CHEMICAL EVOLUTION OF H2O:CO2 ICES ON COMETARY SURFACES

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Abstract

This study examines astrophysical ices, such as the H_2O:CO_2 mixture, exposed to cosmic rays, resulting in chemical changes, including desorption into the gas phase. Using the PROCODA code, we understand these reactions by solving coupled differential equations. We quantified the evolution of molecular abundances, providing valuable data on physicochemical and chemical processes. Experiments like those conducted at GANIL help in understanding space chemistry. With this data and using PROCODA to investigate the behavior of H_2O:CO_2 ice under cosmic rays, we can calculate reaction rates and characterize chemical equilibrium. By monitoring reactions among 73 species, we found that 90.4% of the modeled molecules were not observed. The desorption rates (Y) and molecular abundances (EBR) are defined as follows: $Y=1.65\times10^4$ molecules/ion, with H_2O at 87.73% and CO_2 at 8.49%, respectively. This study enhances the understanding of space chemistry, enabling deeper exploration and significant advancement in astrochemistry.

Keywords: PROCODA, astrochemistry, cosmic rays, abundant molecules.

Knowledge Area: Exact and Earth Sciences – Astronomy

Introduction

This study continues an experimental investigation of highly charged heavy ions (52 MeV $^{58}Ni^{13+}$) in mixtures of H_2O and CO_2 in astrophysical ices (H_2O:CO_2). The analysis aims to simulate the chemical and physicochemical characteristics of interactions induced by cosmic rays, as presented by (Pilling et al., 2010) and (Pilling et al., 2011). The goal is to bring these data into the computational field to demonstrate possible molecules present in the ice that could not be experimentally analyzed due to uncertainties and/or equipment limitations. This could contribute to future research with more advanced telescopes, such as the James Webb Space Telescope and ALMA. Molecules in space can be divided into several categories: simple molecules, molecular ions, radicals, cyclic molecules, and stable molecules. Simple molecules are found in various sources, with the most abundant being H_2, which accounts for approximately 99.99% of molecules in space. The next most abundant molecules are H_2O and CO, with relative abundances to H_2 of approximately 10^{-4}. H_2O, CO, and CO_2 are common molecules in the solid phase and are frequently observed in dust mantles, being detected in absorption by bright infrared sources (Ohishi et al., 2016).

In this work, we aim to quantify the evolution of molecular abundances of chemical species observed in the processing of ices irradiated by cosmic rays, using the PROCODA code (Pilling et al., 2022; Carvalho et al., 2022; Carvalho et al., 2024; Da Silveira et al., 2024). The program is intended to provide an understanding of chemical reactions in an astrophysical environment by solving a system of coupled differential equations. Laboratory studies and astronomical observations indicate that the photolysis and radiolysis of ices can generate simple molecules such as CO, CO_3, O_3, H_2CO_3, and H_2O_2, in addition to more complex organic compounds such as CH_2, H_2CO, HOCO, CH_3O, CH_3*, CH_4*, OHCCOH*, and CH_3CH_3* (Pilling et al., 2010). By comparing laboratory data with observational data, we gain a better understanding of physicochemical processes, which can contribute to new investigations in the field of observational astrochemistry, revealing possible new molecules in the interstellar medium.

The motivation for this work is to understand the chemical evolution of astrophysical ices irradiated by cosmic rays, which is important for elucidating the presence and evolution of molecular abundances in interstellar environments. Laboratory experiments are essential for providing information about the physicochemical processes of these ices, such as those conducted at the Grand Accélérateur National d’Ions Lourds (GANIL), a heavy-ion accelerator that plays a significant role in astrochemistry. It is used in astrochemical experiments to investigate the interaction of radiation with astrophysical ices, potentially revealing molecules that are not observed during the experiment due to experimental limitations. The current work aims to address these limiting issues by introducing a methodology that helps clarify and characterize astrophysical ices more precisely, providing more information about these unobserved molecules.

Methodology

We conducted a meticulous investigation into the chemical evolution of ice composed of water (H_2O) and carbon dioxide (CO_2) molecules under the influence of cosmic ray irradiation. To carry out this investigation, we employed the latest version of the PROCODA code, as referenced in the works of (Pilling et al., 2022b, and Pilling et al., 2023a.) This updated version of the PROCODA code incorporates thermochemical data to minimize solution degeneracy. Additionally, the code is capable of calculating effective rate constants (ERCs), which are crucial for characterizing the chemical equilibrium phase of the system under study.

PROCODA solves a system of coupled differential equations. This feature of the code allows us to describe the time-dependent chemical evolution of astrophysical ices during ionizing radiation processing. This aspect is essential for understanding the chemical processes that occur in astrophysical environments. Previous studies by (Carvalho et al., 2022, Pilling et al., 2022b, and Pilling et al., 2023a) provide more detailed information about the PROCODA code. These works are a valuable source of knowledge and offer an in-depth view of the functionality and applicability of the PROCODA code.

It is important to emphasize that the computational methodology employed in this study is of great relevance. It allows for a precise and detailed analysis of chemical processes in astrophysical environments, significantly contributing to the advancement of the field of astrochemistry. The dataset used in this study, related to cosmic rays (CR), was extracted from the work of (Pilling et al., 2010). For sample preparation, a cesium iodide (CsI) substrate was used. This substrate was employed to deposit gas samples with a purity level above 99% at a temperature of 13 Kelvin.

The authors of the original study used a beam containing nickel-58 ions ($^{58}Ni^{13+}$) with an energy of 52 MeV. This ion beam was used to irradiate the pure, amorphous water (H_2O) ice. For in-situ analysis, a Nicolet FTIR spectrometer was used. This instrument allowed measurements in the range of 4000 to 600 cm^{-1}, with a resolution of 1 cm^{-1}. During the analysis process, spectra were recorded at various fluences, reaching a maximum value of 2×10^{13} ions cm^{-2}.

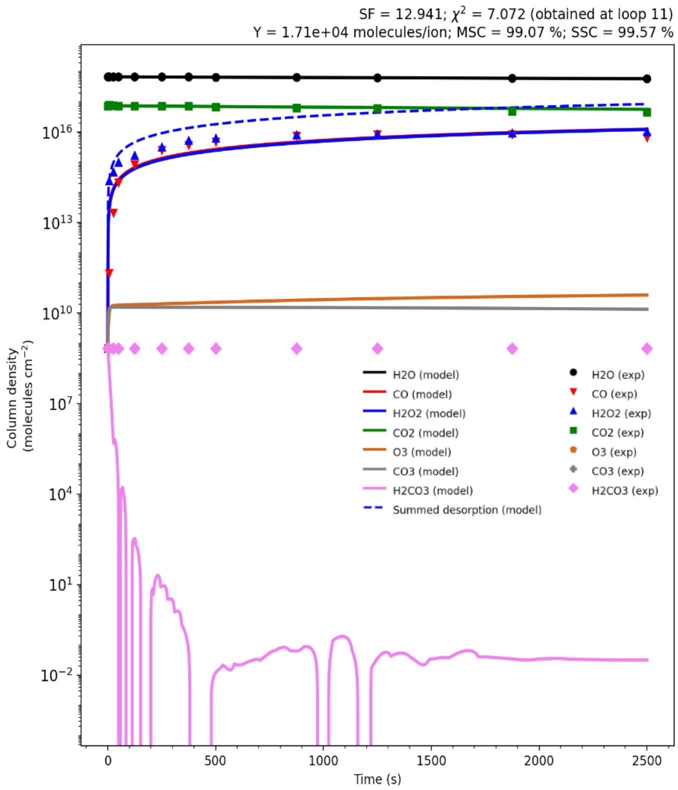
It is important to highlight that, throughout the irradiation process, the nickel ion flux was maintained at a constant value of 2×10^{9} $cm^{-2}s^{-1}$. This rigorous control of the ion flux is crucial to ensure the precision and reproducibility of the experimental results.

This study was conducted to simulate the effects of heavy, highly ionized cosmic rays on cold astrophysical surfaces. For this purpose, a gas sample with a purity greater than 99% was deposited on a CsI substrate at 13K and 80K, after evacuating the chamber to a pressure of 10^{-8} mbar. A front-facing gas inlet was used for deposition. The gas mixtures were prepared by measuring their partial pressures within an auxiliary mixing chamber, which was coupled to the main chamber. During the preparation of the mixture, the mixing chamber and the gas line to the main chamber were kept heated (approximately 80–100 K) to minimize the retention of gas samples on the stainless steel walls.

Results

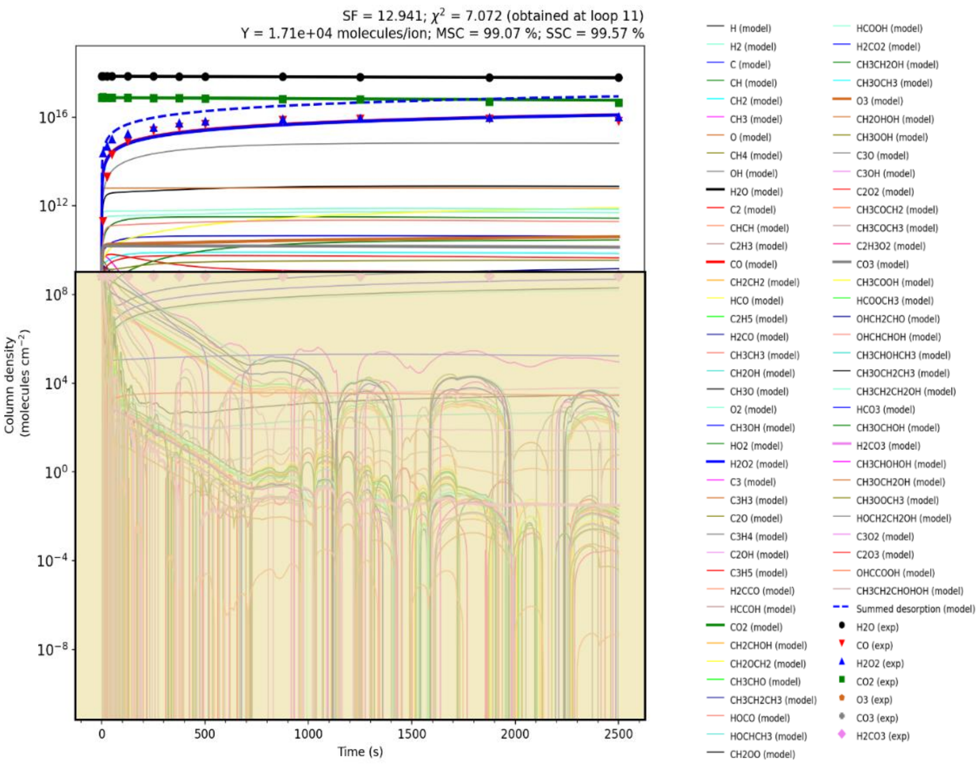
The most appropriate models using the PROCODA code to describe the chemical evolution of $H_2O:CO_2$ ices under the influence of ionizing radiation are illustrated in figures 1, and 2, concerning the interaction with cosmic rays as presented in (Pilling et al., 2010). In these figures, the evolution of column densities over time is detailed. Panel (a) portrays the chemical evolution exclusively of molecules observed experimentally, while panel (b) presents all possible molecules predicted by the PROCODA code.

Figure 1 – Column density (observed species Only)



Souce: The author.

Figure 2 – Column density (all species)



Souce: The author.

In Figure 2, only models with densities above 10^9 cm^{-2} are considered, as they present a formation density more consistent with what is being studied due to the desorption observed.

Desorption refers to the process where atoms, molecules, or particles previously adsorbed on a solid surface, such as dust grains, are released back into the gas phase. This phenomenon is of great relevance in various scientific fields, including surface physics, chemistry, and particularly in astrochemistry and astrophysics.

The gas-phase transition presented in this study occurs due to cosmic rays, which are high-energy particles that can collide with dust grains, causing localized and instantaneous heating, resulting in the desorption of adsorbed molecules. This mechanism is effective even in cold regions of the interstellar medium.

Discussion

Of the 73 species initially proposed to participate in the chemical reactions of the study, only 21 of them, representing 28.76% of the total, proved to be relevant in the coupled chemical system. These chemical species include: H, H_2, C, CH, CH_2, O, OH, H_2O, C_2, CO, HCO, H_2CO, O_2, HO_2, H_2O_2, C_2O, CO_2, HOCO, O_3, C_2O_2, and CO_3. Initially, only 7 species were observed, as cited in (Pilling et al., 2010) and (Pilling et al., 2011). With the use of PROCODA, we were able to analyze three times more species, thus observing what could not be seen through the experiment, either due to experimental limitations or equipment constraints.

Many of these species, such as H, H_2, O, OH, H_2O, CO, and CO_2, have already been identified in various astrochemical environments, including comets, protostars, and frozen surfaces, as documented in previous studies (Mumma et al., 2011). The detection of these molecules in such contexts reinforces their importance and presence in the interstellar medium, highlighting their crucial role in understanding the chemistry that occurs in extreme environments in space.

Conclusion

This study has significantly contributed to understanding the chemical evolution of astrophysical ices irradiated by cosmic rays, using the PROCODA code to overcome the inherent limitations of laboratory experiments. The computational analysis identified 21 relevant chemical species, representing 28.76% of the initially proposed species, many of which have already been detected in astrochemical environments, such as comets and protostars. The comparison between computational data and experimental observations highlights the complexity of the physicochemical processes occurring in the interstellar medium, underscoring the importance of theoretical models in predicting the presence of molecules that might otherwise go unnoticed due to experimental limitations. This work not only enhances the knowledge of cosmic ray-induced interactions in astrophysical ices but also paves the way for future investigations with more advanced telescopes, such as the James Webb Space Telescope and ALMA, enhancing the potential discovery of new molecules and deepening our understanding of chemistry in extreme space environments.

References

CARVALHO, G. A.; PILLING, S.; GERASIMENKO, S. Characterization of acetonitrile ice irradiated by X-rays employing the procoda code–II. Desorption processes. **Monthly Notices of the Royal Astronomical Society**, v. 527, n. 2, p. 2781-2789, 2024.

CARVALHO, Geanderson A.; PILLING, Sérgio; GALVÃO, Breno RL. Characterization of acetonitrile ice irradiated by X-rays employing the procoda code–I. Effective rate constants and abundances at chemical equilibrium. **Monthly Notices of the Royal Astronomical Society**, v. 515, n. 3, p. 3760-3772, 2022.

DA SILVEIRA, Carolina H.; PILLING, Sergio. Modeling the chemical evolution and kinetics of pure H2O Ices under various types of radiation employing the PROCODA code. **Advances in Space Research**, v. 73, n. 1, p. 1149-1169, 2024.

MUMMA, Michael J.; CHARNLEY, Steven B. The chemical composition of comets—emerging taxonomies and natal heritage. **Annual Review of Astronomy and Astrophysics**, v. 49, n. 1, p. 471-524, 2011.

OHISHI, Masatoshi. Search for complex organic molecules in space. In: **Journal of Physics: Conference Series**. IOP Publishing, 2016. p. 052002.

PILLING, Sergio et al. Radiolysis of H2O: CO2 ices by heavy energetic cosmic ray analogs. **Astronomy & Astrophysics**, v. 523, p. A77, 2010.

PILLING, Sergio et al. Radiolysis of astrophysical ice analogs by energetic ions: the effect of projectile mass and ice temperature. **Physical Chemistry Chemical Physics**, v. 13, n. 35, p. 15755-15765, 2011.

PILLING, Sergio; CARVALHO, Geanderson A.; ROCHA, Will RM. Chemical Evolution of CO2 Ices under Processing by Ionizing Radiation: Characterization of Nonobserved Species and Chemical Equilibrium Phase with the Employment of PROCODA Code. **The Astrophysical Journal**, v. 925, n. 2, p. 147, 2022.

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