# The place of Quantum Chemistry in Molecular Astrophysics
## Comment on "A never-ending story in the sky: The secrets of chemical evolution" by Cristina Puzzarini and Vincenzo Barone

The Universe is in a constant state of evolution and, as a result of it, stars and planets are formed from the ashes of previous generations of stars. During most of the key transformations that take place along the life cycle of stars, matter is essentially in molecular state. Therefore, Molecular Astrophysics, which is concerned with the study of molecules in space, emerges as a powerful tool to understand the life cycle of stars. Moreover, during these molecular stages, matter experience chemical transformations which can led to the formation of rather complex molecules, some of them of prebiotic interest. This area of science has evolved into a highly multidisciplinary field in which astronomical observations need the assistance of laboratory experiments and theoretical calculations to maximize the scientific return and gain a deeper understanding of the underlying phenomena [1]. The article by Puzzarini and Barone [2] identify the niches in which Quantum Chemistry can help to solve astrochemical problems and places Quantum Chemistry within the field of Molecular Astrophysics. Among the various examples of how Quantum Chemistry can assist Molecular Astrophysics discussed by Puzzarini and Barone [2], we will comment on two and mention one that has not been covered.

The first example is related with how Quantum Chemistry can help to identify molecules in space through the rotational spectrum. Puzzarini and Barone [2] review the state-of-the-art of *ab initio* calculations and make a fair and realistic discussion of the possibilities of Quantum Chemistry to this respect. It is clearly shown that the current precision that *ab initio* calculations can reach (better than 0.1 %) are far from what is needed to identify a complex molecule in the spectrum of an astronomical source crowded of lines. In those cases, only rotational spectroscopy in the laboratory can reach the accuracy needed. However, quantum chemical calculations can be extraordinarily useful for symmetric molecules with a simple pattern in their rotational spectrum. In fact, some linear molecules for which the rotational spectrum was not available from the laboratory have been identified in space thanks to accurate *ab initio* calculations. This is the case of the negative molecular anion $C_5N^-$. This species was discovered in the circumstellar envelope around the prototypical carbon star IRC +10216 through the observation of a series of lines with harmonically related frequencies which were fitted to rotational and centrifugal distorsion constants in agreement with values from accurate quantum chemical calculations [3]. The perfect agreement together with arguments of chemical plausibility about the presence of this species in IRC +10216 led to a detection that has not been disputed, even if the rotational spectrum of $C_5N^-$ has not been recorded in the laboratory. Recently, two new molecules, $MgC_3N$ and $MgC_4H$, have been identified in the same source thanks again to high level *ab initio* calculations [4].

The second example concerns the computation of reaction rate coefficients, which are essential in Astrochemistry to unveil the chemical routes that form molecules in the interstellar medium. Puzzarini and Barone [2] discuss how relatively transition state theory can provide sufficiently accurate rate coefficients for some reactions at certain temperatures, although in certain cases more computationally expensive methods are needed. One of the main challenges of

quantum chemical calculations concerns the kinetics of reactions at very low temperatures when there is a small barrier that can be surpassed through tunneling or roaming effects. One example is the reaction between the radical OH and methanol ($CH_3OH$). It has been observed in the laboratory that the rate coefficient of this reaction experiences a considerable enhancement when the temperature is lowered down to 22 K [5]. Calculations based on a master equation approach and dynamical calculations successfully reproduced the rise in the rate coefficient with decreasing temperature, although the calculated rate coefficient below 100 K remains about one order of magnitude below the observed values [6,7].

One last example we would like to comment to illustrate the leading role of Quantum Chemistry in Molecular Astrophysics concerns the calculation of rate coefficients for inelastic collisions. Although non reactive, these processes are critical in regulating how the energy levels of molecules are populated in the low density environments usually found in interstellar space, and this information is essential to derive molecular abundances from astronomical spectra. Non reactive collision rate coefficients are very difficult to measure in the laboratory and therefore, quantum chemical calculations are unavoidable. The subject has been reviewed by Roueff and Lique [8].

## References


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