"New tools for the astrochemist: multi-scale computational modelling and helium droplet-based spectroscopy". Comment on: "A never-ending story in the sky: The secrets of chemical evolution" by Cristina Puzzarini and Vicenzo Barone

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In a continuous, rapid learning process, which started in the early 20$^{\text{th}}$ century, our insights into the structure of matter have deepened at incredible speed. The knowledge we gained in this subject now lies at the very heart of all modern sciences, forming the trunk of a widely ramified tree with numerous branches. With the arrival of quantum mechanics our understanding of nature has been pushed far beyond direct accessibility and common intuition. There lies a certain beauty in the fact that sub-atomic physics became so closely linked to cosmology in our quest for the 'origin of everything'. Atomic and molecular physics, on the other hand, are the best tools in our humble attempts to understand the 'origin of life'. Remarkably, even the latter endeavor now seems to lead away from our blue planet and into the cosmos.

The detection of astronomical complex organic molecules (aCOMs), potential building blocks for life as we know it on earth, caught the interest of astrochemists, physicists and biologists likewise. One major goal is to understand the mechanisms governing the genesis of prebiotic molecules, and, most importantly, the chemical evolution from complex, yet still inanimate matter, into life. The review article of Puzzarini and Barone [1] elegantly summarizes the major advancements achieved by joint theoretical and experimental studies, where high level *ab initio* theories, density functional theory (DFT)-based approaches, and accurate quantum treatments of nuclear motion are combined with cutting-edge spectroscopic measurements and astronomical observations of the interstellar medium.

Before commenting on some aspects of their work in greater detail we shall briefly summarize its content. Puzzarini and Barone start with a basic introduction to the energy regimes of astronomical spectroscopy, ranging from the microwave to the optical regime. Most information on molecular systems can be gained from rotational spectra, which indicates already the need for highly accurate computational modeling of the molecular species involved. Vibrations, due to their higher excitation energies, play a minor role in the typically cold environment of the interstellar medium, but can deliver additional information

when e.g. pumped through external radiation fields or in warmer regions; vibrational as well as optical excitations are not restricted to molecules with a permanent dipole moment.

As highlighted by Puzzarini and Barone, whole reactions paths can be derived from spectral analysis in combination with accurate computational modelling. Thus, the authors provide an extensive overview of current computational approaches providing relative energies and spectroscopic parameters of the reactants involved, as well as thermodynamic and kinetic properties [1]. Starting with quantum-chemical predictions of relative energies for small and medium-sized systems, cost-effective schemes are proposed to reduce the errors introduced by finite basis sets and by the typical truncations of determinant-based N-electron wavefunction methods. These schemes are implemented in the quantum-chemistry program package CFOUR [2] along with the so-called HEAT protocol. The composite schemes are well tested for typical molecular species of astrophysics, with the accuracy achieved (well within 0.5 kcal/mol) being particularly reassuring [3].

For large molecules, when computational demands are very high, Puzzarini and Barone propose mixed schemes, employing e.g. DFT approaches for the equilibrium geometries and higher levels of *ab initio* treatments for single-point energy evaluations. In a next step, computational results need to be linked with spectroscopic properties. While rotational constants are easily derived from equilibrium geometries, the vibrational motion is most effectively treated via vibrational perturbation theory of second order [4]. Using the proposed methodological schemes, rotational transitions can be predicted with a relative accuracy better than 0.2% [1]. Mean absolute errors within 8 cm^{-1} are achieved by combining composite schemes for the harmonic frequencies and hybrid DFT/Hartree-Fock approaches for anharmonic corrections when computing vibrational transitions [5].

Particularly challenging is the treatment of electronic excitations, where uncertainties in computation are still much larger due to the increasing complexity of the electronic structure problem. A paradigmatic case of the extreme sensitivity to the underlying quantum-chemical treatment is the simulation of chiroptical properties e.g. of biomolecules such as amino acids. All these requirements triggered the development of a more holistic simulation approach, which has been realized in the form of a software tool named the virtual multifrequency spectrometer by Barone and collaborators [5].

In a later chapter, Puzzarini and Barone propose a novel integrated strategy, which involves theory, experiment, high-performance computing, astronomical data-driven research, as well as augmented and virtual reality technologies as future tools of astrochemistry [1]. The creation of a suitable cyber-infrastructure and the coordinated use of integrated platforms for a joint, concerted data-mining with the help of artificial intelligence are presented as a new 'pillar' of scientific research. In their vision, state-of-the-art computation is combined with human pattern recognition skills and intuition; a concept which would surely help to tackle some of the most puzzling open questions of astrochemistry.

Finally, Puzzarini and Barone [1] compare two possible scenarios which have been suggested as potential explanations for the emergence of life on Earth. According to the *endogenous theory*, life was formed on our planet, and started with the synthesis of simple organic molecules from precursor molecules in the atmosphere in combination with liquid water and energy. Titan, the largest moon of Saturn, is of great interest in this context as it serves as an object comparable to the early Earth due to its complex atmospheric activities and rich chemistry. The *exogeneous delivery* theory, on the other hand, assumes that pre-synthesized molecules have been brought to earth by comets, asteroids or meteorites. In the latter scenario, the catalysis of aCOMs on the surface of the dust grains in interstellar space plays a key role.

This last aspect of their fascinating review brings us to our first comment on

surface-grain chemistry. Current models for the formation and evolution of prebiotic molecules are based on two ingredients. One is the Langmuir-Hinshelwood mechanism, in which the grain plays the simple role of a third body. The other one is the polarizable continuum model[6], employed to simulate the grain mantle of water ice surrounding the grain cores. We believe that descriptions of these locally 'confined' physico-chemical mechanisms would surely benefit from recent developments of multi-scale first-principles modelling. For example, via time-dependent density-functional theory, it has become possible to predict near-IR to UV spectra of biologically relevant molecules and protein-bound optical probes [7], including solvent effects. Also, machine learning techniques now allow for molecular dynamics simulations at high accuracy for flexible molecules consisting of several dozens of atoms [8].

Note that 'multi-scale approach' does not only refer to a spatially layered treatment of a molecular problem e.g by methods of various computational cost. It is a far more flexible concept, and can also refer to the choice of different approaches for certain types of interaction or contributions to the total energy. For instance, one specific protocol is to identify and exploit transferability, i.e. use selected properties obtained by high-level *ab initio* and DFT-based calculations of gas-grain interactions via cluster, periodic, or combined 'cluster-in-solid' modelling [9], and feed them e.g. with continuum models to account for solvent effects. For the concrete case of van-der-Waals-dominated adsorbate/surface interactions [10, 11, 12, 13], the usage of smaller cluster models can be justified as follows. Complicated, dispersionless contributions are mostly of short-range nature. Dispersion, on the other hand, is long-range, but the corresponding parameters show excellent transferability properties upon increasing the size of the surface cluster models [11]. Therefore, these parameters can be calculated at much higher level of *ab initio* theory on small clusters and then scaled to the actual system size. Detailed energy decomposition schemes, an intrinsic feature of methods such as symmetry-adapted perturbation theory[14, 15], are particularly useful in this respect. A logical next step is to derive force-field

expressions from these high-level computations, including parametrizations via machine learning, and to use them for subsequent dynamical studies of molecular motion.

As noted by Puzzarini and Barone [1], there is still much to understand regarding the formation pathways of "astronomical complex organic molecules" (aCOMs) at the extremely low temperatures and densities of the interstellar medium. Here we would like to draw the reader's attention to the niche of helium-droplet-mediated spectroscopy and reaction chemistry [16, 17], an experimental technique which allows molecular studies within the highly inert and cryogenic (about 0.4 K) environment provided by droplets of superfluid helium.

Laboratory experiments have just recently been employed to characterize several diffuse interstellar bands (DIBs). In space, these bands are caused by the photoionization of larger molecules in diffuse interstellar clouds by visible and ultraviolet light. About 500 DIBs, mostly in the visible and infrared regions, have been observed so far. Polycyclic aromatic hydrocarbons (PAHs) and fullerenes are considered to be the main cause of these DIBs as they can survive under extreme interstellar conditions. Indeed, the photodesorption spectrum of the He$-C_{60}^+$ complex revealed the C_{60}^+ ion as the first accepted carrier of DIBs [18]. Independently, Scheier and collaborators were able to assign four interstellar bands to the C_{60}^+ ion via electron ionization of fullerene-doped helium droplets [19]. The C_{60}^+ ion has very recently confirmed as the first carrier of DIBs using the *Hubble Space Telescope* [20].

Very recently, the He droplet isolation technique has been proposed as a tool to characterize low-temperature grain-surface reactivity [21]. Using this technique, the He droplet plays the role of a third body for energy and momentum transfer in the associative reactions between two embedded molecules, and the energy released causes a measurable evaporation of He atoms, which can be compared directly to energy differences obtained in quantum-chemistry calculations. For

instance, the reaction of C atoms with different species such as C_2H_2 has been found to be barrierless, suggesting an efficient formation of prebiotic molecules during the condensation of carbon atoms on grain surfaces. An urgent need to further advance in surface-grain chemistry is a more precise knowledge of the dust grains composition. Thus, Cernicharo and collaborators have just detected the first Ca-bearing molecule in the interestellar space [22], pointing out that a key metal atom in bone structures (calcium) might be as well in the dust grains. This feature indicates that it is also important to model charge-transfer processes in the gas-grain contact region.

Aimed at a first-principles modelling of molecular spectroscopy and reactivity in helium droplets, very accurate characterizations of dispersion-dominated He-molecule and He-surface interactions, are necessary so that cost-effective approaches have been recently developed [10, 23]. To deal with large amplitude motion and related zero-point energy effects [24] special, techniques are necessary, ranging from numerical solutions of the Schödinger equation on a grid [10] to time-dependent density functional theory for the droplet motion [25] with codes that are available to the scientific community. Summarizing, we believe that the experimental and computational advances made in helium droplet research make this somewhat 'exotic' technique a highly useful tool for the astrochemist.

In conclusion, in the quest for the 'origin of life' we have just begun to look beyond our own planet. We found an unexpected molecular complexity that will keep us busy for generations; astronomers, physicists, chemists, biologists and other experts of related fields, are united in their desire to link these findings to the incredible richness of organic life on our planet. Perhaps, knowing more about the 'origin of life' will also help to reveal more about its preservation. Self-awareness, which drives us as scientists and makes us ask all these questions, has developed in a long evolutionary process on this planet, but what about life itself? Chances are, we might find some answers by gazing at the night sky, while our instruments are probing the darkness of interstellar space.

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