

Methanol is one of the most abundant molecule in interstellar medium and in dense molecular clouds. Therefore, even despite the reduced production of $H_3^+$ from X-rays photodissociation process, it is reasonable to expect that at least a fraction of the detected $H_3^+$ in molecular clouds may be produced from this simple methyl compound molecule. Considering methanol as an alternative source of $H_3^+$ inside dense molecular clouds, we derive its reaction scheme by:

$$CH_3OH^* + h\nu \xrightarrow{k_{ph}} H_3^+ + COH \quad (or \ H_3^+ + CO^*)$$

$$H_3^+ + CO \xrightarrow{k_{CO}} COX^+ + H_2$$

where $h\nu$ is the soft X-ray photons, $k_{ph}$ is the $H_3^+$ photoproduction rate [s$^{-1}$] for the dissociation of CH$_3$OH and $k_{CO} \sim 2 \times 10^{-9}$ cm$^{-3}$ s$^{-1}$ is the canonical rate constant for the $H_3^+$ destruction reaction due to CO molecules. As discussed by McCall et al. (1999), others $H_3^+$ destruction processes may also occur inside dense molecular clouds, for example, the dissociation due to electron recombination. However, due to the large abundance of CO in comparison with free electrons, inside dense molecular clouds, it becomes the dominant destruction route of $H_3^+$ (Oka 2006). One can ask about the $H_3^+$ photodestruction rate by the same X-ray field within the cloud, however it certainly must be lower than its UV photodissociation rate $k_{ph} < 10^{-12}$ s$^{-1}$ (van Dishoeck 1987).

Following the above statements, and assuming the steady-state approximation inside dense molecular cloud, the rate of change in the amount of $H_3^+$ coming from methanol due to photodissociation by soft X-rays can be described by:

$$\frac{d[H_3^+]}{dt} = k_{ph}[CH_3OH] - k_{CO}[CO] = 0$$

where $[H_3^+]$, [CH$_3$OH] and [CO] is the number density of photoproduced $H_3^+$, methanol and carbon monoxide inside the molecular cloud.

Assuming a chemical homogeneity into the molecular cloud, Eq. (9) gives the simple relation:

$$N_{H_3^+}^{phot} \sim \frac{k_{ph}}{k_{CO}[CO]} N_{CH_3OH}$$

where $N_{H_3^+}^{phot}$ is the column density of the photoproduced $H_3^+$ from methanol dissociation due to soft X-ray (200-310 eV), and $N_{CH_3OH}$ is the column density of interstellar methyl alcohol. Following Oka (2006), inside dense molecular clouds the CO number density is about 10-0.1 cm$^{-3}$.

In Table 3 we present the methanol column density and the total $H_3^+$ column density, $N_{H_3^+}$, from radioastronomical observations, together with the lower limits for the $H_3^+$ column density resulting from the photodissociation of methanol molecules by soft X-rays inside these clouds. The photoproduced $H_3^+$ fraction over the total observed $H_3^+$ is also showed. We have adopted a typical X-ray luminosity $L_X \geq 10^{31}$ erg s$^{-1}$ which best fit the observational data for AFGL 2591 (Stäuber et al. 2005) as a good approximation of the radiation field also for the others dense molecular clouds. Two lower
limit for averaged soft X-ray flux were considered, $F_{\text{softX}} \gtrsim 2 \times 10^5$ and $\gtrsim 3 \times 10^5$ photons cm$^{-2}$ s$^{-1}$, as discussed before. We adopted the averaged CO number density of about 1 cm$^{-3}$. Assuming a steady state scenario, the highest value for the $H_3^+$ column density from methanol dissociation by soft X-rays was about $N_{H_3^+}^{\text{CH}_3OH} \gtrsim 10^{11}$ cm$^2$, which in the case of AFGL 2591 gives the fraction of the produced $H_3^+$ due to CH$_3$OH photodissociation, $N_{H_3^+}^{\text{ph}} / N_{H_3^+}^{\text{tot}} \approx 0.05\%$. For the lower soft X-ray photon flux the calculated values were about 3 orders of magnitude lower.

Despite the small value of $N_{H_3^+}^{\text{ph}}$ compared with the $H_3^+$ column density from radioastronomical observation, this may represent a new source of $H_3^+$ inside molecular clouds and it is not been considered as yet in interstellar chemistry models. We cannot firmly assert that this will indeed become necessary to create models which fully explain radioastronomical observations, but we consider that our experimental results should be born in mind in those particular circumstances where sources of high energy excitation of extant CH$_3$X could exist.

Based on our experimental data, we expect that in other methanol rich molecular clouds, as pointed out recently in 40 galactic center molecular clouds (Requena-Torres et al. 2006), may also have some amount of $H_3^+$ coming from the soft X-ray (or VUV) photodissociation process of methyl compound molecules.

### 4 CONCLUSIONS

As discussed by Ruhl et al. (1990), the formation of double ionized methyl compound molecules and consequently its dissociation via process like the charge separation and others, requires excitation energies of the order of 30 eV. Within dense clouds, the photon energies of this order of magnitude are not normally available because the absorption by the abundant hydrogen species (and possibly by interstellar grains) in the other layers. However, the H-atom absorption cross section at wavelengths less than 124 eV ($\sim 100$ Å) is small enough to allow soft X-rays to penetrate great depths into these clouds. Therefore, the photochemistry induced by soft X-rays and other sources of energetic radiation like cosmic rays or stellar wind particles should be considered within dense clouds.

The present work points out the importance of the dissociation processes promoted by soft X energy photons on the production of interstellar simply stable polyatomic molecule, $H_3^+$. The production of $H_3^+$ via the photodissociation of interstellar methyl compound organic molecules has been studied using photoelectron-photoion coincidence techniques using soft X-rays photons (200-310 eV).

We have shown that the photodissociation of CH$_3$-X like organic molecules by soft X-rays, leads to the production of $H_3^+$, among the several other dissociation channels, by:

$$\text{CH}_3X + h\nu \rightarrow H_3^+ + CX + e^- \quad \text{(or } H_3^+ + CX^+ + 2e^-) \quad (11)$$

where $h\nu$ = soft X-rays and $X = \text{OH, NH}_2$ and CN.

We have shown that about 0.7% and 3.7% of the single and double photodissociation channels of methanol, respectively, lead to the $H_3^+$ production. As the methanol is one of the most abundant molecule in interstellar medium it is reasonable to expect that at least a fraction of the detected $H_3^+$ could be resultant of this molecule photodecomposition followed by the rearrangement of the H atoms.

The $H_3^+$ photoproduction cross section due to the dissociation of the studied organic molecules by photons over the C1s edge (200-310 eV) were about 0.2-1.4 $\times 10^{-18}$ cm$^2$.

Assuming a steady state scenario and a typical X-ray luminosity of $L_x \gtrsim 10^{31}$ erg s$^{-1}$ as the case for AFGL 2591 (Stäuber et al. 2005), the fraction of the produced $H_3^+$ due to CH$_3$OH photodissociation over the observed value, could reaches up to 0.05%. Despite the extreme small value, this represent a new and alternative source of $H_3^+$ inside dense molecular clouds and it is not been considered as yet in interstellar chemistry models. Moreover, the energetic ionic products released by dissociation of CH$_3$X molecules, including the $H_3^+$ ion, become an alternative and efficient route to complex molecular synthesis, since some ion-molecule reactions do not have an activation barrier and are also very exothermic.

We hope that the $H_3^+$ photoproduction cross section from dissociation of the studied organic molecules by soft X-rays and the photoproduction rate derived in this work will give rise to more precise values for some molecular abundances in interstellar clouds and even in planetary atmosphere models. Better estimative for $H_3^+$ photoproduction rate depends of more accurate soft X-ray radiation field determinations.

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