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Desorption from methanol ice induced by electrons from solar wind or magnetospheres

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Abstract

This work analyzes the physico-chemical effects due to electron irradiation, as e.g. caused by the solar wind, on pure methanol (CH_3-OH) ice. Methanol has been detected in gas and condensed phases in several astrophysical environments, such as comets, asteroids, toward star forming regions and molecular clouds. In some of these environments, methanol is the most abundant specie after water ice. The interaction of ionizing agents with methanol ice induces the production of ionized species, leading to the formation of new compounds. In this work, pure methanol ice (at 142 K) was irradiated, in ultra-high vacuum regime, with 800 eV electrons, thus simulating the wind in frozen surfaces. The desorbed ions were analyzed using time-of-flight mass spectrometry. The results show the formation of protonated species, such as $(CH_3OH)H^+$, H_2COH^+, $C_2H_3^+$ and HCO^+. Absolute desorption yields were determined and compared with results available in the literature from similar experiments. The ionic desorption rate is an important parameter in surface chemistry. It is often approximated in chemical evolution models of astrophysical environments, due to the lack of experimental data.

Keywords: Methanol ice; Mass spectrometry; Astrophysical ices; Desorption stimulated by solar wind

1. Introduction

Methanol (CH_3OH), an organic alcohol, was first detected at 834 MHz with the NRAO radio telescope, toward the center of the galaxy, in the Sagittarius B2 region (Ball et al., 1970). Methanol was also detected in the Solar System in comets (e.g. 1P/Halley, Geiss et al., 1991 and C/1995 O1 Hale Bopp, Crovisier, 1998), in centaur bodies, such as 5145 Pholus (Cruikshank et al., 1998) and in trans-Neptunian objects, such as some Kuiper belt asteroids (Brunetto et al., 2006).

Hodyss et al. (2009) attribute an absorption feature at 3.53 μm in the spectrum of Enceladus to the presence of methanol in this Saturn satellite. In the outer space, methanol was detected toward star forming regions, such as W33A and RAFGL 7009, where the relative abundance of methanol to water is approximately 15% and 30%, respectively (Dartois et al., 1999). Pontoppidan et al. (2003) found young low mass stars (SVS 4-5, SVS 4-9 and a source in the Chameleon I cloud known as Cha INa 2), with a large abundance of methanol compared to water (15–25%). In some low mass star formation regions, and in dark molecular clouds, methanol is found as a minor constituent, usually representing 5% or less in mass (Gibb et al., 2004).

Icy surfaces of Jovian and Saturnian satellites are continually under the influence of ionizing agents from the local magnetospheres and outer space. Examples of these sources of ionization are electrons from solar wind, cosmic rays and photons.

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This paper focuses on the effects due to the impact of 800 eV electrons on methanol ice. Electrons with energies around 1 keV are representative of a fraction of the primary and secondary electron flux incident onto the surfaces of some ice covered bodies in the solar system, like moons and comets (Hand and Carlson, 2011), and they are also compatible with secondary electrons generated by cosmic rays in interstellar clouds.

Irradiation of Methanol ice by electrons, ions or photons has been studied by several authors in the last years. Some of the species detected due to methanol ice processing include CH_4, CO_2, CO and H_2CO by Baratta et al. (1994), Bernstein et al. (1995), Gerakines et al. (1996), Moore et al. (1996), Palumbo et al. (1999) and Hudson and Moore (2000), and de Barros et al. (2011). The HCO molecule was detected by Allamandola et al. (1988), Hudson and Moore (2000), Bernstein et al. (1995), Gerakines et al. (1996) and Bennett et al. (2007). Larger molecules, like C_2H_5OH, among others, were also detected by Bernstein et al. (1995) and Moore et al. (1996). The present work analyses the species produced due to irradiation and calculates the desorption rates of these species. The results may contribute to the development of chemical evolution models for different astrophysical environments.

2. Experimental setup

The electron stimulated ion desorption experiment was carried out in the Surface Chemistry Laboratory, at the Universidade Federal do Rio de Janeiro (UFRJ). The experimental setup consists of an XYZ sample manipulator, a commercial electron gun and a home-made time-of-flight mass spectrometer (TOF-MS) housed in an ultra-high vacuum (UHV) chamber. The vacuum system of the LaQuiS consists of three vacuum pumps: a mechanical rotating palette pump, a turbo molecular pump and a titanium sublimation pump, as described in detail by Mendes et al. (2007). The base pressure in the chamber was about 5×10^{-10} mbar. The TOF-MS consists of an ion extraction system, electrostatic collimating lens, a drift tube and a pair of microchannel plates (MCP) detectors, in chevron configuration. After extraction, the positive ions travel through three metallic grids (each with a nominal transmission of ~90%), before reaching the MCP.

Methanol was purchased commercially from Sigma–Aldrich with purity greater than 99% and degassed through several freeze–pump-thaw cycles before its vapor being admitted into the UHV chamber. The ice preparation begins with the condensation of a thin methanol film on a stainless steel sample holder, connected to a gaseous nitrogen cooling system inside the chamber. The minimum temperature reached was about 140 K. CH_3OH was introduced into the chamber for 12 min at pressure around 1×10^{-8} mbar. Thus, the film is formed *in situ,* under multilayer regime.

The methanol surface was irradiated by a monoenergetic (800 eV) pulsed electron beam (electron gun model ELG-2, Kimball Physics), with frequency of 80 kHz and pulse width of 20 ns. The start signal was provided by a pulse generator, linked to the electron gun. The stop signal corresponds to the output of the detector, processed using a standard system of counting pulses, which consists of a pre-

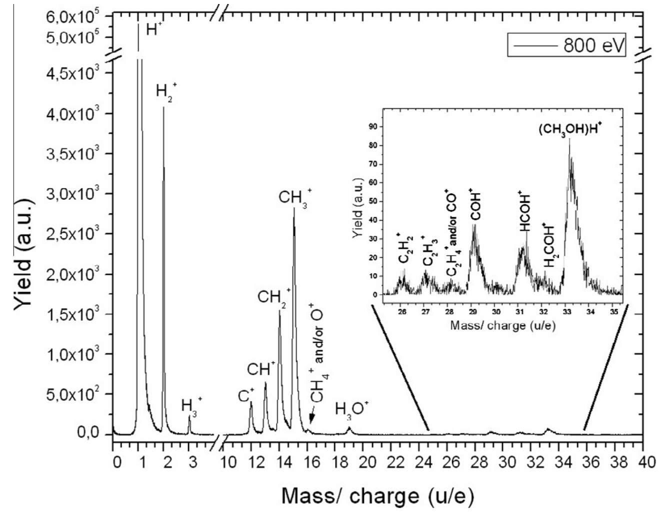

Fig. 1. Mass spectrum of positive desorbed ions from methanol ice due to irradiation with 800 eV electrons.

Table 1
Comparison of the ion/impact ratio of ions desorbed from methanol ice for different ionizing agents: 800 eV electrons (this work) [$Y_{electrons}$], soft X-rays [$Y_{X\text{-}rays}$] and Cosmic rays [Y_{ion}].

m/z	Ion	$Y_{Electrons}$ ($\times 10^{-10}$)	[a]$Y_{X\text{-}rays}$ ($\times 10^{-10}$)	[b]Y_{ions} ($\times 10^{-5}$)
1	H^+	7179.9	100.3	19.2
2	H_2^+	64.8	4.8	5.1
3	H_3^+	3.4	–	1.3
6	C^{++}	Trace	3.5	–
12	C^+	11.1	–	9.5
13	CH^+	17.5	–	8.3
14	CH_2^+	46.0	191.0	22.5
15	CH_3^+	79.3	1.6	39.5
16	CH_4^+ or O^+	2.0	50.1	3.2
17	OH^+	Trace	–	3.8
18	H_2O^+	0.3	–	23.6
19	H_3O^+	2.9	58.8	20.2
25	C_2H^+	Trace	–	3.8
26	$C_2H_2^+$	0.3	–	11.8
27	$C_2H_3^+$	0.4	–	16.4
28	$C_2H_4^+$ or CO^+	0.2	13.4	17.1
29	HCO^+	1.1	16.2	40.7
30	H_2CO^+	0.2	40.9	22.69
31	H_2COH^+	1.2	354.2	48.4
32	H_3COH^+ or CH_3OH^+	0.07	–	3.6
33	$(CH_3OH)H^+$	2.9	–	180
…	…	…	…	…
65	$(CH_3OH)_2H^+$	Trace	–	159.0
97	$(CH_3OH)_3H^+$	Trace	–	100.0
98	$(CH_3OH)_3H_2^+$	Trace	–	5.5
99	$(CH_3OH)_3H_3^+$	Trace	–	3.3

[a] Andrade et al., (2010).
[b] Andrade et al., (2009).