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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 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 molécula 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 vôo. 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 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 a 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-

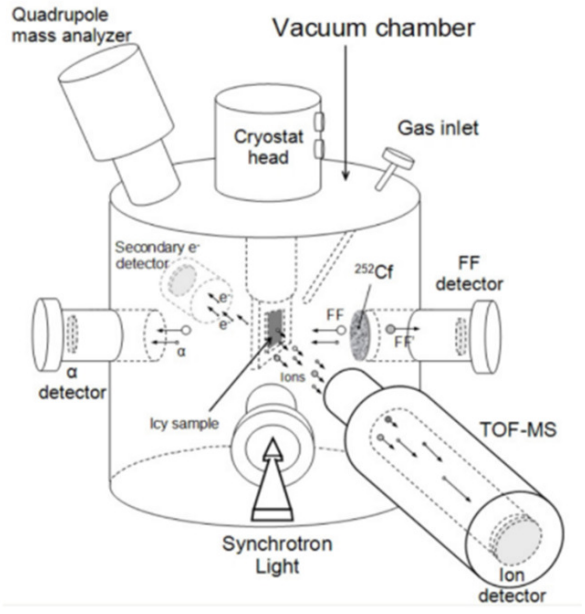

Figura 1. Schematic of the chamber used in the PDMS experiments, containing a TOF-type mass spectrometer, and other mechanisms

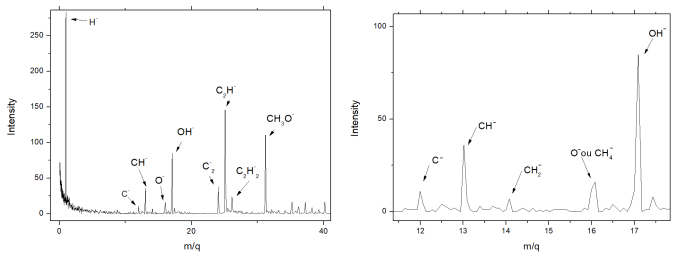

Figura 2. 120 K

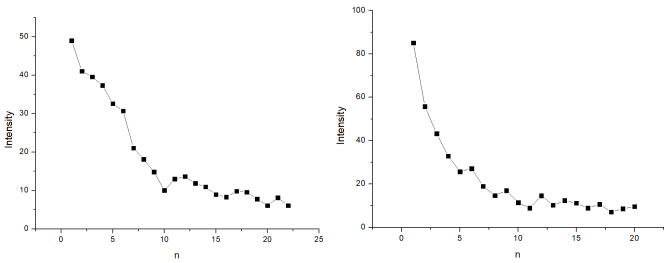

Figura 3. $(CH_3OH)_nOH^-$ and $(CH_3OH)_nCH_3O^-$ series at 55 K.

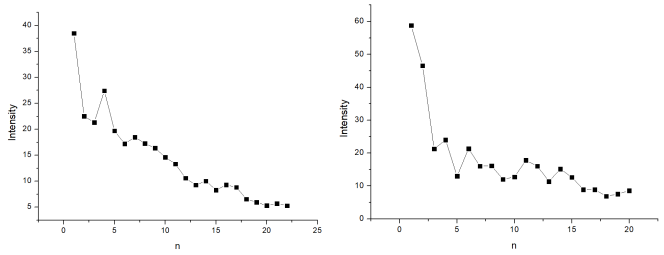

Figura 4. $(CH_3OH)_nOH^-$ and $(CH_3OH)_nCH_3O^-$ series at 100 K.

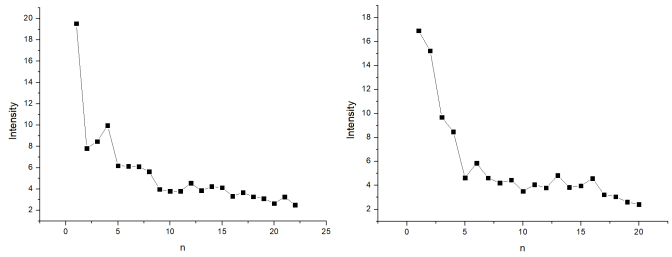

Figura 5. $(CH_3OH)_nOH^-$ and $(CH_3OH)_nCH_3O^-$ series at 120 K.

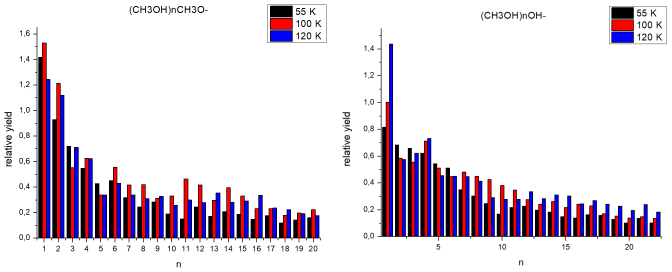

Figura 6. Relative yields.

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 of the desorbed negative ions at three different temperatures: 55 K, 100 K and 120 K. Figure 2 shows the mass 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: $(CH_3OH)_nOH^-$ and $(CH_3OH)_nCH_3O^-$. It was observed that the desorption pattern of clusters changed with the temperature. This change is 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.

The $(CH_3OH)_nCH_3O^-$ series had a higher yield at 100 K, while at 120 K, the yields to the $(CH_3OH)_nOH^-$ 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.

3.3. Breakdown pathways

With all the data collected, it was possible to think about some molecular breakdown pathways and give each path a probability. These probabilities were calculated normalizing the data of both positive and negative ions.

The tables 7 and 8 display the primary pathways of methanol fragmentation when bombarded by californium fission fragments. Next to each fragment, the percentage of breakages has been inserted as a way to indicate the ease or difficulty in the formation of these species. The fracture pathways were chosen taking into account that the interaction of cosmic rays with matter will either excite or positively ionize the molecules, given that the transferred energy is significant.

3.4. Cross-section and Half-life

The decay of californium produces around 96 percent of alpha particles with an avarage energy of 6 MeV. Thus, using the SRIM program, it is possible to find the energy these particles transfer to the methanol target. This energy is known as the eletronic stopping power (Se). The destruction cross-section of a molecule is related to the Se accorting to the law: σ = a . $Se^{3/2}$ (Barros et al, 2011; Andrade et al, 2013). Using data from Barros, who found the power law for methanol irradiated with different ionizing agents, and the alpha particle flux in the interestellar medium given by Shen et al. (2004), it was possible to calculate the half-life of methanol in the interestellar medium due to He particules.

The destruction cross-section found was 1.7 x 10^{-16} cm^2. Although the destruction cross-section of methanol is not constant with the projectile's energy loss and it's initial energy, we can consider the cross-section found here as a good approximation at range of 10^{-3} MeV/nucleon. Using the alpha particle flux in the interstellar medium from Shen et al. (2004) with energy of 6 MeV (1.5 MeV/nucleon) and considering an energy range

$CH_3OH^+ \rightarrow C^-$ (2,2%) + H_3O^+ (21,3%) + H^+ (20,6%)
$CH_3OH^+ \rightarrow C^+$ (3,8%) + H_3O^+ (21,3%) + H^- (17,3%)
$CH_3OH^- \rightarrow CH_3O^-$ (23,5%) + H*
$CH_3OH^* \rightarrow CH_3O$- (23,5%) + H^+ (20,6%)
$CH_3OH^- \rightarrow CH_2^+$ (2,2%) + H^- (17,3%) + OH^- (17,4%)
$CH_3OH^* \rightarrow CH_2$* + H^+ (20,6%) + OH^- (17,4%)
$CH_3OH^- \rightarrow CH_2$- (0,7%) + H^- (20,6%) + OH^- (17,4%)
$CH_3OH^- \rightarrow CH_3$* + OH^- (17,4%)
$CH_3OH^* \rightarrow CH_3^+$ (9,7%) + OH^- (17,4%)
$CH_3OH^+ \rightarrow CH_2^+$ (2,2%) + H^+ (20,6%) + OH^- (17,4%)

Figura 7. Methanol breakdown pathways with highest probabilities.

$CH_3OH^+ \rightarrow C^+$ (3,8%) + H- (17,3%) + H_2O^+ (2,9%) + H*
$CH_3OH^+ \rightarrow C^-$ (2,2%) + H^+ (20,6%) + H_2O^+ (2,9%) + H*
$CH_3OH^+ \rightarrow C^-$ (2,2%) + H_2^+ (5,8%) + H_2O^+ (2,9%)

Figura 8. Methanol breakdown pathways that break into water.

of 10^{-3} up to 10^3 MeV/nucleon, the half-life is 8.2 x 10^{12} s, in other words, 260 thousand years.

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 of desorption at different temperatures. Also, it various methanol breakdown pathways were estimated. To each path a probability was also estimated. Furthermore, it was possible to calculate the stopping power of alpha particles in methanol ice and the destruction cross-section of methanol under the bombardment, the half-life of methanol in the interstellar medium can be estimated as well.

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 or energetic solar particles. 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

Andrade, D. P. P., Boechat-Roberty, H. M., Martinez, R., Homem, M. G. P., da Silveira, E. F., & Rocco, M. L. M. 2009, Surf. Sci., 603, 1190.

Andrade, D. P. P., Rocco M. L. M. , & Boechat-Roberty, H. M. 2010, RAS., 409, 1289.

Dartois E., Schutte, W. A., Geballe T. R., Demyk K., Ehrenfreund P., & d'Hendecourt L. B. 1999, A&A., 342, L32.

Santos, J. C., Andrade D. D. P., da Silveira E. F., Pilling S., & Boechat-Roberty H. M. 2018, UNIVAP., 33, 38.

de Barros, A. L. F. ; Domaracka, A. ; Andrade, D. P. P. ; Boduch, P. ; Rothard, H. & da Silveira, E. F. 2011, RAS., 418, 1363

, Ana L. F. de Barros, Pilling S., Alicja Domaracka, Rothard H., Boduch P. & da Silveira E. F. 2013, RAS., 430, 787-796.