

A Molecular Dynamics Study of the Benzene...Ar₂ Complexes

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Abstract. A simulation of benzene..Ar₂ clusters has been performed using molecular dynamics software. Details on development tools, interaction formulation and calculation parameters are given. Estimates of macroscopic properties as well as elements for understanding the dynamics of the systems are discussed.

1 Introduction

The purpose of this work is twofold. On one side we illustrate our efforts to use and develop object oriented tools and applications to be compared and complemented with the more traditional procedural programming techniques are illustrated. On the other side our efforts to develop computational chemistry applications aimed at producing realistic simulations of complex chemical processes in a priori fashion are discussed. To this end the formulation of the interaction and of the dynamics, the design of the computational algorithms, the averaging over unobserved parameters and the production of visualization tools are developed having in mind the objective of creating an environment enhancing chemical intuition and insight. The context of these efforts is Simbex [1]. Simbex is a Problem solving environment for the simulation of molecular processes at microscopic level using a priori means and aimed at reproducing quantities measured by experimental apparatuses (and in particular molecular beams) that is being assembled at our Laboratory.

The specific process considered here is the formation of benzene-Ar₂ clusters both by considering the C₆H₆ molecule frozen at its equilibrium geometry and by allowing it to deform. Van der Waals clusters formed by the benzene molecule with rare gas atoms have been the focus of a considerable number of experimental and theoretical studies (see for example [2, 3]). These studies were the basis of our investigation.

The computational tools used for the theoretical investigation of these systems are those of Molecular Dynamics (MD) or Monte Carlo (MC) approaches. In the MD approach, the one used in this work, after constructing a proper analytical formulation of the molecular interaction the system is represented as an appropriate set of particles, positions and momenta that is allowed to evolve in time according to the laws of classical mechanics.

In the second section of the paper we describe the object oriented computational procedure. In the third section we describe the construction of the intermolecular interaction. In the fourth section we describe the MD techniques used. In the fifth section we examine the results obtained.

2 The computational procedure

The computational procedure used for the calculations was based entirely on MMTK [4]. MMTK is a set of libraries particularly designed to assemble computational procedures of Molecular Modeling. The novelty of this computational procedure lies in the that it is totally written in Python. Python is a high-level object-oriented general-purpose programming language whose Scientific Python subset [5] has modules suited for integrating differential equations, for interpolating numerical functions, for manipulating geometrical figures, for managing PDB files, for interfacing MPI libraries, etc.. In Python we have integrated C/C++ and Fortran routines as shared libraries (in particular routines from ref. [6]).

This has allowed us to build our own computational procedure by importing from Python almost all modules and writing a few new ones for which we exploited the inheritance properties of MMTK modules. In particular, use has been made of modules for the construction of the chemical universe and chemical objects (atoms, groups, molecules, molecular complexes), for the definition of the force field (Amber and Lennard Jones), for the integration of the trajectories (initial, final and instant positions, integrators, optimizers) and for the analysis of the results (visualization, averaging, integrators).

Due to the particular simplicity of the chemical system under investigation only a few atomic chemical objects were defined and the subset of operations that was considered was also limited. The same is true for the various phases of the MD treatment. The initial conditions of the system were set by defining the universe of initial velocities. This was, eventually, scaled using *thermostat* and *barostat* objects to impose a given distribution of temperature or pressure. In certain runs bond constraints were also imposed. Trajectory data such as atomic positions, velocities, energetic contributions, gradients, etc., were saved using netCDF libraries [7] which allow an economical binary storage of the information for further use in the analysis. The approach used for the energy minimization were based on the conjugate gradient algorithm.

The calculations were performed on a 900Mhz PC with 128 Mb RAM memory and taking each run few ours CPU time.

3 Inter- and intra-molecular potential

Intermolecular interaction of the van der Waals molecule are particularly difficult to characterize. The small value of the binding energy makes the treatments based upon ab initio calculation machinery quite inefficient. At the same time, experimental studies based upon crossed molecular beams are also difficult to perform. For this reason, as is often the case, we addressed ourselves to model

Diatom	σ	ϵ
Ar-Ar	3.35	99.09
Ar-C	3.42	40.20
Ar-Ar	3.21	33.00

Table 1. Lennard-Jones parameters used in this work. σ is given in \AA and ϵ in cm^{-1} .

formulations. In particular, here we deal both with different expansions and model formulations.

The first intermolecular potential used for the simulation of the benzene-Ar system is a pair-additive one obtained by summing all the two body terms of the interaction of the C and H atoms of the benzene molecule with the Argon atoms plus that between the two Ar atoms. For these two body interactions, as usual, a Lennard-Jones 12-6 model potential [8] was adopted

$$V^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

In eq. 1 r is the internuclear distance between the two atoms, ϵ is the energy minimum of the diatomic interaction, σ is the corresponding equilibrium value. As for the intramolecular potential we have either assumed that the benzene is frozen at its equilibrium position (though free of translating and rotating) or allowed the molecule to deform according to a force field of the Amber type [9]. The parameters for the Ar-Ar, Ar-C and Ar-H interactions are given in Table 1 and were taken from Ref. [10]

An extension of the computational procedure to other potentials is being considered using a polynomial in the bond order (BO) coordinates (that has been already extensively used for the study of triatomic and tetratomic systems [11]). Another potential that is also being considered is the product of a Morse-Switching-van der Waals radial term times the spherical harmonics describing the angular dependence of the interaction. Related parameters have been optimized to the reproduction of crossed molecular beam data [12]. A conjugate-gradient technique was used to locate the minima on the potential energy surface. Figure 1 shows these minima corresponding to $R = 3.49 \text{\AA}$ for the (1|1) isomer and $R = 3.70 \text{\AA}$, $r_1 = 3.50 \text{\AA}$ and $r_2 = 3.10 \text{\AA}$ for the (2|0) isomer. In Table 2 these values and the corresponding point groups are given.

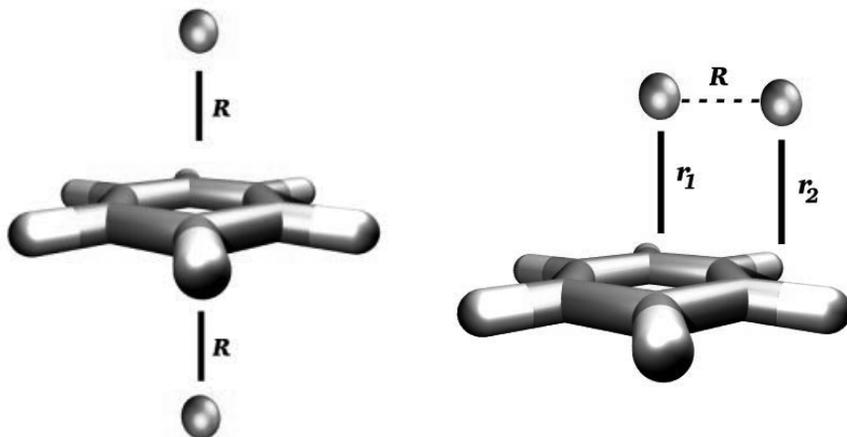


Fig. 1. Location of the energy minima for the benzene-Ar₂ cluster isomer (1|1) (left hand side panel) and isomer (2|0) (right hand side panel).

n	Label	PG	Energy
1	(1 0)	C _{6v}	-356.0
2	(1 1)	D _{6h}	-711.0
	(2 0)	C _s	-665.0

Table 2. Energies (in millihartree) and point groups (PG) for the minima of benzene-Ar_{*n*} clusters. The meaning of the labels is described in the text.

4 Calculations and results

MD simulations were performed using a microcanonical ensemble (NVE). The duration of these simulations was of 100 ns. A timestep of 0.5 fs was adopted to obtain an energy conservation of about 2 cm⁻¹. In the case in which the benzene was kept rigid the timestep was set at 2 fs. Initial positions were chosen so as to start with the isomer (1|1) at the energy global minimum. For this configuration the initial velocities were generated and the system was let to run for about 10⁵ steps in order to allow thermalization and then NVE (microcanonical ensemble) conditions were imposed. When this dynamical balancing process turned out not to be successful velocities were scaled and the balancing process started again. When the balancing process was successful the simulation was run. At the end of the simulation the system is analyzed and relevant parameters calculated.

For our investigation, a temperature range of 10 K starting from 25 K was chosen. The temperature was increased in steps of 1 K up to 35 K.

A first interesting parameter of the process is the number of interconversion (NINT) from isomer (1|1) to the isomer (2|0) observed at the various temperatures. The value of NINT is plotted as a function of the temperature in Fig. 2.

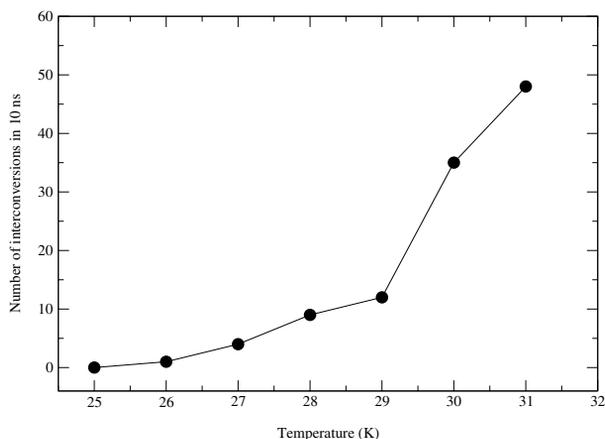


Fig. 2. Number of interconversions as a function of temperature

The figure shows, as expected, an increase of the number of interconversions as the temperature increases. However, there is a sharp variation of the slope of the curve around $T = 29$ K. These values were determined for a simulation time of 10 ns. For each temperature the lifetime of the complex was monitored during the trajectory. The complex dissociates when the distance between the two Argon atoms and the center of mass of benzene molecule is larger than 10 \AA . We found that at temperatures larger than 31 K the lifetime of the complex decreases suddenly. In the 32-40 K temperature range the complex dissociates after 2 ns.

Another relevant property is the relative population (RP) determined as the fraction of time spent by the system in a given configuration with respect to the total time. The value of RP slightly decreases with temperature for isomer (1|1) while it slightly increases for isomer (2|0), the ratio of the relative percentages being 57/43 at 25 K and 62/38 at 31 K.

5 Conclusions

The ability of object oriented programming in allowing the construction of conceptually simple computational procedures has been proven to be successful. In our case, use was made of the object oriented Scientific Python library. The simulator of molecular processes, that was built in this way, allows the reproduction of the signal of molecular beam experiments starting from first principles. The application was shown to be addressable both to the question of building suitable formulations of the interaction of rarified gas systems and to the understanding of the mechanisms leading to the formation of Ar-benzene clusters.

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