Novel SCS-IL-MP2 and SOS-IL-MP2 methods for accurate energetics of large-scale ionic liquid clusters

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ELECTRONIC SUPPLEMENTARY INFORMATION

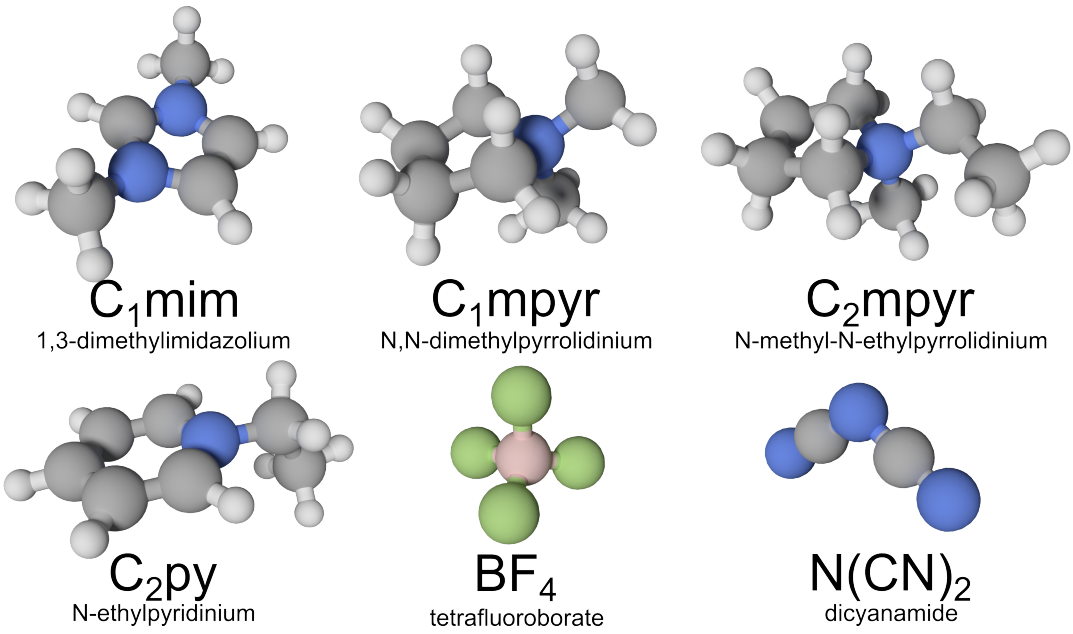

Figure S1. Structures of polyatomic ions used in this study.

Table S1. Total interaction energy, E_{INT}(Tot), (in kJ mol^{-1}) and dispersion contribution, E_{INT}(Disp) (in %)for two and four ion pair clusters as calculated at the CCSD(T)/CBS level of theory. The HF component of total interaction energy was taken from CP-corrected HF/VQZ calculations.

	2 IPs		**4 IPs**	
	E_{INT}(Tot)	**E_{INT}(Disp)**	**E_{INT}(Tot)**	**E_{INT}(Disp)**
$[C_1mim][BF_4]$	-871.4	12.5	-1773.0	13.0
$[C_1mim][Br]$	-910.1	13.5	-1892.5	16.7
$[C_1mim][Cl]$	-948.6	12.1	-1969.0	15.2
$[C_1mim][N(CN)_2]$	-858.7	19.1	-1798.1	23.4
$[C_1mpyr][BF_4]$	-850.8	12.4	-1805.6	14.9
$[C_1mpyr][Br]$	-910.0	14.6	-1889.9	15.8
$[C_1mpyr][Cl]$	-948.2	13.1	-1956.0	15.3
$[C_1mpyr][N(CN)_2]$	-826.8	18.4	-1791.4	22.5
$[C_2mpyr][BF_4]$	-837.7	13.5	-1747.3	15.5
$[C_2mpyr][Br]$	-898.4	15.1	-1863.4	16.7
$[C_2mpyr][Cl]$	-929.6	14.9	-1917.7	16.1
$[C_2mpyr][N(CN)_2]$	-823.9	20.1	-1696.2	21.2
$[C_2Py][BF_4]$	-830.3	13.6	-	-
$[C_2Py][Br]$	-877.3	17.9	-1818.5	22.0
$[C_2Py][Cl]$	-916.8	16.6	-1872.6	18.8
$[C_2Py][N(CN)_2]$	-811.0	21.3	-	-

Table S2. Mean absolute error (MAE), mean (unsigned) error (Mean) and standard deviation (Std. Dev.) for correlation interaction energies of the two- and four-ion pair given in kJ mol^{-1} per ion pair.

	2 IPs			4 IPs		
	MAE	**Mean**	**St. Dev.**	**MAE**	**Mean**	**St. Dev.**
SCS-IL-MP2	1.5	0.9	0.9	1.5	-0.7	0.9
SOS-IL-MP2	1.7	0.9	0.9	1.9	-0.6	0.8
SCS-MP2/VTZ	7.2	7.2	1.8	7.0	7.0	2.5
SCS-MP2/VTZ(CP)	21.2	21.2	1.5	23.7	23.7	2.2
SCS-MP2/VQZ	7.5	7.5	1.6	7.2	7.2	2.2
MP2/VTZ(CP)	6.3	6.2	3.5	5.6	5.2	3.0
MP2/VQZ(CP)	2.9	-0.3	2.3	3.5	-2.5	2.7
MP2/CBS(CP)	5.4	-5.0	3.3	8.2	-8.2	3.8
SCSN/VTZ	5.7	5.7	1.3	4.8	4.8	1.5
SCS-(MI)/VTZ	5.9	5.9	1.3	5.3	5.3	1.7
SCSN/VTZ (CP)	12.7	12.7	1.8	13.1	13.1	1.8
SCS-(MI)/VTZ (CP)	15.3	15.3	1.6	16.4	16.4	1.8

Table S3. Relative errors (mean, with standard deviation in parentheses, and maximum) *given as a percentage* of the total correlation interaction correlation energy according to eq 5. for the two- and four-ion pair clusters.

	2 IPs		4 IPs	
	Mean error	**Max error**	**Mean error**	**Max error**
SCS-IL-MP2	2.3 (1.7)	6.4	1.9 (1.2)	3.6
SOS-IL-MP2	2.6 (1.6)	5.4	2.4 (1.1)	4.3
SCS-MP2/VTZ	10.6 (2.4)	14.4	8.5 (2.1)	12.2
SCS-MP2/VTZ(CP)	32.0 (5.7)	45.1	29.8 (4.6)	38.8
SCS-MP2/VQZ	11.3 (3.0)	19.6	9.0 (2.5)	12.3
MP2/VTZ(CP)	10.2 (6.8)	26.4	7.6 (5.0)	18.5
MP2/VQZ(CP)	4.2 (3.6)	14.6	4.1 (2.7)	9.7
MP2/CBS(CP)	7.5 (3.5)	14.7	9.6 (3.5)	15.0
SCSN/VTZ	8.6 (2.8)	15.8	6.0 (1.8)	8.9
SCS-(MI)/VTZ	8.9 (2.5)	15.0	6.5 (1.7)	9.6
SCSN/VTZ (CP)	19.4 (5.3)	32.6	16.7 (4.2)	25.9
SCS-(MI)/VTZ (CP)	23.3 (5.4)	36.5	20.8 (4.3)	29.9

Table S4. Differences (given per ion pair in kJ mol^{-1}) between FMO3 and FMO2 correlation interaction energies calculated in combination with SCS-IL-MP2 and SOS-IL-MP2 for two and four ion pair clusters.

	2 IPs		**4 IPs**	
	SCS-IL-MP2	**SOS-IL-MP2**	**SCS-IL-MP2**	**SOS-IL-MP2**
$[C_1mim][BF_4]$	0.2	0.1	-0.5	-0.6
$[C_1mim][Br]$	0.2	0.2	1.0	0.9
$[C_1mim][Cl]$	0.2	0.2	0.9	0.6
$[C_1mim][N(CN)_2]$	0.0	0.1	0.8	0.8
$[C_1mpyr][BF_4]$	0.1	0.1	-1.3	-1.7
$[C_1mpyr][Br]$	0.0	0.1	-0.6	-0.9
$[C_1mpyr][Cl]$	0.1	0.0	-1.3	-2.0
$[C_1mpyr][N(CN)_2]$	0.2	0.1	0.2	0.4
$[C_2mpyr][BF_4]$	0.1	0.1	-1.5	-1.7
$[C_2mpyr][Br]$	0.0	0.0	-0.9	-1.1
$[C_2mpyr][Cl]$	0.1	0.0	-1.3	-1.8
$[C_2mpyr][N(CN)_2]$	0.1	0.1	0.7	0.8
$[C_2Py][BF_4]$	0.0	0.0	-0.9	-1.3
$[C_2Py][Br]$	0.0	0.0	0.4	0.1
$[C_2Py][Cl]$	0.0	0.0	0.1	-0.3
$[C_2Py][N(CN)_2]$	0.2	0.1	1.2	1.5