Computational Astrochemistry

Journey towards the molecular universe

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Abstract. In astrochemistry, computational methods play a crucial role in addressing fundamental astronomical questions. Interstellar molecules profoundly influence the chemistry and physics of the interstellar medium (ISM), playing pivotal roles in planet formation and the emergence of life. Understanding their chemistry relies on theoretical approaches such as Density Functional Theory (DFT) and post–Hartree–Fock methods, which are essential for exploring pathways to molecular complexity and determining their interstellar abundances. Various theoretical methods investigate the formation of interstellar molecules in both gaseous and solid states. Molecules in interstellar space may originate from bottom-up processes (building up from CO molecules) or top-down processes (polycyclic aromatic hydrocarbon fragmentation). Here, we present a journey of theoretical investigations aimed at studying the reactivity of interstellar molecules in space.

Key words. Quantum chemistry, ISM, iCOMs, PAHs

1. Introduction

A wide range of organic molecular species have been observed in different regions of the interstellar medium (ISM) and the solar systems, both within our own galaxy and beyond (McGuire 2022; Müller 2019). These molecules serve vital functions in regulating the physical and chemical conditions of the ISM, potentially contributing to the formation of planetary systems and the emergence of life (Tielens 2013). The launch of the high-resolution James Webb Telescope holds promise for revealing organic molecular species in the interstellar space (Fortenberry 2024). As the molecules chemically evolve within the ISM, they become integrated into solar system materials like comets, asteroids, and meteorites (Ehrenfreund & Charnley
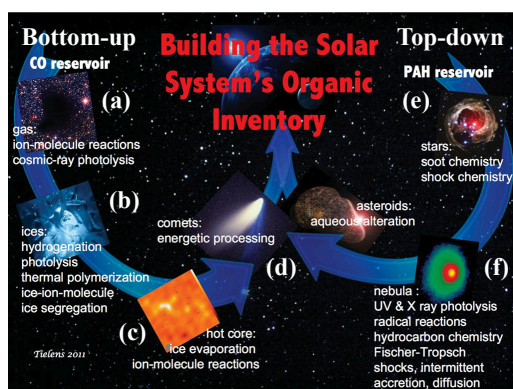
Fig. 1. The schematic explanation of the processes of bottom-up and top-down approaches as reported by Campisi (2021) and Tielens (2013).

2000). The recent NASA mission OSIRIS-REx successfully returned a sample of the asteroid Bennu to Earth (Lauretta et al. 2017; Parker et al. 2023). Examination of these solar system materials promises valuable insights into the origin and chemical evolution of molecular species. Isotopic analysis of these materials has proven crucial in tracing the origin of molecules, believed to have originated in the solar nebula (Sandford et al. 2001). Hence, the molecular species detected in these primitive objects represent a legacy of chemical processes that commenced in the ISM (Tielens 2013). To elucidate this further, most organic molecules are believed to stem from two prevalent entities in space: carbon monoxide (CO) and Polycyclic Aromatic Hydrocarbons (PAHs) (Tielens 2013). According to the bottom-up approach, intriguing chemistry occurs on the surfaces of interstellar grains in cold star-forming regions, where CO undergoes hydrogenation, gradually fostering molecular complexity (Tielens 2013). Conversely, PAHs, constituting approximately 20% of the carbon in space, are thought to form in the outflows of carbon-rich stars (Tielens 2008; Mebel et al. 2017). From a top-down perspective, PAHs fragment via radical and photodissociation processes, producing daughter molecules that act as precursors for biologically relevant molecular structures (Ehrenfreund et al. 2006; Tielens 2013). Eventually, the outcomes of both **bottom-up** and **top-down** processes (Fig. 1) become integrated into cometesimals and planetesimals, potentially delivering them to habitable zones and laying the groundwork for life (Tielens 2013).

Laboratory astrophysics is crucial to understanding the chemical evolution and composition of the cosmos and complements the astronomical approach (Ceccarelli et al. 2023).

Due to the challenges posed by certain reactions of interest, conducting studies in terrestrial laboratories becomes exceedingly difficult. These reactions involve transient species, such as radicals or ions, which are challenging to generate in a controlled manner and in sufficient quantities for reactive experiments. Moreover, experimental approaches often struggle to replicate the authentic conditions of the interstellar medium (ISM). In this context, theoretical calculations play a vital role. They support the interpretation of experimental data and aid in extrapolating results to conditions typical of the ISM. Furthermore, theoretical characterization becomes the sole viable option for investigating reactions that are particularly elusive to study experimentally (Ceccarelli et al. 2023).

Density Functional Theory (DFT), a prominent quantum chemistry approach (Parr 1983), efficiently investigates organic molecules in interstellar environments, providing essential spectroscopic constants, binding and activation energies for astronomical data interpretation. Higher-level methods like coupled-cluster (CC) theory (Čížek 1966) and complete active space perturbation theory (CASPTn) (Roos et al. 1980) may be necessary, particularly for neutral-neutral reactions, where minor energy differences in key transition states significantly influence reaction rate coefficients (Dawes & Ndengué 2016; Balucani et al. 2024).

Below, we outline common computational strategies for studying interstellar molecule reactivity in the ISM.

2. Bottom-up approach

Early astrochemical models focused on gas-phase reactions to derive the abundances of complex molecules. Initially, it was thought that interstellar dust grains only catalyzed H_2 formation, but later, it was proposed that other species could hydrogenate on grain surfaces, increasing molecular complexity (Tielens 2013).

The bottom-up formation of interstellar complex organic molecules (iCOMs) involves the production of hydrogenated species on icy grain mantles, which are then desorbed into the gas phase and undergo reactions. Furthermore, radical-radical couplings occur directly on grain surfaces during the warm-up phase of a newly born protostar, aiding in molecular complexity (Tielens 2013).

In this section, we analyze the role of computational chemistry in substantiating these scenarios.

2.1. Reactions on dust grain surface

Several experimental studies have shown that complex molecules can form on cold ice surfaces (e.g., see Linnartz et al. (2015); Öberg (2016); Marks et al. (2023)). However, these experiments do not fully replicate the conditions of interstellar ice, such as composition, UV and H atom flux, and grain size. Therefore, a theoretical approach is crucial for understanding these processes at an atomic level and their impact on interstellar ice chemistry (Rimola et al. 2018).

A thorough study of radical-radical recombination reactions on ice surfaces uncovered several challenges Garrod & Herbst (2006); Enrique-Romero et al. (2022). First, the coupling of radicals depends on a delicate balance between their diffusion and desorption rates, limiting the temperature range where reactions can occur. For instance, the formation of acetaldehyde from CH_3 and HCO is constrained between the temperatures where CH_3 can diffuse (9-15K) and when methyl radicals desorb, 30K, (Enrique-Romero, Joan et al. 2021). Second, while these couplings are often assumed to be barrierless due to coupling of opposite electronic spins, energy barriers can arise as radicals must break surface interactions to diffuse and react. Third, these reactions can have competing channels, like H-abstractions, hindering the formation of important interstellar iCOMs (Tielens 2013).

An alternative mechanism, the "radical + ice component" scheme, proposes a reaction between a radical (from the gas phase or UV irradiation) and neutral components of ice, like H_2O. This approach, discussed by Rimola et al. (2018), was demonstrated with the formation of formamide (NH_2CHO) from CN radical and water on an ice surface. Despite addressing diffusion and competitive reaction issues, this method faces an energy barrier due to the radical-neutral interaction.

The mentioned scheme shows promise, recently tested with CCH, similar in reactivity to CN, on a water ice surface (Perrero et al. 2022). CCH reacts with H_2O barrierlessly or with a small barrier, forming vinyl alcohol precursors (H_2CCOH and CHCHOH) or C_2H_2 + OH. Hydrogenation of vinyl alcohol to ethanol has a low activation energy barrier, overcome by tunnelling effects. The formation of C_2H_2 + OH is hindered, as the water ice surface efficiently dissipates the energy released (Pantaleone et al. 2020, 2021). Nonetheless, this path can effectively generate OH radicals on ice surfaces without direct energy processing.

Quantum chemical evidence supports the "radical + ice component" scheme as an alternative to classical radical-radical recombination mechanisms. This adds to the various proposed reaction mechanisms explaining the presence of iCOMs in the ISM.

2.2. Gas-phase reactions

The thorough characterization of gas-phase reactions of relevance in astrochemistry hinges upon three fundamental methodologies: 1) the CRESU (Cinetique de Reaction en Ecoulement Supersonique Uniforme) technique yields low-temperature global rate coefficients (Rowe & Marquette 1987; Smith 2006). 2) collision-free experiments determine primary reaction products and their branching ratios (Casavecchia

et al. 2015). Since these techniques are rarely able to reproduce both the low temperature and the low pressure conditions of the interstellar medium, a third approach is necessary based on 3) Quantum theory for chemical reactions aids. This approach is of help in interpreting experimental data and enables extrapolation to interstellar cloud conditions. Additionally, it provides insights for reactive systems inaccessible to experimental investigation.

The quantum characterization of chemical reactions requires electronic structure calculations to derive the potential energy surface (PES) describing the reaction through the stationary point (transition states or bound intermediates) which are formed along the minimum energy path (see, for instance, Dawes & Ndengué (2016) and references therein). Once the PES of a certain reaction has been determined, kinetics calculations can be performed via transition state theory, variational transition state theory or capture theory (Truhlar & Garrett 1984; Truhlar et al. 1996; Clary 1990) depending on the characteristics of the system. In the case of multichannel reactions, a statistical approach can allow to determine the product branching fractions (Miller & Klippenstein 2006).

As already mentioned above, reactions involving two radical species, like $NH + C_2H_5$ (forming mainly $CH_2NH + CH_3$) (Balucani et al. 2018) and $O + CH_2CH_2OH$ (a key route to interstellar glycolaldehyde) (Skouteris et al. 2018; Vazart et al. 2022), lack experimental characterization and are characterized only theoretically. Radiative-association processes, like those discussed in (Antipov et al. 2009; Nyman et al. 2015; Babb et al. 2019; Giani et al. 2024), are also exclusively theoretically characterized due to challenges in lab experiments: it is difficult to disentangle the stabilization of the addition intermediate by spontaneous emission of photons from collisional stabilization.

Recent astrochemical modeling highlighted a significant case involving CH_3O radical in cold or warm regions of the ISM (Balucani et al. 2024). The primary formation pathway for CH_3O involves the reaction $CH_3OH + OH$, extensively studied experi-

mentally and theoretically (Balucani et al. 2024). Understanding this reaction is complex due to its non-Arrhenius behavior, attributed to a pre-reactive complex (Shannon et al. 2013). Klippenstein et al. (Georgievskii & Klippenstein 2005, 2007) showed that for barrierless radical-molecule reactions, the rate-determining step might shift from the formation of a weakly bound van der Waals complex at low temperatures to the passage through a subthreshold saddle point at higher temperatures. The comparison between theoretical calculations and experimental results on several systems suggests a two-transition-states mechanism, necessitating accurate treatments of both inner and outer transition states (Sabbah et al. 2007; Cheikh Sid Ely et al. 2013).

In the $CH_3OH + OH$ case, however, the inner transition state lies above the energy of the reactants, creating a real threshold, resulting in slow kinetics at room temperature and above (Xu & Lin 2007; Roncero et al. 2018; Gao et al. 2018; Nguyen et al. 2019). Experimental data from the CRESU technique show a notable rate coefficient increase below 200 K (Shannon et al. 2013; Antiñolo et al. 2016). And surprisingly, the primary product formed with water is the methoxy radical rather than the anticipated hydroxymethyl radical (CH_2OH) (Shannon et al. 2013). The peculiar behavior is attributed to the pre-reactive complex and efficient tunneling through the outer transition state, facilitating $CH_3O + H_2O$ formation. At very low temperatures, the long-lived pre-reactive complex allows reaching the product asymptote via barrier tunneling, whereas at high temperatures, the pre-reactive complex's short lifetime makes its impact on the rate coefficient negligible. Theoretical approaches incorporating tunneling and a two-transition-states mechanism replicate CRESU experiment trends (Gao et al. 2018; Nguyen et al. 2019). However, experimental and theoretical rate coefficient estimates diverge significantly at the low temperatures relevant to interstellar chemistry (Gao et al. 2018). Partial collisional stabilization of the pre-reactive complex, observed in CRESU experiments, is attributed to
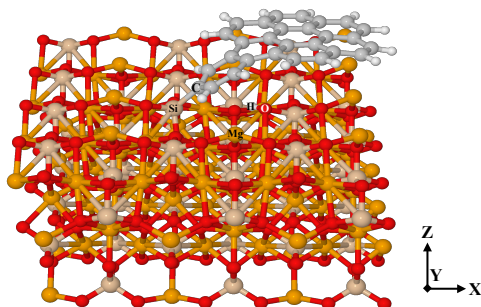
Fig. 2. A large PAH, benzocoronene, adsorbed onto a MgO vacancy on the (010) forsterite surface with a binding energy of 5.48 eV (Campisi et al. 2022). Atomic labels are provided as follows: C (light gray), H (white), O (red), Mg (orange), Si (beige). The surface faces a vacuum region along the z-axis.

conditions incompatible with the highly rarefied ISM environment (Gao et al. 2018).

Intriguingly, comparison between astrochemical model predictions and CH_3O observations in varied temperature regions favors theoretical values derived by Gao et al. (2018) over experimental data, underscoring the significance of theoretical approaches in simulating interstellar conditions.

3. Top-down approach

3.1. Interstellar PAHs

PAHs (Fig. 2), large carbon molecules abundant in our galaxy and beyond, exist in various forms including individual molecules and solid grains. They are present in solar system objects like carbonaceous chondrites meteorites (Sephton 2002), believed to preserve ancient organic compounds formed in the solar nebula. These materials offer insight into early solar system chemistry. PAHs smaller than 6-membered rings are detected in meteorites, suggesting their role as carbon reservoirs and potential association with prebiotic molecules (Tielens 2008, 2013).

After being formed in the surroundings of carbon-rich stars, PAHs are injected into the ISM, where various chemical and photochemical processes can occur (Frenklach & Feigelson 1989; Cherchneff et al. 1992). Thus, Density Functional Theory (DFT) has been extensively used to study both the spectroscopy (Peeters et al. 2021) and reactivity (Jensen et al. (2019); Campisi et al. (2020) and many others) of PAHs in different environments, such as when adsorbed onto grain surfaces or present as gas-phase molecules. The main distinction lies in the treatment of the theoretical model, with periodic DFT (Hasnip et al. 2014) taking into account periodic potentials to simulate solid boundary conditions.

Periodic DFT was used to study PAH adsorption on forsterite surfaces, common in interstellar grains and planetary systems (Campisi et al. 2021, 2022). Forsterite is found in carbonaceous chondrite asteroids and meteorites where PAHs are detected (Sephton 2002). Large PAHs strongly adsorb onto forsterite due to non-covalent aromatic ring interactions (Fig. 2), with binding energies ranging from 1 eV for naphthalene to about 5 eV for benzo-coronene (Campisi et al. 2022). Defects like MgO vacancies enhance reactivity by providing cavities for PAHs to intercalate and dissociate their C-H bonds, potentially explaining the absence of large PAHs in solar system materials.

PAHs play a crucial role in the interstellar medium (ISM) by hosting radicals and undergoing superhydrogenation, a process essential for catalyzing molecular hydrogen formation, the most abundant molecule in space (Jensen et al. 2019; Campisi et al. 2020; Rauls & Hornekær 2008). Non-periodic DFT studies have elucidated the mechanism of PAH superhydrogenation, indicating that odd hydrogenation attachments have barriers approximately 0.20 eV due to involvement of radical neutral species, while even hydrogenation proceeds barrierlessly through radical-radical recombination (Jensen et al. 2019; Campisi et al. 2020). PAH reactivity is shape-dependent, with linear PAHs—where aromatic rings are connected in a straight line—being more reactive than larger, more condensed PAHs. DFT is es-

sential for understanding experimental mass spectra measurements, revealing magic numbers (numbers of hydrogenated species) corresponding to barriers higher than 0.20 eV (Jensen et al. 2019; Campisi et al. 2020). Superhydrogenation not only aids in molecular hydrogen formation but also weakens carbon-carbon bonds in PAHs, converting aromatic bonds into aliphatic ones. Gas-phase studies on cationic pyrene (Tang et al. 2022) indicate that ethyne extraction via fragmentation is possible, but barriers exceed 1.50 eV. Comparing gas-phase studies to reactions on solid surfaces is challenging due to energy dissipation by the grain during exothermic reactions, resulting in a lack of internal energy to overcome the significant barriers.

$N(^2D)$ and $O(^3P)$ are highly reactive toward hydrocarbon molecular species (Balucani et al. 2023; Rosi et al. 2020; Cavallotti et al. 2020), crucial for life-building blocks. Current research focuses on their reactivity with PAHs (Aponte et al. 2017). Computational studies have revealed $N(^2D)$ interactions with small hydrocarbons, leading to N-heterocycle rings and HCN formation, important in Strecker amino acid reactions (Balucani et al. 2023; Aponte et al. 2017). $O(^3P)$ shows promise for PAH fragmentation (Cavallotti et al. 2020), with both experimental and computational studies identifying pathway channels in triplet and singlet states, resulting in CO and small ketene formation (Cavallotti et al. 2020; Dulieu et al. 2019). Further research is needed to explore how PAH size influences O atom reactivity.

Computational studies are pivotal in assessing the photodissociation rate of PAHs by examining their excitation in the UV-visible range ((Joblin et al. 2020; Marciniak et al. 2021) and many others). PAHs are susceptible to photo-destruction, especially in environments like active galactic nuclei or near massive stars, where they can undergo H-loss, fragmentation, and ionization (Zhen et al. 2015). Additionally, collision heating from interactions with cosmic rays, heavy and fast atoms, ions, and shock waves can further contribute to PAH fragmentation by interacting with energetic particles ((Allamandola et al. 1989) and many others).

4. Conclusions

Theoretical methods play a crucial role in studying the chemical evolution reactivity prediction of interstellar molecules. From a bottom-up perspective, complex organic molecule synthesis (iCOMs) results from the collaboration of on-grain and gas-phase reactions. On-grain reactions, like radical-radical couplings, face minimal activation barriers but are constrained by the delicate balance of reactant diffusion and surface desorption. Gas-phase reactions present challenges in determining accurate rate coefficients and simulating realistic interstellar conditions.

Understanding PAH fragmentation is crucial for comprehending the formation of iCOMs, given their high carbon content. Key factors include radical reactions with hydrogen, oxygen, and nitrogen, as well as radiative and ionization processes. Future research should prioritize studying PAH fragmentation induced by oxygen and nitrogen attachment and determining the abundance of resulting products in space.

Moreover, future research should evaluate the delivery of iCOMs formed from both bottom-up and top-down chemistry to understand their presence in solar system objects and their connection with the building blocks of life.

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