MODELING THE CHEMISTRY OF X-RAY-IRRADIATED N_2-CH_4 ICE AND ITS APLICATION TO COLD ASTROPHYSICAL ENVIRONMENTS

Sergio Pilling

[1]Universidade do Vale do Paraíba/Instituto de Pesquisa e Desenvolvimento, Avenida Shishima Hifumi, 2911, Urbanova - 12244-000 - São José dos Campos-SP, Brasil, sergiopilling@yahoo.com.br.

Abstract

Irradiated astrophysical ices represent key chemical reservoirs in interstellar and planetary environments, where they undergo complex radiation-driven reactions and desorption processes. In this work, we present a computational framework based on the PROCODA code, developed to model the temporal evolution of experimentally investigated ices under photolysis and radiolysis until the system reaches chemical equilibrium (CE). The methodology solves a system of coupled differential equations, enabling the quantitative tracking of molecular abundances during radiation processing. As a case study, we apply this approach to mixed N_2–CH_4 ices exposed to X-rays and cosmic rays. The model provides: (i) effective reaction rate coefficients (ERCs) for key processes, (ii) the chemical composition of the CE phase, including both observed and predicted molecular species within the ice, and (iii) the role of radiation-induced desorption in altering ice composition. Importantly, the results reveal the potential formation of prebiotic molecules, including adenine and its precursors, highlighting the astrobiological relevance of radiation-driven chemistry in astrophysical ices.

Palavras-chave: Astrochemistry; Computational Modeling; Astrophysical ices; X-Ray; PROCODA code.

Área do Conhecimento: Astronomia

Introduction

Molecules in space are found both in the gas phase and in cold condensed phases, forming so-called astrophysical ices. These ices are widespread in cold regions of the interstellar medium, in protoplanetary disks, in comets, and on the frozen surfaces of outer Solar System bodies (EHRENFREUND & CHARNLEY, 2000; GIBB et al., 2004; FRASER et al., 2002; ÖBERG et al., 2011; LELLOUCH et al., 2010; BERTRAND & FORGET, 2016; CARLSON et al., 1999). Their physicochemical evolution is largely driven by interactions with ionizing radiation, including ultraviolet photons, cosmic rays, soft X-rays, and secondary fast electrons (MUÑOZ CARO et al., 2002; MEINERT et al., 2016). The processing of these ices by radiation contributes to the molecular diversity observed in astrophysical environments and is therefore central to our understanding of chemical evolution in space (KWOK, 2016; Ehrenfreund & CHARNLEY, 2000).

Nitrogen and methane ices are particularly relevant, as they have been observed on several outer Solar System bodies. Data from the New Horizons mission showed that Pluto's surface is dominated by N_2 and CH_4 ices, while Triton, Eris, and Makemake display similar surface compositions (CRUIKSHANK et al., 1993; OWEN et al., 1993; LICANDRO et al., 2006; GRUNDY et al., 2016). These ices are also expected in the upper atmosphere of Titan (SAMUELSON et al., 1997; NIEMANN et al., 2005). In such environments, energetic photons and charged particles trigger molecular destruction and initiate complex reaction networks, producing radicals, ions, and new molecular species.

Experimental studies have extensively investigated N_2:CH_4 mixtures at cryogenic temperatures to simulate their processing under astrophysical conditions. Photon and ion irradiation experiments consistently demonstrate the formation of a rich variety of organic molecules, including nitriles, hydrocarbons, and even aromatic CN compounds (BOHN et al., 1994; MOORE & HUDSON, 2003;

BRUNETTO et al., 2008; PILLING et al., 2009; WU et al., 2012). In some cases, organic residues analyzed ex situ revealed the presence of adenine, a fundamental nucleobase of DNA (PILLING et al., 2009). These findings underscore the potential role of radiation-driven chemistry in generating prebiotic precursors on icy planetary surfaces.

Despite advances from laboratory studies, significant challenges remain. Many reaction intermediates and products predicted by theory are not directly observed in experiments due to spectroscopic limitations or the transient nature of reactive species. Moreover, reconstructing the complete network of reactions occurring during irradiation is difficult, particularly at the high doses relevant to astrophysical timescales (BARATTA et al., 2002; MUÑOZ CARO et al., 2014). Comparisons between ion and photon irradiation further reveal similarities at low doses but divergences as the ice evolves chemically, highlighting the complexity of radiation-induced processing.

To address these challenges, we employ a computational approach using the PROCODA code, which solves coupled differential equations to model the temporal evolution of irradiated astrophysical ices (e.g., PILLING et al., 2022). In this work, we reanalyzed published experimental data on N_2:CH_4 ices irradiated by X-rays (obtained by VASCONCELOS et al., 2017) to quantify effective reaction rate coefficients (ERCs), equilibrium abundances of observed and predicted species, and desorption dynamics. This methodology complements laboratory experiments, offering new insights into the chemical evolution of astrophysical ices and their potential role in prebiotic chemistry across diverse cosmic environments.

Metodology

In this work, we reanalyzed published experimental data on N_2:CH_4 ices irradiated by X-rays obtained at LNLS/CNPEM, Campinas-SP (VASCONCELOS et al., 2017) using the computational code PROCODA (PROgram for solving COupled Differential equations in Astrochemistry). The code was specifically designed to solve large systems of coupled differential equations, providing a quantitative description of radiation-driven chemistry in astrophysical environments (see also PILLING et al., 2022 for CO_2 ice; PILLING et al., 2023a for CO ice; PILLING et al., 2023b for CO_2 ice; da SILVEIRA & PILLING, 2024 for H_2O ice).

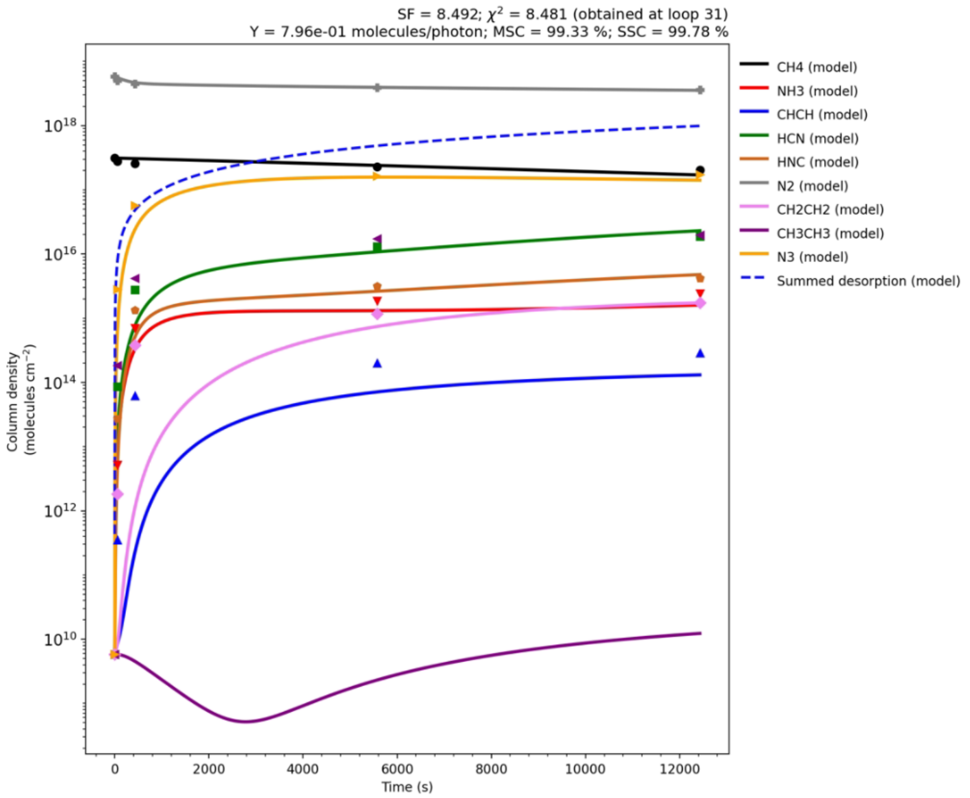
PROCODA calculates effective reaction rate constants (ERCs) for chemical processes in irradiated ices, based on experimental data. It also characterizes the chemical equilibrium (CE) phase, obtained at large radiation fluences, and determines radiation-induced desorption rate constants, thereby providing insights into the molecular kinetics of the system. The code is written in Python and employs the L-BFGS-B minimization algorithm to optimize the solution space (PILLING et al., 2022). The main features of PROCODA can be summarized as follows: (i) Incorporates infrared spectroscopy data (column densities) from laboratory measurements; (ii) Utilizes thermochemical properties of molecular species to pre-rank ERCs during the first stage of calculation; (iii) Accounts for radiation-induced desorption processes and includes non-observed but theoretically predicted species; and (iv) Considers a comprehensive reaction network, including direct dissociation, bimolecular reactions, and desorption processes.

The models incorporated 2,513 coupled differential equations (including desorption processes) and considered a total of 75 distinct chemical species (9 species observed in the experiments + 66 species predicted). The system of equations was solved by minimizing a score function (SF) that quantifies the agreement between modeled and experimental data, guiding the system toward a global minimum solution. Additional constraints were implemented to ensure physically meaningful results, including: (i) conservation of mass, (ii) consistency between experimental and modeled desorption yields, (iii) similarity between modeled and observed column densities, and (iv) attainment of a chemical equilibrium stage at higher fluences, verified through a slope similarity criterion.

Results and discussion

Figure 1 shows the temporal evolution of column densities for N_2:CH_4 (19:1) ices irradiated by X-rays, comparing experimental data (black symbols) from VASCONCELOS et al. (2017) with the best-fit models generated using the PROCODA code. The agreement between models and data is remarkable, capturing the rapid depletion of CH_4 and the formation of new molecular species such as HCN, HNC, NH_3, C_2 hydrocarbons, and N_3. The inclusion of radiation-induced desorption in the model further improves the accuracy, as reflected by the close reproduction of the experimental desorption yields. Importantly, the modeling framework handles both the experimentally detected species and a large set of additional predicted species, even if not directly observable due to spectroscopic limitations. This predictive ability is crucial for reconstructing the hidden chemical complexity of astrophysical ices. The model was unable to reproduce the observed abundances of CH_3CH_3, which may reflect insufficient reaction pathways for this species in the adopted dataset, experimental uncertainties in its measurements, or a combination of both factors. The desorption yield calculated by the model was approximately three times higher than the experimental estimate (0.25×10^{-1} molecules per photon), which may be related to the model's ability to account for unquantified species not resolved in the experiments.

Figure 1 - Evolution of column densities for the best-fit model obtained with the PROCODA code, applied to experimental data of N_2–CH_4 ices irradiated by X-rays (experimental data from VASCONCELOS et al., 2017). Black symbols represent the experimental measurements from the literature, while solid lines correspond to the modeled results. For clarity, only the experimentally observed species are shown; the additional 66 predicted species are omitted.

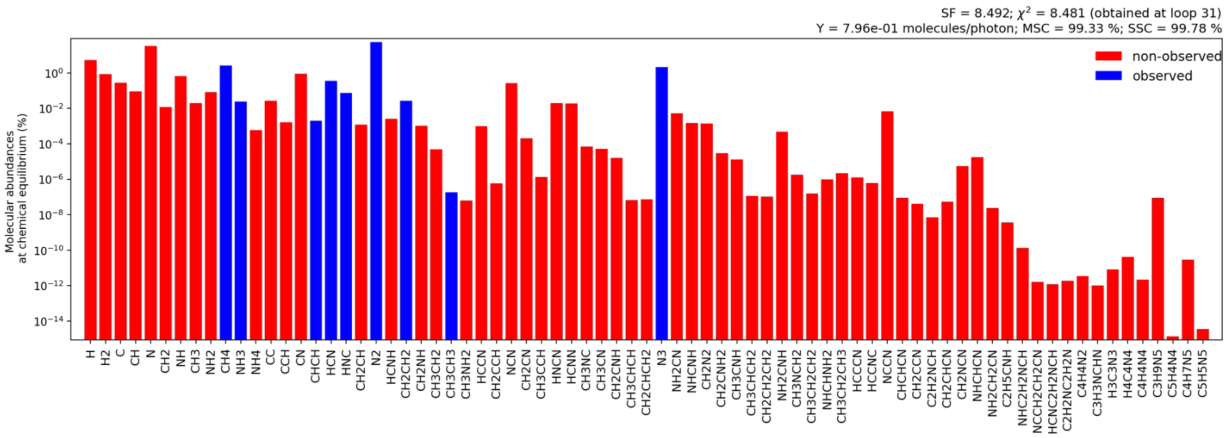


Source: The author

Figure 2 highlights the molecular abundances at the chemical equilibrium (CE) stage for the best-fit model. Blue bars represent experimentally detected species, while red bars correspond to predicted but non-observed products. The results reveal a chemically diverse equilibrium mixture, in which species such as N_3, NH_3, HCN, and hydrocarbons play a central role. The presence of a broad inventory of predicted nitrogen- and carbon-bearing molecules (including nitriles and potential precursors of aromatic and heterocyclic compounds) reinforces the role of N_2–CH_4 ices as fertile chemical reservoirs under astrophysical conditions. Notably, adenine ($C_5H_5N_5$) and other complex prebiotic precursors, previously identified in residues of similar laboratory experiments, are predicted in the computational results, strengthening the astrobiological relevance of these ice mixtures.

From an astrophysical perspective, these results provide insights into the chemical pathways active on Pluto, Triton, Eris, Makemake, and Titan's upper atmosphere, where N_2 and CH_4 dominate the volatile inventory. The modeling demonstrates that radiation-driven processing of such ices leads to a steady-state chemical equilibrium characterized by both volatile species (e.g., HCN, C_2 hydrocarbons) and refractory residues. On icy planetary surfaces, this equilibrium can act as a long-term molecular "signature" of radiation exposure, while in atmospheres (e.g., Titan), photolysis and radiolysis of N_2–CH_4 aerosols could initiate prebiotic chemistry. The integration of PROCODA with laboratory data thus enables extrapolation of laboratory timescales to astrophysical conditions, bridging the gap between experiments and planetary observations

Figure 2 – Molecular Abundances at chemical equilibrium for the best-fit model obtained with the PROCODA code, applied to experimental data of N_2–CH_4 ices irradiated by X-rays (experimental data from VASCONCELOS et al., 2017). Red bars indicate non-observed species, while blue bars represent those detected in the experiments.



Source: The author

Conclusion

This study demonstrates the successful application of the PROCODA computational framework to model the radiation-induced chemistry of N_2–CH_4 ices under astrophysical conditions. By reanalyzing experimental data from X-ray irradiations, PROCODA not only reproduced observed column density trends but also predicted the abundances of dozens of additional species at chemical equilibrium. The models incorporated 2,513 coupled differential equations (including desorption processes) and considered a total of 75 distinct chemical species (9 species observed in the experiments + 66 species predicted). The approach provided effective reaction rate coefficients (ERCs), equilibrium compositions, and desorption yields, thereby offering a comprehensive picture of the molecular kinetics in irradiated astrophysical ices.

The model showed that the system evolves toward a chemical equilibrium, where the abundances of the main species stabilize after the balance between production and destruction processes is achieved. This long-term stabilization is critical for extrapolating the chemistry of astrophysical ices under continuous irradiation.

The results highlight the importance of N_2–CH_4 ices as astrochemical laboratories on outer Solar System bodies. Radiation processing leads to a chemically diverse inventory, including simple volatiles, nitriles, and potential prebiotic precursors such as adenine, pointing to a plausible route for complex organic synthesis beyond Earth. This work underscores the value of combining laboratory experiments and computational modeling to uncover hidden reaction networks and predict the long-term chemical evolution of astrophysical ices exposed to cosmic radiation.

References

BARATTA, G. A.; LETO, G.; PALUMBO, M. E. A comparison of ion irradiation and UV photolysis of CH_4 and CH_3OH. **Astronomy & Astrophysics**, v. 384, p. 343-349, 2002.

BERTRAND, T.; FORGET, F.. Observed glacier and volatile distribution on Pluto from atmosphere–topography processes. **Nature**, v. 540, n. 7631, p. 86-89, 2016.

BOHN, R. B.; SANDFORD, S. A.; ALLAMANDOLA, L. J.; CRUIKSHANK, D. P. Infrared spectroscopy of Triton and Pluto ice analogs: the case for saturated hydrocarbons. **Icarus**, v. 111, n. 1, p. 151-173, 1994.

BRUNETTO, R.; CANIGLIA, G.; BARATTA, G. A.; PALUMBO, M. E. Near-infrared band strengths of icy CH_4 and its mixtures with N_2. **The Astrophysical Journal**, v. 686, p. 1480-1485, 2008.

CARLSON, R. W. et al. Hydrogen peroxide on the surface of Europa. **Science**, v. 283, n. 5410, p. 2062-2064, 1999.

CRUIKSHANK, D. P.; ROUSH, T. L.; OWEN, T. C.; et al. Ices on the surface of Triton. **Science**, v. 261, n. 5122, p. 742-745, 1993.

DA SILVEIRA, C.H.; PILLING, S. 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.

EHRENFREUND, Pascale; CHARNLEY, Steven B. Organic molecules in the interstellar medium, comets, and meteorites: a voyage from dark clouds to the early Earth. **Annual Review of Astronomy and Astrophysics**, v. 38, n. 1, p. 427-483, 2000.

FRASER, H. J.; MCCOUSTRA, M.R.S; WILLIAMS, D. A. The molecular universe. **Astronomy & Geophysics**, v. 43, n. 2, p. 2.10-2.18, 2002.

GIBB, E. L. et al. Interstellar ice: the infrared space observatory legacy. **The astrophysical journal supplement series**, v. 151, n. 1, p. 35, 2004.

GRUNDY, W. M.; BINZEL, R. P.; BURATTI, B. J.; et al. Surface compositions across Pluto and Charon. *Science*, v. 351, n. 6279, aad9189, 2016.

KWOK, S.. Complex organics in space from Solar System to distant galaxies. **The Astronomy and Astrophysics Review**, v. 24, n. 1, p. 8, 2016.

LELLOUCH, E. et al. Detection of CO in Triton's atmosphere and the nature of surface-atmosphere interactions. **Astronomy & Astrophysics**, v. 512, p. L8, 2010.

LICANDRO, J.; PINILLA-ALONSO, N.; PEDANI, M. et al. The methane ice rich surface of large TNO 2005 FY9: a Pluto-twin in the trans-Neptunian belt? **Astronomy & Astrophysics**, v. 445, L35–L38, 2006.

MEINERT, C. et al. Ribose and related sugars from ultraviolet irradiation of interstellar ice analogs. **Science**, v. 352, n. 6282, p. 208-212, 2016.

MOORE, M. H.; HUDSON, R. L. Infrared study of ion-irradiated N_2-dominated ices relevant to Triton and Pluto: formation of HCN and HNC. **Icarus**, v. 161, p. 486–500, 2003.

MUNOZ CARO, G. M. et al. Amino acids from ultraviolet irradiation of interstellar ice analogues. **Nature**, v. 416, n. 6879, p. 403-406, 2002.

MUÑOZ CARO, G. M.; DARTOIS, E.; BODUCH, P. et al. Comparison of UV and high-energy ion irradiation of methanol:ammonia ice. **Astronomy & Astrophysics**, v. 566, A93, 2014.

NIEMANN, H. B.; ATREYA, S. K.; BAUER, S. J. et al. The abundances of constituents of Titan's atmosphere from the GCMS instrument on the Huygens probe. **Nature**, v. 438, n. 7069, p. 779–784, 2005

ÖBERG, K. I. et al. The Spitzer ice legacy: Ice evolution from cores to protostars. **The Astrophysical Journal**, v. 740, n. 2, p. 109, 2011.

OWEN, T. C.; ROUSH, T. L.; CRUIKSHANK, D. P. et al. Surface ices and the atmospheric composition of Pluto. **Science**, v. 261, n. 5122, p. 745–748,. 1993.

PILLING, S.; CARVALHO, G. A.; ROCHA, W. R.M. 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.

PILLING, S. et al. Understanding the Molecular Kinetics and Chemical Equilibrium Phase of Frozen CO during Bombardment by Cosmic Rays by Employing the PROCODA Code. **The Astrophysical Journal**, v. 952, n. 1, p. 17, 2023a.

PILLING, S. et al. Mapping the evolution of pure CO2 ices irradiated by ions, UV, and electrons using the upgraded PROCODA code (employing an effective rate constant ordering by thermochemistry data). **Advances in Space Research**, v. 71, n. 12, p. 5466-5492, 2023b.

PILLING, S. et al. DNA nucleobase synthesis at Titan atmosphere analog by soft X-rays. **The Journal of Physical Chemistry A**, v. 113, n. 42, p. 11161-11166, 2009.

SAMUELSON, R. E.; NATH, N. R.; BORYSOW, A. Gaseous abundances and methane supersaturation in Titan's troposphere. **Planetary and Space Science**, v. 45, n. 8, p. 959–980, 1997.

VASCONCELOS, F. de A. et al. Energetic processing of N2: CH4 ices employing X-Rays and swift ions: implications for icy bodies in the outer solar system. **The Astrophysical Journal**, v. 850, n. 2, p. 174, 2017.

WU, Yu-Jong et al. Spectra and Photolysis of pure nitrogen and methane dispersed in solid nitrogen with vacuum–ultraviolet light. **The Astrophysical Journal**, v. 746, n. 2, p. 175-186 , 2012.

Acknowledgements

The author thank the FVE/UNIVAP and the Brazilian research agencies CNPq #302608/2022-2; and FAPESP (#2024/05115 5).