Anharmonic IR spectra of solvated ammonium and aminium ions: Resemblance between water and bisulfate solvations

Chih-Kai Lin,[a],* and Jer-Lai Kuo[b,c,d],*

[a] Department of Chemistry, National Taiwan University, Taipei, 10617, ROC.

[b] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan, ROC.

[c] Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC.

[d] International Graduate Program of Molecular Science and Technology, National Taiwan University, Taipei, 10617, Taiwan, ROC.

e-mail: ethenel@gmail.com (CKL), jlkuo@pub.iams.sinica.edu.tw (JLK)

Electronic Supplementary Information

This supporting information gives the Cartesian coordinates of optimized geometries, calculated anharmonic bands and assignments, and anharmonic coupling constants of clusters composed of ammonium/aminium solvated by either water or bisulfate investigated in this work.

**Table S1**. Cartesian coordinates of clusters optimized at the MP2/aug-cc-pVDZ level.

$NH_4^+...(H_2O)_2$

N	-0.00881807	1.06215806	0.00000000
H	0.85639895	0.47373110	0.00000000
H	-0.01253205	1.66035810	-0.82974909
H	-0.86479005	0.45966203	0.00000000
H	-0.01253205	1.66035810	0.82974909
O	2.26732499	-0.51414085	0.00000000
H	2.78865896	-0.79026787	0.76684094
H	2.78865896	-0.79026787	-0.76684094
O	-2.26617001	-0.52995902	0.00000000
H	-2.29383398	-1.49696402	0.00000000
H	-3.19294502	-0.25226905	0.00000000

$CH_3NH_3^+...(H_2O)_2$

N	0.00402013	0.47654098	0.53036787
H	-0.85128185	-0.08020408	0.32305395
H	-0.00713383	0.70119305	1.52913785
H	0.84435615	-0.10961198	0.34176486
C	0.03670001	1.72270593	-0.30089021
H	0.05748597	1.42749287	-1.35586820

H	-0.85940502	2.31631889	-0.08834220
H	0.93900399	2.29272300	-0.05359430
O	-2.33436382	-0.93096120	-0.09822492
H	-2.95711987	-0.74894228	-0.81580390
H	-2.73713275	-1.65748819	0.39785215
O	2.30535618	-0.96838092	-0.12014116
H	2.35339520	-1.76733095	-0.66364012
H	3.20155219	-0.85143584	0.22513478

$(CH_3)_2NH_2^+...(H_2O)_2$
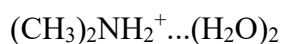
N	0.00000000	0.00000000	0.33627906
H	-0.84051974	0.01246488	-0.27348194
H	0.84051974	-0.01246488	-0.27348194
C	-0.02283574	-1.24551768	1.16002006
H	-0.93006131	-1.24356077	1.77655806
H	-0.02523530	-2.11398862	0.49000906
H	0.86828033	-1.26235578	1.79987706
C	0.02283574	1.24551768	1.16002006
H	0.02523530	2.11398862	0.49000906
H	-0.86828033	1.26235578	1.79987706
H	0.93006131	1.24356077	1.77655806
O	-2.40667401	-0.00450640	-1.12914294
H	-2.64414620	-0.56324013	-1.88243794
H	-3.16554531	0.58444462	-1.01447794
O	2.40667401	0.00450640	-1.12914294
H	3.16554531	-0.58444462	-1.01447794
H	2.64414620	0.56324013	-1.88243794

$(NH_4^+)_3(HSO_4^-)_2$
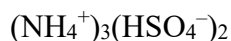
N	-2.37171314	0.05214604	-1.35000896
H	-1.56080336	-0.59757226	-1.48398096
H	-2.12242763	0.69257217	-0.56215196
H	-2.52120521	0.60273675	-2.19751396
H	-3.21136238	-0.48415883	-1.12528496
N	2.37171314	-0.05214604	-1.35000896
H	2.12242763	-0.69257217	-0.56215196
H	1.56080336	0.59757226	-1.48398096
H	3.21136238	0.48415883	-1.12528496
H	2.52120521	-0.60273675	-2.19751396
N	0.00000000	0.00000000	2.72506904
H	-0.52453758	-0.66045210	2.10217904
H	0.52453758	0.66045210	2.10217904

H	0.65190571	-0.52551348	3.30960304
H	-0.65190571	0.52551348	3.30960304
S	-0.01112731	-2.06202598	-0.00299296
O	-0.14016566	-1.58344469	-1.42339896
O	1.30889341	-1.69148970	0.63839204
O	-1.18499227	-1.68266302	0.87470404
O	-0.03890578	-3.69040079	-0.18716396
H	0.04079284	-4.09541476	0.69709304
S	0.01112731	2.06202598	-0.00299296
O	-1.30889341	1.69148970	0.63839204
O	0.14016566	1.58344469	-1.42339896
O	1.18499227	1.68266302	0.87470404
O	0.03890578	3.69040079	-0.18716396
H	-0.04079284	4.09541476	0.69709304

$(CH_3NH_3^+)_3(HSO_4^-)_2$
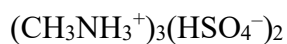
N	-0.09483276	-2.04724491	1.81615047
H	-0.69042495	-1.19201105	1.81201494
H	0.53849431	-1.94508916	0.99444236
H	-0.71268655	-2.84421834	1.64428576
C	0.68097714	-2.18571156	3.08277979
H	1.29526036	-3.09187751	3.02990640
H	-0.01667493	-2.24912128	3.92570582
H	1.31839893	-1.29991025	3.17594934
N	-0.20527674	2.62634735	0.80973147
H	-0.82977056	2.21518397	0.08554211
H	0.42336541	1.84661300	1.10437587
H	-0.79518388	2.87027858	1.60920699
C	0.57706905	3.78767265	0.29665557
H	1.21715287	4.16986718	1.10010699
H	-0.11444210	4.56816592	-0.04083484
H	1.19126622	3.42835737	-0.53614075
N	-0.18736262	-0.57206559	-2.66729606
H	-0.79616261	-0.97213145	-1.92036644
H	0.48976118	0.05045842	-2.17212805
H	-0.78258270	0.01877727	-3.25277713
C	0.51340371	-1.63129976	-3.44723818
H	1.14349468	-1.15942991	-4.21011092
H	-0.23033009	-2.28156074	-3.92214215
H	1.13034577	-2.20270141	-2.74536114
S	-2.18573804	-0.01152043	0.03799577

3

O	-1.69943625	0.22883308	1.44029241
O	-1.83579420	1.10394501	-0.92353810
O	-1.80363567	-1.36818429	-0.51567087
O	-3.81654106	-0.00415047	0.23526858
H	-4.22320893	-0.16060506	-0.63760820
S	1.96006296	0.01683544	-0.01669684
O	1.59689433	-1.41647719	-0.33666743
O	1.48154771	0.46896564	1.33487534
O	1.59013486	0.95518043	-1.14459248
O	3.59226792	0.08792312	0.16009221
H	3.99483308	-0.17559423	-0.68861129

$((CH_3)_2NH_2^+)_3(HSO_4^-)_2$
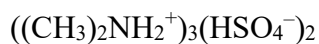
N	2.39602719	-0.48490686	-1.38701208
H	1.70846062	0.29497189	-1.46508808
H	1.98741581	-1.11285526	-0.66411608
C	2.48399480	-1.20976299	-2.68452708
H	3.17777630	-2.05292926	-2.57287308
H	2.85569018	-0.51753719	-3.45091708
H	1.48281111	-1.57332246	-2.94200908
C	3.70024296	0.05322692	-0.91174408
H	3.52880338	0.58265087	0.03248392
H	4.09189550	0.74673140	-1.66697308
H	4.39866903	-0.78173450	-0.77127608
N	-2.39602719	0.48490686	-1.38701208
H	-1.98741581	1.11285526	-0.66411608
H	-1.70846062	-0.29497189	-1.46508808
C	-3.70024296	-0.05322692	-0.91174408
H	-4.09189550	-0.74673140	-1.66697308
H	-4.39866903	0.78173450	-0.77127608
H	-3.52880338	-0.58265087	0.03248392
C	-2.48399480	1.20976299	-2.68452708
H	-1.48281111	1.57332246	-2.94200908
H	-3.17777630	2.05292926	-2.57287308
H	-2.85569018	0.51753719	-3.45091708
N	0.00000000	0.00000000	2.80507592
H	0.54123970	0.62278647	2.16669392
H	-0.54123970	-0.62278647	2.16669392
C	0.94324669	-0.81365947	3.61908692
H	0.36516784	-1.49275581	4.25919392
H	1.54788400	-0.13997233	4.23989992

H	1.57879300	-1.38735594	2.93512692
C	-0.94324669	0.81365947	3.61908692
H	-1.57879300	1.38735594	2.93512692
H	-0.36516784	1.49275581	4.25919392
H	-1.54788400	0.13997233	4.23989992
S	0.36912814	2.08076492	-0.00560808
O	0.48318900	1.55269428	-1.40814208
O	-1.02551198	1.97392736	0.56965792
O	1.41436877	1.54168105	0.94545192
O	0.69152085	3.68087187	-0.22078408
H	0.64897208	4.10923441	0.65453792
S	-0.36912814	-2.08076492	-0.00560808
O	1.02551198	-1.97392736	0.56965792
O	-0.48318900	-1.55269428	-1.40814208
O	-1.41436877	-1.54168105	0.94545192
O	-0.69152085	-3.68087187	-0.22078408
H	-0.64897208	-4.10923441	0.65453792

Table S2. Calculated peak positions (in cm^{-1}), IR intensities (in $km\ mol^{-1}$), and assignments of absorption peaks of ammonium/aminium ions solvated by water and bisulfate.[a]

$NH_4^+...(H_2O)_2$			$(NH_4^+)_3(HSO_4^-)_2$		
wavenumber	IR intensity	assignment	wavenumber	IR intensity	assignment
2790	483	FR_{uu}/S_B	2745	335	FR_{uu}/S_B
2816	341	FR_{uu}/S_B	2830	533	S_B/FR_{uu}
2851	411	S_B/FR_{uu}	2878	266	FR_{uu}/S_B
2901	324	FR_{uu}/S_B	2891	487	S_B/FR_{uu}
2927	583	S_B/FR_{uu}	3008	111	FR_{uu}
3020	72	FR_{uu}	3054	17	FR_{ux}
3113	22	FR_{ux}	3188	11	FR_{ux}
3212	27	FR_{ux}	3333	88	S_{FS}/FR_{xx}
3327	109	S_{FS}	3350	41	FR_{xx}/S_{FS}
3377	100	S_{FA}	3409	80	S_{FA}

$MA–H^+...(H_2O)_2$			$(MA–H^+)_3(HSO_4^-)_2$		
wavenumber	IR intensity	assignment	wavenumber	IR intensity	assignment
2482	11	FR_{ru}	2460	18	FR_{ru}
2522	42	FR_{ru}	2487	34	FR_{ru}
2573	8	FR_{rx}	2575	9	FR_{rx}
2637	22	FR_{rx}	2608	8	FR_{rx}
2833	102	FR_{ru}	2807	76	FR_{ru}
2846	51	FR_{ru}	2824	29	FR_{ru}
2928	116	FR_{rx}	2886	64	FR_{rx}
2938	94	FR_{rx}	2892	27	FR_{rx}
2953	62	FR_{rx}	2917	47	FR_{rx}
2956	47	FR_{rx}	2926	99	FR_{rx}
2996	334	S_{BS}	2972	533	S_{BS}
3057	750	S_{BA}	3027	406	S_{BA}
3123	89	FR_{uu}	3114	125	FR_{uu}
3196	24	FR_{ux}	3164	13	FR_{ux}
3216	10	FR_{ux}	3198	8	FR_{ux}
3285	17	FR_{xx}	3233	14	FR_{xx}
3308	5	FR_{xx}	3269	2	FR_{xx}
3332	6	FR_{xx}	3305	8	FR_{xx}
3344	66	S_F	3356	72	S_F

Table S2 (continued)

DMA–H$^+$...(H$_2$O)$_2$			(DMA–H$^+$)$_3$(HSO$_4^-$)$_2$		
wavenumber	IR intensity	assignment	wavenumber	IR intensity	assignment
2512	55	FR$_{rx}$	2493	48	FR$_{rx}$
2543	8	FR$_{rr}$	2521	16	FR$_{rr}$
2580	7	FR$_{rr}$	2590	8	FR$_{rr}$
2900	194	S$_B$/FR$_{rx}$	2866	166	FR$_{rr}$/S$_B$
2920	114	FR$_{rr}$/S$_B$	2881	211	FR$_{rr}$/S$_B$
2964	38	FR$_{rr}$/FR$_{rx}$	2943	24	FR$_{rr}$/FR$_{rx}$
2992	73	FR$_{rr}$	2972	284	FR$_{rr}$
3125	95	FR$_{rx}$/S$_B$	3085	388	S$_B$/FR$_{rx}$
3135	210	S$_B$/FR$_{rx}$	3096	401	S$_B$/FR$_{rx}$
3145	466	S$_B$/FR$_{rx}$	3108	22	FR$_{rx}$
3175	209	FR$_{rx}$/S$_B$	3165	8	FR$_{rx}$
3310	12	FR$_{xx}$	3313	15	FR$_{xx}$

[a] For the assignments, S$_B$ and S$_F$ denote H-bonded and free NH stretching bands, respectively; the additional subscripts S/A indicate symmetric/antisymmetric stretching modes. FR denotes the Fermi resonance band, and the following subscripts indicate the generalized bending overtone and combination tones that are involved: u, umbrella; x, scissoring; r, rocking (wagging/twisting).

Table S3. The original frequencies (in cm^{-1}) of NH stretching fundamentals and bending overtones/combination tones, the coupling constants (in cm^{-1}) between them, and the original IR intensities of stretching fundamentals (in km mol^{-1}) that involved in Fermi resonance in the clusters of ammonium/aminium cations solvated by water molecules/bisulfate anions.[a]

$NH_4^+\cdots(H_2O)_2$		uu						ux						xx			original
		2850	2894	2939	2943	2987	3035	3134	3140	3180	3184	3228	3231	3421	3428	3431	IR int.
$S_{b,sym}$	2882	2.0	22.6	-29.5	0.0	0.0	37.0	10.2	0.4	-24.2	-1.0	0.3	-8.6	-8.0	0.4	-0.3	912
$S_{b,asym}$	2884	20.8	41.5	-6.8	0.0	0.1	-24.7	20.2	0.8	0.6	0.1	1.1	-29.7	2.0	0.8	-7.9	1322
$S_{f,sym}$	3316	-48.2	4.9	-32.2	-0.1	0.0	-7.2	8.5	0.3	31.6	1.3	0.2	-3.4	-4.8	-0.1	2.7	126
$S_{f,asym}$	3374	0.0	0.0	0.0	14.8	42.4	0.0	1.3	-31.7	-0.4	10.3	13.8	0.6	0.0	0.4	0.0	107

$(NH_4^+)_3(HSO_4^-)_2$		uu						ux						xx			original
		2772	2838	2897	2906	2965	3024	3062	3085	3130	3153	3189	3211	3358	3382	3402	IR int.
$S_{b,sym}$	2840	1.5	44.5	3.1	16.4	-5.1	25.9	-11.1	-11.1	7.7	11.0	10.3	-17.9	-1.4	0.4	-4.7	942
$S_{b,asym}$	2893	-8.2	-36.0	1.4	15.4	2.5	35.4	10.7	9.6	11.1	12.0	-9.4	14.7	-3.3	1.5	-5.6	813
$S_{f,sym}$	3331	55.4	-1.9	-0.2	-33.4	-1.5	7.5	0.9	2.2	23.1	19.5	0.2	0.6	7.6	-1.0	4.8	150
$S_{f,asym}$	3400	1.8	-1.2	-3.5	-2.1	58.2	1.3	35.1	-38.0	-0.9	3.3	-18.0	-14.1	0.0	0.6	-0.1	86

Table S3 (continued)

MA–H⁺...(H₂O)₂		rr			ru				rx								uu	ux		xx			original IR int.
		2632	2645	2660	2556	2595	2900	2915	2625	2665	2973	2987	2647	2690	2996	3011	3161	3235	3258	3312	3337	3359	
$s_{b,sym}$	2989	-55.8	19.3	6.0	35.9	-33.0	7.7	-26.2	-2.6	2.2	-19.3	3.4	17.1	-15.1	-6.9	-13.7	11.3	38.3	4.2	-1.6	-9.4	0.3	625
$s_{b,asym}$	2999	-15.8	3.3	-0.5	9.5	7.6	-56.7	14.5	50.8	-34.1	-4.9	-28.6	8.5	3.3	39.3	-4.3	-40.5	11.1	17.4	-9.5	-13.9	-9.3	1186
s_f	3318	21.0	-30.7	16.3	-16.7	-53.8	-5.9	-43.0	12.9	-10.9	-28.3	-3.6	31.8	-28.2	4.6	-24.5	-1.4	-11.5	1.1	-5.9	12.5	-8.9	85

(MA–H⁺)₃(HSO₄⁻)₂		rr			ru				rx								uu	ux		xx			original IR int.
		2600	2600	2607	2548	2584	2883	2886	2593	2629	2932	2936	2627	2666	2968	2972	3160	3210	3246	3264	3302	3335	
$s_{b,sym}$	2935	7.2	11.7	-20.4	-28.7	-45.2	-41.0	8.1	23.5	22.3	23.1	-11.0	-22.2	21.0	12.4	25.3	25.4	-9.5	5.2	-0.3	6.2	-18.8	848
$s_{b,asym}$	3004	-3.6	-12.7	21.2	20.0	-50.0	-33.5	-26.0	33.7	-9.2	3.8	-28.1	0.9	35.9	30.4	6.9	-28.0	-15.4	11.4	15.3	8.4	5.2	688
s_f	3331	1.4	-7.4	-34.5	61.6	-2.4	13.6	-45.6	14.7	-34.4	-27.5	-20.9	31.1	12.6	19.5	-19.4	11.0	2.5	7.8	-15.0	12.2	2.3	87

DMA–H⁺...(H₂O)₂		rr_N/rt/rw										tt/tw/ww			rx							xx	original IR int.
		2471	2509	2520	2577	2597	2618	2626	2646	2726	2829	2940	2976	3051	2544	2719	2743	2841	2952	3094	3195	3315	
$s_{b,sym}$	2954	0.9	6.2	-9.7	14.7	9.1	0.0	43.7	0.2	0.3	0.1	-0.1	-13.8	-0.6	-58.6	-1.4	4.5	-1.9	-36.6	-2.5	10.2	18.4	968
$s_{b,asym}$	3281	-1.3	55.9	-17.9	23.9	-19.4	0.1	-5.7	1.3	0.5	0.0	-0.4	35.6	0.2	65.3	1.0	-1.5	-2.3	42.1	2.2	-2.9	9.6	73

(DMA–H⁺)₃(HSO₄⁻)₂		rr_N/rt/rw										tt/tw/ww			rx							xx	original IR int.
		2558	2564	2567	2626	2628	2663	2725	2759	2774	2820	2964	3028	3092	2607	2762	2763	2864	2964	3158	3220	3357	
$s_{b,sym}$	2980	-17.5	15.0	-26.2	-5.6	40.4	-0.4	0.1	2.5	1.4	0.0	27.5	56.4	-39.2	-68.5	1.2	3.7	2.4	-47.2	-3.7	7.4	12.0	833
$s_{b,asym}$	3008	21.5	19.5	29.4	30.2	22.3	-0.2	-0.4	1.8	1.1	-2.2	-36.5	50.6	43.5	-59.6	2.9	0.0	-3.0	-41.0	3.2	5.5	-14.0	799

[a] Notations to vibrational modes: s_b, H-bonded NH stretching; s_f, free NH stretching; u, NH₃ umbrella; x, NH₂ scissoring; r, CH₃–NH rocking; r_N, NH₂ rocking; t, NH₂ twisting; w, NH₂ wagging.

Table S4. The original frequencies (in cm^{-1}) of the four NH stretching fundamentals of the ammonium ion and the coupling constants (in cm^{-1}) between the NH stretching modes of two ammonium ions in the $(NH_4^+)_3(HSO_4^-)_2$ cluster. Note that only NH stretching modes are included in this tentative calculation.[a]

NH_4^+ ion 1 \ NH_4^+ ion 2		$s_{b,sym}$	$s_{b,asym}$	$s_{f,sym}$	$s_{f,asym}$
		2894	2944	3377	3451
$s_{b,sym}$	2894	-15.9	9.2	0.7	0.1
$s_{b,asym}$	2944	-9.2	2.4	-1.1	0.4
$s_{f,sym}$	3377	-0.7	-1.1	-0.6	0.1
$s_{f,asym}$	3451	-0.1	0.4	0.1	0.0

[a] Notations to vibrational modes: s_b, H-bonded NH stretching; s_f, free NH stretching.
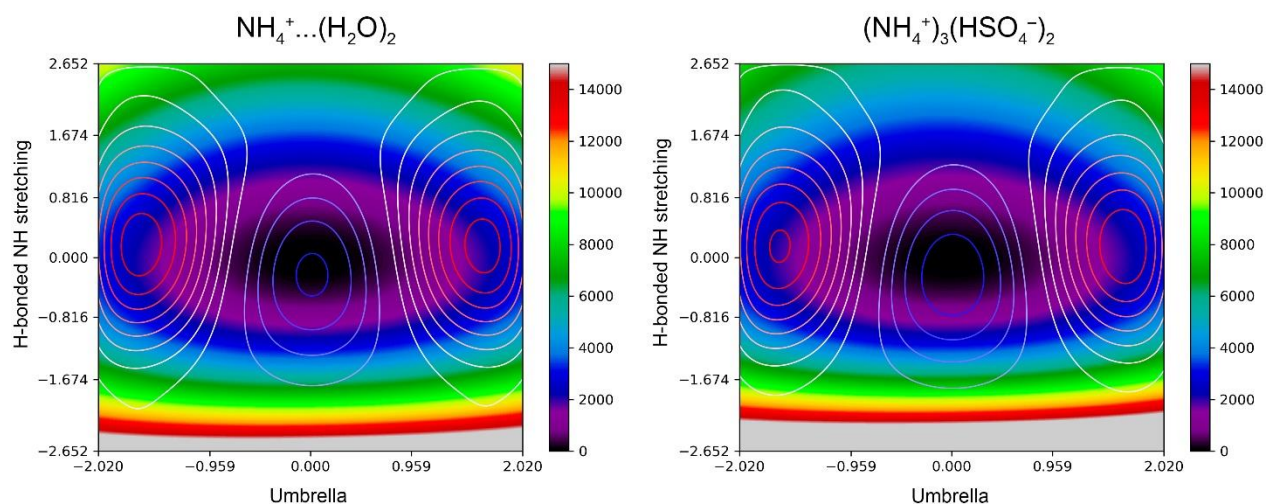
Figure S1. An example diagram showing the similarity between the PES and wavefunctions of $NH_4^+...(H_2O)_2$ and $(NH_4^+)_3(HSO_4^-)_2$ clusters. The PES is a low-dimensional cut regarding the H-bonded NH symmetric stretching mode (vertical axis) and one NH_3 umbrella mode (horizontal axis), and the color map indicates the potential energy. The wavefunction corresponds to the overtone state of the umbrella mode, presenting distortion due to the anharmonic coupling with the stretching mode.