

The GRETOBAPE Gas-phase Reaction Network: The Importance of Being Exothermic

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The gas-phase reaction networks are the backbone of astrochemical models. However, due to their complexity and nonlinear impact on the astrochemical modeling, they can be the first source of error in the simulations if incorrect reactions are present. Over time, following the increasing number of species detected, astrochemists have added new reactions, based on laboratory experiments and quantum mechanics (QM) computations, as well as reactions inferred by chemical intuition and the similarity principle. However, sometimes no verification of their feasibility in the interstellar conditions, namely their exothermicity, was performed. In this work, we present a new gas-phase reaction network, GRETOBAPE, based on the KIDA2014 network and updated with several reactions, cleaned from endothermic reactions not explicitly recognized as such. To this end, we characterized all the species in the GRETOBAPE network with accurate QM calculations. We found that ~5% of the reactions in the original network are endothermic, although most of them are reported as barrierless. The reaction network of Si-bearing species is the most impacted by the endothermicity cleaning process. We also produced a cleaned reduced network, GRETOBAPE-red, to be used to simulate astrochemical situations where only C-, O-, N-, and S-bearing species with less than six atoms are needed. Finally, the new GRETOBAPE network, its reduced version, and the database with all the molecular properties are made publicly available. The species property database can be used in the future to test the feasibility of possibly new reactions.

2023 ApJS 266 38

DOI: [10.3847/1538-4365/accae9](https://doi.org/10.3847/1538-4365/accae9)

Full-text URL: <https://arxiv.org/abs/2302.14799>

Disentangling physics and chemistry in AGB outflows: revealing degeneracies when adding complexity

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Observations of the outflows of asymptotic giant branch (AGB) stars continue to reveal their chemical and dynamical complexity. Spherical asymmetries, such as spirals and disks, are prevalent and thought to be caused by binary interaction with a (sub)stellar companion. Furthermore, high density outflows show evidence of dust-gas interactions. The classical chemical model of these outflows - a gas-phase only, spherically symmetric chemical kinetics model - is hence not appropriate for a majority of observed outflows. We have included several physical and chemical advancements step-by-step: a porous density distribution, dust-gas chemistry, and internal UV photons originating from a close-by stellar companion. Now, we combine these layers of complexity into the most chemically and physically advanced chemical kinetics model of AGB outflows to date. By varying over all model parameters, we obtain a holistic view of the outflow's composition and how it (inter)depends on the different complexities. A stellar companion has the largest influence, especially when combined with a porous outflow. We compile sets of gas-phase molecules that trace the importance of dust-gas chemistry and allow us to infer the presence of a companion and porosity of the outflow. This shows that our new chemical model can be used to infer physical and chemical properties of specific outflows, as long as a suitable range of molecules is observed.

Faraday Discussions 2023

DOI: [10.1039/D3FD00039G](https://doi.org/10.1039/D3FD00039G)

Full-text URL: <https://arxiv.org/abs/2306.05252>

Vacuum UV photodesorption of organics in the interstellar medium: an experimental study of formic acid HCOOH and methyl formate HCOOCH₃-containing ices

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Being a potential process that could explain gas phase abundances of so-called Complex Organic Molecules (COMs) in the cold interstellar medium (ISM), the UV photon-induced desorption from organics-containing molecular ices has been experimentally studied. In this work, we focused on the observation of the photodesorbed products and the measurement of the associated photodesorption yields from pure and mixed molecular ices, each containing organic molecules whose detection has been achieved in the gas phase of the cold ISM, namely formic acid HCOOH and methyl formate HCOOCH₃. Each molecule, in pure ice or in ice mixed with CO or water, was irradiated at 15 K with monochromatic vacuum UV photons in the 7-14 eV range using synchrotron radiation from the SOLEIL synchrotron facility, DESIRS beamline. Photodesorption yields of the intact molecules and of the photoproducts were derived as a function of the incident photon energy. Experiments have revealed that the desorbing species match the photodissociation pattern of each isolated molecule, with little influence of the kind of ice (pure or mixed in CO or H₂O-rich environment). For both species, the photodesorption of the intact organics is found negligible in our experimental conditions, resulting in yields typically below 1E-5 ejected molecules per incident photon. The results obtained on HCOOH and HCOOCH₃-containing ices are similar to what has already been found for methanol-containing ices, but contrast with the case of another complex molecule, CH₃CN, photodesorption of which has been recently studied. Such experimental results may be linked to the observation of COMs in protoplanetary disks, in which CH₃CN is commonly observed whereas HCOOH or methanol are detected only in some sources, HCOOCH₃ not being detected at all.

Faraday Discussions 2023, advanced article

DOI: [10.1039/D3FD00004D](https://doi.org/10.1039/D3FD00004D)

First detection of deuterated methylidyne (CD) in the interstellar medium

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While the abundance of elemental deuterium is relatively low ($D/H \sim$ a few $1e-5$), orders of magnitude higher D/H abundance ratios have been found for many interstellar molecules, enhanced by deuterium fractionation. In cold molecular clouds ($T < 20K$) deuterium fractionation is driven by the H_2D^+ ion, whereas at higher temperatures ($T > 20-30K$) gas-phase deuteration is controlled by reactions with CH_2D^+ and C_2HD^+ . While the role of H_2D^+ in driving cold interstellar deuterium chemistry is well understood, thanks to observational constraints from direct measurements of H_2D^+ , deuteration stemming from CH_2D^+ is far less understood, caused by the absence of direct observational constraints of its key ions. Therefore, making use of chemical surrogates is imperative for exploring deuterium chemistry at intermediate temperatures. Formed at an early stage of ion-molecule chemistry, directly from the dissociative recombination of CH_3^+ (CH_2D^+), CH (CD) is an ideal tracer for investigating deuterium substitution initiated by reactions with CH_2D^+ . This paper reports the first detection of CD in the interstellar medium, carried out using the APEX 12m telescope toward the widely studied low-mass protostellar system IRAS 16293-2422. Gas-phase chemical models reproducing the observed CD/CH abundance ratio of 0.016 suggests that it reflects 'warm deuterium chemistry' (which ensues in moderately warm conditions of the interstellar medium) and illustrates the potential use of the CD/CH ratio in constraining the gas temperatures of the envelope gas clouds it probes.

A&A, accepted, Forthcoming article

DOI: [10.1051/0004-6361/202245209](https://doi.org/10.1051/0004-6361/202245209)

Full-text URL: <https://arxiv.org/abs/2305.07143>

Streamers feeding the SVS13-A protobinary system: astrochemistry reveals accretion shocks?

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We report ALMA high-angular resolution (~ 50 au) observations of the binary system SVS13-A. More specifically, we analyse deuterated water (HDO) and sulfur dioxide (SO_2) emission. The molecular emission is associated with both the components of the binary system, VLA4A and VLA4B. The spatial distribution is compared to that of formamide (NH_2CHO), previously analysed in the system. Deuterated water reveals an additional emitting component spatially coincident with the dust accretion streamer, at a distance larger than 120 au from the protostars, and at blue-shifted velocities (> 3 km/s from the systemic velocities). We investigate the origin of the molecular emission in the streamer, in light of thermal sublimation temperatures calculated using updated binding energies (BE) distributions. We propose that the observed emission is produced by an accretion shock at the interface between the accretion streamer and the disk of VLA4A. Thermal desorption is not completely excluded in case the source is actively experiencing an accretion burst.

Accepted for publication in Faraday Discussions 2023

DOI: [10.1039/D3FD00018D](https://doi.org/10.1039/D3FD00018D)

Full-text URL: <https://arxiv.org/pdf/2306.08539>

Astrochemical models of interstellar ices: History matters

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Ice is ubiquitous in the interstellar medium. We model the formation of the main constituents of interstellar ices, including H_2O , CO_2 , CO , and CH_3OH . We strive to understand what physical or chemical parameters influence the final composition of the ice and how they benchmark to what has already been observed, with the aim of applying these models to the preparation and analysis of JWST observations. We used the Nautilus gas-grain model, which computes the gas and ice composition as a function of time for a set of physical conditions, starting from an initial gas phase composition. All important processes (gas-phase reactions, gas-grain interactions, and grain surface processes) are included and solved with the rate equation approximation. We first ran an astrochemical code for fixed conditions of temperature and density mapped in the cold core L429-C to benchmark the chemistry. One key parameter was revealed to be the dust temperature. When the dust temperature is higher than 12 K, CO_2 will form efficiently at the expense of H_2O , while at temperatures below 12 K, it will not form. Whatever hypothesis we assumed for the chemistry (within realistic conditions), the static simulations failed to reproduce the observed trends of interstellar ices in our target core. In a second step, we simulated the chemical evolution of parcels of gas undergoing different physical and chemical situations throughout the molecular cloud evolution and starting a few $1e7$ yr prior to the core formation (dynamical simulations). Our dynamical simulations satisfactorily reproduce the main trends already observed for interstellar ices. Moreover, we predict that the apparent constant ratio of CO_2/H_2O observed to date is probably not true for regions of low AV, and that the history of the evolution of clouds plays an essential role, even prior to their formation.

Accepted for publication in A&A

Full-text URL: <https://arxiv.org/abs/2306.08346>

Infrared photodesorption of CO from astrophysically relevant ices studied with a free-electron laser

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The infrared excitation and photodesorption of carbon monoxide (CO) and water-containing ices have been investigated using the FEL-2 free-electron laser light source at the FELIX laboratory, Radboud University, The Netherlands. CO-water mixed ices grown on a gold-coated copper substrate at 18 K were investigated. No CO photodesorption was observed, within our detection limits, following irradiation with light resonant with the C-O vibration (4.67 μm). CO photodesorption was seen as a result of irradiation with infrared light resonant with water vibrational modes at 2.9 μm and 12 μm . Changes to the structure of the water ice, which modifies the environment of the CO in the mixed ice, were also seen subsequent to irradiation at these wavelengths. No water desorption was observed at any wavelength of irradiation. Photodesorption at both wavelengths is due to a single photon process. Photodesorption arises due to a combination of fast and slow processes of indirect resonant photodesorption (fast), and photon-induced desorption resulting from energy accumulation in the librational heat bath of the solid water (slow) and metal substrate-mediated laser induced thermal desorption (slow). Estimated cross-sections for the slow processes at 2.9 μm and 12 μm were found to be $\sim 7.5 \times 10^{-18} \text{ cm}^2$ and $\sim 4.5 \times 10^{-19} \text{ cm}^2$ respectively.

Faraday Discussions, 2023

DOI: [10.1039/D3FD00024A](https://doi.org/10.1039/D3FD00024A)

Full-text URL: <https://pubs.rsc.org/en/content/articlelanding/2023/fd/d3fd00024a>

An overview of desorption parameters of Volatile and Complex Organic Molecules: A systematic dig on experimental literature

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Many molecules observed in the interstellar medium are thought to result from thermal desorption of ices. Parameters such as desorption energy and pre-exponential frequency factor are essential to describe the desorption of molecules. Experimental determinations of these parameters are missing for many molecules, including those found in the interstellar medium. The objective of this work is to expand the number of molecules for which desorption parameters are available, by collecting and re-analysing experimental temperature programmed desorption data that are present in the literature. Transition State Theory (TST) is used in combination with the Redhead equation to determine desorption parameters. Experimental data and molecular constants (e.g., mass, moment of inertia) are collected and given as input. Using the Redhead-TST method, the desorption parameters for 133 molecules have been determined. The Redhead-TST method is found to provide reliable results that agree well with desorption parameters determined with more rigorous experimental methods. The importance of using accurately determined pre-exponential frequency factors to simulate desorption profiles is emphasised. The large amount of data allows to look for trends, the most important is the relationship $\log_{10} \nu = 2.65 \ln(m) + 8.07$, where ν is the pre-exponential frequency factor and m the mass of the molecule. The data collected in this work allow to model the thermal desorption of molecules and help understand changes in chemical and elemental composition of interstellar environments.

Accepted in Astronomy & Astrophysics

Full-text URL: <https://arxiv.org/abs/2306.09071>

Investigating the OH-H₂ relation in diffuse Galactic clouds

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We investigate the correlation between OH and H₂ column densities in diffuse Galactic clouds, in order to identify potential molecular tracers of interstellar H₂. For this, we analyse near-UV spectra extracted from the ESO/VLT archives towards seventeen sightlines (five of them new) with known N(H₂), along with nine sightlines with no H₂ information. N(OH) shows only marginal correlation with N(H₂) ($1\text{e}20$ to $2\text{e}21 \text{ cm}^{-2}$), at the 95 per cent confidence level. We use orthogonal distance regression analysis to obtain $N(\text{OH})/N(\text{H}_2) = (1.32 \pm 0.15) \times 10^{-7}$, which is ~ 33 per cent higher than the previous estimates based on near-UV data. We also obtain $N(\text{CH})/N(\text{H}_2) = (3.83 \pm 0.23) \times 10^{-8}$ and a significant correlation between N(OH) and N(CH), with $N(\text{OH}) = (2.61 \pm 0.19) \times N(\text{CH})$, both of which are consistent with previous results. Comparison with predictions of numerical models indicate that OH absorption arises from diffuse gas ($n_{\text{H}} \sim 50 \text{ cm}^{-3}$) illuminated by radiation fields $\sim 0.5\text{-}5 G_0$, while CH is associated with higher density of 500 cm^{-3} . We posit that the apparent dichotomy in the properties of the diffuse clouds giving rise to OH and CH absorption could be due to either (a) the presence of multiple spectroscopically unresolved clouds along the line-of-sight, or, (b) density gradients along the line-of-sight within a single cloud.

Monthly Notices of the Royal Astronomical Society, Volume 523, Issue 3, August 2023, Pages 4593–4602

DOI: [10.1093/mnras/stad1707](https://doi.org/10.1093/mnras/stad1707)

Full-text URL: <https://arxiv.org/abs/2306.05213>

Announcements

PhD position in astrochemistry/planetary atmospheres - Dept. Physics University of Trento, Italy

One Ph.D. position is available in molecular astrophysics/planetary science at the Atomic and Molecular Physics Laboratory, Department of Physics, University of Trento (Italy), within the call for admission to the 39th cycle of the National PhD Program in Space Science and Technology - SST

The position is funded for 3 years (starting from 1st November 2023) and the research topic deals with the study of the physico-chemical processes of formation and destruction of molecular compounds due to energetic reactions of single and multiple-charged ions and/or in electrical discharges.

For further information on the position (Curriculum 4, position 4A) please visit <https://www.unitn.it/phd-sst/784/details-about-funded-positions-39th-cycle-curriculum-4> and/or contact prof. Daniela Ascenzi (daniela.ascenzi@unitn.it)

Requirements are a successful Master of Science degree in Physics, Chemistry, Physical Chemistry and a strong motivation towards experimental work. Deadline for application: July 6th, 2023, hrs. 4.00 PM (Italian time)