

Supporting Information for "Polarisation Corrections and the Hydration Free Energy of Water"

Andrew W. Milne and Miguel Jorge*

Department of Chemical and Process Engineering, University of Strathclyde, Glasgow

E-mail: miguel.jorge@strath.ac.uk

1: Constants and Target Properties

Table 1: Table of constants and experimental values used in this work.

Property	Value
μ_G	1.86 D
α	1.414 Å ³
ε_∞	1.78
ε_0	78.4
C_{QM}	0.29 kJ/mol
ΔH_{Vap}	44.0 kJ/mol
ΔG_{Hyd}	-26.5 kJ/mol

2: Data for Heat of Vaporisation Calculations

Table 2: Raw data from Molecular Dynamics simulations of various water models that were used to calculate the respective heats of vaporisation. All energies are given in units of kJ/mol.

Model	Dipole (D)	U_{El}	U_{LJ}	U_{Total}
SPC	2.27	-48.7	7.02	-41.7
SPCE	2.35	-55.7	8.87	-46.8
TIP3P	2.35	-46.1	6.02	-40.1
TIP4P	2.18	-48.8	7.36	-41.4
TIP4PE _w	2.32	-55.0	8.60	-46.4
TIP4P2005	2.305	-56.0	8.28	-47.8
OPC	2.48	-59.0	7.58	-51.4
TIP4P-FB	2.428	-58.0	8.72	-49.3
H2ODC	2.42	-58.0	9.82	-48.2
TIP4P- ϵ	2.4345	-58.2	8.46	-49.7
TIP4PIce	2.426	-63.4	9.41	-54.0

Table 3: Calculated heat of vaporisation data for various water models with three different polarisation corrections. All energies are given in units of kJ/mol.

Model	Berendsen Correction	ΔH_{vap}			Uncertainty
		None	Berendsen	New	
SPC	3.58	43.9	40.3	45.3	± 0.009
SPCE	5.11	49.0	43.8	50.4	± 0.02
TIP3P	5.11	42.3	37.1	43.7	± 0.011
TIP4P	2.18	43.6	41.4	45.0	± 0.015
TIP4PE _w	4.51	48.6	44.1	50.0	± 0.019
TIP4P2005	4.22	50.0	45.7	51.4	± 0.015
OPC	8.19	53.6	45.4	55.0	± 0.024
TIP4P-FB	6.87	51.4	44.6	52.8	± 0.006
H2ODC	6.68	50.4	43.7	51.8	± 0.013
TIP4P- ϵ	7.03	51.9	44.9	53.3	± 0.010
TIP4PIce	6.82	56.2	49.3	57.6	± 0.03

3: Data for Free Energy of Hydration Calculations

Table 4: Raw data from Molecular Dynamics simulations of various water models that were used to calculate the respective free energies of hydration. All energies are given in units of kJ/mol.

Model	Dipole (D)	ΔG_{El}	ΔG_{LJ}	ΔG_{Total}
SPC	2.27	-35.3	9.17	-25.8
SPCE	2.35	-39.2	9.43	-29.5
TIP3P	2.35	-34.7	9.18	-25.3
TIP4P	2.18	-34.8	9.29	-25.2
TIP4PEw	2.32	-38.5	9.26	-28.9
TIP4P2005	2.305	-38.8	8.79	-29.8
OPC	2.48	-42.0	8.48	-33.2
TIP4P-FB	2.428	-40.9	8.95	-31.7
H2ODC	2.42	-40.7	9.98	-30.4
TIP4P- ϵ	2.4345	-40.8	8.80	-31.7
TIP4PIce	2.426	-42.9	7.93	-34.6

Table 5: Calculated free energy of hydration data for various water models with three different polarisation corrections. All energies are given in units of kJ/mol.

Model	Berendsen Correction	ΔG_{Hyd}			Uncertainty
		None	Berendsen	New	
SPC	3.58	-25.8	-22.3	-27.2	± 0.15
SPCE	5.11	-29.5	-24.4	-30.9	± 0.19
TIP3P	5.11	-25.3	-20.2	-26.7	± 0.14
TIP4P	2.18	-25.2	-23.0	-26.6	± 0.17
TIP4PEw	4.51	-28.9	-24.4	-30.3	± 0.18
TIP4P2005	4.22	-29.8	-25.5	-31.2	± 0.2
OPC	8.19	-33.2	-25.0	-34.6	± 0.19
TIP4P-FB	6.87	-31.7	-24.8	-33.1	± 0.2
H2ODC	6.68	-30.4	-23.7	-31.8	± 0.17
TIP4P- ϵ	7.03	-31.7	-24.7	-33.1	± 0.2
TIP4PIce	6.82	-34.6	-27.8	-36.0	± 0.3

4: Polarisability Tensors

Table 6: All non-zero components of the polarization tensors used in this work **given in atomic units**. α = dipole-dipole polarizability matrix, A = dipole-quadrupole and C = quadrupole-quadrupole. * = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3], † = cc-pv(t+d)z, ‡ = [5s3p2d/3s2p], \diamond = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3].

Component	Polarisability Tensor					
	B3LYP†	B3LYP*	MP2*	CCSD*	CCSD(T)‡	CCSD(T)◇
$\alpha_{x,x}$	5.517	9.769	9.488	8.976	9.70	9.25
$\alpha_{y,y}$	8.510	10.204	9.942	9.712	10.06	9.874
$\alpha_{z,z}$	7.285	9.965	9.691	9.310	9.71	9.529
$A_{x,xz}$	-1.42	-1.12	-1.08	-0.88	0.98	-1.04
$A_{y,yz}$	-6.50	-5.47	-4.96	-5.01	-2.08	-5.11
$A_{z,xx}$	3.93	2.96	2.65	2.65	3.64	2.72
$A_{z,yy}$	-3.57	-2.06	-1.79	-2.00	-3.25	-1.93
$A_{z,zz}$	0.36	-0.89	-0.86	-0.65	-0.39	-0.79
$C_{xx,xx}$	5.97	18.23	16.27	15.18	13.73	15.65
$C_{xx,yy}$	-4.63	-9.26	-8.31	-7.87	-8.44	-8.09
$C_{xx,zz}$	-1.34	-8.96	-7.96	-7.30	-5.29	-7.57
$C_{yy,yy}$	8.75	16.55	15.03	14.29	13.58	14.67
$C_{yy,zz}$	-4.12	-7.29	-6.72	-6.42	-5.14	-6.59
$C_{zz,zz}$	5.46	16.26	14.68	13.72	10.43	14.15
$C_{xy,xy}$	4.63	12.84	11.51	10.73	6.90	11.10
$C_{xz,xz}$	3.20	12.97	11.59	10.75	5.99	11.13
$C_{yz,yz}$	7.82	13.96	12.56	12.03	8.02	12.34

5: Detailed Polarisation Corrections

Table 7: Distortion correction for different sets of multipoles and polarisability matrices at various levels of theory. * = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3], † = cc-pv(t+d)z, ‡ = [5s3p2d/3s2p], ◇ = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3].

Calculation	Multipole Distortion Correction (kJ/mol)					
	B3LYP †	B3LYP *	MP2 *	CCSD *	CCSD(T) ‡	CCSD(T) ◇
AIMD (2)	13.4	7.8	8.2	8.3	8.6	8.2
QM/4MM	23.9	12.0	12.6	12.9	13.5	12.8
QM/230TIP5P	21.7	11.8	12.4	12.7	13.1	12.5
QM/4TIP5P	36.7	18.5	19.5	20.3	21.0	19.7
AIMD (3)	80.2	35.9	38.1	40.4	42.5	38.8
AIMD (1)	78.6	37.9	40.1	41.3	43.4	40.7

Table 8: Values of the cavity radius for different sets of multipoles and polarisability matrices at various levels of theory. * = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3], † = cc-pv(t+d)z, ‡ = [5s3p2d/3s2p], ◇ = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3].

Calculation	Cavity Radius (Å)					
	B3LYP †	B3LYP *	MP2 *	CCSD *	CCSD(T) ‡	CCSD(T) ◇
AIMD (2)	1.638	1.835	1.818	1.794	1.825	1.808
QM/4MM	1.598	1.789	1.773	1.750	1.780	1.763
QM/230TIP5P	1.562	1.750	1.734	1.711	1.740	1.724
QM/4TIP5P	1.495	1.675	1.659	1.638	1.666	1.650
AIMD (3)	1.427	1.598	1.584	1.563	1.590	1.575
AIMD (1)	1.408	1.577	1.563	1.537	1.569	1.554

Table 9: Electronic polarisation correction for different sets of multipoles and polarisability matrices at various levels of theory using the cavity radii from **Table 8**: * = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3], † = cc-pv(t+d)z, ‡ = [5s3p2d/3s2p], ◇ = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3]

Calculation	Electronic Solvation Correction (kJ/mol)					
	B3LYP †	B3LYP *	MP2 *	CCSD *	CCSD(T) ‡	CCSD(T) ◇
AIMD(2)	-25.6	-16.5	-17.2	-18.0	-17.0	-17.4
QM/4MM	-31.1	-19.9	-20.8	-21.7	-20.5	-21.1
QM/230TIP5P	-33.5	-21.5	-22.5	-23.5	-22.2	-22.8
QM/4TIP5P	-44.2	-28.3	-29.6	-30.9	-29.1	-29.9
AIMD (3)	-64.6	-40.8	-42.7	-44.7	-42.1	-43.3
AIMD (1)	-68.4	-43.4	-45.4	-48.1	-44.7	-46.0

Table 10: Individual components of the various multipole-multipole interactions of water that arise when they are distorted in moving from the gas to the liquid phase. * = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3], † = cc-pv(t+d)z, ‡ = [5s3p2d/3s2p], ◇ = d-aug-cc-pVQZ = [7s6p5d4f3g/6s5p4d3]

Component	Polarisation Correction (kJ/mol)					
	B3LYP †	B3LYP *	MP2 *	CCSD *	CCSD(T) ‡	CCSD(T) ◇
Dipole-Dipole	64.5	25.9	27.0	28.2	31.3	27.4
Dipole-Quadrupole	-42.3	-4.9	-4.9	-6.1	-10.3	-5.4
Quadrupole-Quadrupole	58.1	14.8	16.0	18.2	21.5	16.8
Multipole Distortion Total	80.2	35.9	38.1	40.4	42.5	38.8
Dipole	-29.1	-20.7	-21.5	-22.1	-21.2	-21.6
Quadrupole	-35.5	-20.2	-21.3	-22.5	-20.9	-21.7
Electronic Solvation Total	-64.6	-40.8	-42.7	-44.7	-42.1	-43.3
Overall Correction	15.6	-5.0	-4.7	-4.3	0.40	-4.5

6: Dipole - Quadrupole Fits Used for Parametric Study

The following plots (**Figures S1 and S2**) and fits were made using the data in **Table 2**.

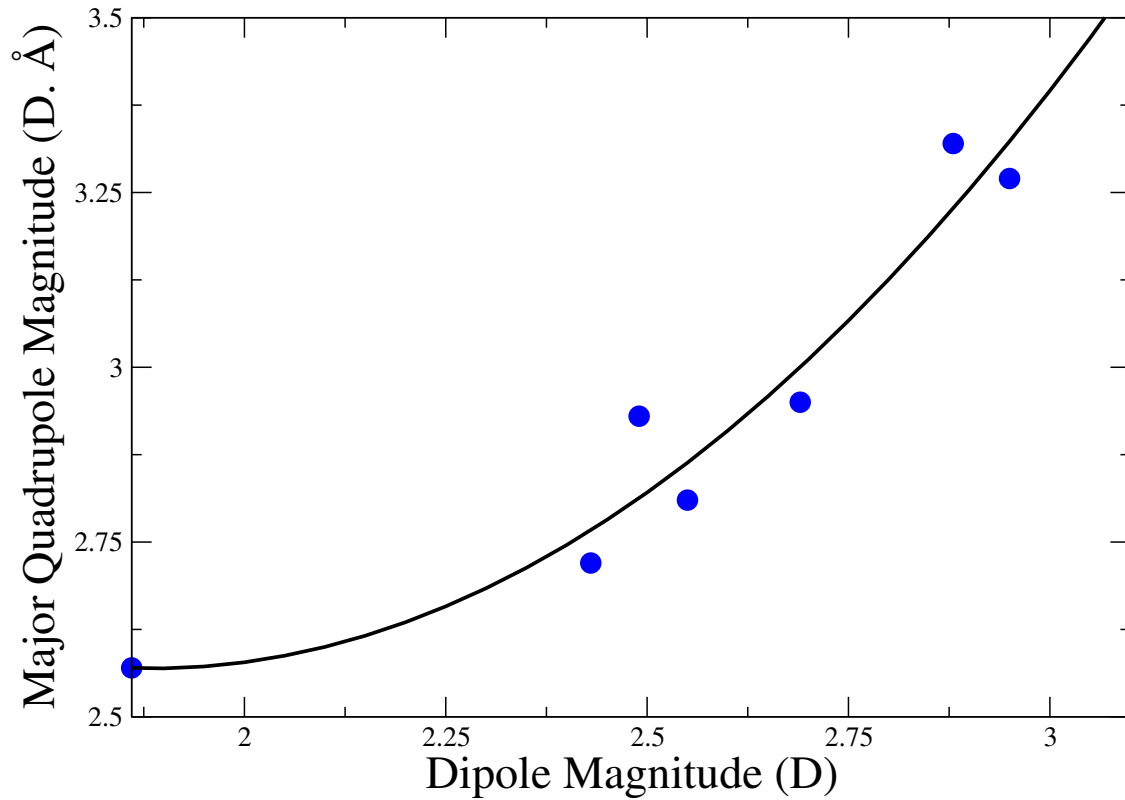


Figure 1: Fit of major quadrupole magnitude (Θ_2) to dipole magnitude (μ) for the parametric study. Fit: $\Theta_2 = 0.664\mu^2 - 2.50\mu + 4.92$, $R^2 = 0.93$.

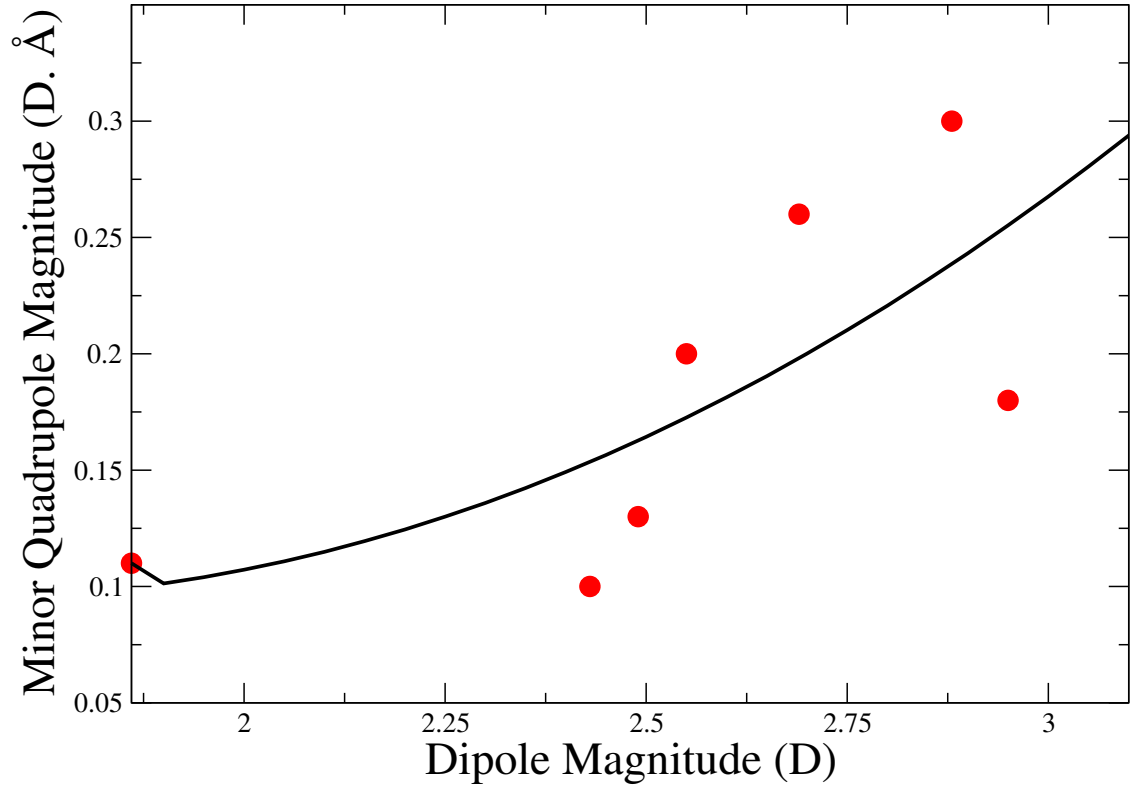


Figure 2: Fit of minor quadrupole magnitude (Θ_0) to dipole magnitude (μ) for the parametric study. Fit: $\Theta_2 = 0.0924\mu^2 - 0.302\mu + 0.341$, $R^2 = 0.48$.

7: Analysis of AIMD Trajectory

The output files provided by Schienbein und Marx consisted of coordinates of all atoms (H and O) and maximally localised Wannier functions (X) from each frame of their trajectory. These were analysed using an in-house Python script. Although the dipole is origin independent, the traceless quadrupole is not. For this reason the coordinates of all water molecules were altered so that the oxygen atom lay at the origin. Then all water molecules were rotated so that they lay along the same plane. Subsequently the dipoles were calculated as:

$$\mu_i = \sum_l r_{i,l} q_l \quad (1)$$

where i refers to the coordinate of the atom along the i -axis and l refers to the atom in the molecule. The overall dipole was then calculated as:

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (2)$$

For quadrupoles:

$$\Theta_{ij} = \sum_l q_l (3r_{i,l}r_{j,l} - ||\mathbf{r}_l||^2 \delta_{ij}) \quad (3)$$

where i and j refer to the coordinates of atom l along the i - and j -axes respectively. δ_{ij} is the Kronecker delta. $||\mathbf{r}_l||$ is the magnitude of the vector \mathbf{r}_l . The charges (q_l) of the ion centres (O and H) correspond to the number of outer electrons of each but positive, since these are treated as nuclei; q_O is hence +6e and q_H is +1e. Each Wannier function has a charge of -2e since it corresponds to a localised coordinate of one orbital.

Since the calculations of Schienbein and Marx were carried out at the quantum level, the angles and bond lengths of the individual water molecules were not constrained. This meant that some were not symmetrical, leading to non-diagonal elements of the 3×3 quadrupole matrix being non-zero. In order to make all molecules comparable the quadrupole matrices

were diagonalised so that all off-diagonal elements were equal to zero. The effect of this was minor (less than a percent difference in the quadrupole magnitudes) and was done purely for the sake of consistency.

The major (Θ_2) and minor (Θ_0) quadrupoles were then computed as

$$\Theta_2 = \Theta_{zz} + \frac{1}{2}\Theta_{xx} \quad (4)$$

$$\Theta_0 = \Theta_{xx} \quad (5)$$

μ , Θ_0 , Θ_2 were calculated for every molecule in every frame of the trajectory, 12,928 in total. These were then summed and divided by the total number of molecules (12,928) to give the average value of each property. These were then binned to provide a distribution of each property. Similarly, for every molecule the necessary polarisation correction was calculated, summed and averaged in order to give the average polarisation correction per molecule.

The distributions for the dipole and major quadrupole seem very similar, both exhibiting a sharp maximum. However, plotting the major quadrupole with respect to the dipole for each molecule showed no correlation between the two properties (see **Figure S3**). The same is true for the minor quadrupole (**Figure S4**), which in any case shows a much wider distribution than the other two multipoles.

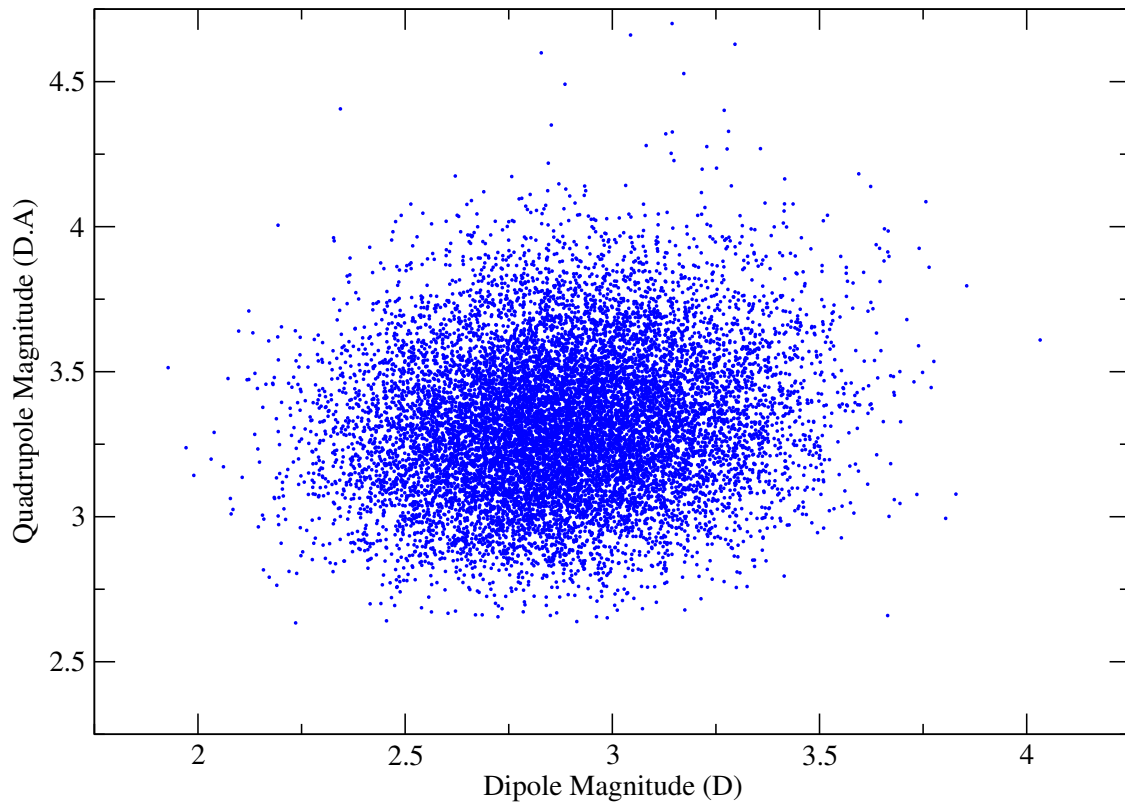


Figure 3: Relationship between the dipole (μ) and the major quadrupole (Θ_2). Calculated from data provided by Schienbein and Marx. There are 12,928 data points (101 frames, 128 water molecules per frame).

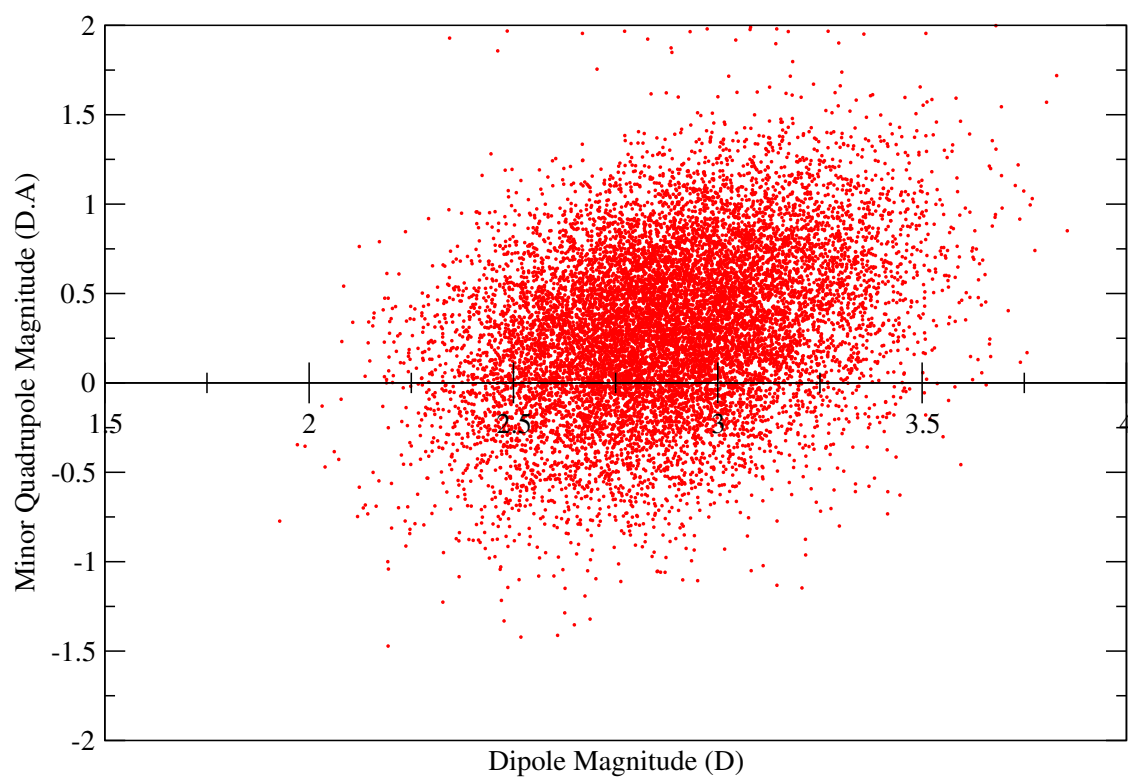


Figure 4: Relationship between the dipole (μ) and the minor quadrupole (Θ_0). Calculated from data provided by Schienbein and Marx. There are 12,928 data points (101 frames, 128 water molecules per frame).

8: Molecular Dynamics Results with Corrections

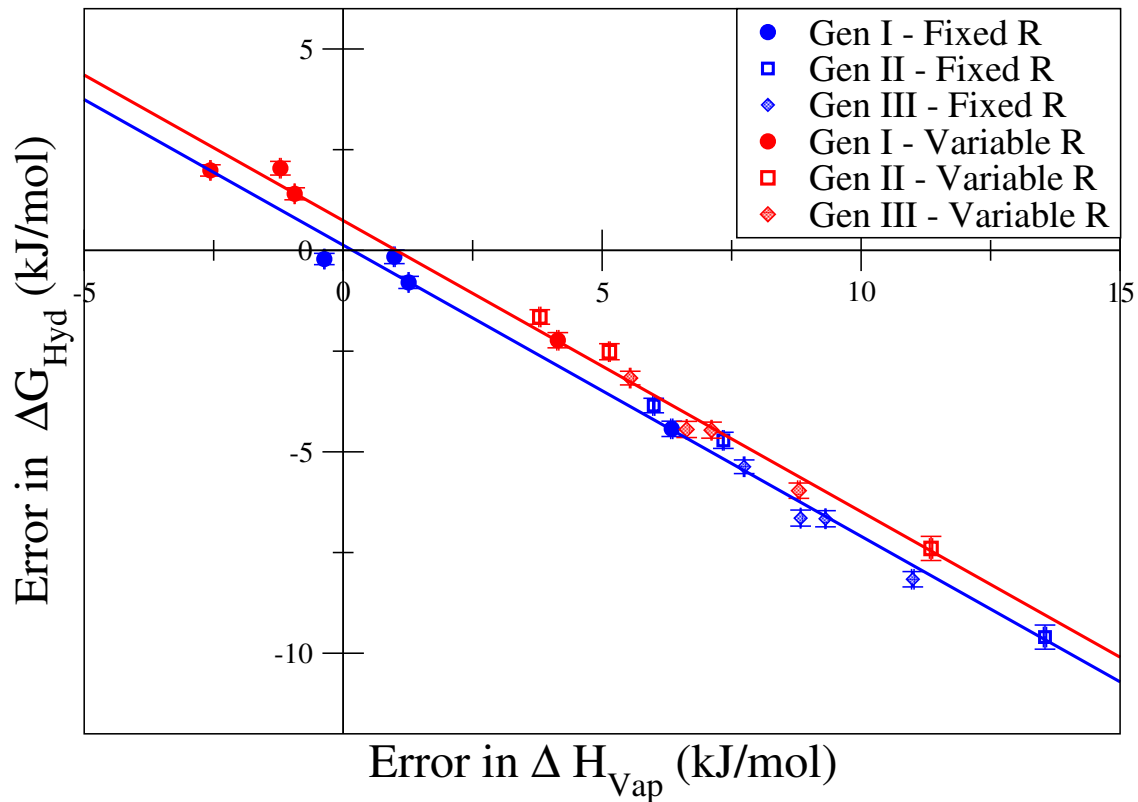


Figure 5: Deviations between simulation and experiment for the hydration free energy and enthalpy of vaporisation of 11 different non-polarisable water models (as shown in **Table 1**) with the polarisation corrections derived in this work applied to them. Fixed R refers to the correction when using a fixed cavity radius corresponding to that of the liquid density. Variable R refers to using a variable cavity radius. Generation I models are represented by solid circles, Generation II by open squares and Generation III models by shaded diamonds.