Electronic structure calculations on the Ar–C$_6$H$_{12}$ interaction: Application to the microsolvation of the chair conformer

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ABSTRACT

We report a theoretical study of the intermolecular potential for Ar–C$_6$H$_{12}$, with the cyclohexane fixed in both chair and twisted-boat conformers; the geometry of these conformers has been optimized at different levels of theory and the results compared with available data in the literature. For constructing the intermolecular potential, we applied the MP2 methodology with two basis from the augmented correlation-consistent basis set family: aug-cc-pVNZ (N = D and T). The accuracy of the MP2 calculations has been checked at the minima geometries obtained with the MP2/aug-cc-pVTZ level of theory, for all lines of approach of argon to cyclohexane considered here, by performing single-point CCSD(T)/aug-cc-pVDZ and MP2/aug-cc-pVQZ calculations. In turn, the best MP2 results (using the aug-cc-pVTZ) for the interaction energy have been fitted to a pairwise analytic potential for Ar–C$_6$H$_{12}$. Then, this potential function was employed in a global geometry optimization of the clusters Ar$_n$ C$_6$H$_{12}$ (n = 1–20), with the cyclohexane fixed in the chair conformer.

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1. Introduction

Cyclohexane is a paradigm of a saturated cyclic hydrocarbon which presents two conformers (chair and twisted-boat) with almost no ring strain and zero dipole moment. The chair conformer is more stable than the twisted-boat one (with $\Delta H°$ estimated [1] to be 5.5 kcal mol^{-1}) and, hence, it is expected to be the most abundant structure at room temperature. As other model systems, cyclohexane has contributed to understand the adsorption phenomena at a molecular level [2]. In addition, it has played an important role to understand the conformers of other saturated carbon compounds, and is also a critical reaction intermediate in catalytic processes used for the production of high octane fuels in the petrochemical industry [3]. Because of this, it has been subjected to many theoretical [4–6] and experimental (Ref. [7] and references therein) studies. In particular, Leong et al. [5] have used experimental geometrical parameters of cyclohexane as starting points for geometry optimization of all conformers at the second-order perturbation theory of Møller-Plesset (MP2) with the 6-31G* basis set. They have also calculated the corresponding harmonic vibrational frequencies at the same level of theory. In a

more recent work, Nori-Shargh et al. [6] have reported a detailed study of the conformational properties of cyclohexane and some of its derivatives by using various *ab initio* and density functional theory (DFT) methods, such as MP2/3-21G* and B3LYP/3-21G*. In turn, Riehn et al. [8] have used femtosecond time-resolved degenerate four-wave mixing spectroscopy to obtain accurate structural information on the symmetric top cyclohexane.

Noncovalent intermolecular interactions are known to have a central role in many chemical processes, *e.g.*, microsolvation of weakly bound clusters. For this reason, molecular clusters involving aromatic and cyclic molecules have been among the most studied (Ref. [9] and references therein). Moreover, the interaction between rare-gas atoms and bound molecules has also received much attention from molecular sciences researchers due to its relevance in the study of collision-induced dissociation and energy transfer phenomena. Small organic molecules (among which one may include cyclohexane) assume special importance because they are more easily dealt with from a theoretical point of view, and since they can be used to characterize the interfacial chemistry occuring in the interaction between rare gases and hydrocarbon surfaces. Particularly relevant are the scattering of rare-gas atoms from self-assembled monolayers (SAMs) absorbed on a metallic surface, which appears to depend on the type of groups terminating the SAM and, hence, are more exposed to the interaction with the incoming atoms [10–12]. In this context, molecules such as CH$_4$ or CF$_4$ have been used as models in the theoretical dynamics

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studies [13–15] of their collision with argon, which may aid in the comprehension of such scattering processes taking place on CH_3-terminated SAMs. In addition, a detailed theoretical study of the interaction of Ar, Kr and Xe with both CH_4 and CF_4 has been published in the literature [16]; another study on Ar + CF_4 has shown that MP2 calculations give energies in very good agreement with CCSD(T) ones [17]. In turn, Hase and collaborators [18] have carried out a detailed theoretical study on the Ar–CH_3OH intermolecular potentials, including MP2/aug-cc-pVTZ geometry optimizations and single-point CCSD(T)/aug-cc-pVTZ calculations (with the CH_3OH molecule fixed at its equilibrium geometry). After the correction for the basis-set superposition error, the CCSD(T) *ab initio* points have been fitted to a sum of two-body analytic functions, and the van der Waals structures predicted by the analytical potential are similar to those obtained by optimization at the MP2/aug-cc-pVTZ level of theory [18]. Cooper and Ahmadi [19] performed a similar study on the interaction of Ar with ethane (CH_3CH_3). More recently, Balabin[20] calculated the interaction energy of *n*-pentane with rare-gas atoms (helium, neon and argon)

using MP2, MP4 and CCSD(T) methods in conjunction with Dunning's correlation-consistent basis sets up to aug-cc-pVQZ.

Concerning energy transfer studies, we stress the abundant use of benzene as target molecule in the collision with argon. Also microsolvation of benzene by rare-gas atoms has been discussed in detail in the literature [21–24]. Then, various analytic potential functions for Ar–benzene have been reported [25–27], but no such functions exist for Ar–cyclohexane. It is worth noting that cyclohexane is a six-carbon ring like benzene, but it is completely saturated and does not present a planar geometry.

To our knowledge, the present work constitutes the first theoretical study on the interaction of argon with cyclohexane. One of the major goals we endeavour is modeling the Ar–cyclohexane interaction with a potential function that can be valid for both chair and twisted-boat conformers; such function can be useful for the study of energy transfer phenomena in the title system. Besides, this work constitutes the first step towards the comprehension of microsolvation of cyclohexane by argon. For that, we have applied the present Ar–C_6H_{12} analytical potential and an accurate
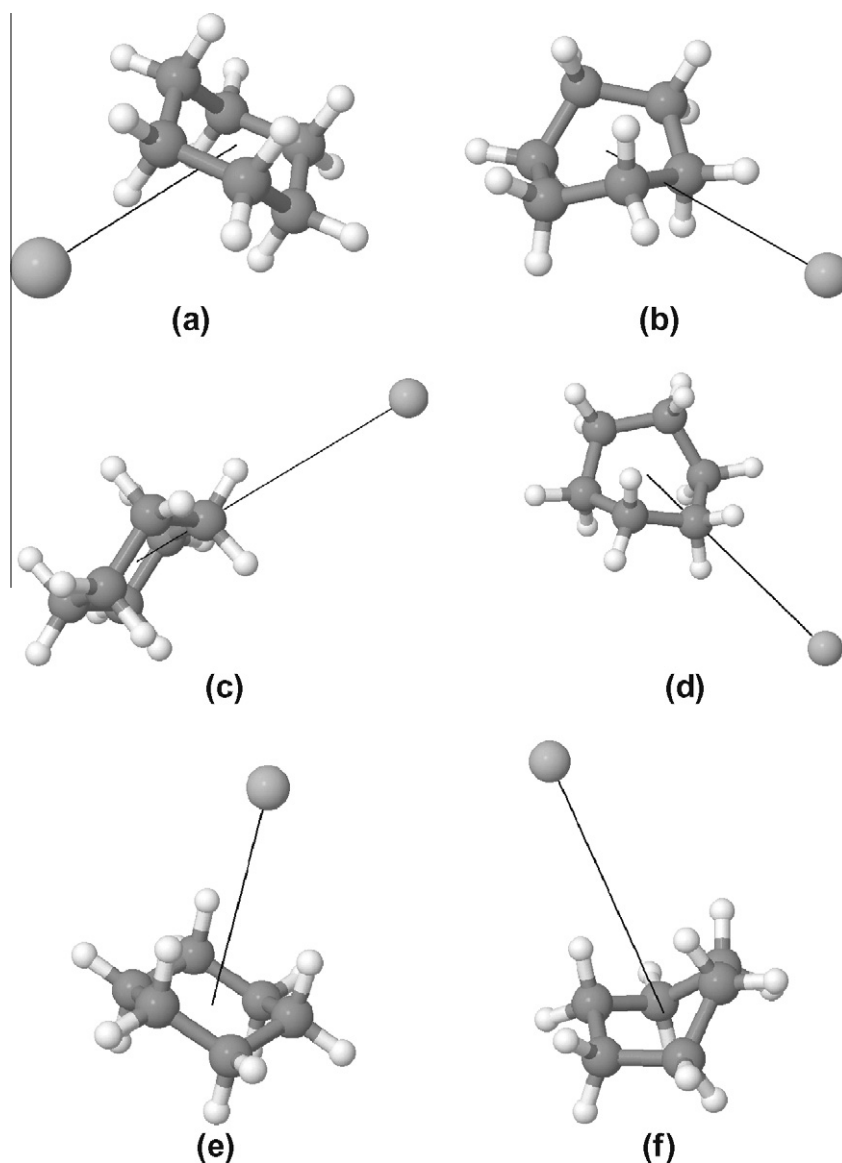
Fig. 1. Definition of the Ar–cyclohexane approaches: (a), (c), and (e) are for chair; (b), (d), and (f) are for twisted-boat. (a and b) Axial approach; (c and d) equatorial through C–C bond approach; (e and f) equatorial through carbon approach. Note that both conformers are fixed in their equilibrium geometries and all lines of approach cross in the center-of-mass of cyclohexane. See the text. Figures produced with Jmol[47].