Bond-Dependent Thole Model for Polarizability and Spectroscopy: Supplemental Information

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TABS Database: CMPD subset

Listed below are the subset of the TABS database for which we generated random configurations using Car-Parinello molecular dynamics in order to test the TholeL method for systems far from the ground state:

Simulation Details - Liquid Water

The initial positions of the H_2O molecules were generated using PACKMOL[1] in a cubic simulation box of length 9.877 Å to achieve a density of 0.998 g/cm³. We equilibrated the system using a Nose-Hoover thermostat[2,3] for 0.5 ps, as at this time the temperature and energy of the system reached equilibrium. We then ran the simulation in the NVE ensemble for 30 ps. All CPMD calculations were performed using the cp.x module of Quantum Espresso (v.6.2.1)[4,5] using the SCAN functional[6] and HSCV psuedopotentials.[7,8]

Table 1: TABS Subset - CPMD Simulations

1-methylimidazole	diacetyl	imidazole	sulfuric-acid
1-methylimidazole	diazene	isobutane	tartaric-acid
2-pyridone	diethylamine	isocyanic-acid	taurine
acetaldehyde	diethyl-ether	isopropyl-alcohol	tert-butyl-alcohol
acetaldoxamine	dimethylamine	isopropylamine	tert-butyl-chloride
acetic-acid	dimethyl-ether	isothiazole	tert-butyl-cyanide
acetone	dimethyl-hydrazine	ketene	tetrahydrofuran
acetonitrile	dimethyl-oxalate	malonic-acid	thiazole
acetyl-chloride	dimethyl-sulfide	methacrylic-acid	thioacetaldehyde
acetylenamine	dimethyl-sulfoxide	methanediol	thioacetamide
acrylamide	dioxane	methane	thioformaldehyde
adenine	dithiooxamide	methanethiol	thiophene
allyl-alcohol	ethanediol	methanol	thymine
aminothiazole	ethane	methyl-acrylate	toluene
aniline	ethanethiol	methylamine	trimethylamine
ascorbic-acid	ethanolamine	methyl-cyanide	uracil
benzene	ethanol	methyl-dicyanide	urea
benzoic-acid	ethyl-acetate	methylhydrazine	vinyl-acetate
butanal	ethylamine	methyl-isothiocyanate	vinyl-acetylene
butane	ethyl-cyanide	N_2	vinyl-alcohol
butanone	ethylene-dichloride	neopentane	vinyl-chloride
butyric-acid	ethylene-gylcol	NH_3	
butyronitrile	ethylene	nitrobenzene	
carbamic-acid	ethyl-formate	nitroethane	
carbonyl-sulfide	ethyl-thiocyanate	nitromethane	
catechol	formaldehyde	nitrous-acid	
CCl_4	formamide	NO_2	
chloramine	formic-acid	NO	
chloroacetic-acid	fulminic-acid	O_2	
chlorobenzene	furan	oxalic-acid	
chloroform	glycerol	oxaziridine	
CO_2	glycine	pentanal	
CO	guanidine	phenol	
crotonic-acid	guanine	phosgene	
CS_2	H_2O_2	propanamide	
cyanamide	H_2O	propane	
cyanic-acid	HCN	propanol	
cyanogen	hexane	propene	
cyanuric-acid	hydrazine	propionitrile	
cyclobutane	hydroxyacetaldehyde	propylene-glycol	
cyclohexane	hydroxyacetonitrile	propyne	
cyclohexanol	hydroxycarbamide	pyridine	
cyclopentane	hydroxylamine	serine	
cyclopropane	hydroxymethylimine	SO_2	
cytosine	hypochlorous-acid	sulfanilamide	

We plot the O-O radial distribution function (RDF) in figure 1. The O-O RDF matches that found using X-ray diffraction quite well, indicating that we have built an accurate model of water.
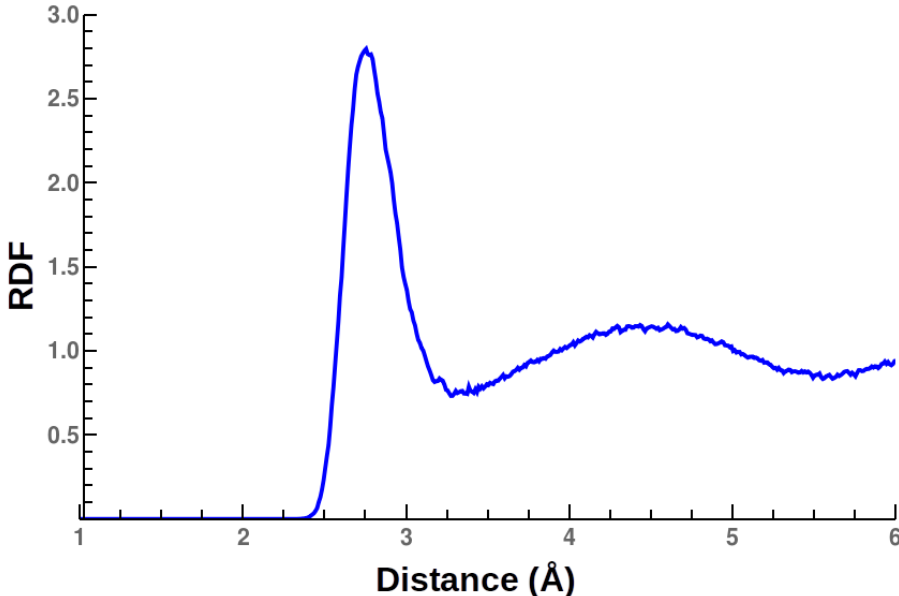

Figure 1: The O-O RDF for liquid water simulated with SCAN at 300K.

Simulation Details - Solvated Urea

The initial positions of the H_2O and urea molecules were generated using PACKMOL[1] in a cubic simulation box of length 10.50 Å to achieve a density of 0.917 g/cm^3. Note that this density is slightly low, but we found that this box length yielded the most accurate structure of water as determined by the O-O RDF. We equilibrated the system using velocity rescaling followed by a Nose-Hoover thermostat[2,3] for 3.8 ps until the temperature and energy of the system reached equilibrium. We then ran the simulation in the NVE ensemble for 30 ps. All CPMD calculations were performed using the cp.x module of Quantum Espresso (v.6.2.1)[4,5] using the SCAN functional[6] and HSCV psuedopotentials.[7,8]

We plot the O-O radial distribution function (RDF) for O in H_2O molecules in figure 2. The O-O RDF, though slightly over-structured, matches that found using X-ray diffraction

quite well, indicating that we have an appropriate volume to accommodate the molecules in the system.
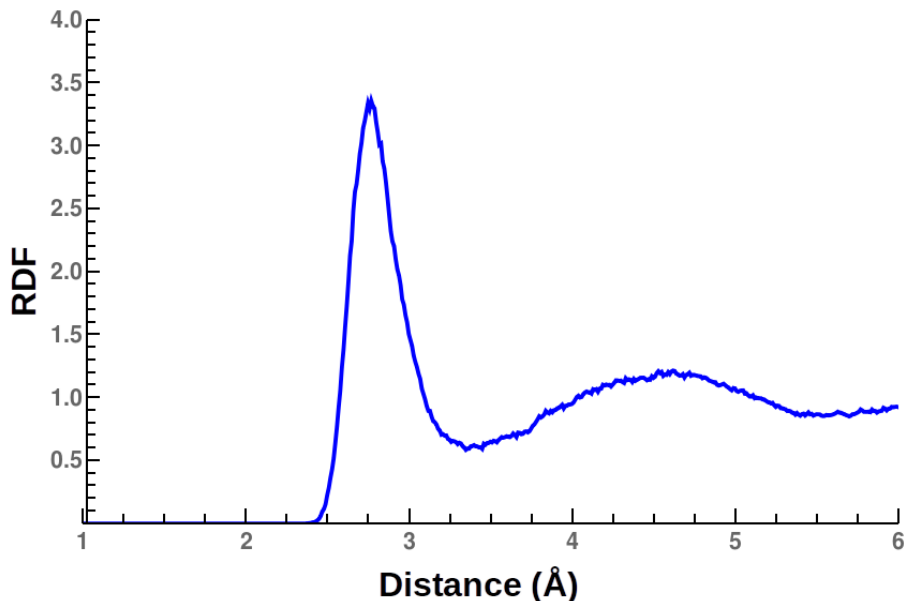

Figure 2: The O-O RDF for H_2O molecules for urea solvated in water simulated with SCAN at 300K.

Simulation Details - Crystalline Urea

The initial configuration was obtained from neutron diffraction experiments[9] and the cell parameters were optimized using the cp.x module of Quantum Espresso (v.6.2.1)[4,5] using the SCAN functional[6] and HSCV psuedopotentials[7,8] to find final cell parameters of (5.661 x 5.661 x 4.712)Å. We then generated a supercell by doubling the lattice vectors, resulting in a cell containing 16 urea molecules. We then equilibrated the system using velocity rescaling followed by a Nose-Hoover thermostat[2,3] for 2.6 ps until the temperature and energy of the system reached equilibrium. We then ran the simulation in the NVE ensemble for 20 ps.

Simulation Details - Gaseous Urea

We simulated a gas-phase urea molecule using the cp.x module of Quantum Espresso (v.6.2.1)[4,5] using the SCAN functional[6] and HSCV psuedopotentials[7,8] in a cubic simulation cell of dimension 10Å. We did not attempt to strictly control temperature, but to get close to 300K we ran the molecule in the NVT ensemble first with velocity rescaling and then with a Nose-Hoover thermostat[2,3] for 1.25 ps in order to initially populate the vibrational modes of the system. We then ran the simulation in the NVE ensemble for 20 ps.

Polarizability Parameters:

We list the optimized parameters for the Thole and TholeL models in the Table 2. The dimensionless constant A is a global scaling factor used for the "Exp" interaction.

Table 2: Atomic Polarizability Parameters (a.u.)

Element	EXP	EXP-L	ERF	ERF-L
A	2.20	2.37	N/A	N/A
O	4.98	6.08	5.44	6.62
H	2.01	2.16	2.76	2.80
C	9.79	9.56	9.45	10.44
N	8.38	9.73	9.71	12.38
Cl	16.65	16.21	16.21	15.89
F	2.65	3.28	3.08	3.49
S	22.77	23.04	23.35	24.29
Br	24.32	23.59	23.78	23.26

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