



Molecular dynamics study on the liquid phosphorus tribromide by applying force-fields derived from quantum chemical approach



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ABSTRACT

The purpose of this paper is to study the molecular dynamics simulation of phosphorus tribromide (PBr₃) as the condensed inorganic liquid. To this aim, four regional intermolecular potential functions of phosphorus tribromide in the gas phase were considered. The potential energy data of 9 phosphorous tribromide configuration dimers were calculated at the B3LYP/6-31 + G (d) level of theory. The calculated potential data were employed to construct a 4-site all-atom force field model. Then, the force field parameters were used to perform the molecular dynamics simulations and compared the simulation results with experimental data. Quantitative agreements for the atomic number density, internal energy, enthalpy, heat capacity and radial distribution function over a wide range of experimental conditions were obtained as a consequence of the parameters force field validation without using experimental data a priori.

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1. Introduction

Computer simulations such as molecular dynamics (MD) and Monte Carlo (MC) simulations have become a very useful tool to understand the dynamics and properties of condensed phases and have been used by chemists, physicists, and molecular biologists at the molecular level [1–3]. Force fields are expressions for the total energy, which primarily control the outcome of the simulations. Most force fields in common application have a similar form including harmonic bond stretching and angle bending, Fourier series for torsion energies, Coulomb plus Lennard-Jones terms for intermolecular and intramolecular nonbonded interactions [4]. As importance of simulations, over the past decades many researches have been performed in this field. Recently, Chao et al. have calculated ab initio potential energy data of dimethyl ether (DME) for seventeen orientations at the MP2/aug-cc-pVQZ level of theory. The calculated MP2 potential data were used to construct a 3-site united atom force field model for MD simulation. Quantitative agreements were obtained for simulation results over a wide range of experimental conditions [5]. Morsali et al. have calculated potential energy for rigid SbF₅ and SbCl₅ using the B3LYP/6-31 + G (d) level of theory. They derived simple six-site force field model to reproduce the results of density functional theory (DFT) calculations. Adjusted force field parameters were used in the MD simulations to obtain density, internal energy, enthalpy and radial distribution function. They found that there is a good agreement between MD results and experimental data

[6]. Abbaspour has performed the molecular dynamics simulation of methane using one site OPLS (optimized potentials for liquid simulations), five sites OPLS-SITE, and two-body HFD (Hartree-Fock dispersion)-like potentials to determine a new equation of state [7]. Vogel et al. presented a new four-dimensional intermolecular potential energy surface for a carbon dioxide dimer on the basis of ab initio calculations using MP2 level including full counterpoise correction with a [5s 4p 3d 2f 1g] basis set. The quality of the new potential was tested by computing values of the second virial coefficient over a wide range of temperatures [8].

There has been a continuing interest in the structure of molecular liquids, especially which their constituent molecules are highly symmetric with a well-defined shape [9]. Phosphorous tribromide (PBr₃) is a colorless liquid at room temperature [10]. PBr₃ is prepared by reacting reaction red phosphorus with bromine in the presence of an inert solvent in order to reduce the violence and resultant danger of the reaction [11,12]. Its main use is for the conversion of primary or secondary alcohols to alkyl bromides, while it is used in the pharmaceuticals manufacture such as alprazolam, methohexital and fenopropfen, on a commercial scale. Another use for PBr₃ is as a potent fire suppression agent marketed under the name Phostrex [10,13]. However, liquid PBr₃ has been investigated by pulsed neutron total scattering technique [14], from X-ray diffraction, molecular dynamics simulations and reverse Monte Carlo (RMC) modeling [15] and also, reverse Monte Carlo [16]. Determination of the intermolecular interaction potentials from experimental measurements is very challenging. Part of the reasons is due to the incompleteness of experimental sampling. For example, experiments using X-ray crystallography or laser luminescence spectroscopy

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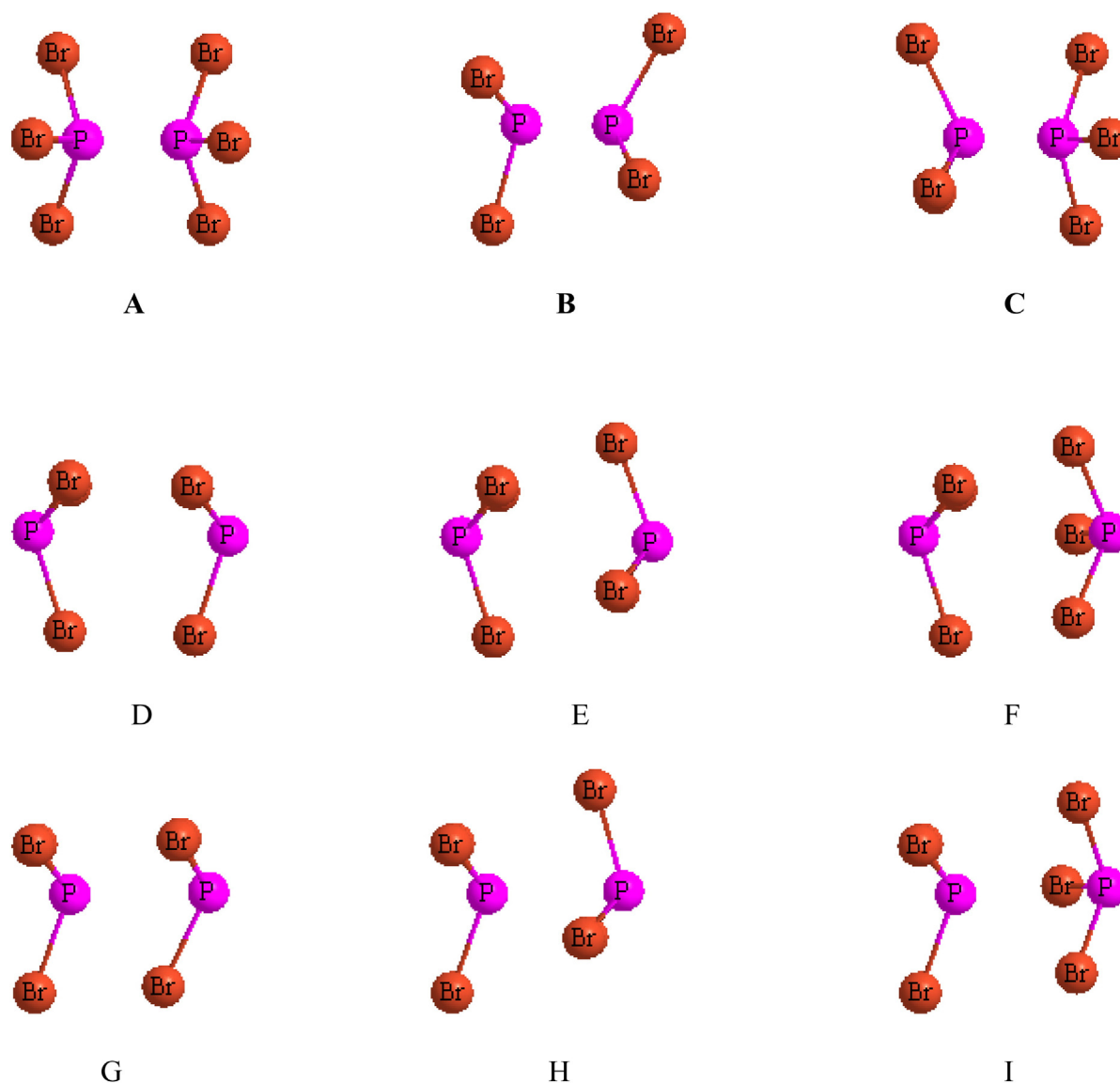


Fig. 1. The 9 symmetric conformers of the PBr_3 dimer (each conformer is shown by a capital letter from A to I).

usually render equilibrium structures, while thermodynamic measurements in the fluid or solid phase often yield isotropic potential data without the desired stereochemical detail [17,18]. Based on mentioned points, we motivated to perform a quantum chemistry calculation and MD simulations for PBr_3 .

In this article, we constructed a DFT force field using a high level of quantum chemistry theory for 9 configurations of the PBr_3 dimer. A procedure has been used to fit the intermolecular potential to reproduce the results from DFT calculations of PBr_3 dimer. We determined the accuracy of the constructed DFT force field through comparison with MD simulation results and experimental data. The major goal of the present study is a development of a new all-atom force field for MD simulation of PBr_3 using quantum mechanical approach. So, we have calculated the potential energy data for several configurations of the PBr_3 dimer.

2. Computational details

The quantum chemistry calculations were performed at the B3LYP/6-31 + G (d) level of theory using the Gaussian 03 program package [19]. First, isolated PBr_3 molecule was optimized at the B3LYP/6-31 + G (d) level and was found to be at the trigonal pyramidal

configuration with the P—Br bond length of 2.25 Å (which is consistent with the experimental data 2.22 Å) and the bond angle for Br—P—Br is 100.93° (which is consistent with the experimental data 101°) [20,21]. We have considered the 9 prime configurations for the PBr_3 dimer that were shown in Fig. 1. Subsequently the Phosphor-Phosphor

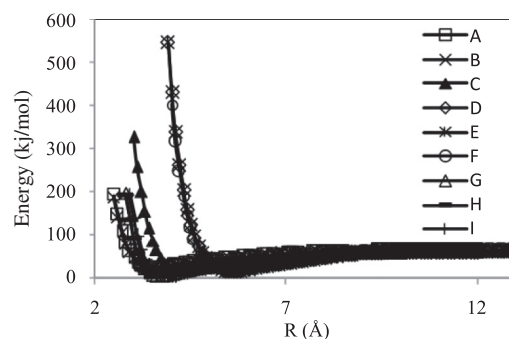


Fig. 2. The curve of E_{total} for the 9 orientations at the B3LYP/6-31 + G (d) level of theory.

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