Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Data

Halocarbons as Hydrogen Bond Acceptors: A Spectroscopic Study of Haloethylbenzenes ($PhCH_2CH_2X$, X=F, Cl, Br) and their Hydrate Clusters

Patrick A. Robertson, Luigi Villani, Uresha L. M. Dissanayake, Luke F. Duncan, Belinda M. Abbott, David J. D. Wilson, Evan G. Robertson*

Table of Contents

* e.robertson@latrobe.edu.au

Simplified anharmonic method

A simplified anharmonic model was used in conjunction with Gaussian 09 harmonic frequency output to predict the aliphatic CH stretch region for conformer specific IR spectra of BrEB, CEB and FEB. This model was shown to give an accurate prediction of the IR spectra of ethylbenzene and propylbenzene, and due to the structural similarity with XEB was deemed suitable for comparison to experimental results.[1]

The Cartesian force constant matrix and dipole derivatives were obtained from vibrational frequency calculations of optimized geometries using B3LYP, B3LYP-D3 and ωB97X-D methods with the 6-311++G(d,p). The Cartesian force constant matrix was mass weighted and the aliphatic CH modes were localised by treating stretches as diatomics and bend modes as triatomics. The resulting localised vibrational modes included CH stretches, bend overtones and bend combinations.[1]

Fermi resonance and anharmonic coupling terms between the modes were used with localised vibrational modes in a Hamiltonian matrix as described in the simplified anharmonic model.[1,2] The addition of these terms leads to a mixing of localised modes giving normalised modes. The dipole derivatives can be used with the normal mode atom displacement to generate mode intensities.[3]

The anharmonicity parameters from the original alkyl systems studied by Tabor *et al*. were backed by repeated testing and Van Vleck perturbation theory calculations.[4] Although the Fermi coupling has been transferrable to date, it is recommended that any new adopters of the model fit against their smallest model system to test for appropriateness. Model Hamiltonian parameters have also been published at the MP2/aug-cc-pVDZ level,[1] and in some cases the additional computational cost may be justified in terms of improved prediction.

References

1. D. P. Tabor, D. M. Hewett, S. Bocklitz, J. A. Korn, A. J. Tomaine, A. K. Ghosh, T. S. Zwier, and E. L. Sibert, J. Chem. Phys. 2016, 144, 224310.
2. E. G. Buchanan, J. C. Dean, T. S. Zwier, and E. L. Sibert, J. Chem. Phys. 2013, 138, 064308.
3. A. Komornicki and R. L. Jaffe, J. Chem. Phys. 1979, 71, 2150-2155
4. E. L. Sibert III, D. P. Tabor, N. M. Kidwell, J. C. Dean, T. S. Zwier, *J. Phys. Chem. A*. 2014, 118, 11272-11281

Stick Spectra from Simplified Anharmonic Method

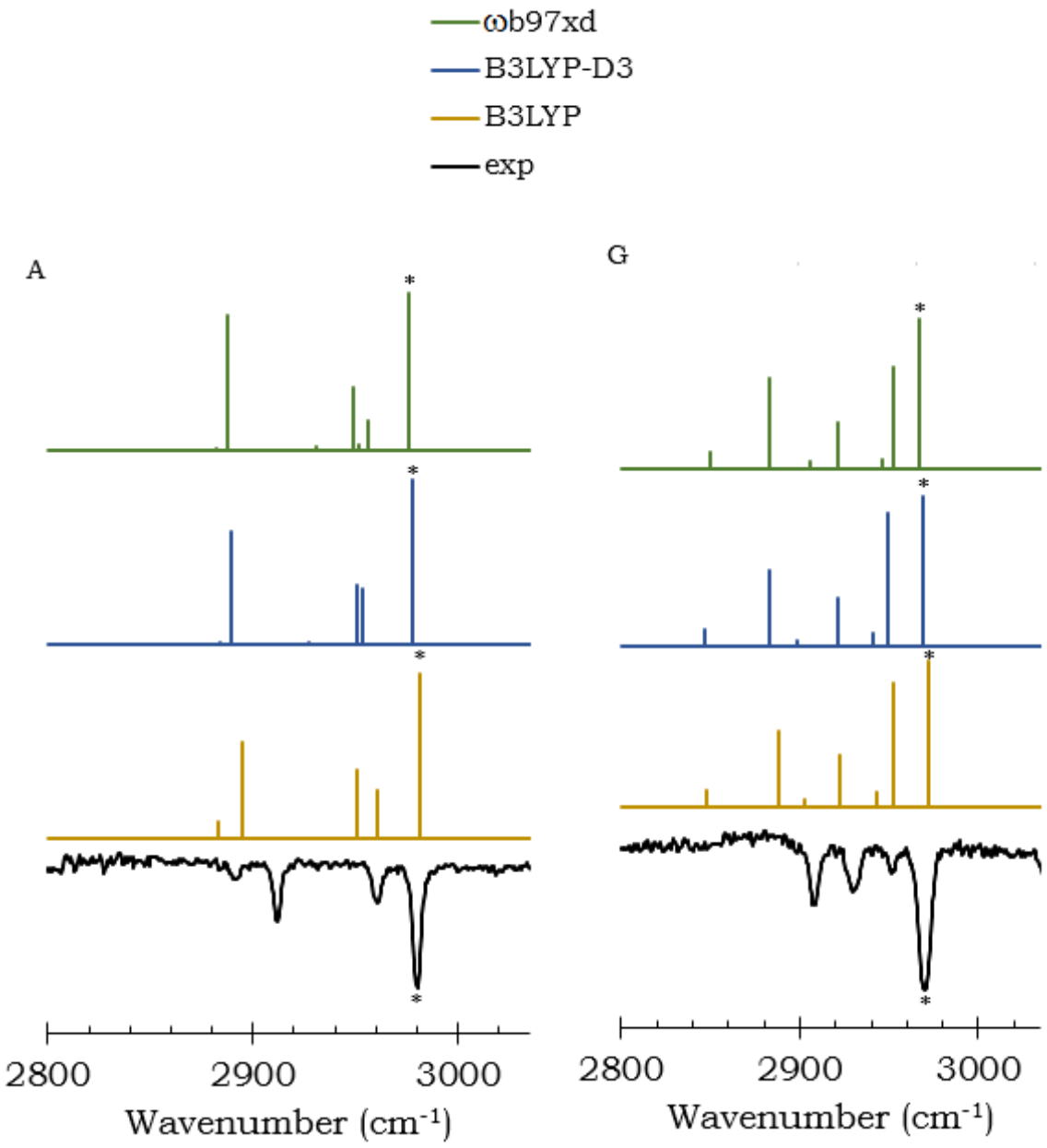

*Figure S1. IR-UV ion-dip spectra of features A and G of FEB and stick spectra based on a simplified anharmonic model for aliphatic modes. Modes marked with an * are assigned to the antisymmetric $C_\beta H_2$ stretch mode.*

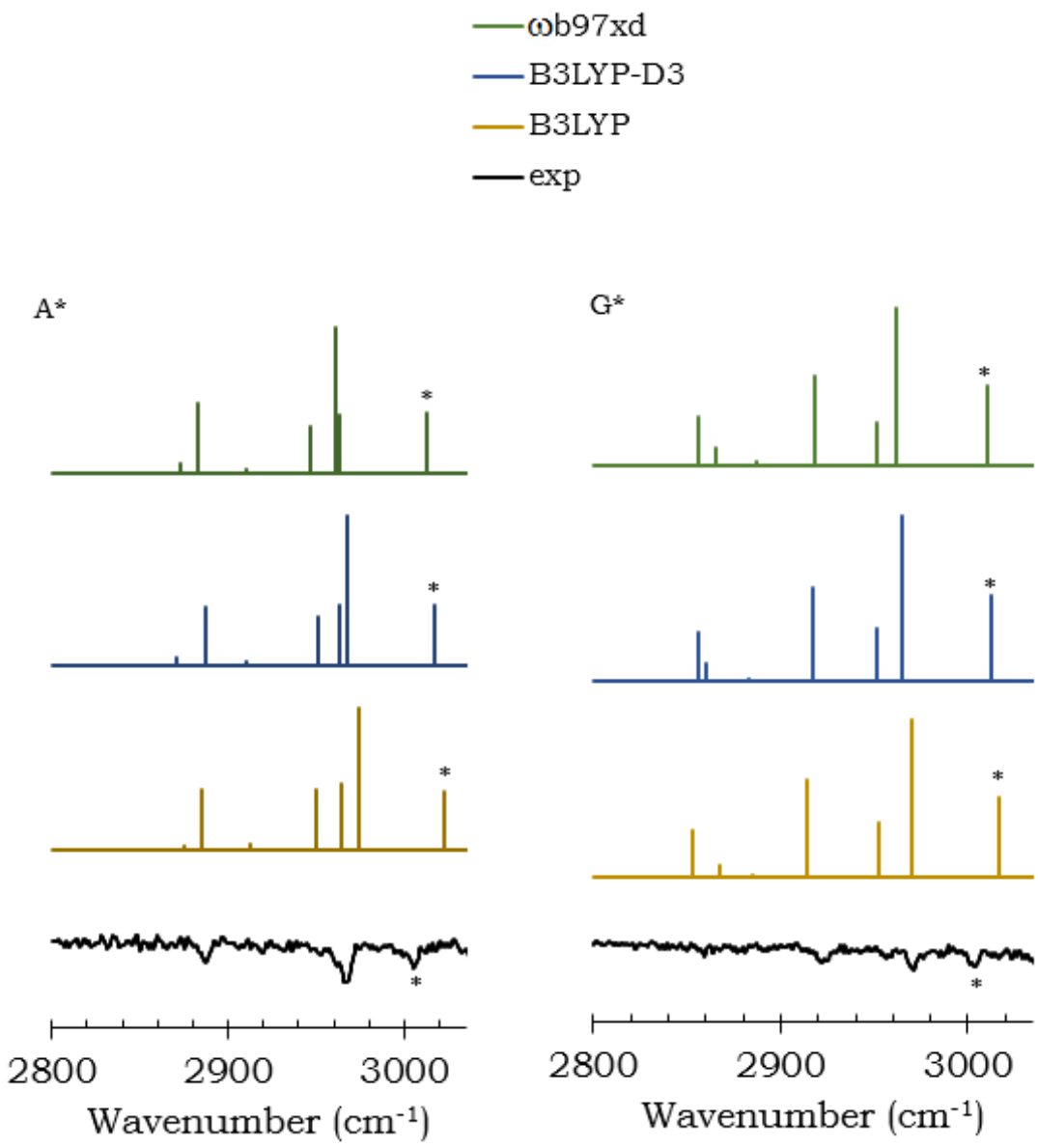

Figure S2. IR-UV ion-dip spectra of features A and G* of CEB and stick spectra based on a simplified anharmonic model for aliphatic modes. Modes marked with an * are assigned to the antisymmetric $C_\beta H_2$ stretch mode.*

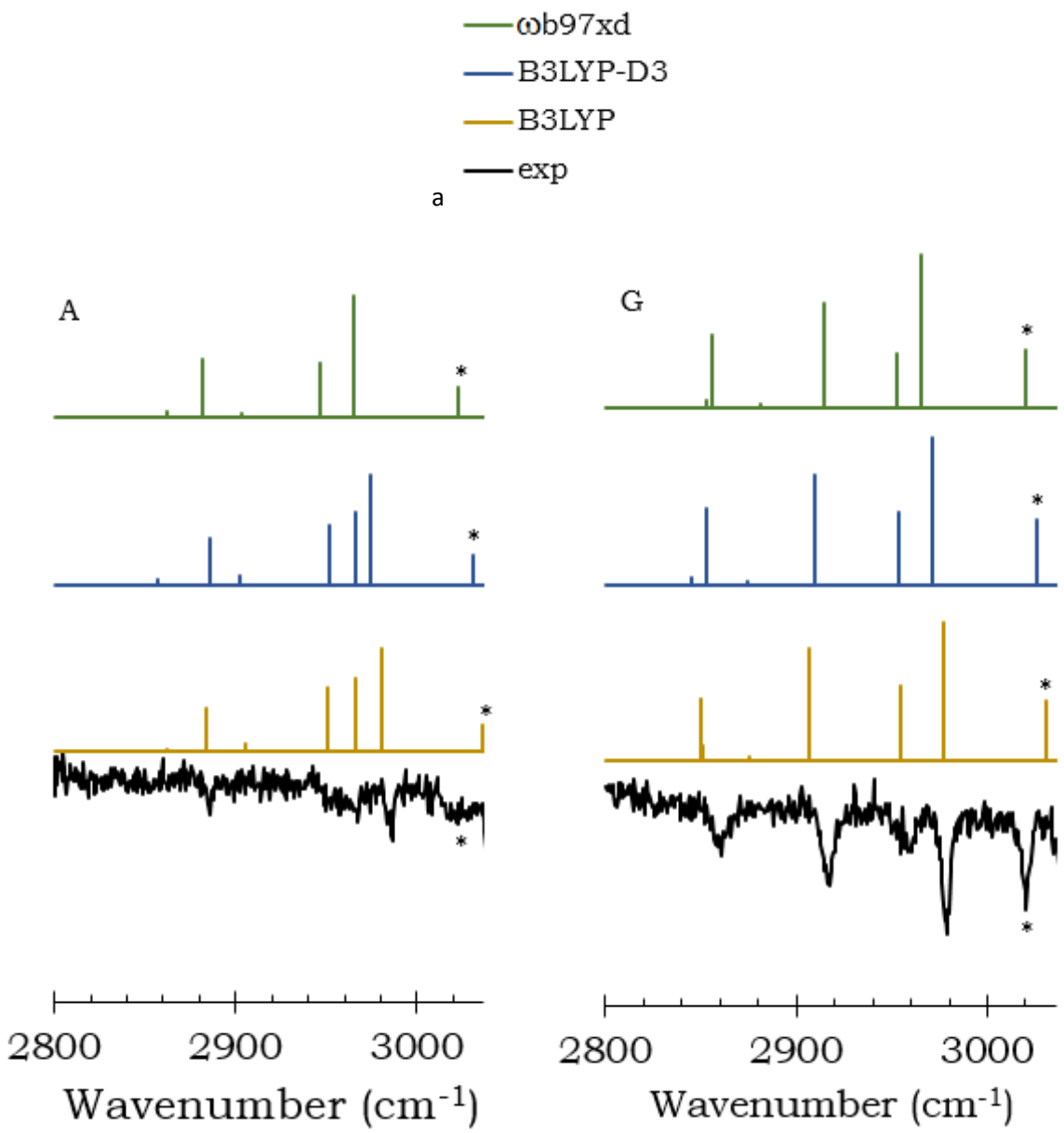

*Figure S3. IR-UV ion-dip spectra of features A and G of BrEB and stick spectra based on a simplified anharmonic model for aliphatic modes. Modes marked with an * are assigned to the antisymmetric $C_\beta H_2$ stretch mode.*

Table S1. Experimental, harmonic (unscaled), and simplified anharmonic band positions in cm^{-1} for the highest wavenumber CH stretch mode of XEB, the antisymmetric $C_\beta H_2$ stretch.

	Anti			*Gauche*		
	FEB	CEB	BrEB	FEB	CEB	BrEB
Experimental	2980	3005	3020	2970	3003	3020
Harmonic (unscaled)						
B3LYP/6-311++G(d,p)	3103	3147	3161	3094	3140	3155
B3LYP-D3/6-311++G(d,p)	3100	3140	3155	3090	3136	3150
ωb97xd/6-311++G(d,p)	3128	3167	3180	3119	3165	3175
B3LYP-GD3(BJ)/aug-cc-pVTZ	3100	3146	3158	3090	3037	3152
MP2/def2-TZVPP	3168	3190	3200	3157	3179	3195
Anharmonic						
B3LYP/6-311++G(d,p)	2981	3023	3036	2972	3017	3031
B3LYP-D3/6-311++G(d,p)	2978	3017	3031	2969	3012	3026
ωb97xd/6-311++G(d,p)	2976	3013	3023	2967	3010	3020

Table S2. Experimental and theoretical v_1 OH stretch band positions (cm^{-1}) used in Figure 9.

OH…X	Experimental	MP2 / TZVPP unscaled	Reference
Water Monomer	3657	3854	
H2O.PET-r	3540	3714	unpublished result
$H_2O.NH_3$	3485	3646	[1]
H_2O.BPN-g	3592	3762	[2]
H_2O.BPN-a linear	3599	3782	[2]
H_2O.BPN-a side	3628	3810	[2]
BPN Aw2	3499 3563	3626 3728	[2]
CEB.w1 side	3621	3796	
CEB.w1 pi	-	3809	
BrEB.w1 side	3618	3792	
BrEB.w1 pi	-	3809	
FEB.w1 side	-	3808	
FEB.w1 pi	-	3809.5	
Benzene.H_2O	3634	3808.5	[3]

[1] A. K. Mollner, B. E. Casterline, L. C. Ch'ng, H. Reisler, *J. Phys. Chem. A* **2009,** *113*, 10174-10183.

[2] P. A. Robertson, I. A. Lobo, D. J. D. Wilson, E. G. Robertson, *Chem. Phys. Lett.* **2016**, 660, 221-227.

[3] T. S. Zwier, R. N. Pribble, Science, **1994**, 265, 75-79.

Cartesian Coordinates

Geometries listed have been optimized at the B3LYP-D3(BJ)/aug-cc-pVTZ level of theory. Coordinates are given in Angstroms.

F-Ethylbenzene (anti)

0 1

6	-2.790297	-0.000106	-0.307781
6	-2.113135	1.200997	-0.133606
6	-0.767201	1.198530	0.210575
6	-0.076837	0.000075	0.388674
6	-0.767067	-1.198462	0.210679
6	-2.113006	-1.201110	-0.133523
1	-3.838364	-0.000171	-0.573254
1	-2.633598	2.140217	-0.262234
1	-0.246910	2.137751	0.349878
1	-0.246692	-2.137624	0.350070
1	-2.633355	-2.140404	-0.262079
6	1.394550	0.000181	0.713184
1	1.656652	0.880317	1.301530
1	1.656683	-0.879688	1.301924
6	2.224071	0.000019	-0.560550
1	2.026097	0.888474	-1.161676
1	2.026012	-0.888559	-1.161453
9	3.587445	-0.000117	-0.245402

F- Ethylbenzene (gauche)

0 1

6	-2.593137	-0.326037	-0.312467
6	-2.138937	0.984749	-0.390038
6	-0.835548	1.292351	-0.019356
6	0.032781	0.300010	0.433356
6	-0.434489	-1.011528	0.508620
6	-1.736386	-1.323367	0.138712
1	-3.607474	-0.567956	-0.598244
1	-2.799731	1.768383	-0.734932
1	-0.490000	2.317018	-0.077717
1	0.229932	-1.792318	0.852477
1	-2.082245	-2.346040	0.202763
6	1.457020	0.632757	0.793632
1	1.532349	1.682443	1.087228
1	1.786801	0.036934	1.646592
6	2.435183	0.413391	-0.348244
1	3.436931	0.750828	-0.078003
1	2.109175	0.923492	-1.255758
9	2.529482	-0.949638	-0.652189

F-Ethylbenzene - water cluster (bound to ring)

0 1

6	2.763908	-0.183372	-0.061547
6	2.054845	-0.767439	-1.105080
6	0.702433	-1.047594	-0.958435
6	0.033658	-0.752320	0.229428
6	0.755928	-0.169702	1.271106
6	2.110436	0.113344	1.129584
1	3.817308	0.032886	-0.172624
1	2.555750	-1.005758	-2.033288
1	0.156845	-1.500862	-1.775990
1	0.252574	0.066341	2.199554
1	2.653971	0.562269	1.949575
6	-1.445376	-1.001783	0.361640
1	-1.731373	-1.894287	-0.196561
1	-1.711351	-1.167821	1.406128
6	-2.247701	0.179053	-0.165417
1	-2.042352	0.361605	-1.220317
1	-2.038648	1.091307	0.391809
9	-3.615403	-0.096089	-0.040531
8	0.110141	2.621339	-0.425787
1	0.669902	1.904652	-0.103992
1	0.706081	3.222636	-0.880901

F-Ethylbenzene - water cluster (bound to halogen)

0 1

6	3.241714	0.492982	-0.270155
6	2.918277	-0.821141	0.044836
6	1.606714	-1.160253	0.354715
6	0.601799	-0.194284	0.357809
6	0.937413	1.121588	0.039285
6	2.247074	1.464263	-0.271296
1	4.262052	0.759418	-0.508807
1	3.687039	-1.581733	0.052759
1	1.361336	-2.184709	0.604985
1	0.165485	1.880450	0.042355
1	2.492012	2.490115	-0.510416
6	-0.830251	-0.564962	0.647755
1	-0.876372	-1.436629	1.301501
1	-1.342414	0.258554	1.144821
6	-1.561036	-0.875136	-0.645425
1	-1.150297	-1.750971	-1.146359
1	-1.548350	-0.023141	-1.323559
9	-2.919821	-1.161431	-0.373703
8	-3.471264	1.578230	0.231516
1	-3.636335	0.640140	0.069947
1	-4.335881	1.997192	0.238826

Cl- Ethylbenzene (anti)

0 1

6	-2.591145	-1.201299	-0.150555
6	-3.265210	0.000063	-0.335400
6	-2.591062	1.201365	-0.150477
6	-1.250672	1.198830	0.214417
6	-0.563850	-0.000056	0.402569
6	-1.250755	-1.198883	0.214339
1	-3.109844	-2.140326	-0.287155
1	-4.308936	0.000107	-0.617358
1	-3.109694	2.140437	-0.287014
1	-0.732253	2.137878	0.361763
1	-0.732399	-2.137975	0.361621
6	0.903517	-0.000114	0.749270
1	1.155468	-0.878648	1.343019
1	1.155480	0.878236	1.343287
6	1.740374	0.000072	-0.522044
1	1.554745	0.885434	-1.122646
1	1.554732	-0.885108	-1.122909
17	3.516795	0.000006	-0.147372

Cl- Ethylbenzene (gauche)

0 1

6	-2.009845	-1.326467	0.335062
6	-2.828571	-0.492491	-0.416099
6	-2.414434	0.804305	-0.697706
6	-1.188854	1.259172	-0.229507
6	-0.358102	0.429872	0.523526
6	-0.783705	-0.867075	0.800186
1	-2.324738	-2.336605	0.558487
1	-3.783580	-0.848505	-0.776988
1	-3.047804	1.462335	-1.276850
1	-0.876358	2.273342	-0.446412
1	-0.146744	-1.522895	1.377909
6	0.983281	0.923806	0.996738
1	1.316692	0.350768	1.861848
1	0.898191	1.966430	1.316900
6	2.066396	0.886666	-0.072209
1	2.988494	1.337464	0.282452
1	1.746092	1.381142	-0.984657
17	2.496045	-0.810012	-0.550155

Cl-Ethylbenzene - water cluster (bound to ring)

0 1

6	2.545814	0.120894	1.117946
6	3.190909	-0.200913	-0.071313
6	2.472281	-0.796034	-1.102108
6	1.118287	-1.061842	-0.944818
6	0.458189	-0.741015	0.241172
6	1.189606	-0.148052	1.270292
1	3.097239	0.578125	1.928037
1	4.245580	0.004380	-0.190747
1	2.967049	-1.053806	-2.028374
1	0.564778	-1.523539	-1.752358
1	0.692178	0.107716	2.196734
6	-1.023702	-0.975293	0.383749
1	-1.286307	-1.114797	1.432176
1	-1.316879	-1.880215	-0.148616
6	-1.804337	0.207484	-0.174751
1	-1.606538	0.357634	-1.231222
1	-1.583387	1.128858	0.353238
17	-3.592307	-0.067419	-0.019950
8	0.524971	2.616079	-0.445162
1	1.105837	3.267849	-0.847225
1	1.107612	1.913907	-0.132223

Cl-Ethylbenzene - water cluster (bound to halogen)

0 1

6	2.600517	1.322892	-0.297115
6	3.540878	0.298695	-0.328311
6	3.156918	-0.997352	-0.007339
6	1.838341	-1.266490	0.340778
6	0.889496	-0.246868	0.377095
6	1.284332	1.051691	0.052181
1	2.894070	2.334570	-0.542103
1	4.566369	0.510479	-0.597854
1	3.883295	-1.798378	-0.025287
1	1.544325	-2.277265	0.594176
1	0.551853	1.848396	0.079269
6	-0.552312	-0.533645	0.713156
1	-0.967647	0.281993	1.302756
1	-0.637540	-1.449248	1.297810
6	-1.356291	-0.672389	-0.569490
1	-1.063936	-1.544499	-1.145967
1	-1.282981	0.218167	-1.184105
17	-3.136986	-0.881520	-0.216485
8	-2.340398	2.308671	0.218906
1	-2.894721	3.091494	0.280106
1	-2.952409	1.561561	0.184472

Br- Ethylbenzene (anti)

0 1

6	-3.335037	-1.201392	-0.162428
6	-1.998997	-1.199031	0.217723
6	-1.314564	-0.000016	0.413750
6	-1.998973	1.199016	0.217746
6	-3.335013	1.201412	-0.162405
6	-4.006961	0.000018	-0.354882
1	-3.852206	-2.140388	-0.305005
1	-1.482070	-2.138034	0.370508
1	-1.482027	2.138006	0.370550
1	-3.852163	2.140420	-0.304964
1	-5.047354	0.000031	-0.648924
6	0.149456	-0.000033	0.776508
1	0.394238	0.878113	1.373489
1	0.394235	-0.878232	1.373412
6	0.992108	0.000021	-0.489769
1	0.822079	0.886524	-1.091449
1	0.822076	-0.886429	-1.091525
35	2.924888	0.000001	-0.079530

Br- Ethylbenzene (gauche)

0 1

6	-2.419169	-1.344876	0.515679
6	-1.297465	-0.675321	0.989529
6	-0.977669	0.596914	0.522458
6	-1.807622	1.187335	-0.430092
6	-2.928328	0.521661	-0.908219
6	-3.237246	-0.748966	-0.435770
1	-2.652157	-2.332880	0.888460
1	-0.658383	-1.147049	1.723600
1	-1.577266	2.179647	-0.798177
1	-3.562535	0.995193	-1.645169
1	-4.110603	-1.268555	-0.804881
6	0.255628	1.312497	1.006181
1	0.019213	2.365902	1.188574
1	0.589312	0.893846	1.955250
6	1.409371	1.298930	0.015595
1	2.252094	1.883862	0.368708
1	1.107223	1.641493	-0.968595
35	2.131660	-0.517157	-0.273141

Br-Ethylbenzene - water cluster (bound to ring)

0 1

6	3.240311	0.120291	1.102909
6	1.882104	-0.129406	1.270458
6	1.136162	-0.732913	0.258295
6	1.782911	-1.084344	-0.926521
6	3.138521	-0.837345	-1.098993
6	3.872112	-0.231425	-0.084809
1	3.802945	0.586965	1.899685
1	1.394432	0.150742	2.195047
1	1.217821	-1.555835	-1.720351
1	3.623620	-1.119220	-2.023393
1	4.928063	-0.040736	-0.216326
6	-0.348190	-0.946715	0.415348
1	-0.650599	-1.870965	-0.076990
1	-0.606905	-1.040311	1.469561
6	-1.111321	0.221872	-0.191474
1	-0.926923	0.322585	-1.255244
1	-0.887943	1.163533	0.296269
35	-3.062537	-0.033317	-0.011817
8	1.266181	2.655717	-0.426128
1	1.791005	3.123333	-1.081663
1	1.818164	1.920181	-0.135247

Br-Ethylbenzene - water cluster (bound to halogen)

0 1

6	-3.659272	-1.176840	-0.021634
6	-2.328127	-1.321299	0.351523
6	-1.477999	-0.218228	0.394271
6	-1.983454	1.036035	0.049315
6	-3.312573	1.182504	-0.324587
6	-4.154388	0.076017	-0.361639
1	-4.309008	-2.041099	-0.044288
1	-1.947267	-2.298728	0.619609
1	-1.326472	1.895793	0.079953
1	-3.693177	2.160858	-0.584646
1	-5.189947	0.190398	-0.650916
6	-0.021255	-0.368478	0.757584
1	0.306901	0.490038	1.341021
1	0.135496	-1.263717	1.358434
6	0.803598	-0.452992	-0.515051
1	0.671581	0.420838	-1.142115
1	0.606726	-1.356445	-1.082003
35	2.751300	-0.503149	-0.118782
8	1.410308	2.665141	0.228198
1	1.834913	3.527536	0.229195
1	2.133111	2.023298	0.228860