Communications to the Editor

Conformations of 1,2-Dimethoxyethane in the Gas and Liquid Phases from Molecular Dynamics Simulations

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We have recently conducted ab initio electronic structure calculations of the geometries and energies of the conformers of 1,2-dimethoxyethane (DME).[1,2] We found that the *ttt* conformer is the lowest in energy, while the *tgt* and $tg^{\pm}g^{\mp}$ conformers are only 0.1−0.2 kcal/mol higher in energy. The conformer energies yield conformer populations consistent with gas phase electron diffraction studies[3] that predict the order of conformer populations to be $tg^{\pm}g^{\mp} + tg^{\pm}g^{\pm} > tgt > ttt$ at 273 K.

Both experiment (e.g., refs 4−6) and simulation (e.g., refs 7 and 8) indicate that the conformations of DME are different in the liquid and solid phases compared to the gas phase; i.e., there are condensed phase effects in DME which change the conformational populations of the molecule. Matrix isolation studies[6] indicate that the *ttt* conformer is the most stable conformer in an argon matrix at 34 K, consistent with our findings that this is the lowest energy conformer. In the liquid and crystalline states, spectroscopic studies indicate that the *tgt* conformer[4] is preferred. The population of the $tg^{\pm}g^{\mp}$ conformer, the most populous conformer in the gas phase,[1−3] is found to decrease on going from the gas to the liquid.[4,9] The stabilization of the *tgt* conformer in the liquid or solid state is easily understood in terms of polar interactions; the *tgt* conformer has an appreciable dipole moment while the *ttt* conformer has a zero dipole moment. Considering the significant dipole moment of the $tg^{\pm}g^{\mp}$ conformer, the decrease in population in going from the gas to the liquid phase is not as easily understood.

A previous Monte Carlo (MC) simulation[8] demonstrated the stabilization of the *tgt* conformer in the liquid at the expense of the *ttt* conformer. However, the force field used was not parametrized to reproduce gas phase populations accurately and did not include hydrogen atoms. We and others have indicated that strong 1,5 $C\underline{H}\cdots O$ electrostatic interactions are responsible for stabilizing the important $tg^{\pm}g^{\mp}$ conformer.[1,2,6,10]

Table 1. Properties and Populations of 1,2-Dimethoxyethane (DME) Conformers at 300 K

			populations		
			gas		
conformer	energy[a] (kcal/mol)	dipole moment[b] (D)	with DDC[c]	without DDC	liquid
ttt	0.00 (0.00)	0.0 (0.0)	0.25	0.21	0.18
tgt	0.14 (0.10)	1.7 (1.5)	0.25	0.28	0.45
$tg^{\pm}g^{\mp}$	0.19 (0.23)	1.6 (1.7)	0.32	0.34	0.17
ttg	1.38 (1.41)	2.0 (1.9)	0.11	0.09	0.09
$tg^{\pm}g^{\pm}$	1.74 (1.51)	2.9 (2.7)	0.04	0.04	0.08
other			0.04	0.04	0.04

[a] Relative conformer energies are for isolated DME molecules from the atomistic force field (ref 2) in kcal/mol. Numbers in parentheses are ab initio values from ref 1. [b] Conformer dipole moments for isolated DME molecules using the atomistic force field. The numbers in parentheses are from ab initio calculations using SCF wave functions (ref 1). [c] Distance-dependent dielectric constant (see text).

We have parametrized a force field which accurately reproduces the conformational geometries, energies, dipole moments, and gas phase electron diffraction patterns of DME.[2] Values for the important conformers are summarized in Table 1. In the present work, we use this force field to study the conformer populations of DME in the liquid and gas phases and the static structure of liquid DME.

Molecular dynamics simulations of liquid DME were performed at constant volume and temperature with a 1 fs time step, employing periodic boundary conditions using the algorithm described previously.[11] Nonbonded interactions were cut off at 9 Å using a spline function which gradually reduces the forces to 0 at the cutoff.[11] All intramolecular nonbonded interactions fall within the cutoff distance. In addition, a distance-dependent dielectric constant was used[11] as a crude model for dielectric screening effects in the bulk. Simulations were performed at 300 K at experimental density.[12] The simulation pressure, corrected for truncated dispersion interactions but not coulomb interactions, was about 40 atm. The system consisted of 150 DME molecules, yielding a periodic box dimension of 29.63 Å. The force field is described in detail elsewhere.[2] Equilibration time was 600 ps, and sampling time was 800 ps, yielding an average of 140 conformational transitions per bond. Simulations of gas phase DME were performed using the stochastic dynamics algorithms described elsewhere.[2,11,13] The same ensemble as for the liquid simulations was utilized, but the intermolecular nonbonded interactions were excluded. Simulations were performed with and without the distance-dependent dielectric constant (DDC). Equilibration time was 400 ps, with 600 ps of sampling time.

The resulting conformer populations are given in Table 1. The DDC increases from 1.0 for interatomic separations less than 4 Å to 3.5 at long separation (see ref 11). The DDC is employed to crudely account for screening effects which would result from atoms from other molecules lying between the interacting atoms in the liquid state. As these effects will not

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(9) The original assignment of peaks was to the $tg^{\pm}g^{\pm}$ conformer. Discrimination of the assignments between the $tg^{\pm}g^{\pm}$ and $tg^{\pm}g^{\mp}$ conformers is not conclusive from normal coordinate analysis alone.[6] Both experimental[3] and theoretical[1,2] results point to the predominance of the latter conformer.

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occur in the gas phase, we believe that it is best to compare results of the liquid simulation with results from gas phase simulation without the DDC. In either case, the $tg^{\pm}g^{\mp}$ conformer is preferred in the gas phase, in agreement with electron diffraction studies.[3]

In the liquid, the *tgt* conformer is the most populous, in agreement with experiment,[4] with a population about 50% greater than in the gas phase. In contrast, the population of the $tg^{\pm}g^{\mp}$ conformer is about 50% less in the liquid phase. This trend is in agreement with experimental observations.[4] The population of the *ttt* conformation also decreases in going from the gas phase to the liquid phase. In the liquid, we find the conformer populations to be $tgt > ttt > tg^{\pm}g^{\mp} > ttg$, in agreement with estimates based on the temperature dependence of the liquid state IR spectra.[4]

The fractional population of total gauche states of the OC—CO bond is greater in the liquid than in the gas phase, 0.73 vs 0.69, respectively, reflecting the large *tgt* population in the liquid phase. This result is consistent with experimental measurements of NMR vicinal coupling in DME,[5] which indicate that the gauche state of the OC—CO bond is stabilized in polar solvents relative to the gas phase and nonpolar solvents. The gauche fraction of the CO—CC bond, in contrast to the OC—CO bond, is less in the liquid than in the gas phase, 0.20 vs 0.27, respectively. This is a result of the decrease in the $tg^{\pm}g^{\mp}$ population in the liquid state. The predicted behavior of CO—CC bond is also consistent with NMR vicinal coupling experiments,[5] which indicate that the gauche conformation of this bond is less favored in some polar solvents than in nonpolar solvents.

The intermolecular pair distribution functions for liquid DME, determined using standard methods,[14] are shown in Figure 1 along with previous simulations of *n*-tridecane ($C_{13}H_{28}$).[15] The O··H pair distribution function shows a shoulder which begins at separations of less than 3 Å, consistent with the intramolecular 1,5-CH··O distance of 2.6 Å seen in the $tg^{\pm}g^{\mp}$ conformer.[1] No analogous interaction was seen in *n*-tridecane; i.e., no equivalent C··H approaches were seen. The C··H pair distribution function in DME shows structure at small separations not seen in *n*-tridecane, but no features at separations less than 3 Å. The C··O pair distribution function shows a shoulder between 3 and 4 Å, consistent with the intramolecular 1,5 CH··O distance of 3.2 Å seen in the $tg^{\pm}g^{\mp}$ conformer.[1] Such structure is not seen in the DME C··C or O··O pairs, or the C··C pair in *n*-alkanes. We conclude that strong intermolecular CH··O interactions, like the 1,5 C*H*··O intramolecular interactions in the $tg^{\pm}g^{\mp}$ conformer, are present in liquid DME. These intermolecular interactions occur to some extent at the expense of the 1,5 CH··O intramolecular interactions, accounting for the observed decrease in population of the $tg^{\pm}g^{\mp}$ conformer in going from the gas to the liquid state.

In conclusion, comparison of conformer populations of DME in the liquid and gas phases shows significant condensed phase effects in agreement with experiment. The population of the *tgt* conformer, which has a relatively large dipole moment, increases significantly in the liquid state compared to the gas phase. In contrast, the population of $tg^{\pm}g^{\mp}$ conformer decreases significantly in the liquid state compared to the gas phase, apparently due to strong intermolecular electrostatic interactions. This latter effect appears to have significant implications for poly(oxyethylene) (POE). Initial simulations[16] of POE using the same force field show a decrease in the frequency of $g^{\pm}g^{\mp}$ OC—C—OC conformations in the polymer melt relative to unperturbed (ideal) polymer chains. This effect could account for the greater mean-square radius of gyration of POE chains in the melt[17] relative to unperturbed chains because of the compact nature of the $g^{\pm}g^{\mp}$ conformations.

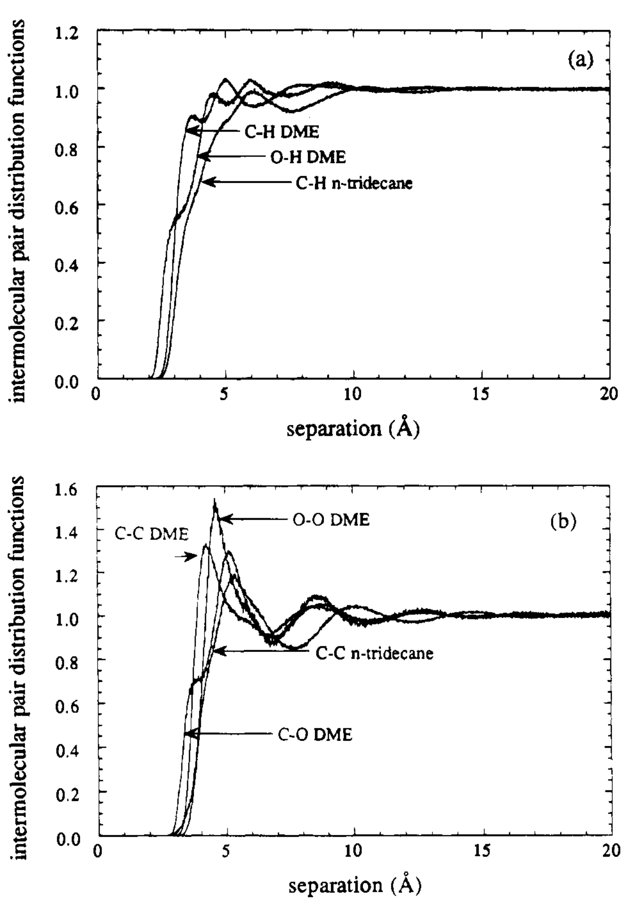

Figure 1. Intermolecular pair distribution functions for DME in the liquid state from simulations. Shown for comparison are results from simulations of *n*-tridecane melts. Pairs are (a) O··H and C··H and (b) C··O, O··O, and C··C.

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