Interfacial structure and orientation of confined ionic liquids on charged quartz surfaces

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1 Atomistic ionic liquid models

1.1 [BF_4] anion

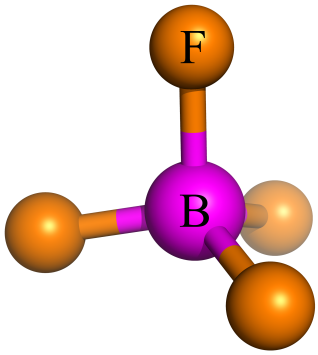

Fig. S1 The [BF_4] anion. The four F atoms connected to the central B atom are characterized with the same atom type.

Table S1 Force field parameters of [BF_4] anion [1–3].

Atoms	σ_{ii}(Å)	ε_{ii}(kJ/mol)	Charge (e)
B	3.5810	0.3974	1.1504
F	3.1181	0.2552	-0.5376

Bonds	r_0(Å)	K_r(kJ/mol Å^2)
B-F	1.389	1213.0

Angles	θ_0 (deg)	K_θ(kJ/mol rad^2)
F-B-F	109.5	209.0

1.2 [PF_6] anion

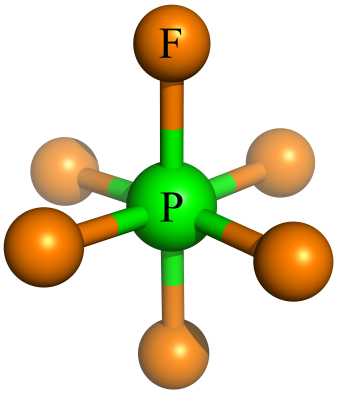

Fig. S2 The [PF_6] anion. The six F atoms connected to the central P atom are characterized with the same atom type.

Table S2 Force field parameters of [PF_6] anion [1–3].

Atom	σ_{ii}(Å)	ε_{ii}(kJ/mol)	Charge (e)
P	3.7418	0.8368	0.7562
F	3.1181	0.2552	-0.2927

Bonds	r_0(Å)	K_r(kJ/mol Å^2)
P-F	1.600	795.0

Angles	θ_0 (deg)	K_θ(kJ/mol rad^2)
F-P-F	90.0	334.7

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1.3 [TFO] anion

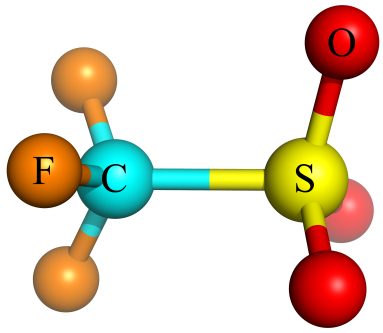

Fig. S3 The [TFO] anion. The F atoms connected to the C atom, and the O atoms connected to the S atom, are characterized with the same atom type, respectively.

Table S3 Force field parameters of [TFO] anion[4].

Atom	σ_{ii}(Å)	ε_{ii}(kJ/mol)	Charge (e)
C	3.4001	0.2762	0.4000
F	3.1185	0.2552	-0.1900
S	3.3640	1.0467	1.0600
O	2.9800	0.8786	-0.6300

Bonds	r_0(Å)	K_r(kJ/mol Å^2)
C-F	1.340	1848.5
C-S	1.835	984.8
S-O	1.450	2664.2

Angles	θ_0 (deg)	K_θ(kJ/mol rad^2)
F-C-F	107.6	390.3
F-C-S	110.4	346.9
C-S-O	102.6	434.9
O-S-O	119.2	484.7

Proper torsions	γ(deg)	K_ϕ(kJ/mol)	n
F-C-S-O	0.0	0.725	3

1.4 [TF_2N] anion

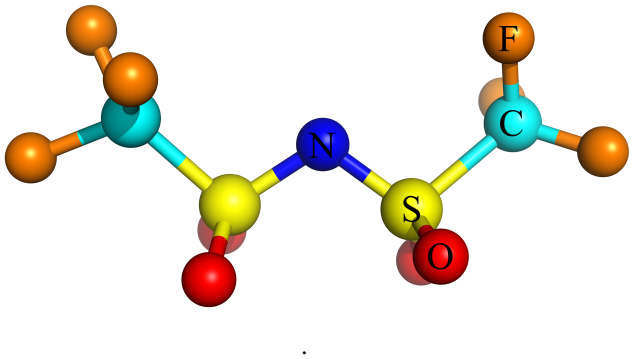

Fig. S4 The [TF_2N] anion. The F atoms connected to the C atoms and the O atoms connected to the S atoms are characterized with the same atom type, respectively.

Table S4 Force field parameters of [TF_2N] anion[4].

Atom	σ_{ii}(Å)	ε_{ii}(kJ/mol)	Charge (e)
N	3.2504	0.7118	-0.7200
S	3.3640	1.0467	0.9600
O	2.9800	0.8786	-0.5400
C	3.4001	0.2762	0.5200
F	3.1185	0.2552	-0.1800

Bonds	r_0(Å)	K_r(kJ/mol Å^2)
N-S	1.600	1555.8
S-O	1.450	2664.2
S-C	1.835	984.8
C-F	1.340	1848.5

Angles	θ_0 (deg)	K_θ(kJ/mol rad^2)
S-N-S	123.2	167.6
N-S-O	113.6	394.6
N-S-C	100.2	407.8
O-S-O	119.2	484.7
O-S-C	102.6	434.9
S-C-F	110.4	346.9
F-C-F	107.6	390.3

Proper torsions	γ(deg)	K_ϕ(kJ/mol)	n
S-N-S-O	0.0	-0.017	3
S-N-S-C	0.0	32.758	1
S-N-S-C	0.0	10.415	2
S-N-S-C	0.0	3.195	3
N-S-C-F	0.0	0.661	3
O-S-C-F	0.0	0.725	3

1.5 [BMIM] cation

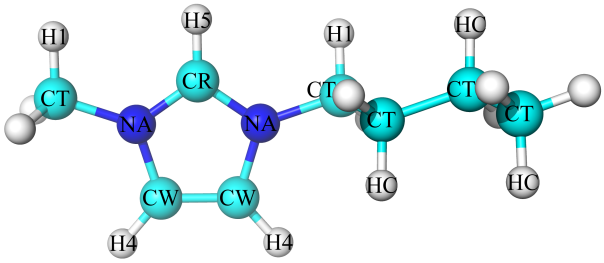

Fig. S5 The [BMIM] cation. The hydrogen atoms connected to the same carbon atoms are characterized with the same atom type.

Table S5 Force field parameters of [BMIM] cation [1–3].

Atom	σ_{ii}(Å)	ε_{ii}(kJ/mol)	Charge (e)
CR	3.400	0.3598	-0.0055
H5	1.782	0.0628	0.2258
NA(m)	3.250	0.7113	0.0596
CW(m)	3.400	0.3598	-0.1426
H4(m)	2.511	0.0628	0.2340
CT(m)	3.400	0.4577	-0.0846
H1	2.471	0.0657	0.1085
NA(b)	3.250	0.7113	0.0682
CW(b)	3.400	0.3598	-0.2183
H4(b)	2.511	0.0628	0.2633
CT(b1)	3.400	0.4577	-0.0153
H1	2.471	0.0657	0.0796
CT(b2)	3.400	0.4577	0.0107
HC	2.650	0.0657	0.0204
CT(b3)	3.400	0.4577	0.0309
HC	2.650	0.0657	0.0157
CT(b4)	3.400	0.4577	-0.0713
HC	2.650	0.0657	0.0294

Bonds	r_0(Å)	K_r(kJ/mol Å^2)
CR-H5	1.070	1589.9
CR-NA	1.322	1673.6
NA-CW	1.378	1506.2
CW-CW	1.343	1715.4
CW-H4	1.070	1610.8
NA-CT	1.472	1171.5
CT-CT	1.526	1297.0
CT-H1	1.080	1422.6
CT-HC	1.090	1422.6

Angles	θ_0 (deg)	K_θ(kJ/mol rad^2)
CR-NA-CW	108.0	502.0
CR-NA-CT	126.3	209.0
NA-CR-NA	109.9	502.0
NA-CR-H5	125.7	126.0
NA-CW-CW	107.1	502.0
NA-CW-H4	122.1	126.0
NA-CT-H1	109.5	230.0
NA-CT-CT	112.2	293.0
CW-NA-CT	125.7	209.0
CW-CW-H4	130.7	126.0
CT-CT-CT	109.5	167.0
CT-CT-H1	109.5	159.0
CT-CT-HC	109.5	155.0
H1-CT-H1	109.5	146.0
HC-CT-HC	109.5	142.0

Proper Torsions	γ(deg)	K_ϕ(kJ/mol)	n
CR-NA-CW-CW	180.0	50.210	2
CR-NA-CW-H4	180.0	8.368	2
CR-NA-CT-CT	0.0	-0.987	1
CR-NA-CT-H1	0.0	0.686	3
NA-CR-NA-CW	180.0	50.210	2
NA-CR-NA-CT	180.0	8.368	2
NA-CW-CW-NA	180.0	50.210	2
NA-CW-CW-H4	180.0	6.276	2
NA-CT-CT-CT	0.0	1.046	3
NA-CT-CT-HC	0.0	0.669	3
CW-NA-CR-H5	180.0	6.276	2
CW-NA-CT-CT	0.0	-0.745	1
CW-NA-CT-H1	0.0	1.021	3
CW-CW-NA-CT	180.0	8.368	2
CT-NA-CR-H5	180.0	6.276	2
CT-NA-CW-H4	180.0	6.276	2
CT-CT-CT-CT	0.0	1.046	3
CT-CT-CT-H1	0.0	0.669	3
CT-CT-CT-HC	0.0	0.669	3
H1-CT-CT-HC	0.0	0.628	3
H4-CW-CW-H4	180.0	6.276	2
HC-CT-CT-HC	0.0	0.628	3

Improper Torsions	γ(deg)	K_ϕ(kJ/mol)	n
CR-CW-NA-CT	180.0	8.368	2
NA-NA-CR-H5	180.0	4.602	2
CW-NA-CW-H4	180.0	4.602	2

2 Atomistic quartz model

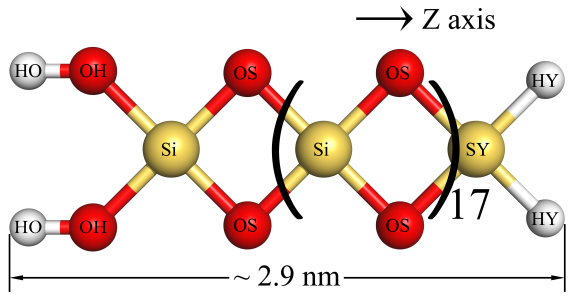

Fig. S6 Schematic structures of quartz $Si(OH)_2$ and SiH_2 surface models. The interpenetrating OS-Si-OS network in bulk quartz is simplified and represented by $Si(OS)_2$ groups.

Table S6 Force field parameters of quartz $Si(OH)_2$ and SiH_2 surface models[5].

Atom	σ_{ii}(Å)	ε_{ii}(kJ/mol)	Charge (e)
Si	3.920	2.5104	1.3333
SY	3.920	2.5104	1.1223
OS	3.367	0.7109	-0.6797
OH	3.442	0.8799	-0.7707
HO	0.000	0.0000	0.2893
HY	2.511	0.0657	0.1552

Bonds	r_0(Å)	K_r(kJ/mol Å^2)
Si-OH	1.680	—
Si-OS	1.635	—
SY-OS	1.635	—
SY-HY	1.486	—
OH-HO	0.975	—

Angles	θ_0 (deg)	K_θ(kJ/mol rad^2)
Si-OS-Si	162.2	—
Si-OS-SY	162.2	—
OS-Si-OS	111.4	—
OS-SY-OS	111.4	—
OH-Si-OH	117.0	—
OH-Si-OS	126.0	—
Si-OH-HO	122.5	—
HY-SY-OS	118.0	—
HY-SY-HY	111.1	—

3 Functional form of potential energy

The force field for ionic liquid groups employs the following functional form for potential energy U:

$$\begin{aligned} U_{total} &= \sum_{bonds} K_r(r-r_0)^2 + \sum_{angles} K_\theta(\theta-\theta_0)^2 \\ &+ \sum_{torsions} \frac{K_\phi}{2}[1+\cos(n\phi-\gamma)] \\ &+ \sum_{i<j}\left\{4\varepsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12}-(\frac{\sigma_{ij}}{r_{ij}})^{6}] \right. \\ &+ \left. \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r_{ij}}\right\}. \end{aligned} \quad (1)$$

The first three terms represent the bonded interactions, *i.e.*, bonds, angles and torsions, and corresponding potential parameters have their usual meaning. The nonbonded interactions are described in the last term, including Van der Waals (VdW, here the Lennard-Jones 12-6 form) and Coulombic interactions of atom-centered point charges. The VdW interactions are calculated between atoms in different molecules or atoms in the same molecule that are separated by more than three consecutive bonds. The VdW interaction parameters between different atoms are obtained from the Lorentz-Berthelot combining rules with

$$\begin{aligned} \varepsilon_{ij} &= \sqrt{\varepsilon_{ii}\varepsilon_{jj}}, \\ \sigma_{ij} &= \frac{\sigma_{ii}+\sigma_{jj}}{2}. \end{aligned} \quad (2)$$

The nonbonded interactions separated by exactly three consecutive bonds (1-4 interaction) are reduced by related scaling factors, which are optimized as 0.50 for VdW interactions and 0.83 for electrostatic interactions, respectively.

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