EXPERIMENTAL SIMULATION OF FAST ELECTRON BOMBARDMENT OF METHANOL ICE AND ITS IMPLICATIONS IN ASTROCHEMISTRY

SIMULAÇÃO EXPERIMENTAL DO BOMBARDEIO DE GELO DE METANOL POR ELÉTRONS RÁPIDOS E SUA IMPLICAÇÃO EM ASTROQUÍMICA

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Abstract - In this work, we experimentally simulate the methanol (CH_3OH) ice behavior (12 K) through the bombarded by fast electrons (4.9 keV) in an attempt to simulate radiation chemistry induced by radiation in space environments. The sample analysis by infrared spectroscopy reveals the appearance of new species, including CO_2, CO, H_2O, and CH_4, during the sample bombardment. We have quantified the effective destruction cross-section of methanol (5.5×10^{-19} cm2) and determined the formation cross-section for these newly produced species. Additionally, we have characterized the chemical equilibrium (CE) phase, which becomes evident at higher fluences. We have also calculated molecular abundances and assessed the desorption yield induced by fast electrons within the same sample. Furthermore, we estimated the timescale required to achieve chemical equilibrium in specific astrophysical environments impacted by electrons. This study significantly contributes to our comprehension of electron bombardment behavior in astrophysical ices and allows for meaningful comparisons with organic-rich ices in space environments.

Keywords: Astrochemistry; Methanol; Astrophysical Ice, Desorption; Laboratory experiments; Electron bombardment.

Resumo - Neste trabalho, simulamos experimentalmente o comportamento do gelo de metanol (CH_3OH) numa temperatura de 12 K sob bombardeio de um feixe de elétrons rápidos (4.9 keV) na tentativa de reproduzir os processos fisioquímicos induzidos por elétrons em ambientes espaciais. A análise da amostra por espectroscopia infravermelha revela o surgimento de novas espécies, incluindo CO_2, CO, H_2O e CH_4, devido ao processamento pela radiação ionizante. Quantificamos a seção de choque efetiva de destruição do metanol (5.5×10^{-19} cm^2) e determinamos a seção choque efetiva de formação para as novas espécies produzidas. Além disso, caracterizamos a fase de equilíbrio químico (EQ), que se torna evidente em fluências mais altas. Calculamos também as abundâncias moleculares e avaliamos o rendimento de dessorção induzido por elétrons rápidos na amostra. Também foi estimado a escala de tempo necessária para atingir o equilíbrio químico em ambientes astrofísicos específicos impactados por elétrons. Este estudo contribui para uma melhor compreensão do efeito do bombardeio de elétrons em gelos astrofísicos e permite comparações significativas com os gelos ricos em compostos orgânicos em ambientes espaciais.

Palavras-chave: Astroquímica; Metanol; Gelo astrofísico; Dessorção; Experimentos de laboratório; Bombardeio por elétrons.

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Data de submissão: 20.06.2022
Data de aprovação: 14.11.2023

Identificação e disponibilidade:
(https://revista.univap.br/index.php/revistaunivap/article/view/4401,
http://dx.doi.org/10.18066/revistaunivap.v29i61.4401).

Introduction

Methanol (CH_3OH), the simplest alcohol, is prominently observed within various celestial settings, including protostellar clouds, molecular clouds, and comets (Parise et al., 2006; Friberg et al., 1988; Bockeleé-Morvan et al., 1994). The formation of interstellar methanol can transpire in both the gaseous phase and on the surfaces of astrophysical ices. However, it is worth noting that reactions occurring solely in the gaseous phase are insufficient to account for the observed abundance of methanol. Therefore, reactions involving solid grains are imperative (Millar et al., 1991).

Notably, methanol detection in the gaseous phase has been documented (Wang et al., 2011; Walsh et al., 2016). The initial detection took place using the NRAO radio telescope, precisely in Sagittarius B2, at a frequency of 834 MHz (Ball et al., 1970). Subsequent detections were achieved in dense molecular clouds (Irvine et al., 1987; Tielens & Allamandola, 1987). More recently, significant milestones in methanol detection include its observation in the circumstellar gas of a proto-star, TW Hya, measured using the Atacama Large Millimeter Array (ALMA) (Walsh et al., 2016), and the identification of a methanol concentration in a prestellar core during the protostellar phases within a Very Low Luminosity Object (VeLLO) known as L1521F (Favre et al., 2020).

Molecules in space environments are continuously subjected to radiation, making their study vital for a better understanding of the molecular evolution within the interstellar medium. This research not only aids in elucidating astronomical observations but also contributes to our comprehension of the intricate processes shaping the cosmos.

This research analyzes an analysis of methanol's solid-phase destruction at 12 K under the influence of fast electrons with an energy of 4.9 keV, akin to the conditions found in the interstellar and interplanetary mediums. Additionally, we investigate the concurrent formation of daughter species over time.

It's worth noting that the same technique employed in this study, albeit using a different ionizing agent, has proven valuable for assessing the destruction and formation processes of various molecules in previous experiments conducted by the LASA workgroup. These experiments encompassed the study of SO_2 ice at 12 K (Bonfim et al., 2017), pure $HCOOCH_3$ ice at 12 K (Rachid et al., 2017), a binary ice mixture of N_2:CH_4 (19:1) at 12 K (Vasconcelos et al., 2017), a quaternary ice mixture of H_2O:CO_2:NH_3:SO_2 (10:1:1:1) at two distinct temperatures (50 K and 90 K) (Pilling & Bergantini, 2015), and CH_3OH pure ice at 12 K subjected to soft X-rays (6 to 2000 eV) (Freitas & Pilling, 2020).

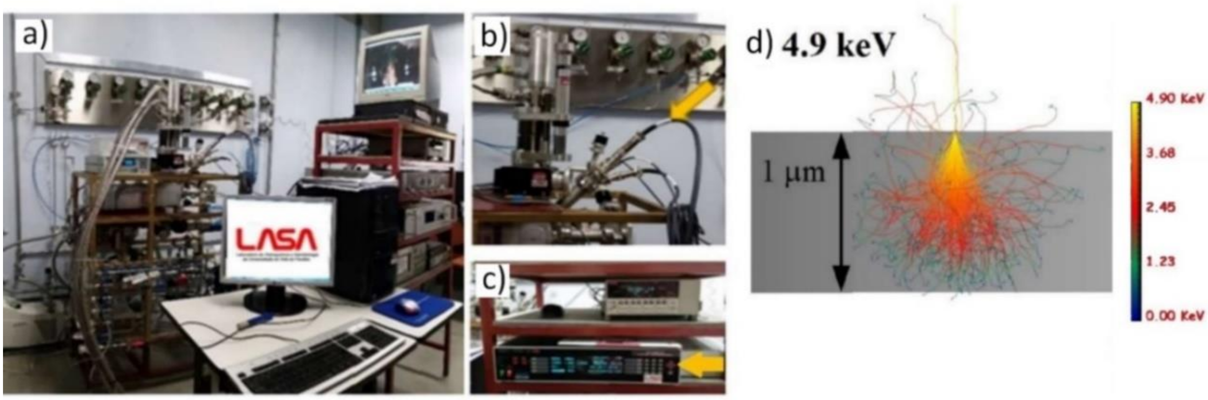
Methodology

In this manuscript, we conducted our experiments within the vacuum chamber at the Laboratory of Astrochemistry and Astrobiology at the Universidade do Vale do Paraiba (LASA/UNIVAP). Our setup involved the integration of a helium closed-cycle Cryostat (ARS Inc.) and an electron gun (Kimball Physics).

Gaseous CH_3OH was methodically deposited onto a pristine ZnSe substrate crystal affixed to the cryostat head within the vacuum chamber to provide a brief overview of our experimental procedure. This deposition process was achieved using a capillary tube positioned approximately 0.5 cm away from the crystal and took approximately 5 minutes to form an ice layer with an initial thickness of 1 μm. The experiments were carried out at a temperature of 12 K, maintaining a base pressure of approximately 2×10^{-8} mbar throughout. During the experiments, the sample was subjected to irradiation by 4.9 keV electrons and meticulously monitored using Fourier-transformed Infrared spectroscopy (FTIR) at various radiation fluences.

Figure 1 illustrates several key components used in this study: (a) an image of the experimental chamber at LASA laboratory at Univap, (b) a close-up highlighting the electron gun, (c) the electronic interface of the electron gun during the experiment, and (d) a simulation depicting the penetration depth of fast electrons into the sample, carried out using CASINO software (Hovington & Drouin, 2007). In panel (d), the simulation demonstrates a multitude of potential electron trajectories when subjected to bombardment at 4.9 keV as they penetrate a sample of pure methanol. Based on this simulation, we defined the ionizing agent's penetration depth as encompassing 90% of the sample's volume. The remaining 10%, which remained unaffected and unchanged, was excluded from our analysis of chemical alterations.

Figure 1 - Several key components used in this study. a) A photograph featuring the LASA setup, including the experimental chamber and the electron gun. b) A close-up view highlighting the electron gun. c) The electronic interface of the electron gun during the experiment, indicated by the arrow, with an ammeter in operation. d) A simulation illustrating the penetration depth of fast electrons, conducted using CASINO software (Hovington & Drouin, 2007).



Results and Discussions

The infrared spectrum of unirradiated methanol ice is depicted in Figure 2 (a), accompanied by the prominent vibrational bands and their respective attributions. It is important to note that each band exhibits distinct intensities stemming from varied band strengths, influencing their interactions with incident infrared radiation.

Here, we quantitatively assess alterations in methanol abundance by focusing on three distinct vibrational modes. Firstly, the OH stretch corresponds to the band at 3347 cm^{-1}. Secondly, the symmetrical and antisymmetric stretch of CH_3 within the 2900 cm^{-1} region. Finally, the CO stretches at the 1030 cm^{-1} region. We calculate the column densities using the Lambert-Beer law as outlined in (Bouilloud et al., 2015).

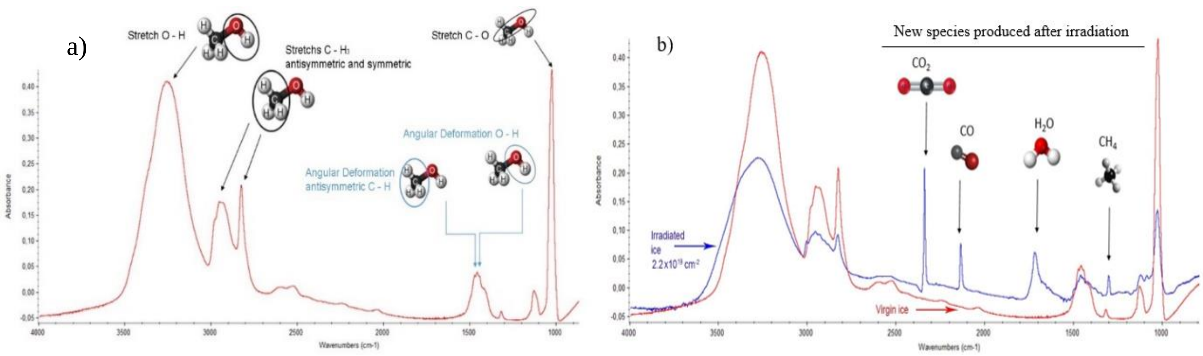
In Figure 2 (b), the most recent spectra of ice following 260 minutes of bombardment by fast electrons are depicted (highlighted in blue), overlaid with the spectra of unirradiated ice (displayed in red). The bands related to the vibration modes of the newly formed daughter species are readily discernible. Molecular assignments and band strengths used in this study were sourced from Hudgins et al., 1993.

According to Pilling and Bergantini, 2015 the change of molecular abundance as a function of radiation fluence (destruction or production) was evaluated by the analysis of infrared area evolution with fluence using:

$$S - S_0 = S_\infty \times \left[1 - e^{(-\sigma_{d,f} \times F)}\right] \quad [\mathrm{cm}^{-1}] \tag{1}$$

where F is the fluence, in units of cm^{-2}, S, S_0 and S_∞ are related to the band areas of the infrared spectrum, at a given fluence, for the un-irradiated sample, and at the highest fluence, respectively. In this equation, $\sigma_{d,f}$ represents the effective formation cross section (σ_f) new-formed species or the effective destruction cross section (σ_d) parent species, both in units of cm^2 (Pilling & Bergantini, 2015).

Figure 2 - a) The infrared spectrum of amorphous methanol ice at 12K obtained in the current study, before irradiation. The main vibrational modes are indicated. b) Overlap of the virgin methanol ice (red line) and irradiated ice spectra after 260 minutes of exposure to fast electrons (4.9 keV)



In Figure 3, we present a graphical representation of the subtracted band area, a metric that directly correlates with the molecular abundances of both the measured methanol bands and the identified daughter species. This visual depiction serves as a valuable tool for understanding the impact of electron bombardment on the composition of methanol ice as a function of fluence. The lines within the graph represent the best-fit curves generated using Equation 1, allowing us to derive crucial insights from the data. Additionally, the values for the effective cross-section, a fundamental parameter in this study, are thoughtfully included for reference.

Figure 3 is divided into two panels: the upper panel and the lower panel. In the upper panel, we focus on the newly generated species as a result of fast electron bombardment. These species, including CO_2, CO, H_2O, and CH_4, play a pivotal role in reshaping the molecular landscape of methanol ice under irradiation conditions. By analyzing the numerical evolution of the abundance of each of these indicated daughter species, we gain valuable insights into the complex chemical transformations occurring during the experiment. In the lower panel, our attention shifts to the destruction and dissociation processes within the methanol molecule itself. Here, we quantify these transformations by tracking the reduction in bands associated with the vibration modes of specific segments of the molecule. In this context, we specifically focus on the C-O stretch, a crucial component often considered as the "backbone" of the methanol molecule (Portugal et al., 2014). This choice is particularly significant as it represents the effective destruction of methanol ice, symbolizing the cleavage of the carbon-oxygen bond—a fundamental chemical alteration during the irradiation process.

It's worth noting that our findings align with previous observations made by Ciaravella et al. (2018), who also detected the presence of CO and CO_2 molecules when irradiating CH_3OH with ultraviolet light in their samples. This convergence of results further underscores the significance of our research in shedding light on the intricate chemistry taking place in astrophysical environments.

Figure 3 – Quantification of changes in the IR spectrum of irradiated methanol ice. The top panel presents the evolution IR bands (in terms of subtracted band area) of the new produced species and bottom panel presents the methanol band evolution during irradiation by 4.9 keV electrons. The band areas are proportional to molecular abundances. The cross section are indicated in the figure and discussed in the text.

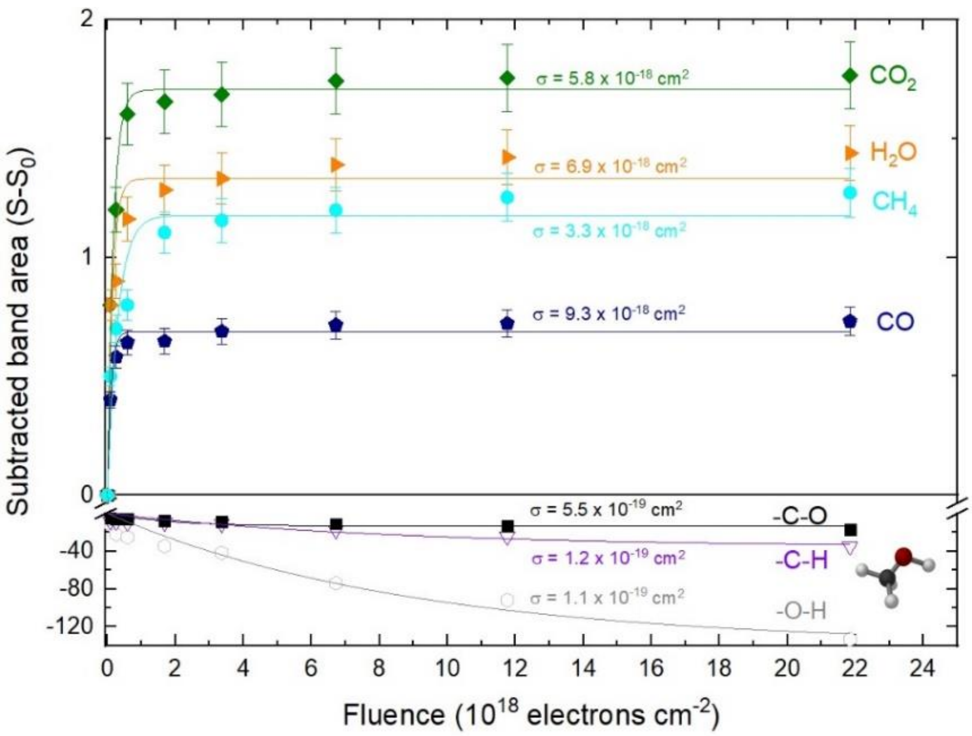
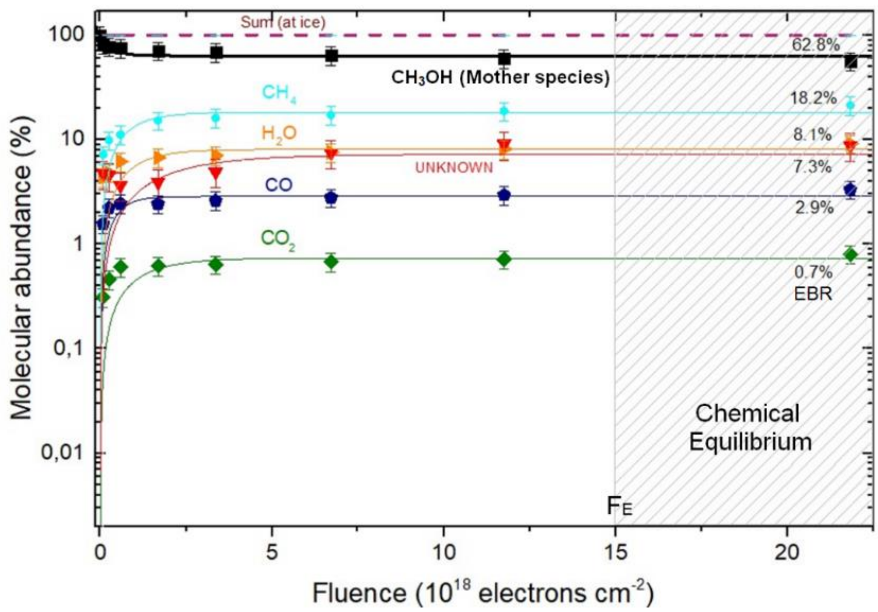


Figure 4 presents the molecular abundance (in percentage) as a function of electrons fluence obtained by the expression indicated in Pilling et al. (2019). In the right part, dashed regions indicate the equilibrium fluence (F_E) of the system (Pilling & Bergantini, 2015). At this fluence, chemical changes are no longer observed with IR spectroscopy, indicating that molecular abundances are virtually constant as well as similar destruction and formation rate at each molecular. In this equilibrium stage, the parent species produce the daughter molecules, which can also be intermediated in forming the new species and their parent molecules (Vasconcelos et al., 2017). In this figure we clearly observe that the evolution of molecular abundances as a function of radiation fluence tends to reach a plateau, indicating the appearance of chemical equilibrium in the sample. In the current experiment, this occurs at fluences of about 15 x 10^{18} electrons cm^{-2}.

The chemical equilibrium phase of irradiated ice in space, shaped by radiation flux and temperature fluctuations, embodies the intricate equilibrium between molecular formation and destruction processes. In the interstellar and interplanetary medium, where cosmic rays and stellar radiation are pervasive, these ices dynamically balance the rates of chemical reactions, radiative interactions, and thermal influences. This equilibrium is a crucial window into the celestial molecular compositions, shedding light on the origins and evolution of complex cosmic molecules that are fundamental to astrochemical investigations.

Figure 4 - Percentage evolution and percentage destruction of the abundance of species of methanol irradiated with electrons indicated as a function of electron fluence. The gray rectangle shows the estimated region of the chemical equilibrium fluence (F_E).



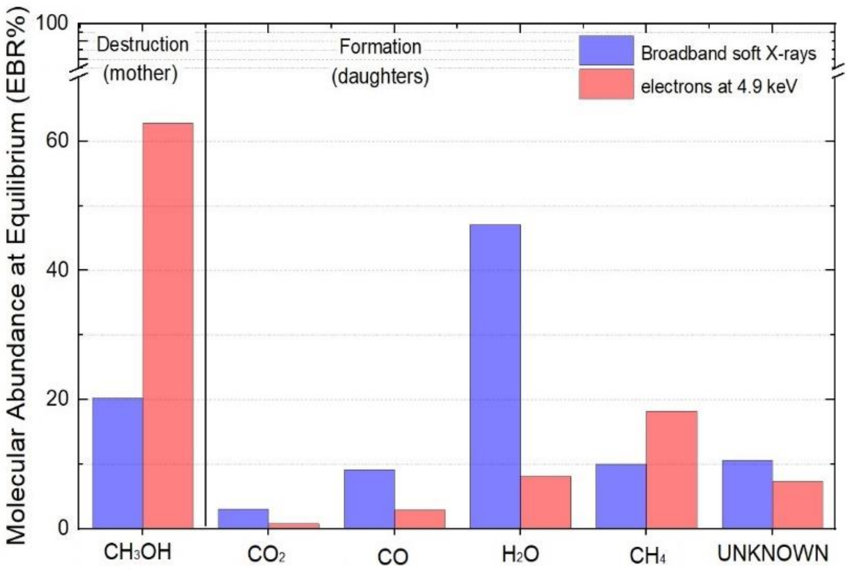
Astrophysical implications

Figure 5 compares the effectiveness destruction cross-section of CH_3OH, and the effective formation cross-section of selected daughter species observed in the two experiments (employing electrons and soft X-rays). The selected band to quantify the methanol molecular abundances in both works was the C-O stretch mode at 1030 cm^{-1}. We observed that methanol is more destroyed by X-rays than fast electrons.

Concerning the produced species, the amount of H_2O, CO_2, and CO was also larger in the experiment employing soft X-rays. This indicates that such incoming energy induced more chemical processes within the ice (mainly due to emitted secondary electrons, which also trigger chemical reactions). Curiously, the production of CH_4 is enhanced in the case of electron bombardment suggesting that some reaction pathways to produce CH_4 might be enhanced due to the presence of fast electron in the bombardment of methanol ice. The nature of the unknown species is under investigation and will be the subject of future publication.

Figure 6 illustrates the timescale necessary for methanol ice to reach chemical equilibrium when subjected to 4.9 keV electron bombardment at a constant temperature of 12 K, as a function of electron flux. Vertical lines on the graph represent the flux levels found in selected space environments exposed to fast electrons alongside the electron flux utilized in our laboratory experiments for comparative purposes. In certain instances, we have estimated approximate values using an r^{-2} law, referencing the electron flux in Earth's orbit (which includes both photons and electrons). Notably, this figure reveals that the impact of electron bombardment on the methanol sample yields effects similar to those induced by soft X-rays, employing the same experimental technique.

Figure 5 - Comparison between the molecular abundance at the chemical equilibrium of CH_3OH in the experiment carried out with electron bombardment (this work) and broadband soft X-rays (6-2000 eV), both at 12 K and employing the same instrumentation. The selected band to quantify the methanol molecular abundances in both works was the C-O stretch mode at 1030 cm^{-1}.

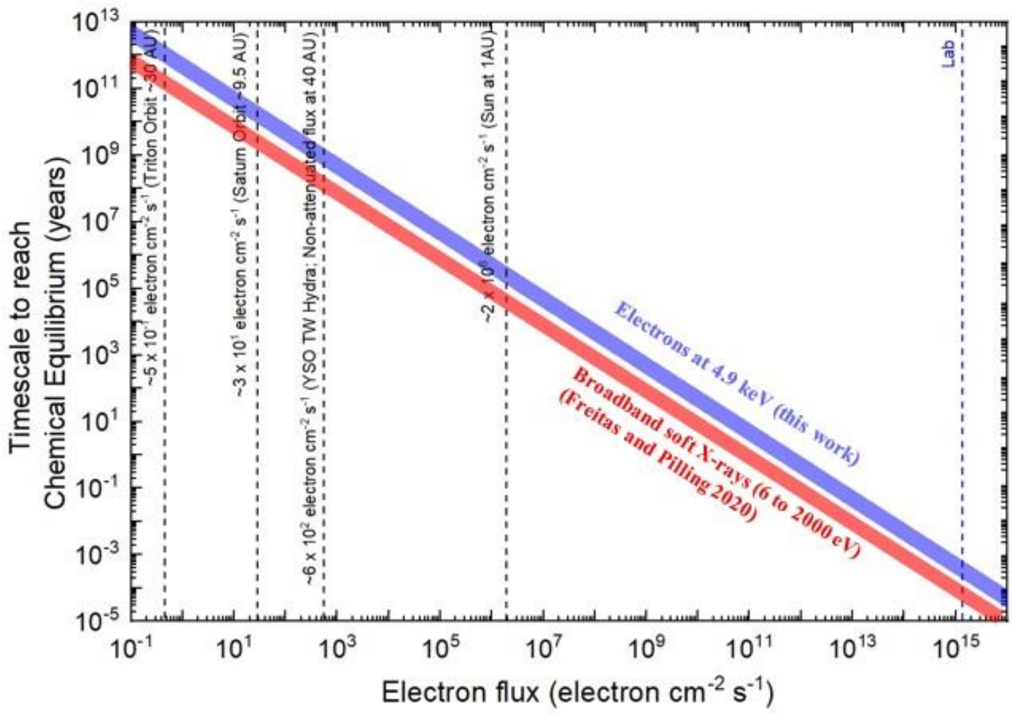


The results indicated that the time to reach chemical equilibrium with electrons in the laboratory is about three times higher. For the Earth orbit, the timescale to reach the chemical equilibrium (with ionizing agent flux of 2×10^6 $cm^{-2}s^{-1}$) was roughly 2.4×10^5 years, while in Saturn orbit (with flux of 3×10^1 $cm^{-2}s^{-1}$) was approximately 1.8×10^{10} years. In the experiment utilizing soft X-rays, the timescale to reach the chemical equilibrium for the Earth, for example, was just roughly 5.1×10^{-3} years. However, when irradiated by broadband soft X-rays (6 – 2000 eV) on methanol ice, the illuminated fraction of the sample is approximately 90%, while with fast electrons of 4.9 keV is 10%.

Future observations utilizing instruments such as the JWST (James Webb Space Telescope) MIRI/NIRSpec hold the potential to investigate more locations with defined electron fluxes, providing valuable insights into the timescales required to attain chemical equilibrium in various astrophysical environments.

The current research shows that employing different ionizing agents (such as keV electrons and soft X-rays) yields a similar effect on astrophysical ices. This might be related with the fact that the incoming soft X-rays produce a lot of secondary electrons inside the ices during irradiation (Pilling & Bergantini, 2015). Considering that in space, both ionizing agents act simultaneously in the processing of ices, a question about the synergy between involving these projectiles might also arise. Upcoming experiments may consider synergizing these approaches to emulate space environments with enhanced realism. In exploring the interplay between temperature and radiation in chemical equilibrium, forthcoming studies may extend their scope to simulate ices under varying temperature conditions. This broader perspective could provide valuable insights into the chemistry of frozen surfaces characterized by temperature gradients, such as those found on planets, asteroids, moons, and within distinct regions of protoplanetary disks.

Figure 6 - Timescale required for the methanol ice reaches chemical equilibrium under bombardment of 4.9 keV electrons at constant temperature of 12 K, as a function of electron flux. Rightmost vertical line shows laboratory electron flux and the other vertical lines indicate estimated electron fluxes in selected space environments in the same selected energy. The sloped red line indicates the timescales obtained broadband X-rays (6-2000 eV) taken from (Freitas & Pilling, 2020) for comparison purpose.



CONCLUSIONS

In this study, we have conducted experiments to investigate the irradiation of methanol ice at a temperature of 12K, simulating the effects of ionizing radiation in space environments using fast electron bombardment. These experiments were conducted within a high vacuum chamber at LASA Laboratory at Univap, employing an infrared spectrometer (FTIR) coupled to an electron gun for precise analysis. The key findings and conclusions of this research are as follows:

i) The irradiation of methanol ice led to the production of new molecules, including CO, CO_2, H_2O, and CH_4.

ii) We estimated the desorption yield to be approximately 0.04 molecules per electron;

iii) The effective destruction cross-section for methanol, induced by fast electrons at 4.9 keV, was determined to be approximately 5.5×10^{-19} cm^2. The effective formation cross-sections for daughter species, identified by visible bands in the infrared spectra, were as follows: 5.8×10^{-18} cm^2 (CO_2), 9.3×10^{-18} cm^2 (CO), 6.9×10^{-18} cm^2 (H_2O), and 3.3×10^{-18} cm^2 (CH_4);

iv) At chemical equilibrium, the primary product of fast electron impact was CH_4, accounting for 18.2% of the assigned species, followed by H_2O and CO at 8.1% and 2.9%, respectively. Approximately 7.3% of the species remained unidentified at equilibrium;

v) We estimated the timescale to reach chemical equilibrium (TSE) for pure methanol ice irradiated by fast electrons in various astrophysical environments. For instance, in Earth's orbit (with an ionizing agent flux of 2×10^6 cm^{-2} s^{-1}), the TSE was approximately 2.4×10^5 years.

This study contributes significantly to our understanding of the effects of ionizing radiation on methanol-rich ices and sheds light on the equilibrium chemistry that occurs on icy surfaces in space. It underscores the vital role of radiation-induced chemistry by fast electrons in astrophysical environments.

ACKNOWLEDGEMENT

We thank the financial support from the agencies FAPESP (#2009/18304-0), FINEP, CAPES and CNPQ (#PQ306145/2015-4; #PQ302985/2018-2; #PQ302608/2022-2). The authors also acknowledge the staff of LNLS/CNPEM and FVE/UNIVAP for their support in this scientific production.

REFERENCES

Ball, J. A., Gottlieb, C. A., Lilley, A. E., & Radford, H. E. (1970). Detection of methyl alcohol in Sagittarius. *Astrophysical Journal*, *162*, L203.

Bockelée-Morvan, D., Crovisier, J., Colom, P., & Despois, D. (1994). The rotational lines of methanol in comets Austin 1990 V and Levy 1990 XX. *Astronomy and Astrophysics*, *287*, 647-665.

Bonfim, V. S., Castilho, R. B., Baptista, L., & Pilling, S. (2017). SO 3 formation from the X-ray photolysis of SO 2 astrophysical ice analogues: FTIR spectroscopy and thermodynamic investigations. *Physical Chemistry Chemical Physics, 19*(39), 26906-26917.

Bouilloud, M., Fray, N., Bénilan, Y., Cottin, H., Gazeau, M. C., & Jolly, A. (2015). Bibliographic review and new measurements of the infrared band strengths of pure molecules at 25 K: H2O, CO2, CO, CH4, NH3, CH3OH, HCOOH and H2CO. *Monthly Notices of the Royal Astronomical Society, 451*(2), 2145-2160.

Ciaravella, A., Jiménez-Escobar, A., Cosentino, G., Cecchi-Pestellini, C., Peres, G., Candia, R., Collura, A., Barbera, M., Di Cicca, G., Varisco, S., & Venezia, A. M. (2018). Chemical evolution of interstellar methanol ice analogs upon ultraviolet irradiation: the role of the substrate. *The Astrophysical Journal, 858*(1), 35.

Favre, C., Vastel, C., Jimenez-Serra, I., Quénard, D., Caselli, P., Ceccarelli, C., Chacón-Tanarro, A., Fontani, F., Holdship, J., Oya, Y., Punanova, A., Sakai, N., Spezzano, S., Yamamoto, S., Neri, R., López-Sepulcre, A., Alves, F., Bachiller, R., Balucani, N., … Witzel, A. (2020). Seeds of Life in Space (SOLIS*). Astronomy & Astrophysics, 635*, A189. https://doi.org/10.1051/0004-6361/201937297

Freitas, F. M., & Pilling, S. (2020). Laboratory investigation of X-ray photolysis of methanol ice and its implication on astrophysical environments. *Química nova*, *43*, 521-527. https://doi.org/10.21577/0100-4042.20170510.

Friberg, P., Madden, S. C., Hjalmarson, A., & Irvine, W. M. (1988). Methanol in dark clouds. *Astronomy and Astrophysics*, *195*, 281-289.

Hovongton, P., & Drouin, D. (2007). *Casino*: Monte Carlo simulation of electron trajectory in solids. http://www.gel.usherbrooke.ca/casino/.

Hudgins, D. M., Sandford, S. A., Allamandola, L. J., & Tielens, A. G. G. M. (1993). Mid- and far-infrared spectroscopy of ices-Optical constants and integrated absorbances. *Astrophysical Journal Supplement Series*, *86,* (2), 713-870.

Irvine, W. M., Goldsmith, P. F., & Hjalmarson, Å. (1987). Chemical abundances in molecular clouds. In D. J. Hollenbach & H. A, Thronson Jr*. (*Eds)*. Proceedings of the Symposium on Interstellar Processes* (pp. 560-609). Springer.

Millar, T. J., Bennett, A., Rawlings, J. M. C., Brown, P. D., & Charnley, S. B. (1991). Gas phase reactions and rate coefficients for use in astrochemistry-The UMIST ratefile*. Astronomy and Astrophysics Supplement Series*, *87*, 3, 585-619. SERC-supported research., 87, 585-619.

Parise, B., Ceccarelli, C., Tielens, A. G. G. M., Castets, A., Caux, E., Lefloch, B., & Maret, S. (2006). Testing grain surface chemistry: a survey of deuterated formaldehyde and methanol in low-mass class 0 protostars*. Astronomy & Astrophysics*, *453*(3), 949-958.

Pilling, S., & Bergantini, A. (2015). The effect of broadband soft X-rays in SO2-containing ices: implications on the photochemistry of ices toward young stellar objects. *The Astrophysical Journal, 811*(2), 151.

Pilling, S., Rocha, W. R. M., Freitas, F. M., & Da Silva, P. A. (2019). Photochemistry and desorption induced by X-rays in water rich astrophysical ice analogs: implications for the moon Enceladus and other frozen space environments. *Royal Society of Chemistry Advances*, 9(49), 28823-28840.

Portugal, W., Pilling, S., Boduch, P., Rothard, H., & Andrade, D. P. (2014). Radiolysis of amino acids by heavy and energetic cosmic ray analogues in simulated space environments: α-glycine zwitterion form. *Monthly Notices of the Royal Astronomical Society, 441*(4), 3209-3225.

Rachid, M. G., Faquine, K., & Pilling, S. (2017). Destruction of C2H4O2 isomers in ice-phase by X-rays: Implication on the abundance of acetic acid and methyl formate in the interstellar medium. *Planetary and Space Science, 149*, 83-93.

Tielens, A.G.G.M., & Allamandola, L.J. (1987). Composition, Structure, and Chemistry of Interstellar Dust. In: D.J. Hollenbach & H.A. Thronson, (eds) *Proceedings of the Symposium on Interstellar Processes* (pp 397–470). Springer.

Vasconcelos, F. D. A., Pilling, S., Rocha, W. R., Rothard, H., & Boduch, P. (2017). Energetic processing of N2: CH4 ices employing X-Rays and swift ions: implications for icy bodies in the outer solar system. T*he Astrophysical Journal, 850*(2), 174.

Walsh, C., Loomis, R. A., Öberg, K. I., Kama, M., van't Hoff, M. L., Millar, T. J., Aikawa, Y., Herbst, E., Weaver, S. L. W., & Nomura, H. (2016). First detection of gas-phase methanol in a protoplanetary disk. *The Astrophysical Journal Letters*, *823*(1), L10.

Wang, S., Bergin, E. A., Crockett, N. R., Goldsmith, P. F., Lis, D. C., Pearson, J. C., ... & Zmuidzinas, J. (2011). Herschel observations of EXtra-Ordinary Sources (HEXOS): Methanol as a probe of physical conditions in Orion KL. *Astronomy & Astrophysics, 527*, A95.