3P038 Global mapping of small carbon clusters using the scaled hypersphere search method

(Tohoku University, Graduate School of Science) ○Balázs Hajgató, Satoshi Maeda, Koichi Ohno

Introduction:

The study of pure carbon molecules has engaged great interest for many decades. Molecules of this kind were first detected in astrophysical sources over a century ago and continue to be intensely studied in connection with the chemistry of carbon stars, comets, and interstellar molecular clouds. In particular, long carbon chains have recently been proposed as possible carriers of the diffuse interstellar bands. Carbon clusters are known to be present in hydrocarbon flames and other soot-forming systems, and the study of these species is necessary for acquiring a thorough understanding of these complex chemical environments. Carbon clusters are also thought to be intermediates in the gas-phase chemistry taking place in chemical vapor deposition systems for production of thin diamond and silicon carbide films. Clearly, a detailed knowledge of the physical and chemical properties of carbon clusters is important for understanding a large variety of chemical systems.

In addition to such practical considerations, carbon clusters are fascinating examples of the richness and variety of carbon chemistry itself. Due to the enormous bonding flexibility of carbon, its unique ability to form stable single, double, or triple bonds, carbon clusters appear in a wide range of structural forms that are synthesized spontaneously in hot carbon plasmas. For example, researchers have been puzzling for more than a decade over the ability of a molecule as symmetric as the icosahedral C_{60} cluster to form in such spontaneous way. Elucidating the evolution of carbon cluster structure, from linear chains to rings to closed sphenoidal cages to nanotubes, that takes place as the cluster size increases constitutes a major scientific challenge and requires an intimate interplay of state of the art experimental and theoretical techniques. While great progress has been made in recent years, many unanswered questions still remain[1,2].

As the first and basic step towards understanding the great variety of chemistry and astrochemistry involving small carbon clusters it is necessary to make a theoretical study. To achieve a better understanding of these systems, I have investigated small carbon clusters, of up to six atoms. The main focus of this work has been the extrema on the potential energy surface (PES) of the clusters along with

their corresponding reaction and dissociation channels. This treatment can be coupled with remote sensing experimental data, such as spectroscopic measurements, in order to help us to understand the reactions taking place in outer space, even though it is physically impossible to collect suitable sample materials.

Computational methods:

Both singlet and triplet PES were investigated at the B3LYP/6-311+G* level of theory. Energy refinements were also performed using CCSD(T) calculations. The global PES search technique employed was the Scaled Hypersphere Search (SHS) method[3,4]. This algorithm searches the pathways leading to transition states and dissociation channels from an arbitrary equilibrium structure. Combining the SHS technique with a downhill-walk algorithm allows a full topographic analysis of the PES to be obtained for any given chemical composition.

Results:

The triplet results for C_4 and singlet results for C_5 are given in figures 1 and 2, respectively. In the case of small carbon clusters the linear ones are the most stable isomers and in the case of the even numbered clusters the linear triplet one is the global minimum while in the case of odd numbered clusters the linear singlet species. Some compounds seem to be enough stable against monomolecular reactions so their experimental detection might be possible.
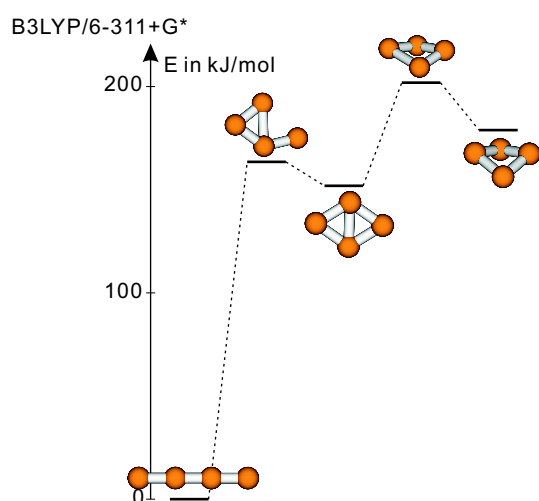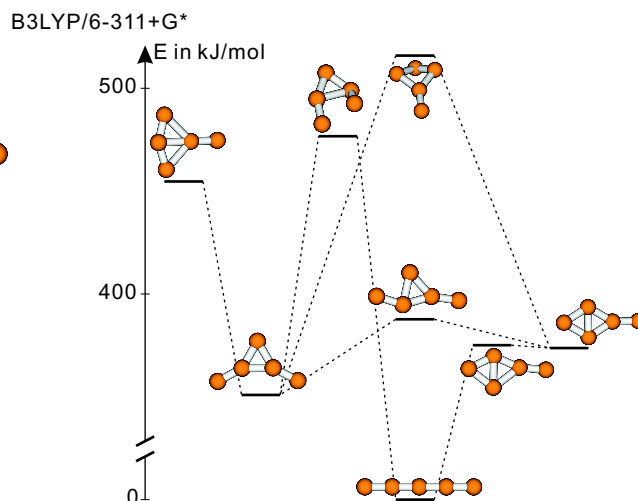

Figure 1: Triplet PES of C_4

Figure 1: Singlet PES of C_5

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