On the interaction of various gases with all-boron fullerene B\(_{80}\): Rovibrational, Thermodynamics and QTAIM analysis

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Abstract: The experimental observation, by photoelectron spectroscopy, of an all-boron fullerene anion, named B\(_{40}\), gave rise to a whole new chemistry concerning boron-based fullerenes for various applications such as hydrogen storage [1]. The aesthetically attractive cluster of boron B\(_{80}\), a fullerene-like hollow shell, inspired research to design B\(_{80}\)-based macrostructures. Just as thin films of conventional buckyballs have been explored as adsorbent of gases, these new boron cage clusters are potential molecular architectures for gas detection and/or uptaking applications. Herein, we employed a minimalist two-dimensional approach to assess and characterize the intermolecular interactions along the potential energy curve of a single B\(_{80}\) cluster with six different light gas molecules: H\(_2\), HF, NH\(_3\), CO\(_2\), SH\(_2\) and SO\(_2\). Rovibrational analysis was carried out by solving the radial nuclear Schrödinger utilizing the Discrete Variable Representation method, which enables the computation of the rovibrational spectroscopic constants characterizing the intermolecular interaction. The spectroscopic constants enable the computation of the thermodynamics properties, including anharmonic and non-rigid rotator effects, highlighting qualitatively the spontaneity and energetics involved in gas adsorption. Additionally, we put these interactions under scrutiny to unravel the nature of such interactions, i.e., van der Waals type or with some fraction of covalency. To disclose possible preferences for interaction sites (whether pentagonal of hexagonal faces) we performed additional calculations considering the gases to bind via the pentagonal as well as the hexagonal face of the B\(_{80}\) fullerene. Our results suggest that all gases bind strongly via hexagonal sites, especially for HF (~6kcal/mol more attached to the B\(_{80}\) surface). Thermodynamics of adsorption were all favorable at room temperature except for H\(_2\). QTAIM analysis indicated that the curved bond paths (with a bond critical point) will take place not along the approaching axis, but with a curvature towards the edges of the hexagonal faces, not along the central boron atom lying in the hexagonal face. For the pentagonal faces, the bond paths are also curved, pointing to the atoms of the pentagonal site.

Key-words: Boron Fullerene, Intermolecular Interactions, Spectroscopic Rovibrational Constants, QTAIM.

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References: