Nuclear Quantum Effects and Isotope Effects for Vaporation of Dibromomethane

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Brominated hydrocarbons such as bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) are considered characteristic atmospheric pollutants, harmful to humans, as well as known by their catalytic properties in reactions that damage the stratospheric ozone [1]. Oceanic macro-algae and industrial processes are the main sources of dibromomethane (DBM) [2]. DBM is the part of research regarding environmental impact and remediation [1], degradation [2], chemical transport models [2], and solvation effects [3]. Up to date, explicit solvent models of DBM have not been developed, therefore little or nothing is known about the DBM behaviour and influence of specific interactions between solvent molecules on processes like vaporization from pure organic phase, for instance. For this purpose equilibrium isotope effects have been predicted and compared to the available experimental data.

In this work, four models based on several levels of theory for the initial geometry optimisation, were developed in order to estimate basic DBM physical properties. Consequently, Quantum Mechanics/Molecular Mechanics (QM/MM) MD simulations were performed for subsequent estimation of isotope effects using path integral formalism by thermodynamic integration. Results show that conserved energy is preserved differently depending on the initial level of theory used during geometry optimisation. Thus, models optimised with higher levels of theory display more consisted energy values. Estimated Carbon equilibrium isotope effect agrees with experimental results, while bromine isotope effects are more spread.

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