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Solvent Dependence on Conformational Transition, Dipole Moment, and Molecular Geometry of 1,2-Dichloroethane: Insight from Car–Parrinello Molecular Dynamics Calculations

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We have investigated the molecular geometry and dipole moment distribution for the major conformational states of 1,2-dichloroethane (DCE) in three different solvents under ambient conditions using the Car–Parrinello mixed quantum mechanics/molecular mechanics method. The solvents studied were water, DCE, and chloroform. Within the time scale investigated, we find a conformational equilibrium existing between the gauche and trans forms of DCE in all three solvents. In the chloroform solvent, the conformational transition occurs more frequently than in water solvent and in liquid DCE (i.e., DCE solute in DCE solvent). The population of gauche conformer is more in the case of water solvent, while the trans conformer dominates in chloroform solvent. We report a bimodal nature of the dipole moment distribution for DCE in all three solute–solvents studied, where the peaks are attributed to the trans and gauche conformational states. The dipole moments of both of the conformational states increase with increasing polarity of the solvent. Also, with an increase in solvent polarity, an increase in the C–Cl bond length and magnitude of atomic charges in DCE has been observed. The increase in atomic charges of DCE is almost twice when the solvent is changed from chloroform to water.

1. Introduction

Alkanes and substituted alkanes exist in numerous conformational states due to the conformational mobility of the torsional degrees of freedom. The relative stability and the population of different conformations are decided by contributions from many sources, like electrostatic interaction, van der Waals interaction, solute–solvent interaction, solvent polarization energies, and the thermodynamic state of the system defined by temperature and pressure.^{1–4} Many experimental and theoretical studies have been carried out to understand the conformational polymorphism of 1,2-disubstituted ethanes. This holds in particular for 1,2-dichloroethane (DCE) which is one of the simpler molecules in the series. Experimentally, the molecular geometry and population of different conformational states of DCE have been studied in its gaseous phase,⁵ condensed phase,^{6–8} and in the solution phase of polar and nonpolar solvents.^{1,9,10} The confinement effect on the conformational equilibrium of DCE in nanoconfined methanol has been investigated;¹¹ likewise, the structure and dynamics of DCE on metal surface¹² and protein surface¹³ have also been theoretically investigated. Moreover, there are studies investigating the pressure effect on the conformational equilibrium.^{14,15} In the gaseous phase, the trans form has been reported to be more stable than the gauche form, something that has been attributed to the electrostatic energy which is more favorable when similar charges are separated by long distances. However, in the solution phase, the relative energies of the gauche (see Figure 1a) and

trans (see Figure 1b) forms are decided also by the solute–solvent interaction terms.¹⁶ Experimentally, it has been reported that the conformational equilibrium in solution strongly depends on the dielectric property of the medium.¹⁷ The solvent dependence on the conformational equilibrium of DCE has been probed using various experimental techniques such as NMR, IR, and Raman spectroscopies.^{1,18} Molecular dynamics calculations and Monte Carlo simulations have been used to study the conformational distribution of DCE in solvents such as carbon tetrachloride, benzene, and methyl chloride.^{19–23} These simulations may, however, suffer due to the inaccuracy of the force field used to describe the molecular interactions. The solvent dependence of molecular geometry and C–Cl stretching frequencies have been reported for DCE based on *ab initio* electronic structure calculations that include solvent effects through the polarizable continuum model and reaction field theory in general.^{1,3,9,24}

The conformational distribution and hence the dipole moment of DCE has been reported to strongly depend on the nature of the solvent.³ This arises mainly due to the considerable difference in the dipole moment of the gauche and trans forms of DCE. In the ideal trans form (where ϕ , the dihedral angle between Cl–C–C–Cl, is 180°), the dipole moment is zero. For the gauche form in the gas phase, where the dihedral angle is $\pm 60^\circ$, the dipole moment for this conformation is reported to be 1.34 au (i.e., 3.5 D). Due to the dipole–dipole interaction, the gauche form is stabilized in polar solvents and in its condensed phase.¹⁷ It has been experimentally reported that the population of trans conformers increases significantly in the nonpolar solvents. Even though there are many theoretical and

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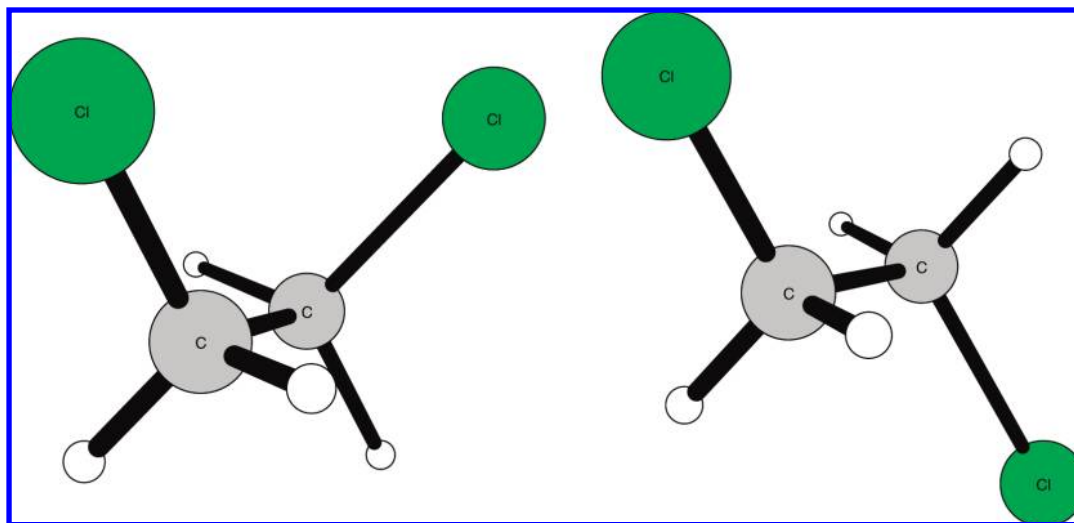


Figure 1. Molecular geometry of the two most stable conformations, namely, the gauche and trans forms of DCE.

experimental reports available for DCE, we are not aware of any study that investigates the solvent dependence on the rate of conformational transition, dipole moment distribution, average dipole moment, and the molecular geometry. Such studies demand quantum mechanical treatment of the solute molecule with the solvent molecules included explicitly. Also, the conformational transitions are thermally activated molecular processes that require the simulations to be carried out either in the NVT or the NPT ensemble. On the basis of all these requirements, we decided to do Car–Parrinello molecular dynamics (CPMD)^{25,26} calculations in a quantum mechanics/molecular mechanics (QM/MM) setup which has been successfully used to study many solute–solvent systems.^{27–31} The QM/MM implementation also takes care of the charge evolution in the solute molecule based on the instantaneous solvent environment.³² We use the QM/MM setup in CPMD to study three different solute–solvent systems where DCE is the solute and water, DCE, and chloroform are the solvents. The second solute–solvent system can be simply described as liquid DCE as the solute and solvent molecules are of the same type. We have used the CPMD method to investigate these systems as this technique does not suffer from the inaccuracy of empirical force fields which are commonly applied in molecular dynamics (MD) calculations.³³ Due to the computational expense of these calculations, we have for all the three solute–solvent systems limited the study to a time scale between 100 and 150 ps.

2. Computational Details

Three different solute–solvent systems were prepared with DCE as a solute and water (now onward referred as system I), DCE (system II), and chloroform (system III) as solvents. The gauche or trans form of the DCE has been used as the solute. The number of solvent molecules included were 8891, 1090, and 1947 in the cases of systems I, II, and III, respectively. First, all three solute–solvent systems were equilibrated by carrying out MD calculations under ambient conditions using the Amber software.³⁴ We have used the TIP3P force field for the description of water; for all other molecules, the generalized amber force field (GAFF)³⁵ has been used. The equilibrated structures from the MD simulations for the systems I, II, and III have been used as the initial structure for CPMD³⁶ calculations. In our present calculations, we have used the Becke, Lee, Yang, and Parr (BLYP) gradient corrected functional^{37,38} and the Troullier–Martins norm conserving pseudopotentials.³⁹

Here, the electronic wave function is expanded in a plane wave basis set and the cutoff used was 80 Ry. We have used 5 au as the time step for the integration of the equation of motion and 600 amu as the fictitious electronic mass. The calculations were carried out in a QM/MM setup,³² where the solute molecule (here, the DCE molecule) is treated at the density functional theory level while the solvents (water, DCE, and chloroform) are treated with a less accurate molecular mechanics force field (either TIP3P or GAFF). The interaction between the QM and MM systems involves electrostatic, short-range repulsion, and long-range dispersion interaction terms (using the empirical van der Waals parameters). The CPMD calculations involve the following three procedures: (1) Quenching run: the electronic and ionic temperature of the initial structure is quenched to remove any hot spot in the system due to inaccurate starting molecular geometry. (2) Scaled temperature run: a short run using temperature scaled dynamics carried out to bring the system to the required temperature and pressure. (3) Nose run: in this run, the system is kept to interact with a Nose–Hoover thermostat at the required temperature. The Nose thermostat mimics the real system connected to a heat bath to maintain the system temperature. The total time scale for the Nose production runs is between 100 and 150 ps.

3. Results and Discussion

3.1. Solvent Dependence on Conformational Transition.

The conformational transitions are usually considered as rare events, as these involve a kinetic barrier which is considerably larger than the thermal energy, $k_B T$, available to a system under ambient conditions. Thus, to understand the systems with conformational disorder through molecular simulations, one has to use different sampling techniques (such as the umbrella sampling technique) or enhanced molecular dynamics calculations.³³ The reaction coordinate approach and metadynamics based approach⁴⁰ are implemented in the CPMD code³⁶ to investigate such rare events or to study the reaction mechanisms and molecular processes with energy barriers at the order of many kcal/mol. We have still adopted a regular molecular dynamics approach, as we can access qualitatively the solvent dependence on conformational transitions and quantitatively the molecular geometries and dipole moments of individual conformational states. Thus, we acknowledge the limitation of the present computational tool in studies of molecular processes involving a larger time scale.

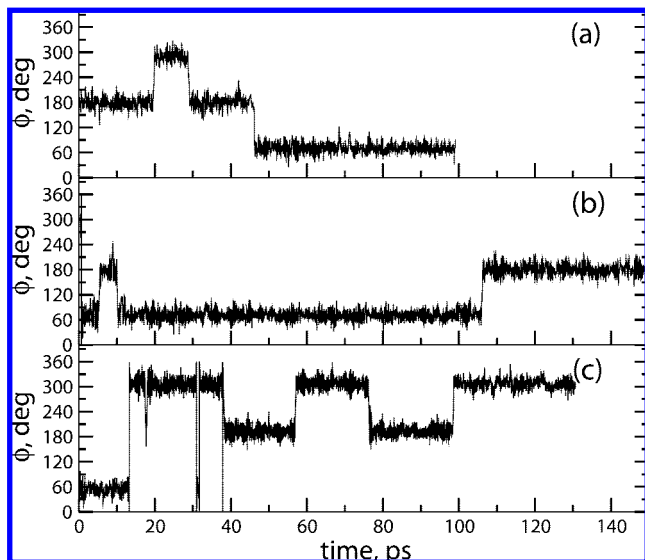


Figure 2. Dynamical evolution of dihedral angle $\phi_{\text{Cl-C-C-Cl}}$ of DCE in different solvents such as water, DCE, and chloroform.

TABLE 1: Percentage Population of trans and gauche Conformers

system	DCE in water	liquid DCE	DCE in chloroform
trans	41.4	32.2	61.1
gauche	58.6	67.8	38.9

The conformational state of the DCE can be conveniently discussed using the angle, ϕ , which is the dihedral angle between the atoms Cl–C–C–Cl. When the angle, ϕ , is 180° , the DCE is said to be in the trans form, and when the angle is $\pm 60^\circ$, it is said to be in the gauche state. The dihedral angle, 300° , is equivalent to -60° and means a gauche conformation. Figure 2 shows the time evolution of the angle, ϕ , as a function of time step for all three solute–solvent systems. In all three systems, we see conformational transitions between the gauche and trans forms. In the case of systems I and II, we see infrequent jumps. In the case of the chloroform solvent, the picture is entirely different and we see many such conformational transitions between gauche and trans forms. This clearly explains that the barrier between the gauche and trans forms in chloroform solvent is considerably decreased when compared to the other two cases (i.e., systems I and II). Our calculations clearly show that the time scale for the interconversion process is very much affected by the nature of the solvent. In a less polar solvent, the conformational transition seems to occur frequently when compared to the case of polar solvent. The solvent dependence of the time scale for the interconversion process has yet to be verified experimentally from NMR measurements or from ultrasonic relaxation studies. We also observe a marked effect of solvent polarity on the population of different conformational states. Here, it is important to note the dielectric constants (which is a rough measure of the polarity) of water, DCE, and chloroform, which have the values 78.4, 10.4, and 5.0, respectively.⁴¹ Table 1 displays the percentage population of gauche and trans conformers of DCE in systems I–III. The percentage population of trans conformer (which is reported to have less dipole moment than the gauche conformer) is more in the case of less polar chloroform solvent.

In the case of water solvent, the percentage population of gauche conformer is more. We emphasize that while the values in Table 1 may not be accurate due to poor statistics including only a few conformational transitions, still the solvent depen-

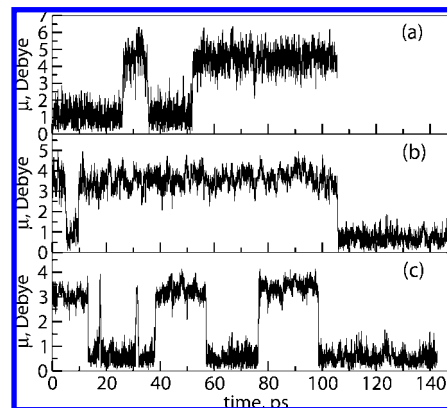


Figure 3. Dynamical evolution of dipole moment of DCE in different solvents such as water, DCE, and chloroform.

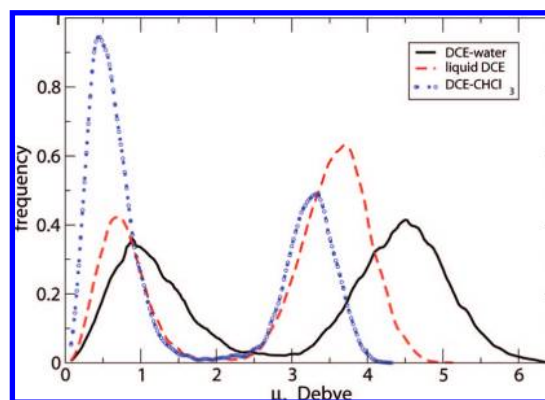


Figure 4. Dipole moment distribution of DCE in different solvents such as water, DCE, and chloroform.

dence of the percentage population of gauche and trans conformers in water and chloroform solvents is reproduced qualitatively in comparison with the experiments.¹⁷ For quantitative reproduction of the population of states, one has to do a long simulation of a few nanoseconds which is not feasible with the available computational resources. Still, in our present calculations, the simulation time scale used is 5–20 times larger than the usual time scale employed by others.^{42–44} Parts a, b, and c of Figure 3 show the time evolution of the dipole moment of DCE in the case of systems I, II, and III, respectively. This again displays similar features as the time evolution of ϕ . It is clearly shown that the gauche conformer in different solvents has different magnitudes for the dipole moment. Also, the conformer with $\phi = 60^\circ$ and $\phi = 300^\circ$ has the same magnitude for the dipole moment.

3.2. Solvent Dependence on Molecular Geometry and Dipole Moment. In this section, we will discuss the solvent dependence on the molecular geometry, charge distribution, and dipole moment for the two major conformational states. Figure 4 displays the dipole moment distribution for systems I–III. In all three systems, the dipole moment distribution curve is bimodal in nature. The peak appearing close to 0 D in these cases is due to the trans conformer, and the peak appearing beyond 2.5 D is due to the gauche conformer. We have calculated (by integrating the two peaks separately using the formula $\int x f(x) dx / \int f(x) dx$) the average dipole moments for the trans and gauche forms of DCE in water, liquid DCE, and in chloroform solvents, and the values are shown in Table 2. The dipole moments for the trans form in water, liquid DCE, and chloroform are, respectively, 1.17, 0.77, and 0.61 D. Similarly, the dipole moments for the gauche form are 4.50, 3.60, and

TABLE 2: Average Dipole Moments for trans and gauche Conformers

trans			
system	DCE in water	liquid DCE	DCE in chloroform
debye	1.17	0.77	0.61
gauche			
system	DCE in water	liquid DCE	DCE in chloroform
debye	4.50	3.60	3.25

TABLE 3: Average D-RESP Charges for trans and gauche Conformers

atom	q (DCE in water)	q (liquid DCE)	q (DCE in chloroform)
trans			
Cl	-0.2044	-0.1299	-0.1062
C	0.0374	0.0221	0.0176
H	0.0837	0.0543	0.0453
gauche			
Cl	-0.2413	-0.1816	-0.1527
C	0.0353	0.0252	0.0201
H ₁	0.1235	0.1103	0.0847
H ₂	0.0829	0.0463	0.0492

TABLE 4: Average Bond Distances for trans and gauche Conformers

system	$R_{\text{Cl-Cl}}$	$R_{\text{C-C}}$	$R_{\text{C-H}}$
trans			
DCE in water	1.8850	1.5175	1.0903
liquid DCE	1.8749	1.5186	1.0911
DCE in chloroform	1.8695	1.5172	1.0905
gauche			
DCE in water	1.8797	1.5116	1.0958
liquid DCE	1.8663	1.5147	1.0934
DCE in chloroform	1.8578	1.5138	1.0922

3.25 D. An interesting observation is that the dipole moment of the gauche and trans forms increases with increasing polarity of the solvent. A polar solvent polarizes a solute more significantly than a nonpolar solvent and hence results in a larger charge separation which in turn leads to a higher dipole moment. It is important to notice that the average dipole moment of the trans form is not zero, albeit close to zero. This is because the molecule does not adopt a fixed conformation with dihedral angle 180° but exhibits small amplitude torsional motion around this angle and the resulting conformations lead to a nonzero average dipole moment. This result is much different to the static *ab initio* electronic structure calculations which usually report zero dipole moment for the trans conformer.⁹ However, at finite temperature, the torsional motion along the C–C bond leads to conformations that do not have zero dipole moment and hence the average value for the dipole moment of the trans form is not exactly zero.

We have also investigated the solvent effect on the atomic charges and molecular geometry for DCE; Tables 3 and 4 show these quantities. Table 3 displays the D-*resp* charges⁴⁵ on all atoms of DCE. These are the charges obtained by fitting to the molecular electrostatic potential and that take into account the dynamic solvent environment. The results in Table 3 can be discussed as follows: (1) The charges on all atomic sites, namely, Cl, C, and H, increase with increasing polarity. Due to the reason stated earlier, the polar solvents polarize the solute molecule more significantly than the less polar solvents and hence we see increasing charge density at the atomic sites with increasing

polarity. Interestingly, the charge on each atomic site is increased by almost 2 times when the solvent environment is changed from chloroform to water. For example, the charge on the Cl atom of DCE in chloroform solvent is -0.1 which increases to -0.2 in the case of water solvent. (2) The net atomic charges of trans and gauche forms are significantly different, and overall, the gauche form is more polarized by the solvents than the trans conformer. The conformation dependence of atomic charges and dipole moments is less discussed in the literature. Here, we provide an example of a case where the charges and dipole moments can be significantly affected by the conformation. We recommend that it is necessary to treat such systems at a quantum mechanical level for the correct description of charge distribution and its higher order moments. (3) Another interesting aspect to notice is that the hydrogen atoms of the gauche form have two different charges. In the trans form, both of the hydrogens in the CH_2Cl group are equivalent and in the gauche form this equivalence is lifted. The hydrogen atom (of the first CH_2Cl group) that is trans in position to the Cl atom of the neighboring CH_2Cl group has a different charge when compared to the hydrogen atom that is related to the Cl atom by a dihedral angle of 120° (see Figure 1a).

Table 4 displays the solvent effect on different bond lengths in DCE. First, it is seen that the C–Cl bond length increases with the solvent polarity. For example, the C–Cl bond length for the trans form in chloroform solvent is 1.8695 \AA and in water solvent the value is 1.8850 \AA . Similarly, the C–Cl bond length for the gauche form in chloroform solvent is 1.8578 \AA and in water solvent the value is 1.8797 \AA . Second, the C–Cl bond length is larger for the trans form when compared to the gauche form. The C–Cl bond length for the trans form in water solvent is 1.8850 \AA , and for the gauche form, the value is 1.8797 \AA . The C–C and C–H bonds do not show significant solvent dependence like the C–Cl bond. These results are consistent with the high-level *ab initio* reaction field theory calculations which suggest an increase in C–Cl bond with increasing dielectric constant of the media.³ In comparison to our results, these self-consistent reaction field calculations (SCRf) do not report any increase for the bond lengths such as C–C and C–H with increasing dielectric constant.³ Overall, the dielectric constant dependence of different bond lengths appears to be similar from the SCRf calculations and the present CPMD calculations. The actual magnitude of the bond lengths in our calculations is at the higher side, since our results are for DCE at finite temperature, while the geometrical parameters from SCRf calculations correspond to zero temperature.

3.3. Conclusions. The solvent dependence on the conformational transition for DCE has been investigated in chloroform and water solvents as well as for the case of liquid DCE. In the chloroform solvent, we observe many interconversion processes between gauche and trans forms which indirectly reveals the lower barrier for conformational transition. However, we rarely find such interconversion in the cases of liquid DCE and in water solvent. We have also investigated the solvent dependence of the dipole moment distribution. The dipole moments of the gauche and trans forms of DCE increase with increasing polarity of the solvents. The atomic charges in DCE also show a dramatic increase with increasing solvent polarity. The trans form has a single hydrogen atom type with respect to the magnitude of charge, while the gauche form has two different hydrogen atom types. We also report a strong conformation dependence on the net atomic charges where the atoms in the gauche form appear to have larger charges than the trans form. Also, the atomic charge values of DCE increase almost twice in quantity when

the solvent is changed from chloroform to water. We also report an increasing C–Cl bond length (for both trans and gauche conformers) with increasing solvent polarity, while the C–C and C–H bond lengths are not altered.

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