The solvation structure of CO_2 in dichloromethane – A comparative correlated, semi-empirical and classical MD simulation study

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ABSTRACT

In this work the structural and dynamical properties of CO_2 in dichloromethane were studied via classical and QMCF MD simulations employing a variety of increasingly complex computational methods, namely correlated resolution-of-identity second-order Møller-Plesset perturbation theory (RI MP2), resolution-of-identity density functional theory (DFT) using the B3LYP functional with and without dispersion correction, semi-empirical self consistent density-functional tight-binding (SCC DFTB) as well as the second-generation geometries, vibrational frequencies, and non-covalent interaction extended tight-binding (GFN2-xTB) approach. All levels of theory yield a similar description of the spherically-shaped first solvation layer found in the range of 6.4 to 6.9 Å. The structural and dynamical data obtained via RI B3LYP-D3 are found in good agreement with the high level RI MP2 reference, whereas the SCC DFTB/3ob and GFN2-xTB methods displayed minor deficiencies in the description of halogen-based interactions. Despite the observed structural differences both the vibrational frequencies of the solute as well as the first shell mean ligand residence times show similar values, pointing towards rapid exchange reactions of first shell ligands with the bulk. In addition several classical potential models for the description of the system have been assessed and adjusted MM potential parameters providing structural and dynamical data comparable to the much more expensive quantum chemical methods are provided.

1. Introduction

The recent report by the Intergovernmental Panel on Climate Change (IPCC) [1,2] has once more demonstrated that climate change becomes an increasing global problem due to the impact of various human activities. Among the different factors contributing to climate change the increase in greenhouse gas concentration is proven to be a key element associated to climate change. Carbon dioxide (CO_2) is the main compound contributing to the greenhouse effect next to CH_4 [3]. Massive emission of CO_2 into the atmosphere is produced from natural gas and fossil fuel burning in various technological sectors and CO_2 capture from the atmosphere and subsequent activation is considered as a promising solution to reduce its overall concentration [4]. CO_2 can be captured via absorption in materials [5] and converted to other substrates e.g., methane [6], methanol [7], dimethyl ether (DME) [8], dimethyl carbonate [9] and formic acid [10].

Experimental studies of CO_2 reduction using transition metal catalysts in solution had been performed in water [11] as well as various organic solvents such as acetonitrile [12,13], dimethyleformamide [14], tetracyanoborates [15], tetrahydrofuran (THF) [16,17] and dichloromethane (DCM) [18]. In particular, it is noted that CO_2 reduction using zinc-based catalysts can be successfully performed in DCM [19–21]. The knowledge of the structural and dynamical properties of CO_2 in DCM is a key prerequisite to understand the associated activation mechanism thus aiding in the development of prospective CO_2 capture materials. This is particularly true when aiming at computational investigations of catalytic processes considering an explicit description of the surrounding solvent.

In the past, computational approaches have been successfully employed to study the physio-chemical properties of CO_2 in solution. Molecular simulations can provide estimates for the reaction dynamics and structure of the reacted species [22,23]. Molecular dynamics (MD) simulations play an essential role in this context to investigate the impact of solute–solvent interactions and can provide a description of structural and dynamics properties at the molecular level. Combining MD with different methods e.g. quantum mechanics (QM), molecular mechanics (MM) or even hybrid QM/MM simulation protocols have the potential to provide an accurate representation of the chemical system and the

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