

# Chemical Evolution in Space: The Case of Imines

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**Abstract.** One of the main aims of astrochemistry is to understand the chemical evolution occurring in space: from diatomics to molecules of a certain degree of complexity and beyond. A significant number of features in astronomical spectra are still unassigned, thus pointing out that we are far from a complete census of interstellar molecules. This calls for new laboratory (experimental-computational) efforts. In parallel, the identification of an increasing number of molecules raises the issue of how these species can be produced in the typical harsh conditions of the interstellar medium. On these grounds, this contribution presents some results obtained by applying a new computational strategy to the specific case of imines, a prototypical class of prebiotic molecules.

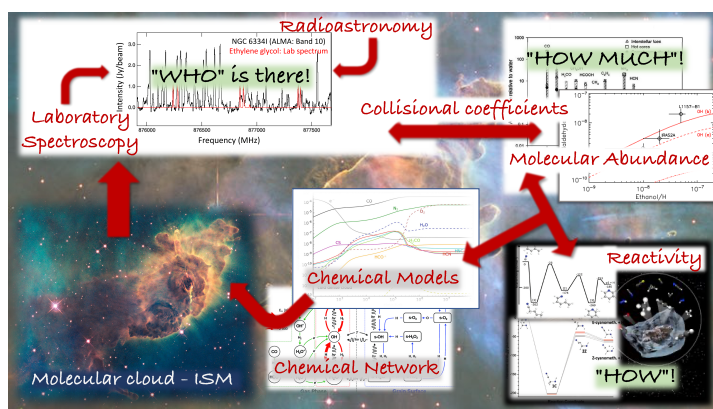
**Key words.** ISM: molecules – astrochemistry – molecular processes – molecular data

## 1. Introduction

Cosmic evolution is the tale of progressive transition from simplicity to complexity. The newborn universe starts with the simplest atoms formed after the Big Bang and proceeds toward “astronomically” complex organic molecules (COMs; Herbst & Dishoeck (2009)). Understanding the chemical evolution of the universe is one of the main aims of astrochemistry (Puzzarini 2020), with the starting point being the knowledge whether a molecule is present in the astronomical environment under consideration and, if so, its abundance. In this context, molecular spectroscopy plays the central role: the astronomical observation of the spectroscopic features of a given molecule is the definitive, unequivocal proof of its presence, with the overwhelming majority of gas-phase chemical species be-

ing discovered via their rotational signatures (McGuire 2018). However, the interpretation of astronomical detections and the identification of molecules is not straightforward at all, indeed requiring huge laboratory efforts which are increasingly supported by computational studies (Puzzarini et al. 2019; Puzzarini & Barone 2020). While the search for molecules in the interstellar medium (ISM) is one of the astrochemical challenges that we address in our laboratory by combining computational and experimental rotational spectroscopy with radioastronomical observations (Melosso et al. 2020; Melli et al. 2018; Cazzoli et al. 2016), here we focus on the reactivity.

Molecules can exist in a wide range of astrophysical environments, from the extremely cold regions between stars to the atmospheres of stars themselves. The evidence for molecular complexity in the universe is undisputed;



**Fig. 1.** An astrochemical grand challenge: the complete chemical characterization of a molecular cloud.

however, there is still much to be understood about how prebiotic molecules are formed in the typically cold and (largely) collision free environment of the interstellar medium. State-of-the-art computational approaches allow the proposal and validation of reliable formation pathways for the detected molecules, but an important result is also the rationalization of interstellar chemistry in terms of a limited number of general reaction mechanisms. In addressing these points, a specific class of molecules will be considered: imines, i.e. those species containing the  $>C=N-$  moiety, some of which are key intermediates toward the main building blocks of biomolecules, like amino acids and nucleobases (see Balucani (2009) and references therein).

## 2. Grand challenges in astrochemistry

In order to derive the chemical composition of an astronomical object a synergistic interplay of radioastronomical observations and laboratory spectroscopy is required. The intensity of the observed/assigned lines needs then to be converted into a species abundance. To complete the picture, chemical reactivity needs to be unveiled and chemical modeling to be theorized. These processes and their interconnection are sketched in Figure 1, and require a strong interplay of different communities: astronomy, astrophysics, and chemistry. These

considerations lead to the definition of the following grand challenges:

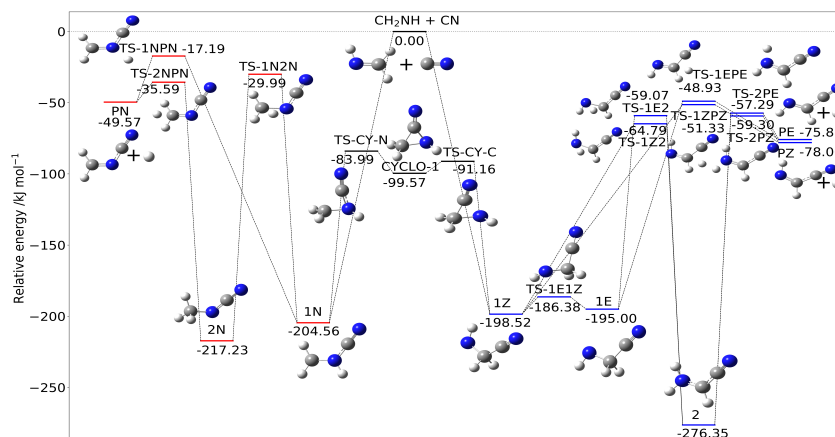
- The census of the interstellar molecules.
- The mechanisms of formation of molecules.
- The chemical evolution of astronomical objects.

As mentioned above, here, we focus on the contributions that our groups can provide on the second issue in the list above, which is also somehow connected to the first.

### 2.1. Gas-phase chemical reactivity: the methodology

Understanding the chemical processes in space is one of the main goals of astrochemistry. Focusing on prebiotic molecules, the most widespread investigated reactions to form COMs are based on grain-surface chemistry because radical species trapped in icy mantles can easily react and give rise to a rich chemistry (see, e.g., Garrod, R. T. & Herbst, E. (2006); Garrod et al. (2008)). However, several studies have pointed out that gas-phase reactions play a role that could have been much overlooked (Codella, C et al. 2017; Skouteris et al. 2018, 2017; Vazart et al. 2016; Lupi et al. 2020a).

The extreme conditions of the ISM (i.e., very low temperatures and very low density) pose strong limitations on the feasibility of chemical reactions in the gas phase: all transition states should be submerged with re-



**Fig. 2.** Pathways of the  $\text{CH}_2\text{NH} + \text{CN}$  reaction showing submerged barriers

spect to reactants' energy. To derive accessible pathways, the key point is to accurately characterize a reactive potential energy surface (PES). The approach followed in our laboratories (Lupi et al. 2020a; Tonolo et al. 2020; Baiano et al. 2020; Lupi et al. 2020b) involves the following steps:

- Preliminary investigation of the reactive PES using a cost-effective level of theory in order to locate the stationary points (a global-hybrid density functional used with a double-zeta basis set).
- Improved description of the relevant channels using a double-hybrid density functional in conjunction with a triple-zeta basis set.
- Accurate energy evaluations of the relevant stationary points using quantum-chemical composite schemes (Puzzarini 2011; Császár et al. 1998; Tajti et al. 2004; Alessandrini et al. 2019).

Since thermochemistry is not sufficient to determine whether a formation pathway might take place in the ISM or not, kinetic computations are then required. A remarkably effective option is offered by calculations of global rate constants using a master equation (ME) approach based on ab initio transition state theory (the MESS software being used as ME solver; Georgievskii et al. (2013)). For elementary reactions involving a transition state, rate constants can be evaluated using transition state

theory, while for barrierless elementary reactions, phase space theory (Pechukas & Light 1965; Chesnavich 1986) often provides reliable results (see, e.g., Tonolo et al. (2020); Baiano et al. (2020); Lupi et al. (2020b)).

## 2.2. Gas-phase chemical reactivity: complex imines

The work reported in Bizzocchi et al. (2020) is a nice example of the integration of experiment and theory for the identification of new molecules in space: an accurate computational characterization of the spectroscopic parameters of propargylimine (PGIM) guided the recording and assignment of its rotational spectrum, thus leading to the accurate knowledge of the rotational features required for the detection (in the G+0.693-0.027 molecular cloud). However, at that time, there was no clue about how PGIM could be formed in the ISM. The answer (at least partial) to this question was provided by Lupi et al. (2020a), who applied the methodology described above to the ethynyl radical ( $\text{C}_2\text{H}$ ) + methanimine ( $\text{CH}_2\text{NH}$ ) reaction.

In analogy to the addition of the CN radical to  $\text{CH}_2\text{NH}$  (see Figure 2) leading to cyanomethanimine, the addition of the isoelectronic  $\text{C}_2\text{H}$  radical leads to PGIM through a reaction mechanism that involves the forma-

tion of a stable pre-reactive complex and its successive evolution ruled by submerged transition states. A completely analogous mechanism has also been found for the reaction between CH<sub>2</sub>NH and the CP (Alessandrini et al. 2021b) or OH (Alessandrini et al. 2021a) radical. Therefore, in a more general perspective, the results of our computational investigations on the CH<sub>2</sub>NH + X (with X being a small radical) reactive systems support a general addition/elimination mechanism for the formation of complex imines, which starts from methanimine as a precursor and involves reactive radicals abundantly present in the interstellar space.

Lupi et al. (2020a) and Alessandrini et al. (2021b) suggest new potential interstellar molecules that require, first of all, a computational characterization to guide the spectroscopic (experimental) investigation. Then, if the species is experimentally (rotational spectroscopy) observed as product of the reaction under consideration, the reaction mechanism is somehow validated. Moving to space, the experimental-spectroscopic characterization in the laboratory opens the way to the detection in the ISM. If this is successful, a further validation of the mechanism is obtained.

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