# EXPLORING THE CHEMICAL DYNAMICS OF ASTROPHYSICAL ICES EXPOSED TO IONIZING RADIATION: A COMPUTATIONAL ANALYSIS WITH PROCODA

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**Abstract**
Astrophysical ices play a crucial role in the chemical evolution of space environments, as they undergo ionizing radiation-induced reactions and desorption processes. Here, we present our pioneering computational methodology, PROCODA, aimed to elucidates the intricate chemical evolution of experimentally investigated ices under photolysis/radiolysis processes until chemical equilibrium (CE) phase is attained. The code solves a system of coupled differential equations, effectively traces the evolution of molecular abundances over time during the radiation processing of ices. Here we present some results for the employ of PROCODA code on pure ices (CO, $CO_2$, and $H_2O$) subjected to different types of ionizing radiation, such as cosmic rays, UV and energetic electrons. This methodology provides the values of the reaction coefficient rates (named here as ERC – Effective rate coefficients), the characterization of CE phase with the values of molecular abundances of both observed and non-observed (but predicted) species within the ice and the characterization of desorption processes due to incoming radiation.

**Palavras-chave**: Astrochemistry; Computational Modeling; Astrophysical ices; Laboratory Experiments.

**Área do Conhecimento:** Astronomia

## Introduction

In space molecules are usually observed in gas-phase and in cold solid-phase (named as astrophysical ices). The most abundant species in ices are $H_2O$, $CO_2$ and CO and the study of its chemical evolution under the presence if space radiation is highly needed to better characterize such ices and also their environments (e.g. HERBST and VAN DISHOECK, 2009; BOOGERT et al. 2015). These ices can be detected in the cold regions of interstellar medium, in protoplanetary discs, in comets and frozen surfaces of solar system (e.g. EHRENFREUND and CHARNLEY, 2000; GIBB, et al. 2004; FRASER et al. 2002; ÖBERG et al. 2011; LELLOUCH et al. 2010; BERTRAND and FORGET 2016; CARLSON et al., 1999)

The ionizing radiation that primarily triggers chemical reactions within astrophysical ices comprises cosmic rays, UV, and soft X-rays, and fast electrons (e.g., MUNOZ CARO et al. 2002; MEINERT et al. 2016). Studies have suggested that the bombardment of frozen species, including CO, by incoming radiation from the ISM can augment the molecular complexity of these regions (e.g., VASCONCELOS et al. 2017; Pilling et al. 2009, 2010; ANDRADE et al. 2008, and references therein)

The understanding of chemical abundance evolution of astrophysical ices under the presence of ionizing radiation is important to clarify the presence and the evolution of molecular abundances in space environments (e.g. KWOK 2016; EHRENFREUND and CHARNLEY 2000). Laboratory experiments are essential to provide information about physicochemical processes of such ices including spectroscopy features and interaction cross-sections with radiation (e.g. PILLING et al. 2009; PILLING et al. 2010). However some molecules produced (or predicted to be produced) in the lab are not observed during the ice processing experiments due to experimental limitations. Additionally, the characterization of the chemical reaction set happening during ice-processing experiments are a big challenge. The current work aims to navigate along these issues introducing a new computational methodology that helps to clarify and characterize astrophysical ices under processing by radiation.

**Metodology**

In this work we employ the PROCODA (Acronym for PROgram for solving COupled Differential equations in Astrochemistry) to solves a system of coupled differential equations, providing a comprehensive understanding of chemical reactions in astrophysical environments. Specifically, it calculates effective rates constants (ERC) for chemical systems involved in ice processing by ionizing radiation in laboratory experiments based on experimental data. Additionally, PROCODA describes the ice composition at the chemical equilibrium (CE) phase obtained at large radiation fluence and the radiation-induced desorption reaction rates constants, providing valuable information about the molecular kinetics of the system. The code was developed in Python language using L-BFGS-B minimization algorithm (see details at PILLING et al. 2022).

The main features of this procedure are: 1) consider laboratory data in the Infrared (column densities); 2) consider the thermochemistry data of molecular species to pre-rank the ERCs (in the phase 1 calculation); 3) consider desorption induce processes and also non-observed (but predicted) species in the experiments; 4) consider a set chemical reactions including direct dissociation, bimolecular, and radiation-induced desorption reactions.

Here, we present models considering data from 3 different experiments: i) pure CO ice at 13 K irradiated by 50 MeV Ni ions obtained at GANIL laboratory/France (from DUARTE et al. 2010); ii) pure $CO_2$ ice at 8 K ice irradiated by UV photons of 10 eV (from MARTÍN-DOMÉNECH et al. 2015) and iii) pure $H_2O$ ice at 20 K irradiated by 2 keV electrons (MIFSUD et al. (2022)). The model for the irradiated CO ice, employed a chemical network considers 156 coupled equations (with desorption included) and 18 different molecular species. The model for the irradiated $CO_2$ ice, employed a chemical network considering 111 coupled equations (with desorption included) and 11 different molecular species. The model for the irradiated $H_2O$ ice, employed a chemical network considering 61 coupled equations (with desorption included) and 9 different molecular species.

To solve the coupled chemical equations set, the code employs a minimization process of a score function (SF) that evaluates how close the system is to its minimum global solution. In the minimization processes, the code also incorporates other constraints to ensure accuracy in the modeling of astrophysical ices. These include maintaining mass conservation and mass similarity between the model and experiments, as well as ensuring similarity between experimental and modeled desorption yields, and achieving a chemical equilibrium stage at larger fluences using a slope similarity criterion. The SF employed in the minimization algorithm during the search of best solution of coupled as well as the list of all equations employed are presented with details on the published papers related with this work (PILLING et al. 2023a (for CO ice), PILLING et al. 2023b ($CO_2$); DA SILVEIRA and PILLING 2024 ($H_2O$)).

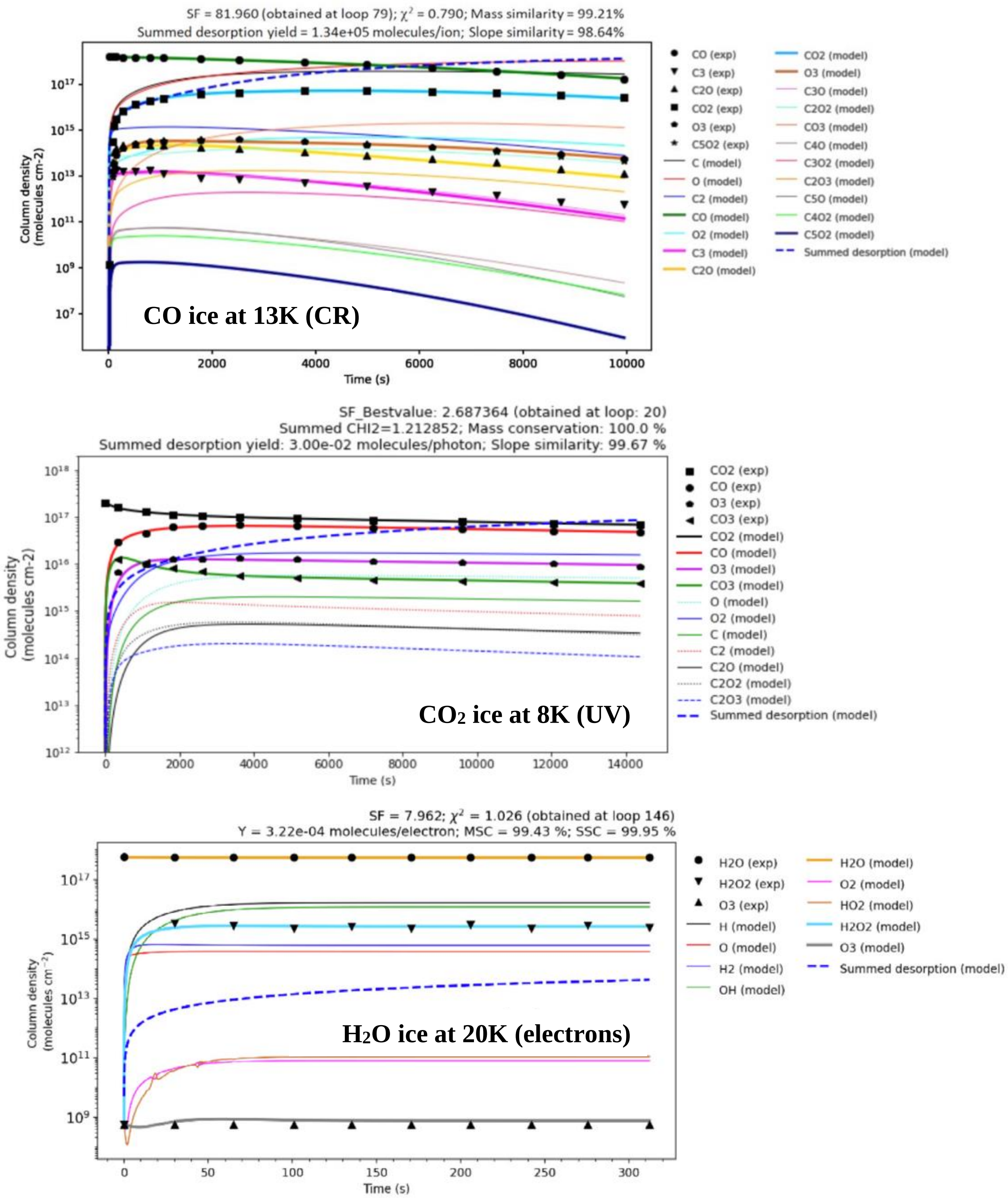
**Results**

Figure 1 presents the evolution of column density obtained for the best-fit models employing the PROCODA code on experimental data of pure CO, $CO_2$ and H2O ices at cryogenic temperatures irradiated by different ionized sources. The black symbols represent the experimental data (taken from DUARTE et al. 2010 (CO); MARTÍN-DOMÉNECH et al. 2015 ($CO_2$) and MIFSUD et al. 2022 ($H_2O$)). The bold-dashed blue line represents the summed desorption column density calculated in each model. In all panels, important output parameters for the best-fit models are displayed in the header.

The models are in a very good match with the experimental data and also reproduce the CE behavior (a slighted sloped plateau observed at large fluences). As discussed by PILLING et al. (2022), with this methodology, we are able to quantify both the abundances of observable and nonobserved species in the IR spectra irradiated ices. Such characterization helps us to better understand the underlying chemistry within the ice during the laboratory experiments and also helps to put constrain in astrochemical observations.

The list with all outputs from the models including the numerical values for the effective rate coefficients (ERCs), the employed equations, the numerical values for the abundances at the chemical equilibrium phase (large irradiation times) and desorption parameters are given in the respective published papers (PILLING et al. 2023a (for CO ice), PILLING et al. 2023b ($CO_2$); DA SILVEIRA, and PILLING 2024 ($H_2O$)).

Figure 1 - The evolution of column density obtained for the best-fit models employing the PROCODA code on experimental data of pure CO, $CO_2$ and H2O ices at cryogenic temperatures irradiated by different ionized sources. The black symbols represent the experimental data taken from literature.




Source: PILLING et al. 2023a (for CO ice), PILLING et al. 2023b (CO2); DA SILVEIRA and PILLING 2024 (H2O)

**Discussion**

As higlihter by PILLING et al (2023a), the main astrochemical implication of current work is the employ of the calculated values of ERC in an astrochemical models to map chemical evolution of such species in space environmetns. In this direction, the PROCODA code is not only important to map the chemical evolution of simple ices under processing of radiation in the laboratory but also important to characterize the evolution of more complex ices (e.g. $H_2O$:CO:$NH_3$ ices, mixed ices containing water and organic species, etc.). This could allow the characterization of important organic species in the ices that were not detected by the experiments, with also important implications in the astrobiology field.

Moreover, this study also has implications for the observation of frozen and desorbed molecules in cold space environments. These observations provide valuable information about the chemical composition of the ISM and the physical conditions in which the molecules are formed and evolve. The results of this study may help explain some of the observed molecular species and their abundances, as well as the mechanisms behind their formation and desorption. We hope the current methodology helps to clarify the solid-state astrochemistry models of ices under the presence of radiation, as well as, helps to explain the observations of frozen and desorbed molecules in cold space environments.

In addition, by analyzing the behavior of these molecules and their reaction rates, the methodology provides crucial insights into the chemical processes that occur in astrophysical environments. Additionally, this computational tool might be very useful in the understanding of the chemistry of astrophysical environments that the James Webb Space Telescope (JWST) will observe (e g. MCCLURE et al., 2023). Through a comparative analysis of PROCODA's outputs, derived from laboratory radiolysis and photolysis experiments, with the data obtained from JWST, we can validate and enhance our understanding of the chemistry within astrophysical environments. Consequently, we can improve the interpretation of astronomical observations and gain profound insights into the formation and evolution of celestial bodies. The combination of PROCODA and JWST data thus holds great potential in advancing astrochemistry.

**Conclusion**

This work presents a theoretical model (PROCODA) to map the chemical evolution and kinetics in pure CO, $CO_2$ and $H_2O$ ice under various types of radiation (CR, UV, and electron). The experimental data were taken from different sources (DUARTE et al. 2010; MARTÍN-DOMÉNECH et al. 2015; MIFSUD et al. 2022). Some selected conclusions of our study are as follows:

The results indicate that ionizign radiation can produce severel new species in the irradiated ices. The PROCODA code is usefull tool to caracterize the reacion kinetics providing values for the Effective rate coeficients (ERCs) and the chemical equilibrum (CE) phase of irradiated ices.

In the case of CO ice, the most abundant species in the ice at the CE phase were atomic oxygen (18.2%) and carbon (68.2%), followed by CO (11.8%) and $CO_2$ (1.6%). The molecular desorption at the CE phase was dominated mainly by atomic carbon and oxygen, followed by the parent species CO (~4.9%) and CO2 (~0.6%). For the $CO_2$ ice, the calculated average direct ERC was 1.6e-3 $s^{-1}$ and the average bimolecular ERC 1.0e-25 $cm^3$ $molecule^{-1}$ $s^{-1}$.The most abundant species in the irradiated $H_2O$ ice at the CE phase were $H_2O$, H and OH. The yield of $H_2O_2$ per $H_2O$ molecule (initially in the ice) was 4.5e-3.

The results of this study provide valuable insights into the chemical evolution of astrophysical ices under radiation, which is a crucial aspect of astrochemistry. The studied molecules are of particular interest to astronomers as they are important precursors to complex organic molecules that are potential building blocks of life. By elucidating the reaction pathways and rates of such ices (and its mixed) under irradiation, this study helps to refine and improve solid-state astrochemistry models, which can aid in the interpretation of astronomical observations.

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