SUPPORTING INFORMATION FOR:

Comparison of the Blue-Shifted C-D Stretching Vibrations for DMSO-d_6 in Imidazolium-based Room Temperature Ionic Liquids and in Water

Liqun Zhang,[a] Yong Wang [a], Zheng Xu, [b] and Haoran Li*, [a]

[a]Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

[b]Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou 310012, P. R. China

1. The cartesian coordinates of the optimized structures for Il/DMSO complexes shown in Figure 6.

(1) [Bmim][BF_4] /DMSO (shown in Figure 6(a))

C	1.604734	-0.380509	0.142705
N	2.696390	0.333302	-0.154024
C	3.399084	0.577597	1.012351
C	2.710592	-0.021682	2.024401
N	1.594086	-0.616805	1.460027
C	2.998207	0.873431	-1.483228
C	0.529921	-1.338201	2.188223
C	-0.156949	-0.461111	3.239025
C	-1.329097	-1.198684	3.900587
C	-2.031200	-0.343629	4.961622
H	0.863671	-0.689030	-0.584929
H	4.312964	1.149458	1.021966
H	2.916029	-0.071813	3.080946
H	2.399922	0.325367	-2.212992
H	2.732854	1.932955	-1.507468
H	4.062658	0.742490	-1.688188
H	0.982083	-2.228690	2.639278

*Corresponding author. Fax: +86-571-8795-1895
Email Address: lihr@zju.edu.cn

H	-0.193970	-1.649814	1.434739
H	0.567236	-0.161129	4.009244
H	-0.525817	0.448359	2.754294
H	-2.051932	-1.478748	3.124153
H	-0.974009	-2.134721	4.355803
H	-1.342778	-0.067022	5.769355
H	-2.871319	-0.883706	5.410680
H	-2.420912	0.579566	4.520300
F	-0.073588	1.815558	-0.163455
B	-1.398623	1.350753	0.052454
F	-1.871316	1.801551	1.286616
F	-1.356674	-0.089096	0.065266
F	-2.222541	1.760666	-1.006687
C	-1.885975	-1.690845	-2.732437
S	-0.441279	-1.074482	-3.667846
O	0.743749	-1.067419	-2.686213
C	-0.994763	0.658577	-3.851584
H	-1.698267	-2.746278	-2.523893
H	-2.776708	-1.591198	-3.359276
H	-1.983078	-1.121556	-1.804585
H	-1.248683	1.086328	-2.878215
H	-0.169028	1.201835	-4.315933
H	-1.860927	0.671385	-4.519985

ΔG=-1400.8912 (Hartree/Particle)

(2) [Bmim][BF_4] /DMSO (shown in Figure 6(b))

C	1.283547	-1.066987	0.368026
N	2.617357	-1.007027	0.279850
C	3.146544	-0.999743	1.557006
C	2.097453	-1.062849	2.425238
N	0.944324	-1.110680	1.662347
C	3.385960	-0.904720	-0.964989
C	-0.442211	-1.104727	2.169510
C	-0.846448	0.269885	2.712958
C	-2.296284	0.274185	3.216082
C	-2.725719	1.640174	3.763495
H	0.570221	-1.078282	-0.449072
H	4.208063	-0.938724	1.734529
H	2.073118	-1.070581	3.502831
H	2.699769	-0.645321	-1.769236
H	4.107486	-0.093792	-0.861756
H	3.893555	-1.852031	-1.163687
H	-0.506434	-1.877841	2.942794

H	-1.073286	-1.401946	1.328008
H	-0.174517	0.556914	3.533597
H	-0.716410	1.010611	1.916403
H	-2.963746	-0.016653	2.393877
H	-2.420728	-0.489465	3.997058
H	-2.098952	1.942395	4.610693
H	-3.764681	1.619301	4.108867
H	-2.641218	2.416453	2.995282
F	1.004682	0.755788	-2.117936
B	0.957514	1.877148	-1.214203
F	2.150845	1.881143	-0.462740
F	-0.142977	1.658261	-0.334948
F	0.788825	3.052811	-1.927786
C	-2.874603	0.322826	-1.520940
S	-2.360680	-1.373005	-1.974939
O	-1.354390	-1.832386	-0.905922
C	-1.385767	-0.939893	-3.459445
H	-3.521384	0.232837	-0.645380
H	-3.442815	0.751498	-2.351369
H	-1.991900	0.923302	-1.283622
H	-0.603672	-0.226591	-3.186984
H	-0.950164	-1.870697	-3.828987
H	-2.062854	-0.526936	-4.212759

ΔG= -1400.8914(Hartree/Particle)

(3) [Bm_2im][BF_4] /DMSO (shown in Figure 6(c))

C	-1.483261	1.131495	1.021401
N	-1.698288	0.961958	-0.295843
C	-2.091366	-0.342120	-0.534928
C	-2.126296	-0.970137	0.670738
N	-1.751199	-0.042464	1.628975
C	-1.466681	1.963879	-1.345630
C	-1.537960	-0.353553	3.051915
C	-0.226091	-1.108940	3.298721
C	0.016152	-1.347694	4.795086
C	1.317138	-2.113975	5.061374
C	-1.028690	2.380467	1.689102
H	-2.237391	-0.696276	-1.545845
H	-2.360670	-1.989867	0.928725
H	-0.458528	2.364643	-1.229163
H	-1.543330	1.449799	-2.304335
H	-2.217499	2.755904	-1.279525
H	-2.403598	-0.934090	3.388422

H	-1.545910	0.591241	3.600055
H	-0.259271	-2.069892	2.769197
H	0.600493	-0.538661	2.862755
H	0.052733	-0.379953	5.314294
H	-0.830761	-1.899264	5.228620
H	1.298448	-3.101470	4.586100
H	1.475660	-2.262357	6.134660
H	2.180184	-1.570166	4.663347
H	-1.680240	2.632538	2.531833
H	-1.040843	3.210348	0.983087
H	0.000683	2.260161	2.043471
F	1.891536	1.076842	1.797833
B	1.987541	0.874358	0.396208
F	3.293121	0.598482	0.011548
F	1.503484	2.038775	-0.264013
F	1.130926	-0.214638	0.044722
C	0.295208	-1.032085	-5.650479
S	0.000176	-1.324858	-3.868115
O	-1.252595	-0.508156	-3.516834
C	1.440850	-0.407952	-3.227047
H	-0.536579	-1.485377	-6.192706
H	1.236737	-1.503860	-5.944966
H	0.320910	0.045093	-5.834152
H	1.418050	0.618235	-3.602850
H	1.378728	-0.412662	-2.136255
H	2.353004	-0.920801	-3.545536

ΔG= -1440.1895 (Hartree/Particle)

2. The cartesian coordinates of the optimized structures for DMSO-$(H2O)_n$ complexes (n=1, 2, 3) shown in Figure 7.

(1) pure DMSO (shown in Figure 7(a))

C	-0.814613	0.185058	1.369849
S	0.233653	-0.445267	0.000026
O	1.504650	0.387066	0.000391
C	-0.814035	0.185093	-1.370203
H	-0.297110	-0.058408	2.299697
H	-1.790848	-0.307680	1.346187
H	-0.914938	1.269551	1.274795
H	-0.915253	1.269485	-1.274954
H	-0.295697	-0.057742	-2.299757

H	-1.789924	-0.308377	-1.347388

(2) DMSO-1w (shown in Figure 7(b))

C	-1.373038	-0.768267	0.646602
S	0.000011	0.410908	0.931800
O	-0.003817	1.378863	-0.258675
C	1.376861	-0.762815	0.642507
H	-2.300008	-0.200215	0.746463
H	-1.335004	-1.553097	1.407262
H	-1.286176	-1.178021	-0.363043
H	1.288643	-1.173339	-0.366700
H	2.301849	-0.191014	0.739297
H	1.344298	-1.547473	1.403599
O	0.000806	-0.367939	-2.379119
H	-0.010761	-0.069154	-3.295298
H	-0.001864	0.436888	-1.812686

(3) DMSO-1w (shown in Figure 7(c))

C	1.369384	0.716438	-0.144087
S	-0.000238	-0.405046	-0.620872
O	-0.001332	-0.493040	-2.140232
C	-1.368126	0.717724	-0.142081
H	2.297625	0.217380	-0.429575
H	1.336777	0.871888	0.937012
H	1.270675	1.655409	-0.695439
H	-1.267893	1.657960	-0.690999
H	-2.296989	0.220747	-0.429184
H	-1.335511	0.870330	0.939427
O	0.001060	-0.282620	2.834207
H	-0.002530	-1.235680	2.674109
H	-0.003718	-0.176986	3.793808

(4) DMSO-1w (shown in Figure 7(d))

C	-0.223021	0.484499	-2.167199
S	-0.137908	-0.518697	-0.639506
O	-1.169911	0.092173	0.314359
C	1.506136	0.054114	-0.071019
H	-1.199747	0.296604	-2.616709
H	0.570299	0.173395	-2.852675
H	-0.129168	1.541219	-1.904623
H	1.514562	1.146102	-0.027176
H	1.650372	-0.350342	0.932771

H	2.271682	-0.323046	-0.754953
O	0.034669	0.198123	2.837773
H	-0.526029	0.044012	3.606462
H	-0.562200	0.217162	2.061240

(5) DMSO-2w (shown in Figure 7(e))

C	-1.479935	0.301276	1.381566
S	-0.641073	-0.548329	0.000195
O	0.807182	-0.005290	0.000272
C	-1.479157	0.299241	-1.382952
H	-0.968506	-0.004385	2.296561
H	-2.528456	-0.008895	1.399839
H	-1.387082	1.381835	1.248853
H	-1.386469	1.379997	-1.251755
H	-0.967131	-0.007685	-2.297186
H	-2.527634	-0.011064	-1.401358
O	1.477330	0.150399	-2.717020
H	1.476794	0.130106	-1.738637
H	2.368379	-0.087803	-2.996787
O	1.476519	0.149622	2.717820
H	2.367313	-0.089427	2.997684
H	1.476264	0.129633	1.739417

(6) DMSO-3w (shown in Figure 7(f))

O	0.000626	-0.108721	-1.364737
S	-0.000293	-0.269547	0.177089
C	1.380748	0.757746	0.778611
C	-1.382144	0.757625	0.776953
H	2.295639	0.329791	0.363989
H	-2.296499	0.329590	0.361233
H	1.378873	0.711608	1.870165
H	-1.381575	0.711488	1.868508
H	1.251372	1.779171	0.412511
H	-1.252418	1.779062	0.411008
H	1.715910	-0.149222	-2.053677
H	-1.713826	-0.149372	-2.055735
O	2.693541	-0.147275	-2.118362
O	-2.691379	-0.147510	-2.121594
H	2.912611	-0.597106	-2.942132
H	-2.909421	-0.597360	-2.945626
O	-0.000820	-0.495345	3.648273
H	-0.001267	-0.275676	4.588565
H	-0.002084	-1.460646	3.605743

3. C-D asymmetric stretching vibrational frequencies (ν_{as}, cm^{-1}) and their changes of DMSO-d_6 in DMSO-d_6…$(H_2O)n$ (n= 1, 2, 3) complexes obtained at B3LYP/6-31++G** level.

Table 1. C-D asymmetric stretching vibrational frequencies (ν_{as}, cm^{-1}) and their changes of DMSO-d_6 in DMSO-d_6…$(H_2O)n$ (n= 1, 2, 3) complexes obtained at B3LYP/6-31++G** level.

Vibrational modes	(a)	(b)	$\Delta\nu^a$	(c)	$\Delta\nu^a$	(d)	$\Delta\nu^a$	(e)	$\Delta\nu^a$	(f)	$\Delta\nu^a$
ν_{as}	2183	2183	0	2184	1	2185	2	2185	2	2186	3
ν_{as}	2339	2341	2	2342	3	2342	3	2344	5	2349	10
ν_{as}	2342	2344	2	2344	2	2344	2	2345	3	2350	8
ν_{as}	2347	2350	3	2350	3	2350	3	2353	6	2356	9
ν_{as}	2349	2352	3	2353	4	2353	4	2356	7	2359	10

[a]Complexation shift relative to the monomer $\Delta\nu=\nu-\nu(a)$

4. The changes of bond distances of DMSO-d_6

Table 1. The bond distances(*r*, in Å) of DMSO-d_6 in pure DMSO-d_6, [Bmim][BF_4]/DMSO-d_6 mixtures and [Bm_2im][BF_4]/DMSO-d_6 mixtures as shown in Fig.6 in the paper.

	DMSO-d_6	[Bmim][BF_4]/DMSO-d_6 Shown in Fig.6(a)	[Bmim][BF_4]/DMSO-d_6 Shown in Fig.6(b)	[Bm_2im][BF_4]/DMSO-d_6 Shown in Fig.6(c)
$r_{C\text{-}D}$	1.093	1.092	1.093	1.093
$r_{C\text{-}D}$	1.093	1.092	1.093	1.093
$r_{C\text{-}D}$	1.093	1.092	1.093	1.093
$r_{C\text{-}D}$	1.093	1.092	1.093	1.093
$r_{C\text{-}D}$	1.093	1.092	1.093	1.093
$r_{C\text{-}D}$	1.093	1.092	1.093	1.093
$r_{S=O}$	1.510	1.530	1.530	1.530
$r_{C\text{-}S}$	1.830	1.820	1.820	1.830

5. IR spectra of ternary solutions of [Bmim][BF_4]/DMSO-d_6/H_2O with a mole fraction of 1:1:1.