Supporting Information
for
Polarizable Force Field for Molecular Ions Based on the Classical Drude Oscillator

Fang-Yu Lin,[a] Pedro E. M. Lopes,[a] Edward Harder,[b] Benoît Roux,[b, †] and

Alexander D. MacKerell, Jr.[a, ‡]

[a]Department of Pharmaceutical Sciences, School of Pharmacy, University of Maryland, 20 Penn Street, Baltimore, MD 21201, USA.

[b]Department of Biochemistry and Molecular Biology, University of Chicago, Chicago, IL, 60637, USA.

Corresponding author: [†]roux@uchicago.edu; [‡]alex@outerbanks.umaryland.edu

Table S1. Calculation of target hydration free energies $\Delta G(Y^{-/+}_{target})$ for the respective molecular ions ($Y^{-/+}$) used in the additive model.

Molecule ($Y^{-/+}$)	($X^{-/+}$)	$\Delta G(Y^{-/+}_{ref})$	$\Delta G(X^{-/+}_{ref})$	$\Delta G(X^{-/+}_{CGenFF})$	$\Delta G(Y^{-/+}_{target})$	Method[a]
NH4	Chloride	-85.2[1, 2]	-74.6[1, 2]	-79.4[3]	-80.4	2
NC1	Chloride	-76.5[1, 2]	-74.6[1, 2]	-79.4[3]	-71.7	2
NC2	Chloride	-68.6[1, 2]	-74.6[1, 2]	-79.4[3]	-63.8	2
NC3	Chloride	-61.2[1, 2]	-74.6[1, 2]	-79.4[3]	-56.4	2
NC4	Chloride	-50.4[4]	-76.0[4]	-79.4[3]	-47.0	2
IMIM	Ammonium	-63.1[5]	-82.2[5]	-78.8[b]	-59.7	1
GUAN	Ammonium	-64.3[5]	-82.2[5]	-78.8[b]	-60.9	1
MGUAN	Methylammonium	-62.0[6]	-73.1[6]	-69.6[c]	-58.5	1
ETS	Chloride	-73.4[1, 7]	-73.0[1, 7]	-79.4[3]	-79.8	1
MES	Chloride	-75.4[1, 7]	-73.0[1, 7]	-79.4[3]	-81.8	1
ACET	Chloride	-79.2[1, 7]	-73.0[1, 7]	-79.4[3]	-85.6	1
PHET	Chloride	-73.5[1, 7]	-73.0[1, 7]	-79.4[3]	-79.9	1

[a] Method 1: $\Delta G(Y^{-/+}_{target}) = \Delta G(X^{-/+}_{CGenFF}) + \Delta G(Y^{-/+}_{ref}) - \Delta G(X^{-/+}_{ref})$.

Method 2: $\Delta G(Y^{-/+}_{target}) = \Delta G(X^{-/+}_{ref}) + \Delta G(Y^{-/+}_{ref}) - \Delta G(X^{-/+}_{CGenFF})$.

[b] $\Delta G(NH4)_{hyd, CGenFF}$ is used to normalized. Value is obtained from $\Delta G(NH4)^{real}_{hyd, CGenFF}$ in Table 9.

[c] $\Delta G(NC1)_{hyd, CGenFF}$ is used to normalized. Value is obtained from $\Delta G(NC1)^{real}_{hyd, CGenFF}$ in Table 9.

Table S2. Water minimum interaction energies (E_{min}, kcal/mol) and distances (R, Å) for molecular ions from QM, Drude model (Drude) and additive model (CGenFF) and their differences ($\triangle E_{min}$ and ΔR) compared to QM values**.**

Mol.	QM		Drude		CGenFF		$Difference_{Drude}$		$Difference_{CGenFF}$		Orientations
	E_{min}	R	E_{min}	R	E_{min}	R	$\triangle E_{min}$	$\triangle R$	$\triangle E_{min}$	$\triangle R$	
NH4	-20.34	1.7	-19.91	1.8	-19.98	1.7	0.43	0.1	0.36	0.0	Fig. 1a
NC1	-18.27	1.7	-16.53	1.8	-19.11	1.7	1.74	0.1	-0.84	0.0	Fig. 1b
NC2	-16.91	1.8	-15.77	1.8	-15.95	1.8	1.14	0.0	0.96	0.0	Fig. 1c
NC3	-16.05	1.8	-14.23	1.9	-13.90	1.8	1.82	0.1	2.15	0.0	Fig. 1e
NC4	-8.11	2.2	-7.29	2.3	-9.21	2.1	0.82	0.1	-1.10	-0.1	Fig. 1f
IMIM	-9.65	2.0	-9.35	2.1	-9.28	2.2	0.30	0.1	0.37	0.2	Fig. S1a
	-16.40	1.7	-15.73	1.7	-16.54	1.7	0.67	0.0	-0.14	0.0	Fig. S1b
	-11.32	2.0	-11.21	1.9	-11.88	2.0	0.11	-0.1	-0.56	0.0	Fig. S1c
	-6.74	3.1	-6.64	3.2	-7.67	3.2	0.10	0.1	-0.93	0.1	Fig. S1d
	-7.75	3.0	-7.20	3.2	-7.55	3.2	0.55	0.2	0.20	0.2	Fig. S1e
	-8.43	2.9	-7.68	3.2	-7.79	3.2	0.75	0.3	0.64	0.3	Fig. S1f
GUAN	-14.98	1.8	-13.01	1.9	-16.49	1.8	1.97	0.1	-1.51	0.0	Fig. S2a
	-6.52	3.1	-7.45	3.1	-6.86	3.2	-0.93	0.0	-0.34	0.1	Fig. S2b
	-7.37	3.0	-7.92	3.2	-6.71	3.3	-0.55	0.2	0.66	0.3	Fig. S2c
MGUAN	-14.28	1.8	-12.70	1.9	-16.34	1.8	1.58	0.1	-2.06	0.0	Fig. S3a
	-6.01	3.1	-6.53	3.1	-6.63	3.2	-0.52	0.0	-0.62	0.1	Fig. S3b
	-7.25	3.0	-6.80	3.2	-6.36	3.4	0.45	0.2	0.89	0.4	Fig. S3c
	-14.61	1.8	-14.60	1.9	-15.54	1.8	0.01	0.1	-0.93	0.0	Fig. S3d
	-7.44	2.2	-6.30	2.3	-6.33	2.5	1.14	0.1	1.11	0.3	Fig. S3e
ACET	-13.63	1.8	-14.27	1.8	-14.85	1.7	-0.64	0.0	-1.22	-0.1	Fig. S4a
	-13.69	1.8	-13.09	1.8	-13.05	1.7	0.60	0.0	0.64	-0.1	Fig. S4b
	-11.07	1.9	-9.42	2.0	-11.19	1.8	1.65	0.1	-0.12	-0.1	Fig. S4c
MES	-9.74	2.3	-10.20	2.5	-11.07	2.3	-0.46	0.2	-1.33	0.0	Fig. S5a
	-13.95	2.3	-14.22	2.1	-11.46	2.3	-0.27	-0.2	2.49	0.0	Fig. S5b
ETS	-9.42	2.3	-10.17	2.4	-11.09	2.3	-0.75	0.1	-1.67	0.0	Fig. S5c
	-13.44	2.3	-13.28	2.1	-11.44	2.3	0.16	-0.2	2.00	0.0	Fig. S5d
PHET	-13.55	1.8	-14.59	1.7	-15.18	1.7	-1.04	-0.1	-1.63	-0.1	Fig. S7a
	-11.25	1.9	-11.18	1.8	-11.88	1.8	0.07	-0.1	-0.63	-0.1	Fig. S7b
	-8.15	2.3	-8.45	2.2	-11.67	2.1	-0.30	-0.1	-3.52	-0.2	Fig. S7c
AVE							0.37	0.1	-0.23	0.0	
AUE							0.74	0.1	1.09	0.1	
RMSD							0.92	0.1	1.34	0.1	

Figure S1. Water interaction energy surfaces as a function of distance from the QM, Drude and additive (CGenFF) models with imidazolium (IMIM) with different water orientations in **a.** to **f.** respectively. Distances are labeled between the hydrogen (H), nitrogen (N), or carbon (C) on IMIM and water oxygen (O_{water}). Carbons are label in green, nitrogens in blue, oxygen in red, and hydrogens in white.

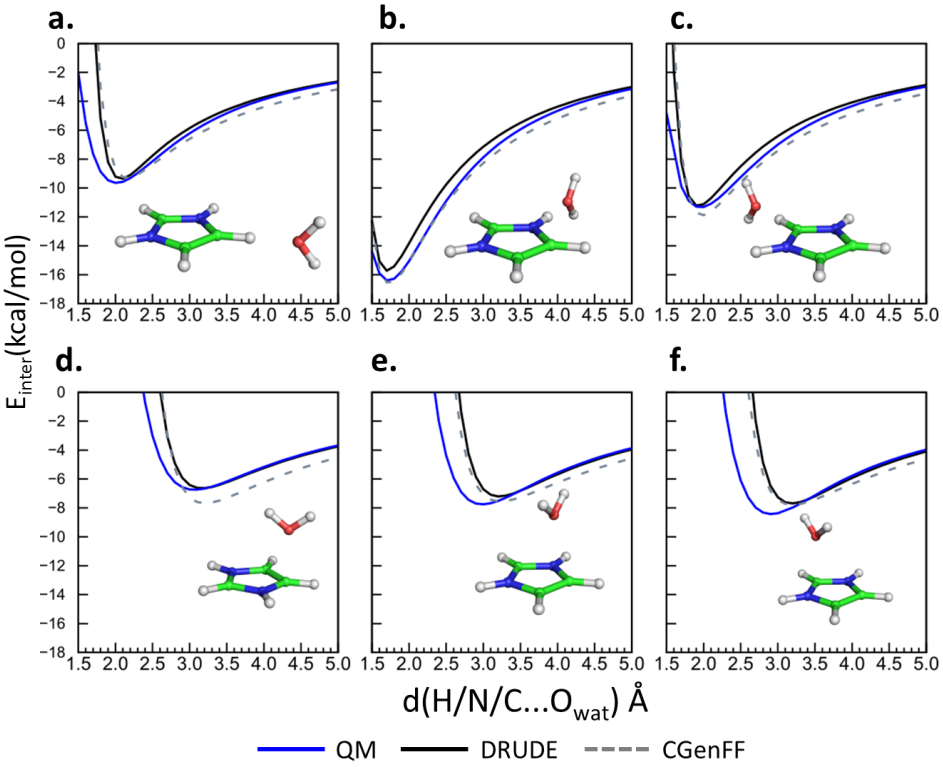

Figure S2. Water interaction energy surfaces as a function of distance from the QM, Drude and additive (CGenFF) models with guanidinium (GUAN) with different water orientations in **a.** to **c.** respectively. Distances are labeled between the hydrogen (H), nitrogen (N), or carbon (C) on GUAN and water oxygen (O_{water}). Carbons are label in green, nitrogens in blue, oxygen in red, and hydrogens in white.

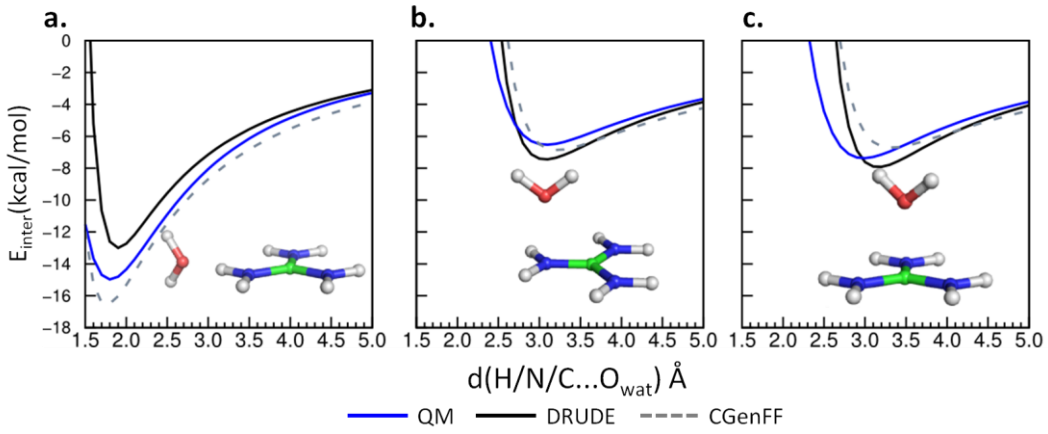

Figure S3. Water interaction energy surfaces as a function of distance from the QM, Drude and additive (CGenFF) models with methylguanidinium (MGUAN) with different water orientations in **a.** to **e.** respectively. Distances are labeled between the hydrogen (H), nitrogen (N), or carbon (C) on MGUAN and water oxygen (O_{water}). Carbons are label in green, nitrogens in blue, oxygen in red, and hydrogens in white.

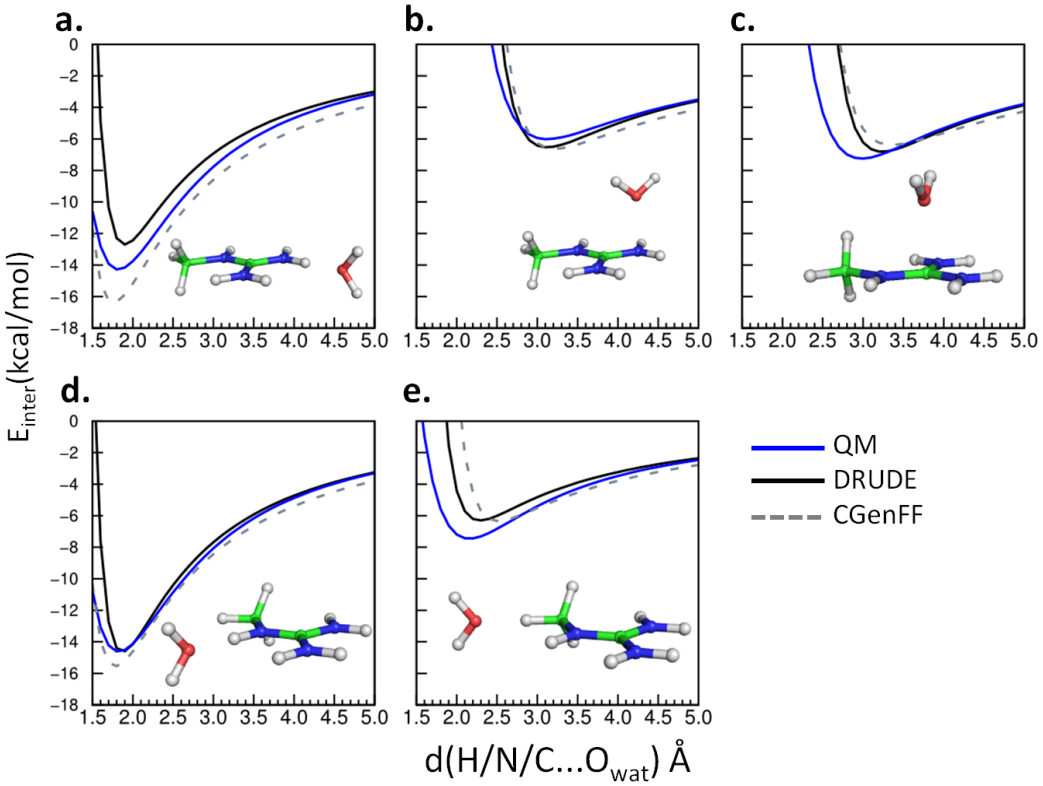

Figure S4. Water interaction energy surfaces as a function of distance from the QM, Drude and additive (CGenFF) models with acetate (ACET) with different water orientations in **a.**, **b.** and **c.** respectively. Distances are labeled between the oxygen (O) on ACET and water hydrogen (H_{water}). Carbons are label in green, oxygen in red, and hydrogens in white.

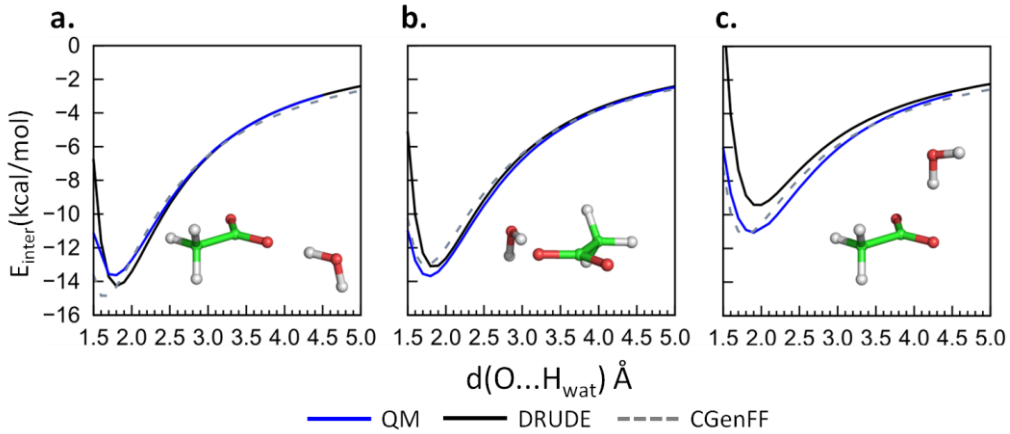

Figure S5. Water interaction energy surfaces as a function of distance from the QM, Drude and additive (CGenFF) models with methanethiolate (MES) and ethanethiolate (ETS) with different water orientations in **a.** to **d.** respectively. Distances are labeled between the sulfur (S) on the model compounds and water hydrogen (H_{water}). Carbons are label in green, sulfur in yellow, oxygen in red, and hydrogens in white.

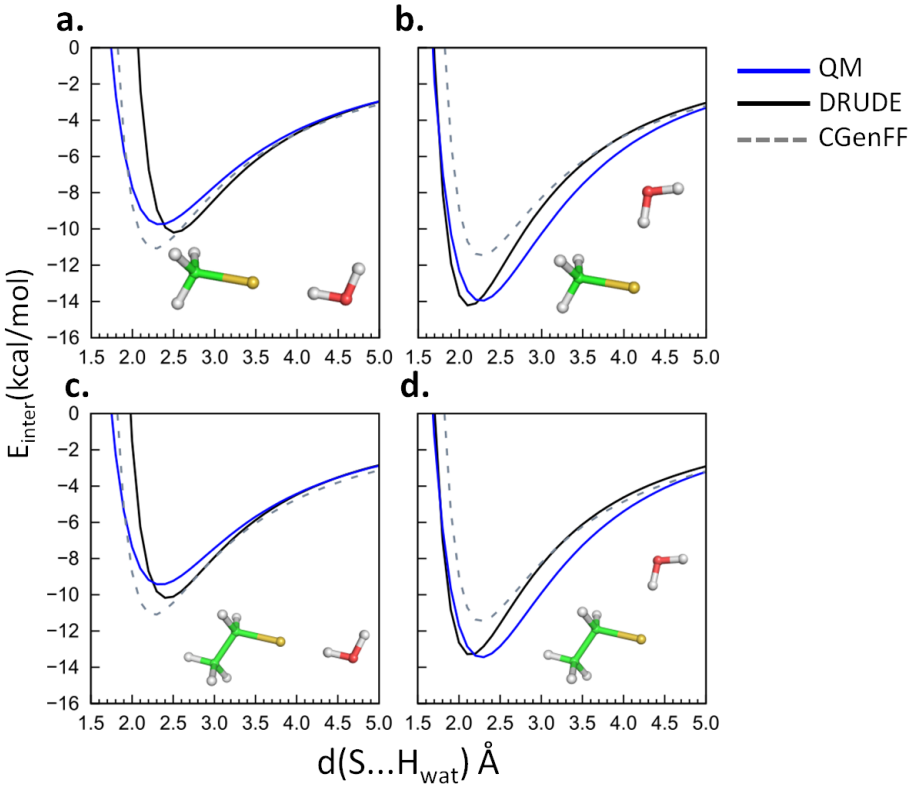

Figure S6. Water interaction energy surfaces as a function of distance from the QM, Drude and additive (CGenFF) models with phenolate (PHET) with different water orientations in **a.** to **c.** respectively. Distances are labeled between the oxygen (O) or carbon (C) on PHET and water hydrogen (H_{water}). Carbons are label in green, oxygen in red, and hydrogens in white.

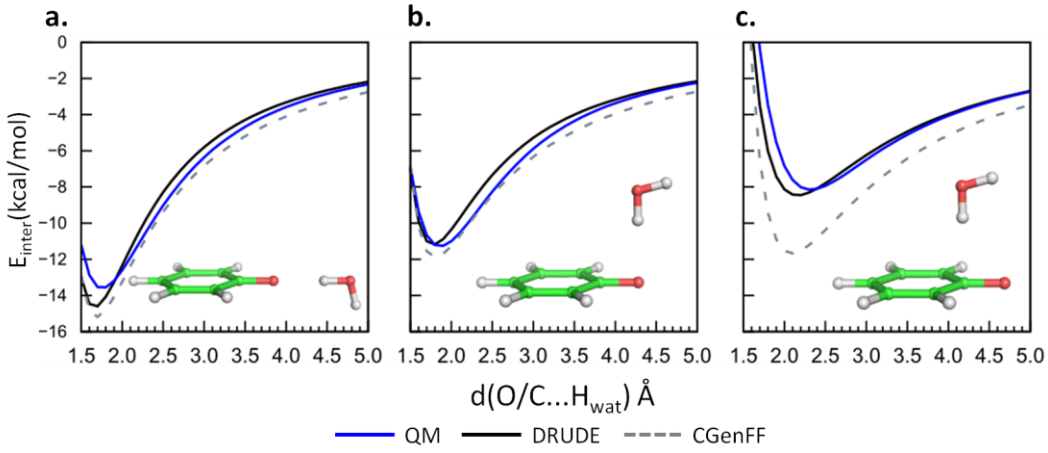

Table S3. Internal parameters of bond lengths (Å) and angles (°) from QM and Drude model for each molecular ion with differences (Diff.) compared to QM values. The atoms of the corresponding bonds/angles are provided based on their atom names in the topology file in Table S5. Repeated bonds/angles in the same molecular ion are not shown.

Bond/Angle	Atoms	QM	Drude	Diff.	Atoms	QM	Drude	Diff.
Mol.	**NH4**							
Bond	N-HN1	1.03	1.03	0.00				
Angle	HN1-N-HN2	109.47	109.47	0.00				
Mol.	**NC1**				**NC2**			
Bond	N-C1	1.51	1.53	0.02	N-C1	1.51	1.52	0.01
	N-HN2	1.03	1.03	0.00	N-HN3	1.03	1.03	0.00
	C1-H11	1.10	1.09	-0.01	C1-H11	1.10	1.08	-0.01
Angle	C1-N-HN2	111.49	111.17	-0.32	C1-N-HN3	109.32	109.93	0.61
	HN2-N-HN3	107.38	107.72	0.34	HN3-N-HN4	105.83	107.99	2.16
	N-C1-H11	108.04	110.89	2.86	N-C1-H11	108.04	110.14	2.10
	H11-C1-H12	110.87	108.01	-2.85	H11-C1-H12	110.52	108.72	-1.81
					C1-N-C2	113.46	109.14	-4.32
Mol.	**NC3**				**NC4**			
Bond	N-C1	1.50	1.51	0.01	N-C1	1.50	1.49	-0.01
	C1-H11	1.10	1.08	-0.02	C1-H11	1.10	1.08	-0.02
	N-HN4	1.03	1.03	0.00				
Angle	C1-N-C2	111.32	108.96	-2.35	C1-N-C2	109.47	109.47	0.00
	N-C1-H11	108.81	109.94	1.13	N-C1-H11	108.62	110.35	1.73
	H11-C1-H12	110.40	109.05	-1.35	H11-C1-H12	110.31	108.58	-1.73
	C1-N-HN4	107.56	109.98	2.42				
Mol.	**IMIM**				**ACET**			
Bond	CG-HG	1.09	1.09	0.00	C1-H1	1.10	1.11	0.01
	CG-CD2	1.38	1.37	-0.02	C1-C2	1.56	1.55	-0.01
	CG-ND1	1.38	1.38	0.00	C2-O1	1.27	1.27	0.00
	ND1-HD1	1.02	1.01	-0.01				
	ND1-CE1	1.35	1.35	0.00				
Angle	HG-CG-CD2	130.97	129.05	-1.92	H1-C1-H2	109.65	108.83	-0.82
	HG-CG-ND1	122.74	124.31	1.58	H1-C1-C2	111.50	111.34	-0.16
	CD2-CG-ND1	106.29	106.64	0.35	C1-C2-O1	114.98	114.89	-0.09
	CG-ND1-HD1	125.55	124.20	-1.35	O1-C2-O2	128.64	128.74	0.09
	CG-ND1-CE1	110.45	110.13	-0.32				
	HD1-ND1-CE1	124.01	125.68	1.67				
	ND1-CE1-NE2	106.52	106.47	-0.05				
	ND1-CE1-HE1	126.74	126.77	0.03				
Mol.	**GUAN**				**MGUAN**			
Bond	C-N1	1.34	1.35	0.01	C-N1	1.35	1.35	0.00
	N1-H11	1.01	1.00	-0.01	N1-H11	1.01	1.00	-0.01
					C2-HC1	1.10	1.08	-0.02
Angle	N1-C-N2	120.00	120.00	0.00	N1-C-N2	119.60	118.84	-0.76
	C-N1-H11	121.23	121.79	0.56	C-N1-H11	121.26	121.79	0.53
	H11-N1-H12	117.55	116.41	-1.14	H11-N1-H12	117.53	115.63	-1.90
					C-N3-C2	123.60	121.34	-2.26
					H31-N3-C2	118.64	119.86	1.22
					N3-C2-HC1	107.74	108.87	1.13
					HC1-C2-HC2	108.48	109.61	1.13
Mol.	**MES**				**ETS**			
Bond	C1-H11	1.11	1.11	0.00	C1-H11	1.11	1.11	0.00
	C1-S1	1.85	1.83	-0.01	C1-S1	1.84	1.81	-0.03
					C1-C2	1.54	1.53	-0.01
Angle	H11-C1-H12	107.15	107.50	0.34	H11-C1-H12	106.65	109.02	2.37
	H11-C1-S1	111.70	111.38	-0.32	H11-C1-S1	110.07	106.54	-3.53

					S1-C1-C2	112.87	113.28	0.41
					H11-C1-C2	108.48	110.62	2.14
					C1-C2-H21	112.06	110.89	-1.17
					H21-C2-H22	108.83	107.91	-0.92
Mol.	**PHET**							
Bond	CG-HG	1.10	1.08	-0.02				
	CG-CD1	1.41	1.40	-0.01				
	CE1-CZ	1.45	1.44	-0.02				
	CZ-OH	1.29	1.27	-0.02				
Angle	HG-CG-CD1	121.15	119.17	-1.98				
	CD1-CG-CD2	117.69	121.66	3.97				
	CD1-CE1-CZ	122.99	122.43	-0.55				
	HE1-CE1-CZ	116.94	116.71	-0.24				
	CE1-CZ-CE2	113.61	115.87	2.26				
	CE1-CZ-OH	123.20	122.07	-1.13				

Table S4. QM and Drude vibrational spectra of molecular ions. Frequencies in cm^{-1} with the percent contribution, %, of the reported normal mode to the associated frequency shown.

NH4	QM	Assignment	%	Assignment	%	DRUDE	Assignment	%	Assignment	%
1	1431.1	daNH	38	rNH	38	1462.8	daNH	34	rNH	34
2	1431.1	dsNH	76			1462.9	dsNH	68	rNH	16
3	1431.2	daNH'	50	rNH'	50	1462.9	rNH'	50	daNH'	50
4	1683.6	rNH	50	daNH	50	1654.8	daNH	50	rNH	50
5	1683.6	rNH'	50	daNH'	50	1654.9	daNH'	50	rNH'	50
6	3308.1	sN-H	100			3208.4	sN-H	100		
7	3460.3	sN-H	100			3364.5	sN-H	100		
8	3460.3	sN-H	100			3364.5	sN-H	100		
9	3460.3	sN-H	100			3364.5	sN-H	100		
NC1	QM					DRUDE				
1	295.8	torN-C1	100			267.4	torN-C1	100		
2	891.8	rNH	59	rC1H	36	915.2	sN-C1	94		
3	891.8	rNH'	59	rC1H'	36	918.5	rNH	70		
4	943.6	sN-C1	102			918.6	rNH'	70		
5	1252.2	rC1H	48	rNH	32	1112.9	rC1H	60		
6	1252.2	rC1H'	48	rNH'	32	1112.9	rC1H'	60		
7	1428.9	dsC1H	99			1422.6	daC1H	54	daC1H'	30
8	1468.3	daC1H	68	daC1H'	18	1422.6	daC1H'	54	daC1H	30
9	1468.3	daC1H'	68	daC1H	18	1497.2	dsC1H	98		
10	1485.0	dsNH	97			1522.9	dsNH	92		
11	1628.5	daNH'	86			1572.6	daNH	58	daNH'	37
12	1628.5	daNH	86			1572.6	daNH'	58	daNH	37
13	3059.1	sC1-H	100			2924.5	sC1-H	100		
14	3180.9	sC1-H	100			2924.5	sC1-H	100		
15	3180.9	sC1-H	100			3049.0	sC1-H	100		
16	3339.9	sN-H	100			3264.6	sN-H	100		
17	3446.0	sN-H	100			3368.6	sN-H	100		
18	3446.0	sN-H	100			3368.6	sN-H	100		
NC2	QM					DRUDE				
1	196.6	torN-C1	50	torN-C2	50	216.5	torN-C1	50	torN-C2	50
2	272.4	torN-C2	48	torN-C1	48	243.1	torN-C2	48	torN-C1	48
3	378.2	dNCC	90			416.4	dNCC	94		
4	798.7	rNH	70			780.7	rNH	86		
5	861.4	sN-C1	92			869.4	sN-C1	88		
6	998.7	sN-C1	61			924.0	sN-C1	77	wNH	17
7	1003.5	rC2H	27	rC1H	27	1039.0	rC2H	26	rC1H	26
8	1058.1	sN-C1	40	rC2H'	16	1058.5	rC1H'	28	rC2H'	28
9	1222.4	rC1H'	26	rC2H'	26	1134.5	rC2H	28	rC1H	28
10	1246.9	rNH	26	rC2H	23	1138.8	iNH	80		
11	1361.8	iNH	71			1138.8	rC1H'	27	rC2H'	27
12	1385.4	wNH	79			1334.2	wNH	68	sN-C1	21
13	1410.1	dsC1H	51	dsC2H	51	1424.5	daC1H	33	daC2H	33
14	1438.6	dsC2H	51	dsC1H	51	1428.1	daC1H'	31	daC2H'	31
15	1458.3	daC1H	30	daC2H	30	1428.2	daC2H'	32	daC1H'	32
16	1459.3	daC2H'	30	daC1H'	30	1429.9	daC2H	32	daC1H	32
17	1471.1	daC1H'	32	daC2H'	32	1471.3	dsC1H	50	dsC2H	50
18	1475.5	daC2H	32	daC1H	32	1477.5	dsC2H	49	dsC1H	49
19	1619.1	cN-H	101			1574.4	cN-H	98		
20	3045.1	sC2-H	50	sC1-H	50	2924.0	sC1-H	50	sC2-H	50
21	3046.0	sC1-H	50	sC2-H	50	2924.4	sC2-H	50	sC1-H	50
22	3164.3	sC1-H	50	sC2-H	50	2925.1	sC1-H	50	sC2-H	50
23	3164.4	sC2-H	50	sC1-H	50	2926.3	sC2-H	50	sC1-H	50
24	3164.5	sC1-H	50	sC2-H	50	3047.5	sC1-H	50	sC2-H	50
25	3165.1	sC2-H	50	sC1-H	50	3048.6	sC2-H	50	sC1-H	50
26	3361.7	sN-H	100			3307.7	sN-H	100		

27	3426.7	sN-H	100			3375.2	sN-H	100		
NC3	QM					DRUDE				
1	184.0	torN-C1	33	torN-C3	33	233.2	torN-C2	34	torN-C3	33
2	266.0	torN-C1	62	torN-C3	25	254.5	torN-C2	61	torN-C3	34
3	266.0	torN-C2	55	torN-C3	39	254.6	torN-C1	62	torN-C3	32
4	389.4	dC3NC1	58	dC1NC2	19	393.4	dC3NC1	58	dC1NC2	29
5	389.4	dC2NC3	47	dC1NC2	39	393.4	dC2NC3	57	dC1NC2	32
6	447.4	dC2NC3	28	dC3NC1	28	453.6	dC2NC3	30	dC1NC2	30
7	798.3	sN-C1	93			839.1	sN-C1	88		
8	974.6	sN-C1	73			925.1	sN-C1	69		
9	974.6	sN-C1	73			925.1	sN-C1	69		
10	1029.3	rC1H'	35			1042.6	rC1H'	38	rC3H'	22
11	1029.3	rC3H'	28	rC2H'	25	1042.6	rC2H'	37	rC3H'	19
12	1046.0	rC3H	23	rC1H	23	1046.2	rC1H	22	rC2H	22
13	1228.4	rC1H	28	sN-C1	16	1131.4	rNH	32	rC2H	23
14	1228.4	rC3H	20	sN-C1	16	1131.4	rNH'	32	rC1H	23
15	1248.4	rC3H'	17	rC2H'	17	1181.4	rC2H'	17	rC3H'	17
16	1389.2	rNH	71			1314.9	rNH	46	sN-C1	21
17	1389.2	rNH'	71			1314.9	rNH'	46	sN-C1	21
18	1405.5	dsC1H	60	dsC2H	37	1422.9	daC3H	22	daC2H	22
19	1405.5	dsC3H	64	dsC2H	30	1424.5	daC2H'	38	daC3H'	19
20	1438.9	daC2H	23	daC3H	23	1424.5	daC1H'	39	daC3H'	24
21	1449.4	dsC2H	33	dsC3H	33	1436.8	daC1H'	20	daC3H'	20
22	1454.5	daC2H'	35	daC1H'	34	1442.9	daC1H	38	daC3H	19
23	1454.5	daC3H'	36			1442.9	daC2H	38	daC3H	21
24	1471.2	daC1H	23	daC2H	19	1464.9	dsC2H	60	dsC3H	33
25	1471.2	daC3H	36	daC2H	18	1464.9	dsC1H	60	dsC3H	31
26	1485.8	daC2H'	21	daC1H'	21	1485.4	dsC1H	32	dsC3H	32
27	3034.5	sC1-H	61	sC3-H	36	2921.8	sC2-H	34	sC3-H	33
28	3034.5	sC2-H	64	sC3-H	30	2922.4	sC2-H	62	sC3-H	34
29	3035.7	sC3-H	33	sC1-H	33	2922.4	sC1-H	62	sC3-H	33
30	3149.3	sC1-H	57	sC3-H	41	2925.8	sC2-H	62	sC3-H	34
31	3149.3	sC2-H	65	sC3-H	26	2925.9	sC1-H	63	sC3-H	33
32	3151.0	sC3-H	33	sC1-H	33	2927.2	sC1-H	33	sC3-H	33
33	3153.1	sC3-H	33	sC1-H	33	3044.9	sC2-H	62	sC3-H	34
34	3156.2	sC2-H	66	sC3-H	24	3044.9	sC1-H	63	sC3-H	33
35	3156.2	sC1-H	56	sC3-H	43	3050.7	sC1-H	33	sC3-H	33
36	3373.8	sN-H	100			3353.6	sN-H	100		
NC4	QM					DRUDE				
1	167.1	torN-C1	25	torN-C3	25	260.6	torN-C3	25	torN-C2	25
2	295.3	torN-C3	62	torN-C1	30	289.3	torN-C3	59	torN-C2	39
3	295.3	torN-C1	45	torN-C4	35	289.3	torN-C4	61	torN-C2	29
4	295.3	torN-C2	62	torN-C4	32	289.4	torN-C1	75		
5	358.6	rNC	41	daNC	41	381.0	rNC	47	daNC	47
6	358.6	daNC'	41	rNC'	41	381.0	daNC'	47	rNC'	47
7	444.7	daNC'	33	rNC'	33	435.4	daNC	44	rNC	44
8	444.7	daNC	41	rNC	41	435.4	dsNC	85		
9	444.7	dsNC	66			435.4	rNC'	42	daNC'	42
10	737.7	sN-C1	101			764.8	sN-C1	98		
11	950.9	sN-C1	76			943.6	sN-C1	58		
12	950.9	sN-C1	76			943.6	sN-C1	58		
13	950.9	sN-C1	76			943.6	sN-C1	58		
14	1044.0	rC1H'	23	rC4H	18	1027.1	rC2H	25	rC1H	25
15	1044.0	rC2H'	21	rC3H	18	1027.1	rC4H	33	rC1H'	26
16	1044.0	rC1H	23	rC2H	23	1027.1	rC2H'	30	rC3H'	30
17	1152.8	rC3H'	21	rC2H	17	1072.6	rC4H'	22	rC3H	17
18	1152.8	rC3H	21	rC1H'	17	1072.6	rC4H	22	rC3H'	17
19	1280.0	sN-C1	18			1290.4	sN-C1	30		
20	1280.0	rC3H	18	sN-C1	18	1290.4	sN-C1	30		

21	1280.0	rC1H	18	sN-C1	18	1290.4	sN-C1	30		
22	1403.6	dsC3H	58	dsC4H	42	1422.9	daC3H'	30	daC2H'	30
23	1403.6	dsC1H	64	dsC4H	26	1422.9	daC3H	32	daC1H'	23
24	1403.6	dsC2H	76			1422.9	daC4H	26	daC1H	23
25	1440.7	daC1H'	34	daC3H	27	1437.9	daC4H	23	daC2H'	17
26	1440.7	daC3H'	32	daC2H'	30	1437.9	daC4H'	23	daC2H	17
27	1440.7	daC1H	32	daC2H	32	1451.6	daC1H'	20	daC2H'	20
28	1450.4	daC2H'	22	daC1H'	22	1451.6	daC4H'	28	daC1H	22
29	1450.4	daC2H	22	daC1H	22	1451.6	daC3H	25	daC2H	25
30	1462.3	dsC2H	25	dsC1H	25	1467.9	dsC3H	56	dsC2H	39
31	1485.7	daC2H'	27	daC1H'	27	1467.9	dsC4H	59	dsC2H	26
32	1485.7	daC4H'	20	daC1H	18	1467.9	dsC1H	71		
33	1485.7	daC2H	27			1498.8	dsC1H	24	dsC4H	24
34	3026.7	sC3-H	75			2918.0	sC1-H	37	sC4-H	37
35	3026.7	sC2-H	64	sC1-H	20	2918.0	sC1-H	37	sC3-H	33
36	3026.7	sC1-H	50	sC4-H	49	2918.0	sC3-H	35	sC2-H	34
37	3031.2	sC4-H	25	sC1-H	25	2920.9	sC1-H	25	sC4-H	25
38	3141.7	sC1-H	32	sC4-H	26	2920.9	sC1-H	25	sC2-H	25
39	3141.7	sC3-H	35	sC1-H	33	2924.6	sC3-H	35	sC2-H	34
40	3141.7	sC4-H	36	sC2-H	30	2924.6	sC1-H	37	sC3-H	33
41	3143.6	sC2-H	25	sC1-H	25	2924.6	sC1-H	38	sC4-H	37
42	3143.6	sC1-H	25	sC4-H	25	3041.5	sC3-H	59	sC2-H	40
43	3147.3	sC4-H	37	sC3-H	35	3041.5	sC4-H	62	sC2-H	28
44	3147.3	sC3-H	37	sC2-H	30	3041.6	sC1-H	75		
45	3147.3	sC1-H	37	sC4-H	33	3050.5	sC1-H	25	sC4-H	25
IMIM	QM					DRUDE				
1	605.7	t5RNG1	75	t5RNG1a	40	507.0	wNE2H	39	wND1H	39
2	618.0	t5RNG1a	67	t5RNG1	35	530.9	wND1H	36	wNE2H	36
3	687.8	wND1H	49	wNE2H	49	645.9	wCE1H	35	wCGH	18
4	723.1	wCE1H	40	wNE2H	16	704.7	t5RNG1	45	t5RNG1a	24
5	745.5	wCGH	34	wCD2H	34	714.0	wCD2H	32	wCGH	32
6	808.7	wCE1H	61	wND1H	19	865.8	wCE1H	44	t5RNG1a	24
7	828.9	wCD2H	55	wCGH	55	886.3	d5RNG1a	46	d5RNG1	24
8	886.1	d5RNG1a	59	d5RNG1	31	887.3	d5RNG1	46	d5RNG1a	24
9	908.1	d5RNG1	57	d5RNG1a	30	951.4	wCD2H	48	wCGH	48
10	1049.7	sCG-ND1	21	sNE2-CD2	21	1018.8	sNE2-CD2	24	sCG-ND1	24
11	1083.3	sCD2-CG	24	dCGH	20	1032.8	dCE1H	33		
12	1121.7	sNE2-CD2	24	sCG-ND1	24	1081.4	dCD2H	30	dCGH	30
13	1163.1	dCE1H	45			1169.3	dCE1H	45	dCD2H	17
14	1180.4	sCE1-NE2	26	sND1-CE1	26	1195.2	dNE2H	19	dND1H	19
15	1310.9	dCGH	26	dCD2H	26	1379.2	dNE2H	32	dND1H	32
16	1430.9	sCD2-CG	26			1495.8	dCE1H	19	sCE1-NE2	16
17	1446.3	sNE2-CD2	21	sCG-ND1	21	1561.5	sCD2-CG	33	dND1H	21
18	1538.3	sCE1-NE2	35	sND1-CE1	35	1593.8	sCE1-NE2	16	sND1-CE1	16
19	1568.2	sCD2-CG	37			1600.0	sCD2-CG	20	sCG-ND1	16
20	3249.0	sCD2-HD2	50	sCG-HG	50	3062.5	sCE1-HE1	99		
21	3254.6	sCE1-HE1	95			3160.7	sCD2-HD2	50	sCG-HG	50
22	3266.9	sCG-HG	48	sCD2-HD2	48	3165.9	sCG-HG	50	sCD2-HD2	50
23	3531.2	sND1-HD1	50	sNE2-HE2	50	3513.9	sNE2-HE2	50	sND1-HD1	50
24	3537.2	sNE2-HE2	50	sND1-HD1	50	3519.8	sND1-HD1	50	sNE2-HE2	50
GUAN	QM					DRUDE				
1	229.5	torC-N3	33	torC-N1	33	370.5	wCN1	57		
2	300.2	wN3C	53	wN1C	45	386.6	wN3C	53		
3	300.2	wN2C	65	wN1C	21	386.6	wN1C	40	wN2C	39
4	386.8	wN3C	35	wN2C	35	452.7	torC-N2	33	torC-N1	33
5	482	dN2CN3	73			495.3	dN2CN3	88		
6	482	dCN	73			495.4	dCN	88		
7	557	torC-N2	51	torC-N1	37	529.6	torC-N2	48	torC-N3	27
8	557	torC-N3	58	torC-N1	22	529.6	torC-N1	50	torC-N3	25

9	683.8	wCN1	100			687	wCN1	43	wN3C	19
10	1007.6	sC-N1	97			975.4	sC-N1	89		
11	1018.3	dN2C	32	dN3C	32	1056.5	dN3C	33	dN2C	33
12	1092.8	dN3C	39	dN1C	32	1096.8	dN3C	39	sC-N1	28
13	1092.8	dN2C	47	sC-N1	22	1096.8	dN1C	41	sC-N1	28
14	1557	dN2H21	37	dN1H11	28	1472.1	dN1H11	33	sC-N1	20
15	1557	dN3H31	43	sC-N1	21	1472.1	dN3H31	31	sC-N1	20
16	1655.2	dN2H21	32	dN1H11	32	1638.4	dN3H31	30	dN2H21	30
17	1688.6	sC-N1	54	dN3H31	19	1681.9	sC-N1	50	dN3H31	25
18	1688.6	sC-N1	54	dN2H21	22	1682	sC-N1	50	dN1H11	27
19	3520.8	sN2-H	63	sN3-H	31	3323	sN3-H	60	sN2-H	37
20	3520.8	sN1-H	61	sN3-H	36	3323	sN1-H	64	sN2-H	29
21	3535.5	sN1-H	33	sN3-H	33	3344	sN1-H	33	sN2-H	33
22	3655.8	sN2-H	33	sN3-H	33	3419.5	sN3-H	33	sN2-H	33
23	3658.9	sN2-H	65	sN3-H	28	3431.2	sN3-H	60	sN2-H	37
24	3658.9	sN1-H	59	sN3-H	39	3431.2	sN1-H	64	sN2-H	29
MGUAN	QM					DRUDE				
1	110.4	torC-N3	54	torN3-C2	16	82.7	torN3-C2	101		
2	156.1	torN3-C2	82			127	torC-N3	57	wN3H31	35
3	213.1	wN1C	79	wN2C	17	287.1	dCN3C2	60	dN2CN3	34
4	256.7	wN3H31	41	torC-N1	23	383.4	wN2C	38	wCN1	37
5	277.8	dCN3C2	46	dN2CN3	22	400.7	wN1C	45	wN2C	22
6	318.8	wN2C	62	wN1C	16	435.5	torC-N1	57		
7	458.5	dCN	64			470.8	dCN	77		
8	501	torC-N3	35	torC-N1	30	486.7	torC-N2	57	wN1C	17
9	540.9	torC-N2	66	torC-N1	23	547	torC-N1	36	wN3H31	20
10	571	dN2CN3	49	dCN3C2	21	561	dN2CN3	53	dCN3C2	18
11	690.3	wCN1	99			697.4	wCN1	41	wN3H31	21
12	905.2	sC-N1	47	sN3-C2	27	878.7	sN3-C2	34	sC-N1	28
13	1035.4	dN1C	49	dN2C	34	1015.4	sC-N1	49	sN3-C2	26
14	1058.4	sC-N1	40	dN2C	34	1069.1	dN2C	50	rC2H	17
15	1126	rC2H'	89			1071.8	rC2H'	86		
16	1148.9	rC2H	23	sC-N1	22	1079.8	dN1C	36	rC2H	30
17	1167	rC2H	40	sN3-C2	34	1126.3	dN2C	21	sC-N1	20
18	1398.5	dN3H	52	sC-N1	17	1391.9	sC-N1	27	dN1H11	21
19	1417.5	dsC2H	83			1402.9	daC2H	84		
20	1460.2	daC2H'	86			1409	daC2H'	87		
21	1480	daC2H	76			1476.9	dsC2H	76		
22	1557.8	dN2H21	43	sC-N1	17	1503	dN2H21	33	sC-N1	21
23	1627.4	dN1H11	58	dN2H21	16	1639.6	dN1H11	63		
24	1679.7	sC-N1	50	dN2H21	37	1676	sC-N1	49	dN2H21	44
25	1687.4	sC-N1	56	dN1H11	19	1718.7	sC-N1	47	dN3H	33
26	3015.1	sC2-H	100			2874.9	sC2-H	100		
27	3107.2	sC2-H	100			2874.9	sC2-H	100		
28	3153	sC2-H	100			2995.9	sC2-H	100		
29	3528.4	sN1-H	54	sN2-H	45	3322.8	sN1-H	50	sN2-H	49
30	3535.8	sN2-H	53	sN1-H	44	3336.2	sN2-H	49	sN1-H	47
31	3562.7	sN3-H	97			3381.9	sN3-H	95		
32	3663.5	sN2-H	59	sN1-H	41	3421.8	sN2-H	52	sN1-H	46
33	3665.4	sN1-H	59	sN2-H	41	3430.1	sN1-H	52	sN2-H	47
ACET	QM					DRUDE				
1	26.1	torC1-C2	99			5.5	torC1-C2	98		
2	423.6	dO2C2C1	63	dC2O	25	418	dO2C2C1	71	dC2O	28
3	593.0	wC2O1	71	rC1H'	27	595.6	wC2O1	91		
4	605.3	dC2O	47	sC1-C2	31	629.2	sC1-C2	52	dC2O	34
5	859.0	sC1-C2	55	sC2-O1	22	901	sC1-C2	38	dC2O	31
6	968.2	rC1H	81			976.5	rC1H'	83		
7	999.8	rC1H'	67	wC2O1	29	1005.8	rC1H	89		
8	1270.8	dsC1H	84			1303.8	sC2-O1	74		

9	1321.8	sC2-O1	62			1360.9	dsC1H	75	daC1H	19
10	1419.3	daC1H	94			1420.4	daC1H'	90		
11	1433.8	daC1H'	94			1427.1	daC1H	71	dsC1H	20
12	1589.1	sC2-O1	91			1611.8	sC2-O1	93		
13	2974.0	sC1-H	100			2908.9	sC1-H	100		
14	3060.4	sC1-H	100			2967.8	sC1-H	100		
15	3077.8	sC1-H	100			2968.8	sC1-H	100		
MES	QM					DRUDE				
1	694.3	sC1-S1	103			689.8	sC1-S1	93		
2	911.9	rC1H'	97			831.4	rC1H'	57	rC1H	38
3	911.9	rC1H	97			831.5	rC1H	57	rC1H'	38
4	1270.8	dsC1H	102			1384.9	dsC1H	93		
5	1429.1	daC1H	95			1392.1	daC1H	77	daC1H'	18
6	1429.1	daC1H'	95			1392.1	daC1H'	77	daC1H	18
7	2925.9	sC1-H	100			2851.1	sC1-H	100		
8	2991.3	sC1-H	100			2907.2	sC1-H	100		
9	2991.3	sC1-H	100			2907.2	sC1-H	100		
ETS	QM					DRUDE				
1	262.8	torC1-C2	97			241.3	torC1-C2	94		
2	322.3	dC1CS	89			286.7	dC1CS	90		
3	662.6	sC1-S1	87			643.2	sC1-S1	78		
4	742.9	rC1H	61	rC2H'	33	657.3	rC1H	82		
5	953.1	rC2H	40	sC1-C2	33	953.7	rC2H	37	wC1H	29
6	981.0	iC1H	42	rC2H'	30	966.1	rC2H'	66	iC1H	28
7	1035.0	sC1-C2	58	rC2H	27	1026.4	sC1-C2	52	rC2H	39
8	1218.3	wC1H	84			1121	iC1H	62	rC2H'	23
9	1223.6	iC1H	56	rC2H'	29	1196.5	wC1H	54		
10	1322.5	dsC2H	97			1414.6	daC2H	40	cC1-H	38
11	1422.9	cC1-H	96			1423.5	dsC2H	75	cC1-H	21
12	1426.1	daC2H'	92			1425.1	daC2H'	92		
13	1445.0	daC2H	90			1431	daC2H	53	cC1-H	30
14	2920.8	sC2-H	72	sC1-H	28	2850.4	sC1-H	99		
15	2936.3	sC1-H	71	sC2-H	29	2887.8	sC1-H	99		
16	2968.4	sC1-H	99			2904.5	sC2-H	99		
17	3031.6	sC2-H	100			2958.3	sC2-H	100		
18	3071.2	sC2-H	99			2958.8	sC2-H	99		
PHET	QM					DRUDE				
1	174.6	ta6RNG1a	58	tp6RNG1	26	251.2	ta6RNG1a	54	wCZH	20
2	407.1	ta6RNG1	89	ta6RNG1a	30	395.9	dCZH	77		
3	423.8	dCZH	74			417.2	ta6RNG1	89	ta6RNG1a	30
4	469.1	tp6RNG1	38	ta6RNG1a	26	486.5	wCZH	41	ta6RNG1a	35
5	502.9	da6RNG1a	62	da6RNG1	21	499.2	da6RNG1a	35	sCZ-OH	26
6	584.1	da6RNG1	57	da6RNG1a	19	628.3	tp6RNG1	93	wCZH	15
7	597.5	tp6RNG1	55	wCZH	32	710.2	da6RNG1	59	da6RNG1a	20
8	681.6	wCGH	82			755.9	sCE1-CZ	25	sCZ-CE2	25
9	769.4	wCD1H	26	wCD2H	26	771.3	wCGH	36	wCD1H	21
10	794.0	sCE1-CZ	26	sCZ-CE2	26	864.4	wCD2H	35	wCD1H	35
11	797.1	wCZH	36	wCE1H	34	891.3	dt6RNG1	69		
12	845.7	wCD2H	38	wCD1H	38	967.1	wCGH	40	wCE2H	33
13	869.7	wCE1H	31	wCE2H	31	980.4	sCG-CD1	36	sCD2-CG	36
14	934.1	dt6RNG1	72			1002.8	sCE2-CD2	24	sCD1-CE1	24
15	997.5	sCG-CD1	31	sCD2-CG	31	1007.2	wCGH	34	wCD2H	28
16	1033.4	dCE2H	14	dCE1H	14	1017.0	wCE1H	40	wCE2H	40
17	1107.4	dCGH	46	dCD1H	19	1120.9	sCE2-CD2	20	sCD1-CE1	20
18	1125.3	dCD2H	20	dCD1H	20	1195.3	dCGH	29	dCD1H	20
19	1226.9	dCE2H	25	dCE1H	25	1195.5	sCZ-OH	40	dCE2H	18
20	1334.1	sCZ-OH	32			1222.5	dCE2H	26	dCE1H	26
21	1337.3	dCGH	22	sCZ-CE2	19	1410.3	dCGH	34	dCD2H	14
22	1454.2	sCD1-CE1	30	sCE2-CD2	30	1427.3	sCD1-CE1	19	sCE2-CD2	19

23	1480.7	sCZ-OH	40			1450.1	dCD1H	28	dCD2H	28
24	1524.7	sCD2-CG	32	sCG-CD1	32	1485.9	dCGH	25	sCG-CD1	17
25	1588.3	sCE2-CD2	20	sCD1-CE1	20	1524.9	sCZ-OH	14		
26	3070.2	sCD2-HD2	40	sCD1-HD1	40	3003.9	sCE1-HE1	50	sCE2-HE2	50
27	3074.8	sCD1-HD1	43	sCD2-HD2	43	3004.7	sCE2-HE2	50	sCE1-HE1	50
28	3106.8	sCE2-HE2	43	sCE1-HE1	42	3051.8	sCG-HG	98		
29	3107.4	sCE1-HE1	41	sCE2-HE2	41	3051.9	sCD2-HD2	50	sCD1-HD1	50
30	3128.7	sCG-HG	81			3055.7	sCD2-HD2	49	sCD1-HD1	49

Figure S7. Radial distribution functions (RDF) between the nitrogen of the positively charged model compounds. **a.** NH4, **b.** NC1, **c.** NC2, **d.** NC3, **e.** NC4, **f.** IMIM, **g.** GUAN and **h.** MGUAN, and water oxygen for the Drude (DRUDE, solid line) and additive (CGenFF, dotted line) models.

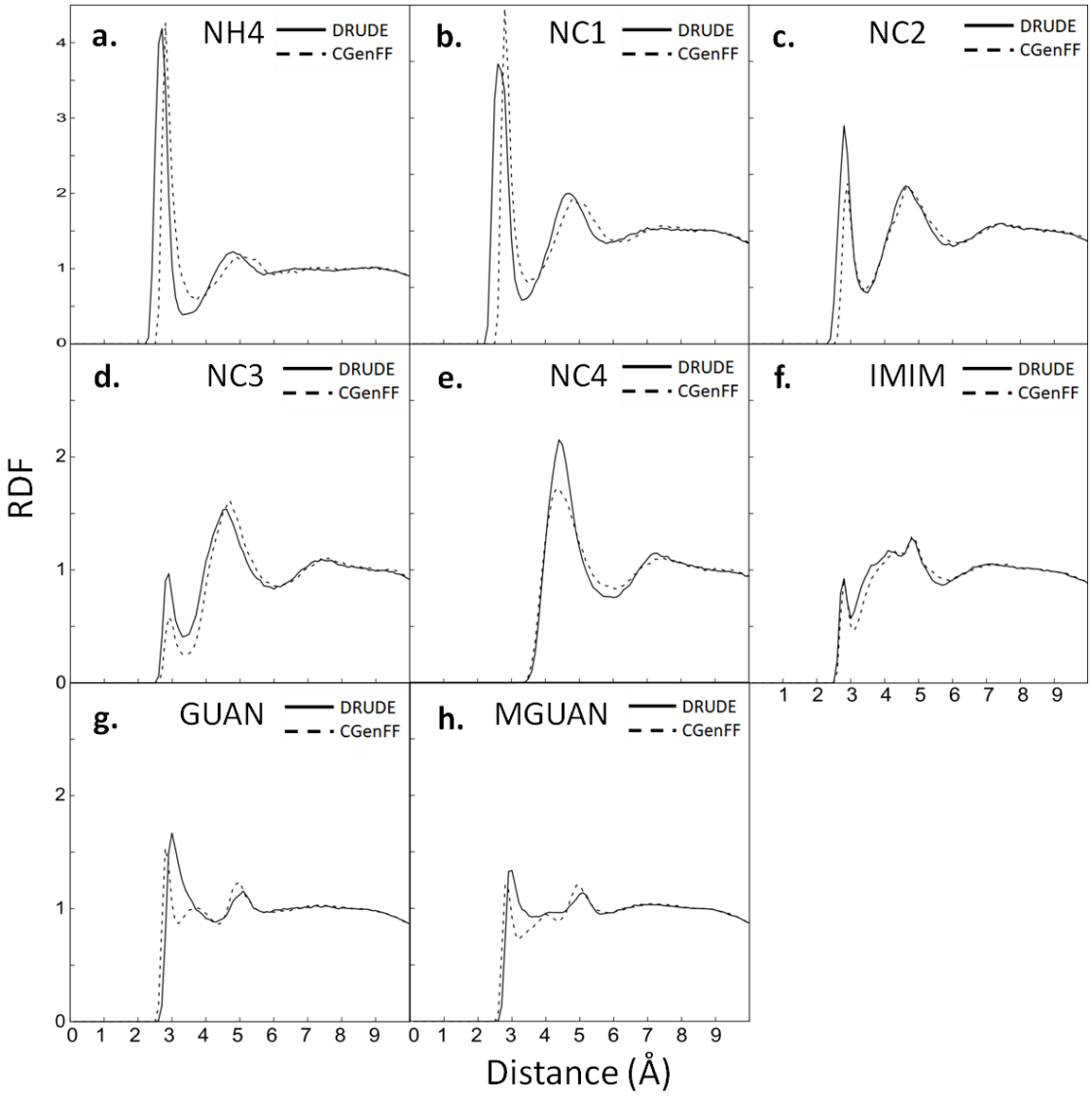

Figure S8. Radial distribution functions (RDF) between the sulfur/oxygen of the negatively charged model compounds. **a.** MES, **b.** ETS, **c.** ACET, and **d.** PHET, and water oxygen for the Drude (DRUDE, solid line) and additive (CGenFF, dotted line) models.

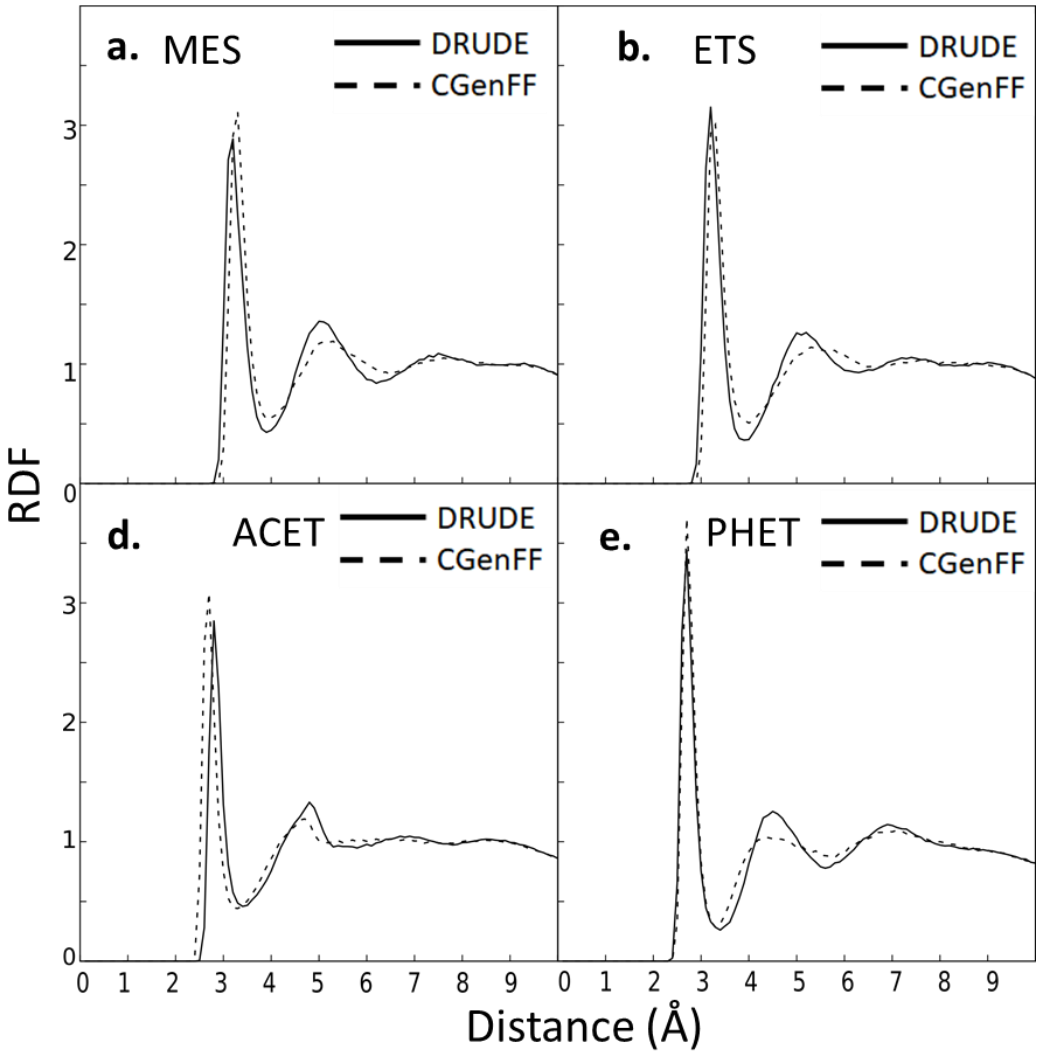

Figure S9. Spatial probability distributions of water molecules in the vicinity of methylammonium (NC1). Drude model of NC1 viewed from three perspectives are shown in **a-c**. Corresponding distributions for the additive CGenFF model are shown in **d-f.** Probabilities are calculated through n_{water_atoms}/N, where n_{water_atom} is the occupancy of water atoms occurring in a voxel of 0.25x0.25x0.25 $Å^3$, and N is the total occupancy over all the voxels. Surfaces are drawn to encompass voxels with probability larger than 0.0055.

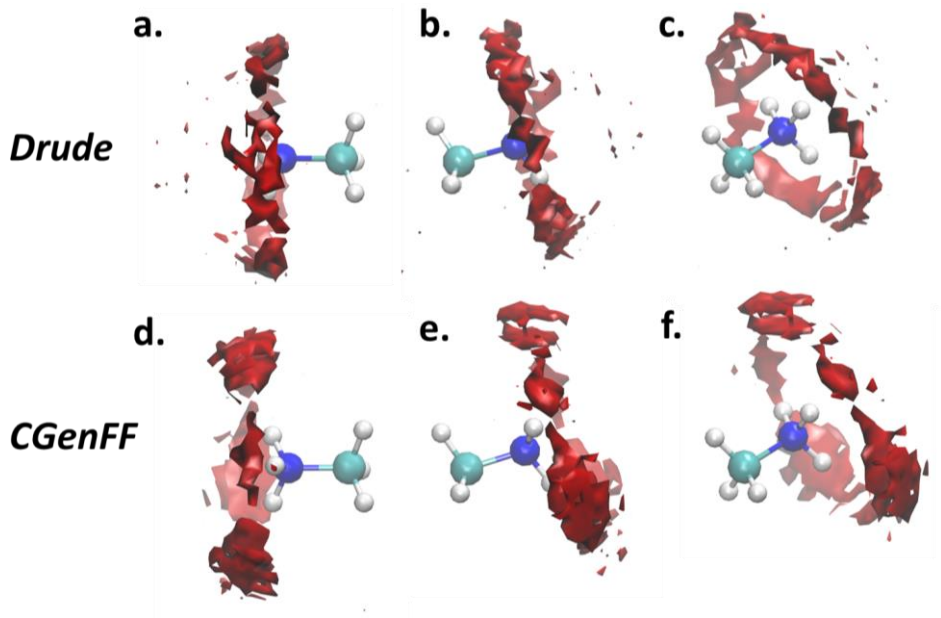

Figure S10. Spatial probability distributions of water molecules in the vicinity of dimethylammonium (NC2). Drude model of NC2 viewed from four perspectives are shown in **a**-**d**. Corresponding distributions for the additive CGenFF model are shown in **e**-**h.** Probabilities are calculated through n_{water_atoms}/N, where n_{water_atom} is the occupancy of water atoms occurring in a voxel of 0.25x0.25x0.25 $Å^3$, and N is the total occupancy over all the voxels. Surfaces are drawn to encompass voxels with probability larger than 0.0055.

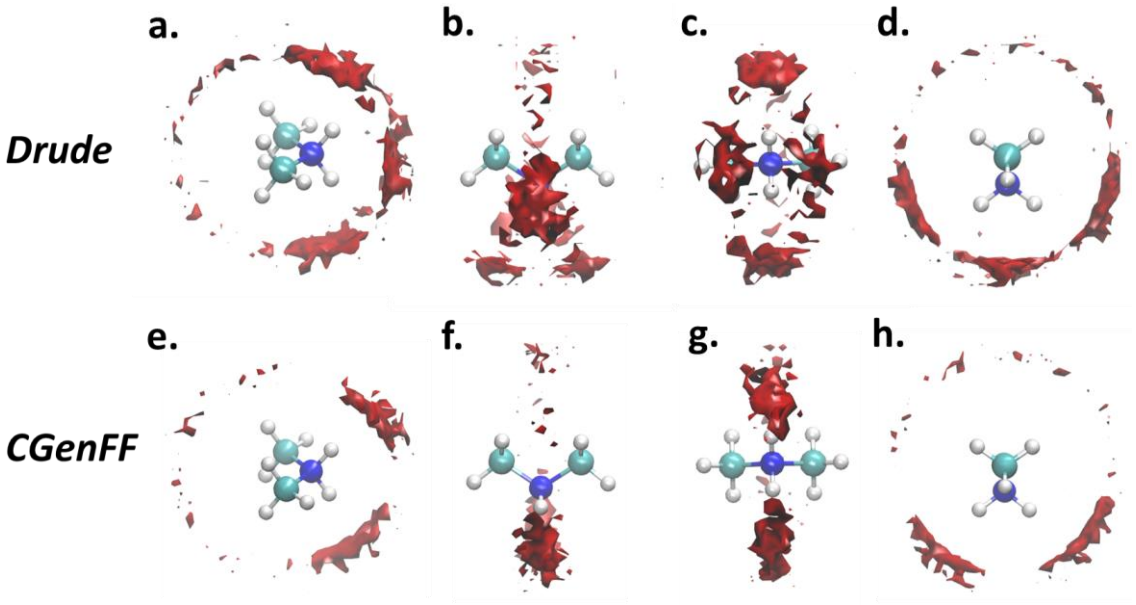

Figure S11. Spatial probability distributions of water molecules in the vicinity of tetramethylammonium (NC4). Drude model of NC4 viewed from two perspectives are shown in **a**-**b**. Corresponding distributions for the additive CGenFF model are shown in **c**-**d.** Probabilities are calculated through n_{water_atoms}/N, where n_{water_atom} is the occupancy of water atoms occurring in a voxel of 0.25x0.25x0.25 $Å^3$, and N is the total occupancy over all the voxels. Surfaces are drawn to encompass voxels with probability larger than 0.0055.

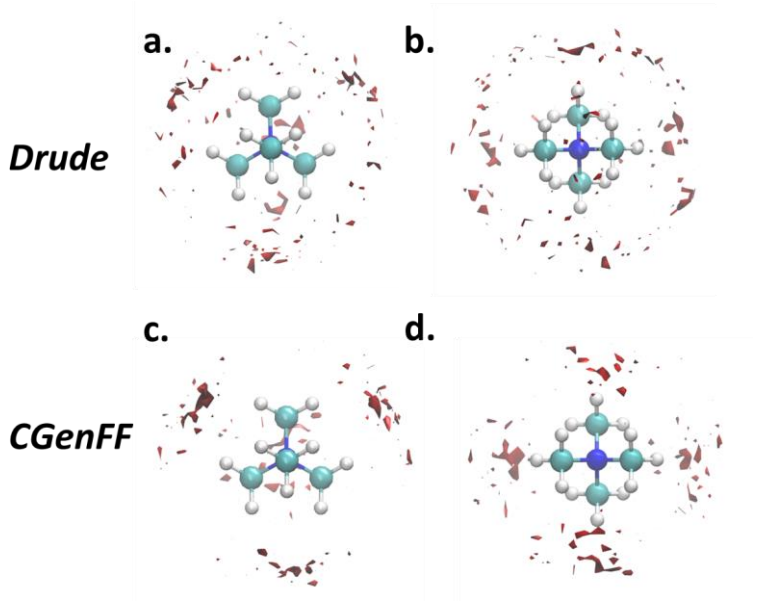

Figure S12. Spatial probability distributions of water molecules in the vicinity of imidazolium (IMIM). Drude model of IMIM viewed from two perspectives are shown in **a**-**b**. Corresponding distributions for the additive CGenFF model are shown in **c**-**d.** Probabilities are calculated through n_{water_atoms}/N, where n_{water_atom} is the occupancy of water atoms occurring in a voxel of 0.25x0.25x0.25 $Å^3$, and N is the total occupancy over all the voxels. Surfaces are drawn to encompass voxels with probability larger than 0.0055.

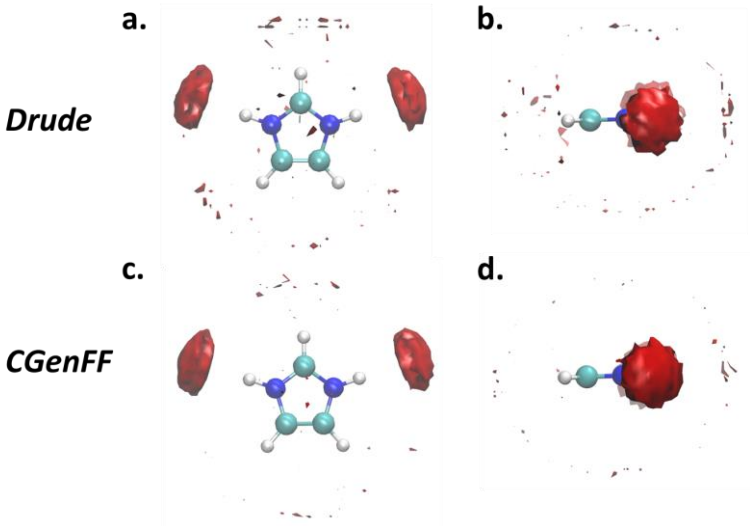

Figure S13. Spatial probability distributions of water molecules in the vicinity of methanethiolate (MES) and ethanethiolate (ETS). Drude model of MES viewed from orthogonal perspectives are shown in **a**-**b** and for ETS in **c**-**d.** Corresponding distributions for the additive CGenFF model are shown in **e**-**h.** Probabilities are calculated through n_{water_atoms}/N, where n_{water_atom} is the occupancy of water atoms occurring in a voxel of 0.25x0.25x0.25 $Å^3$, and N is the total occupancy over all the voxels. Surfaces are drawn to encompass voxels with probability larger than 0.0055.

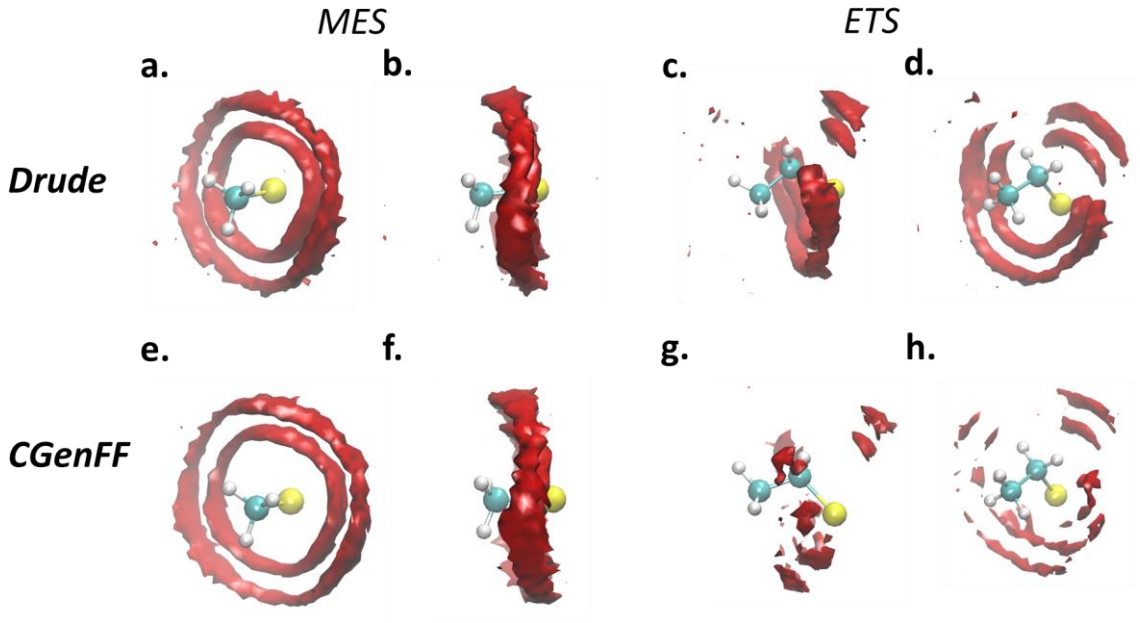

Table S5. Drude topology and parameter stream file for molecular ions.

```
* DRUDE topology and parameter stream file for molecular ions
* January 2018
*

read rtf card append
* Topology for drude model compounds
*
40

DEFA FIRS NONE LAST NONE
AUTOGENERATE ANGLES DIHEDRALS PATCH DRUDE

!molecular ions

RESI ACET         -1.000 ! acetate, Harder, Sep 09, fylin, jan16 only change the charges
!
!   H1      O1
!     \    //
! H2--C1--C2 (-1)
!     /    \
!   H3      O2
!
GROUP
ATOM C1   CD33A   -0.253  ALPHA -2.528  THOLE 1.414
ATOM H1   HDA3A    0.007
ATOM H2   HDA3A    0.007
ATOM H3   HDA3A    0.007
ATOM C2   CD2O2A   0.758  ALPHA -1.016  THOLE 0.899
ATOM O1   OD2C2A   0.003  ALPHA -0.699  THOLE 2.399
ATOM O2   OD2C2A   0.003  ALPHA -0.699  THOLE 2.399
ATOM LP1A LPD     -0.383
ATOM LP1B LPD     -0.383
ATOM LP2A LPD     -0.383
ATOM LP2B LPD     -0.383
BOND C1 C2  C2 O1  C2 O2
BOND C1 H1  C1 H2  C1 H3
BOND O1 LP1A O1 LP1B
BOND O2 LP2A O2 LP2B
IMPR O1 C1 O2 C2
LONEPAIR relative LP1A O1 C2 C1  distance 0.35 angle 110.0 dihe   0.0
LONEPAIR relative LP1B O1 C2 C1  distance 0.35 angle 110.0 dihe 180.0
ANISOTROPY O1 C2 LP1A LP1B A11 0.7229 A22 1.265
LONEPAIR relative LP2A O2 C2 C1  distance 0.35 angle 110.0 dihe   0.0
LONEPAIR relative LP2B O2 C2 C1  distance 0.35 angle 110.0 dihe 180.0
ANISOTROPY O2 C2 LP2A LP2B A11 0.7229 A22 1.265
IC  O1  C2 C1  H1   1.2543  118.04  180.00  111.57   1.1108
IC  O1  O2 *C2 C1   1.2543  122.88  180.00  119.08   1.5229
IC  H1  C2 *C1 H2   1.1108  111.57  120.15  110.12   1.1112
IC  H1  C2 *C1 H3   1.1108  111.57 -120.15  110.12   1.1112
IC  H1  C1 C2  O2   1.1108  111.57    0.00  119.08   1.2536
PATCH FIRST NONE LAST NONE

RESI PHET         -1.000 ! Phenolate, SXZ, fylin only change the charges
```

```
!RING p 6 CG CD1 CD2 CE1 CE2 CZ
!
!            HD1  HE1
!             |    |
!            CD1--CE1
!            /      \
!       HG--CG      CZ--O (-)
!            \      /
!            CD2--CE2
!             |    |
!            HD2  HE2
!
GROUP
ATOM CG   CD2R6A  -0.122   ALPHA -1.286   THOLE 1.210
ATOM HG   HDR6A    0.080
ATOM CD1  CD2R6A  -0.358   ALPHA -1.331   THOLE 1.364
ATOM HD1  HDR6A    0.222
ATOM CD2  CD2R6A  -0.358   ALPHA -1.331   THOLE 1.364
ATOM HD2  HDR6A    0.222
ATOM CE1  CD2R6A  -0.250   ALPHA -1.340   THOLE 1.394
ATOM HE1  HDR6A    0.030
ATOM CE2  CD2R6A  -0.250   ALPHA -1.340   THOLE 1.394
ATOM HE2  HDR6A    0.030
ATOM CZ   CD2R6I   0.390   ALPHA -1.169   THOLE 1.131
ATOM OH   OD31D   -0.636   ALPHA -0.728   THOLE 1.109
BOND CD1 CG CD2 CG CE1 CD1
BOND CE2 CD2 CZ CE1 CZ CE2
BOND CG HG CD1 HD1 CD2 HD2 CE1 HE1
BOND CE2 HE2 CZ OH
IC CG     CD1    CE1    CZ       0.0000    0.00    0.00    0.00   0.0000
IC CD1    CE1    CZ     CE2      0.0000    0.00    0.00    0.00   0.0000
IC CE1    CZ     CE2    CD2      0.0000    0.00    0.00    0.00   0.0000
IC CD1    CD2    *CG    HG       0.0000    0.00  180.00    0.00   0.0000
IC CE1    CG     *CD1   HD1      0.0000    0.00  180.00    0.00   0.0000
IC CE2    CG     *CD2   HD2      0.0000    0.00  180.00    0.00   0.0000
IC CZ     CD1    *CE1   HE1      0.0000    0.00  180.00    0.00   0.0000
IC CZ     CD2    *CE2   HE2      0.0000    0.00  180.00    0.00   0.0000
IC CE2    CE1    *CZ    OH       0.0000    0.00  180.00    0.00   0.0000
PATCH FIRST NONE LAST NONE

RESI MES          -1.000 ! methanethiolate, fylin, jan09, only change the charges
!
!  H1A
!     \
! H1B--C1--S1 (-)
!     /
!  H1C
!
GROUP
ATOM H11  HDA3A    0.071
ATOM H12  HDA3A    0.071
ATOM H13  HDA3A    0.071
ATOM C1   CD33A   -0.325  ALPHA -1.553  THOLE 1.300
ATOM S1   SD2C2A  -0.888  ALPHA -2.313  THOLE 1.300
```

```
ATOM LP1A LPR      0.000
BOND C1  S1
BOND C1  H11  C1 H12  C1  H13
BOND S1  LP1A
LONEPAIR relative LP1A S1 C1 H11 distance 0.45 angle 180.0 dihe 180.0
IC H11    C1     H12    S1       2.3848  143.76    0.00  109.54   1.8127
IC S1     H11    *C1    H12      1.8110  108.69   90.00  108.40   1.1110
IC S1     H11    *C1    H13      1.8110  108.69  180.00  108.40   1.1110
IC S1     H11    *C1    H12      0.0000    0.00   90.00    0.00   0.0000
IC S1     H11    *C1    H13      0.0000    0.00  180.00    0.00   0.0000
PATCH FIRST NONE LAST NONE

RESI ETS          -1.000 ! ethanethiolate, fylin, jan09, only change the charges
!
!  H21  H11  H12
!     \   \  /
! H22--C2--C1
!     /      \
!  H23        S1 (-)
!
GROUP
ATOM C1   CD32A  -0.428  ALPHA -1.404  THOLE 1.300
ATOM S1   SD2C2B -0.824  ALPHA -2.323  THOLE 1.300
ATOM H11  HDA2A   0.126
ATOM H12  HDA2A   0.126
ATOM C2   CD33A  -0.090  ALPHA -1.435  THOLE 1.496
ATOM H21  HDA3A   0.030
ATOM H22  HDA3A   0.030
ATOM H23  HDA3A   0.030
ATOM LP1A LPR     0.000
BOND C1  C2   C1  S1   C1  H11  C1  H12
BOND C2  H21  C2  H22  C2  H23
BOND S1  LP1A
LONEPAIR relative LP1A S1 C1 H11 distance 0.35 angle 180.0 dihe 180.0
IC C2     S1     *C1    H11      1.5264  113.24  121.62  106.59   1.1111
IC C2     S1     *C1    H12      1.5264  113.24 -121.62  106.59   1.1111
IC S1     C1     C2     H21      1.8093  113.24  180.00  110.86   1.1105
IC H21    C1     *C2    H22      1.1105  110.86  119.94  111.04   1.1111
IC H21    C1     *C2    H23      1.1105  110.86 -119.94  111.04   1.1111
IC C2     S1     *C1    H11      0.0000    0.00   90.00    0.00   0.0000
IC C2     S1     *C1    H12      0.0000    0.00  180.00    0.00   0.0000
PATCH FIRST NONE LAST NONE

RESI NH4           1.000 ! ammonium
                         ! LJ parameters of eps = -0.025 and Rmin/2 = 1.76
                         ! yields improved dGhyd of -81.3 kcal/mol for NH4
GROUP                   !                                      HN3
ATOM N    ND3P3A  -0.692  ALPHA -1.400           !              |
ATOM HN1  HDP1B    0.423                         !    HN2------N------HN4  (+)
ATOM HN2  HDP1B    0.423                         !              |
ATOM HN3  HDP1B    0.423                         !              |
ATOM HN4  HDP1B    0.423                         !             HN1
BOND N HN1 N HN2 N HN3 N HN4
PATCH FIRST NONE LAST NONE
```

```
RESI NC1           1.000 ! methylammonium
GROUP                    !                                      HN3
ATOM N    ND3P3A  -0.349 ALPHA -1.298 THOLE 0.895 !              |
ATOM C1   CD33A   -0.100 ALPHA -1.656 THOLE 0.895 !              |
ATOM HN2  HDP1B    0.340                           !    HN2------N------HN4      (+)
ATOM HN3  HDP1B    0.340                           !              |
ATOM HN4  HDP1B    0.340                           !              |
ATOM H11  HDA3C    0.143                           !         H11-C1-H13
ATOM H12  HDA3C    0.143                           !              |
ATOM H13  HDA3C    0.143                           !             H12
BOND N  C1  N  HN2 N  HN3 N HN4
BOND C1 H11 C1 H12 C1 H13
PATCH FIRST NONE LAST NONE

RESI NC2           1.000 ! dimethylammonium
GROUP                    !
ATOM N    ND3P2A  -0.070  ALPHA -1.479  THOLE 0.111 !             HN3
ATOM C1   CD33A   -0.043  ALPHA -1.578  THOLE 1.429 !    H23       |
ATOM C2   CD33A   -0.043  ALPHA -1.578  THOLE 1.429 !      |       |
ATOM HN3  HDP1B    0.266                            ! H22-C2------N------HN4      (+)
ATOM HN4  HDP1B    0.266                            !      |       |
ATOM H11  HDA3C    0.104                            !     H21      |
ATOM H12  HDA3C    0.104                            !        H11-C1-H13
ATOM H13  HDA3C    0.104                            !              |
ATOM H21  HDA3C    0.104                            !             H12
ATOM H22  HDA3C    0.104
ATOM H23  HDA3C    0.104
BOND N  C1  N  C2  N  HN3 N  HN4
BOND C1 H11 C1 H12 C1 H13
BOND C2 H21 C2 H22 C2 H23
PATCH FIRST NONE LAST NONE

RESI NC3           1.000 ! trimethylammonium fylin, new charges, jan9
GROUP                    !                                      H32
ATOM N    ND3P2A   0.209  ALPHA -0.661  THOLE 0.803 !              |
ATOM C1   CD33A   -0.107  ALPHA -1.527  THOLE 2.113 !         H31-C3-H33
ATOM C2   CD33A   -0.107  ALPHA -1.527  THOLE 2.113 !     H23      |
ATOM C3   CD33A   -0.107  ALPHA -1.527  THOLE 2.113 !      |       |
ATOM HN4  HDP1B    0.212                            ! H22-C2------N------HN4    (+)
ATOM H11  HDA3C    0.100                            !      |       |
ATOM H12  HDA3C    0.100                            !     H21      |
ATOM H13  HDA3C    0.100                            !        H11-C1-H13
ATOM H21  HDA3C    0.100                            !              |
ATOM H22  HDA3C    0.100                            !             H12
ATOM H23  HDA3C    0.100                            !
ATOM H31  HDA3C    0.100                            !
ATOM H32  HDA3C    0.100                            !
ATOM H33  HDA3C    0.100                            !
BOND N  C1  N  C2  N  C3  N  HN4
BOND C1 H11 C1 H12 C1 H13
BOND C2 H21 C2 H22 C2 H23
BOND C3 H31 C3 H32 C3 H33
PATCH FIRST NONE LAST NONE
```

```
RESI NC4           1.000 ! tetramethylammonium, fylin new charges
GROUP                    !
ATOM N    ND3P2A  -0.488  ALPHA -0.829  THOLE 0.793 !            H32
ATOM C1   CD33A   -0.288  ALPHA -1.793  THOLE 1.099 !             |
ATOM C2   CD33A   -0.288  ALPHA -1.793  THOLE 1.099 !        H31-C3-H33
ATOM C3   CD33A   -0.288  ALPHA -1.793  THOLE 1.099 !     H23     |      H41
ATOM C4   CD33A   -0.288  ALPHA -1.793  THOLE 1.099 !     |       |      |
ATOM H11  HDA3C    0.220                            ! H22-C2------N------C4-H42 (+)
ATOM H12  HDA3C    0.220                            !     |       |      |
ATOM H13  HDA3C    0.220                            !     H21     |      H43
ATOM H21  HDA3C    0.220                            !        H11-C1-H13
ATOM H22  HDA3C    0.220                            !             |
ATOM H23  HDA3C    0.220                            !             H12
ATOM H31  HDA3C    0.220
ATOM H32  HDA3C    0.220
ATOM H33  HDA3C    0.220
ATOM H41  HDA3C    0.220
ATOM H42  HDA3C    0.220
ATOM H43  HDA3C    0.220
BOND N  C1  N  C2  N  C3  N C4
BOND C1 H11 C1 H12 C1 H13
BOND C2 H21 C2 H22 C2 H23
BOND C3 H31 C3 H32 C3 H33
BOND C4 H41 C4 H42 C4 H43
IC C1    N     C2    H21    1.4948  109.47 -180.00  109.38   1.0795
IC C2    C1    *N    C3     1.4948  109.47  120.00  109.47   1.4948
IC C2    C1    *N    C4     1.4948  109.47 -120.00  109.47   1.4948
IC C2    N     C1    H11    1.4948  109.47 -180.00  109.38   1.0795
IC H11   N     *C1   H12    1.0795  109.38  120.00  109.38   1.0795
IC H11   N     *C1   H13    1.0795  109.38 -120.00  109.38   1.0795
IC H21   N     *C2   H22    1.0795  109.38  120.00  109.38   1.0795
IC H21   N     *C2   H23    1.0795  109.38 -120.00  109.38   1.0795
IC C1    N     C3    H31    1.4948  109.47  180.00  109.38   1.0795
IC H31   N     *C3   H32    1.0795  109.38  120.00  109.38   1.0795
IC H31   N     *C3   H33    1.0795  109.38 -120.00  109.38   1.0795
IC C1    N     C4    H41    1.4948  109.47 -180.00  109.38   1.0795
IC H41   N     *C4   H42    1.0795  109.38  120.00  109.38   1.0795
IC H41   N     *C4   H43    1.0795  109.38 -120.00  109.38   1.0795
PATCH FIRST NONE LAST NONE

RESI GUAN          1.000 ! guanidinium
GROUP
ATOM C    CD2N1A   1.315  ALPHA -1.359  THOLE 0.821 !      H11  H12
ATOM N1   ND2P1A  -0.821  ALPHA -1.155  THOLE 0.953 !        \  /
ATOM H11  HDP1B    0.358                            !         N1
ATOM H12  HDP1B    0.358                            !         |
ATOM N2   ND2P1A  -0.821  ALPHA -1.155  THOLE 0.953 !         C
ATOM H21  HDP1B    0.358                            !        / \
ATOM H22  HDP1B    0.358                            !  H21-N2   N3-H31
ATOM N3   ND2P1A  -0.821  ALPHA -1.155  THOLE 0.953 !       |   |
ATOM H31  HDP1B    0.358                            !     H22   H32
ATOM H32  HDP1B    0.358                            !
BOND C N1   C N2   C N3
```

```
BOND N1 H11 N1 H12 N2 H21  N2 H22  N3 H31  N3 H32
IMPR   C N2 N1 N3
IC N1     C      N2     H21      1.3402  120.00    0.00  121.39   0.9969
IC N2     N1     *C     N3       1.3402  120.00  180.00  120.00   1.3402
IC N2     C      *N1    H11      2.3212   30.00    0.00  121.39   0.9969
IC N2     C      *N1    H12      2.3212   30.00 -180.00  121.39   0.9969
IC N1     C      *N2    H22      2.3212   30.00  180.00  121.39   0.9969
IC N1     C      *N3    H31      2.3212   30.00    0.00  121.39   0.9969
IC N1     C      *N3    H32      2.3212   30.00 -180.00  121.39   0.9969
PATCH FIRST NONE LAST NONE

RESI MGUAN         1.000 ! methylguanidinium, fylin HDA3C is used instead of HDA3A
GROUP
ATOM  C   CD2N1A   1.067  ALPHA -1.418  THOLE 0.849 !      H11  H12
ATOM  N1  ND2P1A  -0.809  ALPHA -1.023  THOLE 0.886 !        \  /
ATOM  H11 HDP1B    0.375                            !         N1
ATOM  H12 HDP1B    0.375                            !         |
ATOM  N2  ND2P1A  -0.809  ALPHA -1.023  THOLE 0.886 !         C
ATOM  H21 HDP1B    0.375                            !        / \
ATOM  H22 HDP1B    0.375                            !  H21-N2   N3-H31
ATOM  N3  ND2P1A  -0.730  ALPHA -1.320  THOLE 0.630 !      |      |
ATOM  H31 HDP1B    0.404                            !    H22 HC2-C2-HC1
ATOM  C2  CD33A    0.173  ALPHA -1.700  THOLE 0.570 !            |
ATOM  HC1 HDA3C    0.068                            !           HC3
ATOM  HC2 HDA3C    0.068                            !
ATOM  HC3 HDA3C    0.068                            !
BOND C  N1   C N2   C N3
BOND N1 H11  N1 H12 N2 H21   N2 H22  N3 H31 N3 C2
BOND C2 HC1  C2 HC2 C2 HC3
IMPR   C N2 N1 N3
IC N1     C      N2     H21      1.3523  118.93    0.00  121.59   0.9999
IC N2     N1     *C     N3       1.3507  118.93  180.00  119.60   1.3613
IC N2     C      *N1    H11      2.3282   30.52    0.00  121.77   1.0000
IC N2     C      *N1    H12      2.3282   30.52 -180.00  122.27   0.9997
IC N1     C      *N2    H22      2.3282   30.55  180.00  122.39   0.9983
IC N1     C      *N3    H31      2.3453   30.09    0.00  118.52   1.0023
IC N1     C      *N3    C2       2.3453   30.09  180.00  121.90   1.5024
IC C      N3     C2     HC1      1.3613  121.90 -180.00  109.19   1.1142
IC HC1    N3     *C2    HC2      1.1142  109.19  119.25  110.12   1.1140
IC HC1    N3     *C2    HC3      1.1142  109.19 -119.25  110.12   1.1140
PATCH FIRST NONE LAST NONE

RESI IMIM          1.000 ! Imidazolium, EH
GROUP
ATOM CG   CD2R5D  -0.012  ALPHA -1.522  THOLE 1.196 !       HD1    HE1
ATOM HG   HDR5D    0.173                            !        |     /
ATOM CD2  CD2R5D  -0.012  ALPHA -1.522  THOLE 1.196 !       ND1--CE1
ATOM HD2  HDR5D    0.173                            !      /      |
ATOM ND1  ND2R5C  -0.171  ALPHA -1.260  THOLE 1.194 ! HG-CG       |
ATOM HD1  HDP1A    0.340                            !      \      |
ATOM NE2  ND2R5C  -0.171  ALPHA -1.260  THOLE 1.194 !      CD2--NE2
ATOM HE2  HDP1A    0.340                            !       |      \
ATOM CE1  CD2R5E   0.170  ALPHA -1.500  THOLE 1.317 !      HD2     HE2
ATOM HE1  HDR5E    0.170
```

```
BOND NE2  CD2       ND1  CG        CD2  CG        CE1  ND1
BOND NE2  CE1       CG   HG
BOND ND1  HD1       CD2  HD2       CE1  HE1       NE2  HE2
IMPR ND1  CE1  CG   HD1       NE2  CE1 CD2  HE2
IMPR CE1  ND1  NE2  HE1       CG   CD2 ND1  HG    CD2  CG  NE2  HD2
DONO HD1  ND1
DONO HE2  NE2
IC CG     CD2    NE2    CE1      0.0000    0.00    0.00    0.00   0.0000
IC CD2      NE2    CE1    ND1      0.0000    0.00    0.00    0.00   0.0000
IC CD2    ND1    *CG    HG       0.0000    0.00  180.00    0.00   0.0000
IC NE2    CG     *CD2   HD2      0.0000    0.00  180.00    0.00   0.0000
IC CE1    CG     *ND1   HD1      0.0000    0.00  180.00    0.00   0.0000
IC CE1    CD2    *NE2   HE2      0.0000    0.00  180.00    0.00   0.0000
IC NE2    ND1    *CE1   HE1      0.0000    0.00  180.00    0.00   0.0000
PATCH FIRST NONE LAST NONE
END

read para card append
* Drude polarizable FF parameters
*
BONDS
!atom type      Kb       b0
!=========================================
! Thiolates, XZ
SD2C2A   CD33A    218.00      1.832 ! MESH
SD2C2A   LPR        0.00      0.000 ! MESH
SD2C2B   CD32A    200.00      1.810 ! ETSH
SD2C2B   LPR        0.00      0.000 ! ETSH
! PHET
OD31D    CD2R6I   334.30      1.262 ! PHET, QM=1.276, XZ
CD2R6I   CD2R6A   305.00      1.384 ! PHET, QM=1.440, XZ

ANGLES
!atom types     Ktheta  Theta0   Kub     S0
!================================================
! Thiolates, XZ
SD2C2A   CD33A    HDA3A     35.00    112.42 ! Optimized, target: 111.38
SD2C2B   CD32A    HDA2A     25.00    106.30 ! from SD31B    CD32A    HDA2A
SD2C2B   CD32A    CD33A     46.00    113.20 ! from SD31B    CD32A    HDA2A
!! PHET
CD2R6A   CD2R6A   CD2R6I    50.00    118.20 ! PHET, QM=122.99, XZ
CD2R6A   CD2R6I   OD31D     55.20    127.80 ! PHET, QM=123.23, XZ
CD2R6A   CD2R6I   CD2R6A    50.00    111.50 ! PHET, QM=113.55, XZ
CD2R6I   CD2R6A   HDR6A     30.00    116.55 ! PHET, QM=116.81, XZ
!! MGUNA
ND2P1A   CD33A    HDA3C     51.50    107.50 ! GUAN, c22 40.00    109.50   27.00   2.1300 ! NC4,
charmm27, ammonium cations

DIHEDRALS
!atom types            Kchi     n     delta
!================================================
!! Thiolates
SD2C2B   CD32A    CD33A    HDA3A       0.175    3      0.0 ! from SD31B   CD32A    CD33A
HDA3A
```

```
!!! PHET
CD2R6A  CD2R6A   CD2R6A   CD2R6I       2.800    2   180.00 ! PHET, from BENZ
CD2R6A  CD2R6A   CD2R6I   CD2R6A       2.800    2   180.00 ! PHET, from BENZ
CD2R6A  CD2R6I   CD2R6A   HDR6A        4.200    2   180.00 ! PHET, from BENZ
CD2R6I  CD2R6A   CD2R6A   HDR6A        4.200    2   180.00 ! PHET, from BENZ
CD2R6A  CD2R6A   CD2R6I   OD31C        2.800    2   180.00 ! PHET, from BENZ
OD31D   CD2R6I   CD2R6A   CD2R6A       3.100    2   180.00 ! PHET, phenolate
OD31D   CD2R6I   CD2R6A   HDR6A        4.200    2   180.00 ! PHET, phenolate
HDP1A   OD31D    CD2R6A   CD2R6A       0.990    2   180.00 ! PHET, phenolate
!!! MGUAN
CD2N1A   ND2P1A   CD33A    HDA3C       0.000    3     0.00 ! MGUAN, ARG, c22
HDP1B    ND2P1A   CD33A    HDA3C       0.000    3     0.00 ! MGUAN, ARG, c22
IMPROPER
!
!V(improper) = Kpsi(psi - psi0)**2
!
!Kpsi: kcal/mole/rad**2
!psi0: degrees
!note that the second column of numbers (0) is ignored
!

NONBONDED nbxmod  5 atom vatom cdiel vdistance switch vswitch -
cutnb 16.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5

! LJ for molecular ions
HDP1B    0.0   -0.0100    0.7500 ! MGUAN/GUAN/NC3/NC2/NC1/NH4, fylin
ND2P1A   0.0   -0.0950    1.8000 ! MGUAN/GUAN, fylin
CD2N1A   0.0   -0.4750    1.8000 ! MGUAN/GUAN, fylin
ND3P2A   0.0   -0.3600    1.3800 ! NC2/NC3/NC4, fylin
ND3P3A   0.0   -0.0250    1.5500 ! NC1/NH4, fylin;  -0.025 1.76 yields better dGhyd for NH4
SD2C2A   0.0   -0.2000    2.1700 ! MES, thiolates, fylin
SD2C2B   0.0   -0.1000    2.2600 ! ETS, fylin
LPR      0.0   -0.1000    2.0500 ! MES/ETS, Repulsive LP, for sulfates, XZ
CD2R6I   0.0   -0.7800    1.5500 ! PHET, fylin
OD31D    0.0   -0.8300    1.5200 ! PHET, fylin
CD2O2A   0.0   -0.4300    1.47 ! ACET, fylin
OD2C2A   0.0   -0.3000    1.82 ! ACET, fylin
END
```

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