

Ionic desorption of methanol ice in different space environments

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Abstract. Methanol is the simplest organic alcohol and is a precursor to many more complex prebiotic species. This substance has already been found in solid phase in several astrophysical environments such as comets and protostars, which in turn are bombarded with different ionizing particles such as, for example, cosmic rays and from stellar winds. In some regions around young stars, such as RAFGL 7009, the Methanol detection showed high abundance, reaching 30 percent in relation to water in the condensed phase. In this work, studies of the desorption induced by energetic particles, simulating the interaction of cosmic rays with methanol ice, were carried out using the technique of time of flight mass spectrometry. Negative ions were analyzed together with their clusters desorbed, thus obtaining the relative yields of each one of them. In this phase of the work, an emphasis will be given to the production of negative ions desorbed from the sample and the possible paths of fragmentation of the molecule. The formation of anions of the hydrogen series (Hn) was not observed, but the formation of anions of hydrocarbons (CnHn), in addition to the formation of the cluster series (CH₃OH)_nCH₃O⁻. A discussion of possible methanol fragmentation pathways, as well as astrophysical implications for this phenomenon will be discussed.

Resumo. O metanol é o álcool orgânico mais simples e é precursor de muitas espécies pré-bióticas mais complexas. Esta substância já foi encontrada em fase sólida em diversos ambientes astrofísicos como cometas e protoestrelas, que por sua vez são bombardeados com diferentes partículas ionizantes como, por exemplo, raios cósmicos e partículas provenientes dos ventos estelares. Em algumas regiões em torno de estrelas jovens, como a RAFGL 7009, a detecção de metanol mostrou alta abundância, chegando a 30 por cento em relação a água na fase condensada. Neste trabalho, estudos da dessorção induzida por partículas energéticas, simulando a interação de raios cósmicos com gelo de metanol foram realizados a partir da técnica espectrometria de massa por tempo de voo. Foram analisados os íons negativos juntamente com os seus clusters dessorvidos, obtendo assim os rendimentos relativos de cada um destes. Nesta fase do trabalho, uma ênfase será dada a produção de íons negativos dessorvidos da amostra e nos possíveis caminhos de fragmentação da molécula. Não foi observada a formação de ânions da série do hidrogênio (Hn), mas foi observada a formação de ânions de hidrocarbonetos (CnHn), além da formação da série de cluster (CH₃OH)_nCH₃O⁻. Uma discussão sobre os possíveis caminhos de fragmentação do metanol, assim como as implicações astrofísicas para este fenômeno serão discutidos.

Keywords: Astrochemistry – Methods: laboratory – Methods: data analysis – Molecular data – Molecular processes

1. Introduction. Why study methanol?

Methanol is the simplest organic alcohol and is a precursor to many more complex prebiotic species. It has already been found in solid form (ice) in various astrophysical environments such as comets and protostars, which in turn are bombarded with different ionizing particles, such as cosmic rays and particles from stellar wind (Andrade et al. 2009).

2. The experiment and methodology

At the Van de Graaf Laboratory, at the Pontifical Catholic University of Rio de Janeiro (PUC – Rio), fission fragments of Californium-252 with energy around 65 MeV were used to simulate the influence of cosmic rays on methanol ice inside an high-vacuum chamber, simulating an astrophysical environment (Andrade et al. 2010). During the procedure, mass spectra of secondary negative ions desorbed by the ice surface were obtained using the Plasma Desorption Mass Spectrometry (PDMS) technique.

The top of figure 1 shows a schematic of the vacuum chamber used in the experiment and, at the bottom, the stages through which the fragments pass from the moment they were formed (after the impact of the ionizing beam) until they reach the detector. This technique uses the time of flight of the fragments to discriminate their masses (Dartois et al. 1999; Santos et al. 2018), since the time of flight can be converted into a mass-

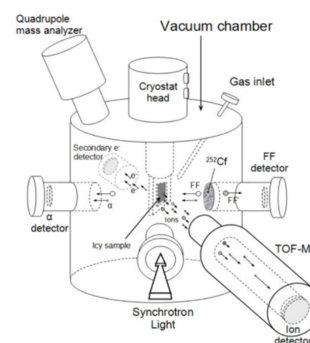


FIGURA 1: Schematic of the chamber used in the PDMS experiments, containing a TOF-type mass spectrometer, and other mechanisms

charge ratio through simple calculations of classical mechanics and electromagnetism.

Since we are working with methanol, the ions formed will be derivatives from Carbon, Oxygen and Hydrogen. Using Origin 8.5 program, it was possible to calibrate the spectra, converting the time of flight in mass/charge ratio (m/q), and to obtain the relative yields to the desorbed negative ions at three different temperatures: 55 K, 100 K and 120 K. Figure 2 shows the mass

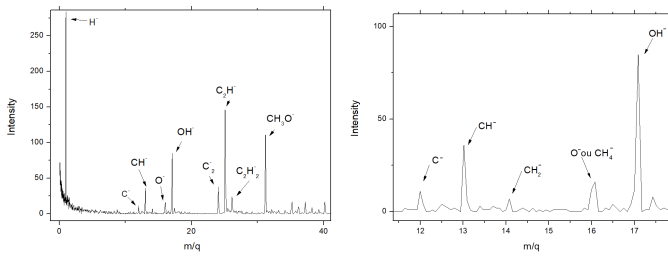


FIGURA 2: 120 K

spectra of the desorbed negative ions at 120 K to $1 < m/q < 40$ u/e (at left) and a zoom at right.

3. Results

3.1. Ions

Observing the ions between 1 and 40 u/e, it was noticeable that in the CH_n^- series, the most intense was CH^- ($m/q = 13$ u/e), and in the C_nH_n^- series, it was C_2H^- ($m/q = 25$ u/e). Also, the ions 13 and 25 u/e had a preference in formation for 120 K temperature, while the ions 17 and 31 u/e for 55 K.

3.2. Clusters

It is possible to notice the formation of cluster series of methanol: $(\text{CH}_3\text{OH})_n\text{OH}^-$ and $(\text{CH}_3\text{OH})_n\text{CH}_3\text{O}^-$. Clusters with up to $n = 22$ were found. It was observed that the desorption pattern of clusters changed with the temperature. This change must be related with the ice structure. At temperature around 55 K, ice with an amorphous structure is expected, while at higher temperatures, around 120 K, the crystalline form appears. Between 55 K and 120 K, a mixture of these forms must be present.

The $(\text{CH}_3\text{OH})_n\text{CH}_3\text{O}^-$ series had a higher yield at 100 K, while at 120 K, the yields to the $(\text{CH}_3\text{OH})_n\text{OH}^-$ series were higher, showing that depending on the temperature, the distribution of clusters changes, producing a different pattern. This result can be seen in Figure 6, where the relative yields to $T = 55$ K, 100 K and 120 K are displayed.

4. Conclusions

In this work, an astrophysical environment containing methanol irradiated by cosmic rays was simulated. The methanol fragmentation pattern was analyzed, as well as the clusters series pattern at different temperatures. These results may help to understand methanol fragmentation in frozen space environments such as ice grains in the interstellar medium under the influence of cosmic rays. Such results can be used in models of chemical evolution of the medium for the formation of more complex molecules from the generated fragments.

References

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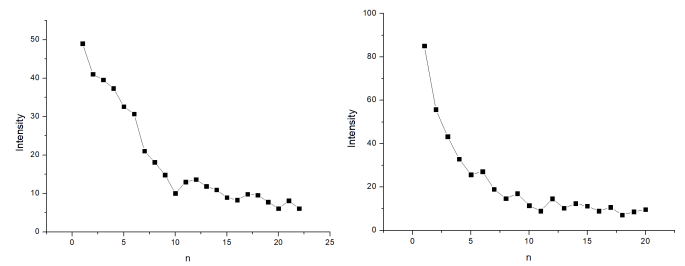
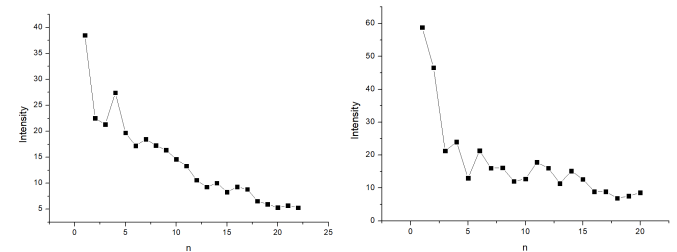
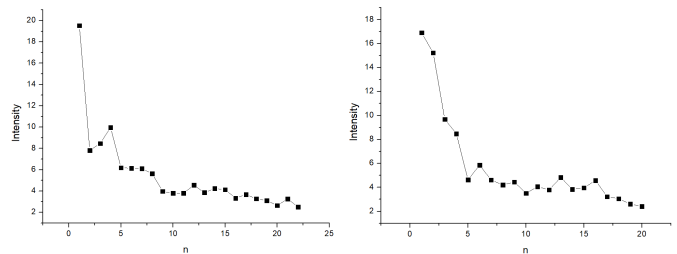
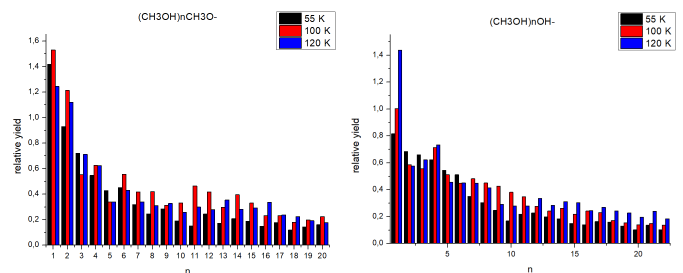

 FIGURA 3: $(\text{CH}_3\text{OH})_n\text{OH}^-$ and $(\text{CH}_3\text{OH})_n\text{CH}_3\text{O}^-$ series at 55 K

 FIGURA 4: $(\text{CH}_3\text{OH})_n\text{OH}^-$ and $(\text{CH}_3\text{OH})_n\text{CH}_3\text{O}^-$ series at 100 K

 FIGURA 5: $(\text{CH}_3\text{OH})_n\text{OH}^-$ and $(\text{CH}_3\text{OH})_n\text{CH}_3\text{O}^-$ series at 120 K


FIGURA 6: Relative yields