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Formation of methyl formate in comets by irradiation of methanol-bearing ices

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ABSTRACT

Methyl formate is a complex organic molecule considered potentially relevant as precursor of biologically active molecules. It has been observed in several astrophysical environments, such as hot cores, hot corinos, and comets.

The processes that drive the formation of molecules in cometary ices are poorly understood. In particular it is not yet clear if molecules are directly accreted from the pre-solar nebula to form comets or are formed after accretion.

The present work analyzes the possible role of cosmic ion irradiation and radioactive decay in methyl formate formation in methanol-bearing ices. The results indicate that cosmic ion irradiation can account for about 12% of the methyl formate observed in comet Hale–Bopp, while radioactive decay can account for about 6% of this amount.

The need of new data coming from earth based and space observational projects as well as from laboratory experiments is outlined.

1. Introduction

Comets are an agglomerate of ices, rocky debris and organic compounds. According to the current theories, they formed from accretion of planetesimals in the proto-planetary disc at the very beginning of the history of the Solar System. They are among the least thermally processed and the most primitive members of the Solar System. Comets contain frozen gases such as water, carbon monoxide, carbon dioxide, methane and ammonia. They also contain a variety of organic compounds some of which are considered as building blocks for biotic molecules, such as methanol, hydrogen cyanide, formaldehyde, ethanol, ethane, and more complex molecules (Irvine et al., 2000; Bockelée-Morvan et al., 2000; Crovisier et al., 2004). Large amounts of these species could have been delivered on the surface of the early Earth after cometary impacts and might have accumulated in the form of surviving organic compounds (Oró, 1961; Chyba and Sagan, 1992). Thus, comets could have played a major role in the development of life on our planet. Because their material is well-preserved, the study of comets nowadays can inform us on the nature of the compounds which could have seeded the Earth in the early times.

Among the cometary molecules which might have contributed to the emergence of life on our planet methyl formate ($HCOOCH_3$) deserves attention. As an isomer of acetic acid (CH_3COOH) and glycolaldehyde ($HOCH_2CHO$), molecules directly linked to the biological evolution, it is of primary importance from an exobiological point of view. Methyl formate is observed in a number of sources such as hot cores and hot corinos (Brown et al., 1975; Bottinelli et al., 2007; Sakai et al., 2007; Favre et al., 2011). It has been also identified in the coma of comet C/1995 O1 (Hale–Bopp) where it presents a relative abundance of 0.08% with respect to water (Bockelée-Morvan et al., 2000). In comet C/2002 T7 (LINEAR) only an upper limit of 1% with respect to water was found (Remijan et al., 2006). Other attempts were made in order to identify this molecule in other comets, like in comet 9P/Tempel 1, where however the identification was not possible (Tozzi et al., 2009). Methyl formate should be widespread in comets, together with other organic compounds, but its low abundance and faint lines (which make it detectable only in unusually strong comets) is probably the reason why methyl formate has not been often detected.

The origin of interstellar and cometary methyl formate is at the present matter of debate. Laboratory experiments have shown that methyl formate can be formed in the solid state after UV photolysis of pure CH_3OH and $CO:CH_3OH$ icy mixtures (Gerakines et al., 1996; Öberg et al., 2009), irradiation with 5 keV electrons of pure CH_3OH and $CO:CH_3OH$ icy mixtures (Bennett and Kaiser, 2007), and irradiation with 16 and 220 MeV oxygen ions of pure

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CH_3OH ice (de Barros et al., 2011). Modica and Palumbo (2010) studied the formation of methyl formate after irradiation of CH_3OH and CO:CH_3OH icy samples with 200 keV protons. They discussed how the results can account for methyl formate abundances observed in different sources in dense molecular clouds and suggested that interstellar methyl formate can be efficiently formed after cosmic ion irradiation of icy grain mantles. Recently Occhiogrosso et al. (2011) have shown that processing of icy mantles due to cosmic ion irradiation can account for the abundance of methyl formate observed in dark dense molecular clouds but not that found in hot cores and corinos. Since the composition of interstellar and cometary ices present similarities, cometary molecules could be directly incorporated from the presolar gas and dust or formed 'in situ' by similar energetic processes. Occhiogrosso et al. (2011) discussed other routes of formation of methyl formate at the stage of the early protoplanetary disk that could also be invoked for explaining the abundance of methyl formate in comets.

In the present work we investigate the formation of methyl formate by energetic processing of cometary nuclei containing CO and CH_3OH, molecules commonly observed in comets. Comparisons of the composition of different Oort Cloud comets indicates that CH_3OH has abundances from 0.5% to 5% relative to water (Mumma et al., 2002; Mumma, 1997; Bockelée-Morvan et al., 1995), while native CO varies between 1.8% and 12% or even 23% in view of the fact that both CO millimeter and infrared lines do not provide compelling evidence for a distributed source of CO in Hale–Bopp atmosphere (Bockelée-Morvan et al., 2010). This comet presents a CO:CH_3OH ratio of 10:1 and abundances of 23% and 2.4% relative to water, respectively (Bockelée-Morvan et al., 2010).

Our aim is to evaluate the amount of methyl formate that can be formed in cometary ices by cosmic ion irradiation and by decay of radioactive nuclei.

2. Experimental set-up

The used experimental apparatus has been already described elsewhere (Strazzulla et al., 2001; Palumbo et al., 2004). In brief it consists of a stainless steel high-vacuum chamber operating at a pressure kept lower than 10^{-7} mbar interfaced with a FTIR spectrometer ($10\,000-400\ \mathrm{cm}^{-1} = 1-25\ \mu\mathrm{m}$) through IR-transparent windows. Inside the vacuum chamber a substrate (Si or KBr) is placed in thermal contact with a cold finger, whose temperature can be varied within the 16–300 K range. A needle valve is used to admit the gas or gas mixture to be investigated into the chamber, where it freezes onto the substrate.

After deposition the samples can be irradiated by energetic (30–400 keV) ions. In this study we have used 200 keV H^+ ions and investigated the effects of irradiation at increasing ion fluences. The beam used produces current densities in the range from 10^{-1} to a few $\mu\mathrm{A\,cm}^{-2}$ in order to avoid macroscopic heating of the sample. The integrated ion flux is directly related to the ion current that is continuously measured during irradiation. The substrate plane forms an angle of 45° with the infrared beam and the ion beam. In this way spectra can be taken before, during, and after irradiation without tilting the sample. The energy released to the sample by impinging ions (dose) is given in eV/16u, where u is the unified atomic mass unit defined as 1/12 of the mass of an isolated atom of carbon-12. As discussed by Strazzulla and Johnson (1991), the dose given in units of eV per small molecule (16u) is a convenient way to characterize chemical changes and compare the results obtained irradiating different samples.

All the spectra shown in this work are ratioed to the corresponding spectrum of the background acquired before deposition and are taken at a resolution of 1 cm^{-1}. Each spectrum is plotted on an optical depth scale using the relation $I = I_0 \cdot e^{-\tau}$ (Beer–Lambert law), where $\tau = \alpha \cdot x$ (α = absorption coefficient; x = path length through the material).

As discussed in a previous paper (Modica and Palumbo, 2010), a He–Ne laser beam was used to monitor the thickness of the samples by watching in real time the interference curve between the reflections at the interfaces vacuum-sample and sample-substrate. We have measured the thickness of pure methyl formate samples and estimated the band strength A (cm molecule^{-1}) of its bands. The detailed description of the procedure can be found in Modica and Palumbo (2010) and in Fulvio et al. (2009). Our experiments enabled us to obtain an estimate of the amount of the most abundant molecules (and methyl formate) present in the sample after each step of irradiation. The column densities were monitored using the equation

$$N = \frac{\int \tau(\nu)\, d\nu}{A}, \tag{1}$$

where A is the band strength value. Table 1 lists the band strength values used in this work along with the spectral characteristics of the bands considered. The thickness of the samples is corrected by a factor of

$$\frac{1}{\cos\theta_r} = \frac{1}{\sqrt{1 - \frac{\sin^2\theta_i}{n_f^2}}}, \tag{2}$$

where θ_r is the refractive angle. This correction takes into account the increased path length of the IR beam at an incidence angle $\theta_i = 45°$.

3. Results

We have performed several laboratory experiments analyzing interstellar and cometary ice analogs by using infrared spectroscopy. In particular, we have studied a pure CH_3OH ice and a CO:CH_3OH ice mixture in the ratio 1.6:1. The samples were deposited on KBr substrates at 16 K and then they were irradiated with 200 keV protons.

The experimental results here described are not new, they have been already discussed in the framework of their relevance in explaining the presence of methyl formate in interstellar clouds

Table 1
Band strength values of reference bands for methyl formate, methanol, and carbon monoxide.

Species	Band position		Assignment	Band strength	Reference
	cm^{-1}	μm		cm molecule^{-1}	
$HCOOCH_3$	1164	8.59	CH_3 rock	1.96×10^{-17}	Modica and Palumbo (2010)
CH_3OH	1033	9.68	C–O str	1.3×10^{-17}	Palumbo et al. (1999)
CO	2137	4.68	C$\equiv$O str	1.1×10^{-17}	Jiang et al. (1975)