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

Ab initio anharmonic approach to IR, Raman and SFG spectra of solvated methylammonium ion

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Electronic Supplementary Information

This supporting information gives the Cartesian coordinates of optimized geometries, anharmonic coupling constants, and scaled harmonic IR and Raman spectra of $CH_3NH_3^+...X_3$ clusters investigated in this work. The adequacy of the current level of theory is also discussed.

A. Harmonic IR and Raman spectra

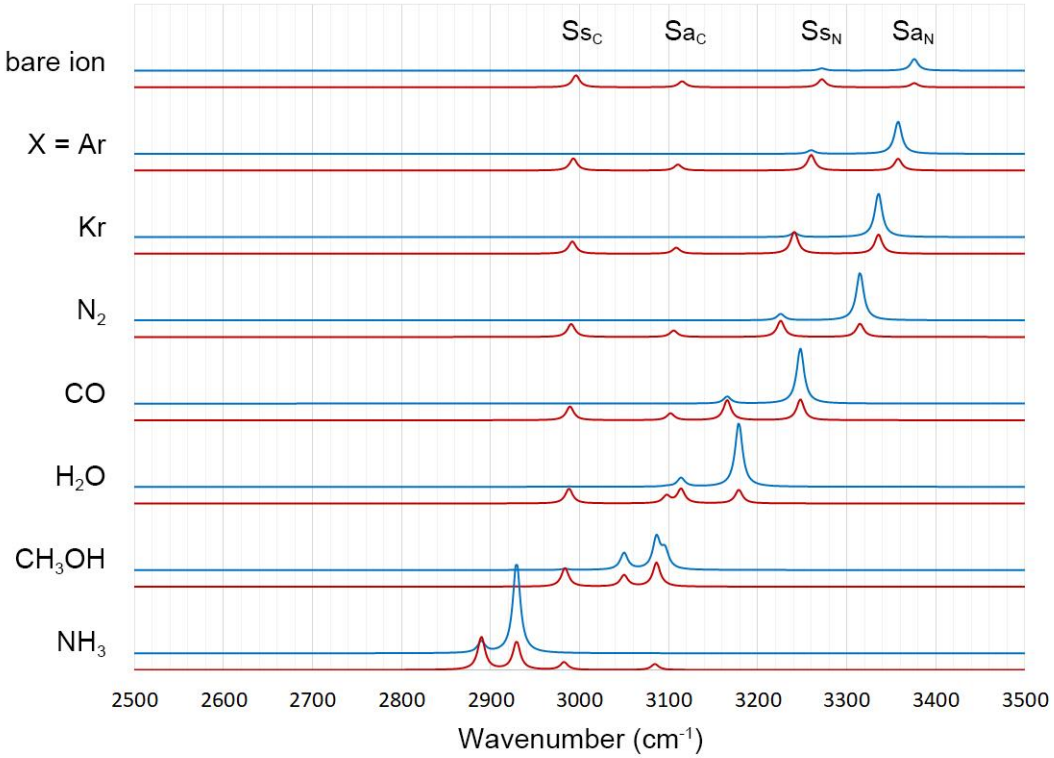

Figure S1. Calculated IR (blue traces) and static Raman (red traces) spectra of $CH_3NH_3^+...X_3$ clusters at the MP2/aug-cc-pVDZ level under the harmonic approximation. The frequencies were scaled by a common factor of 0.959. Ss and Sa denote symmetric and asymmetric stretching modes, and subscripts C and N refer to CH and NH groups, respectively.

B. Adequacy of the current level of theory

In this work, we have carried out the mixed-level scan with the *n*-mode representation (*n*MR) for the PES. The most essential components of PES were calculated using CCSD/aug-cc-pVDZ up to 2MR and the remaining parts using MP2/aug-cc-pVDZ up to 4MR. Although the experimental data of the triply-solvated methylammonium ion clusters ($MA–H^+...X_3$) have not been available yet, we have achieved good agreements between experimental and simulated spectra at this level for protonated amine–water clusters and solvated ammonium clusters.[1,2]

We take the methylammonium–water cluster, $MA–H^+...H_2O$, to test how much a higher level of theory and a larger basis set may improve the simulated results. **Figure S2** shows such a comparison between the IRPD experimental spectrum, the simulated one using CCSD/aug-cc-pVDZ, and the one using DLPNO-CCSD(T)-F12/aug-cc-pVTZ calculated with the ORCA program.[3]

The numbers of the major peaks and their resonance positions calculated by using CCSD/aug-cc-pVDZ are consistent with the experimental result within errors of 10 cm^{-1} (within ~0.3%).[1] Within this accuracy, we conclude that the CCSD/aug-cc-pVDZ level is suitable to construct a vibrational Hamiltonian with our anharmonic algorithm. The DLPNO-CCSD(T)-F12/aug-cc-pVTZ level, on the other hand, predicts peak positions closer to the experimental measurement. Even with this improvement, such a high level is not feasible for us to cope with clusters consisting of more binding partners or heavy atoms such as bromine and iodine studied in this work. Thus, we choose CCSD/aug-cc-pVDZ for this work.

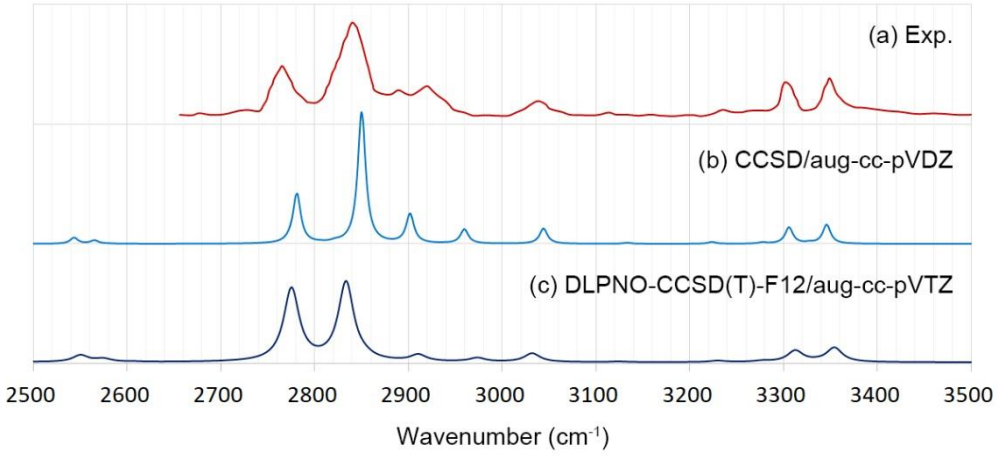

Figure S2. Comparison of experimental and simulated IR spectra of the $MA–H^+...H_2O$ cluster.

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[1] C.-K. Lin, R. Shishido, Q.-R. Huang, A. Fujii and J.-L. Kuo, Vibrational spectroscopy of protonated amine−water clusters: Tuning Fermi resonance and lighting up dark states, *Phys. Chem. Chem. Phys.*, 2020, **22**, 22035−22046.

[2] C.-K. Lin, Q.-R. Huang and J.-L. Kuo, Anharmonic coupling behind vibrational spectra of solvated ammonium: Lighting up overtone states by Fermi resonance through tuning solvation environments, *Phys. Chem. Chem. Phys.*, 2020, **22**, 24059−24069.

[3] F. Neese, The ORCA program system, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73−78.

C. Modeling local environments in perovskite

The local environment of the methylammonium ion in the organic–inorganic halide perovskite lattice, $MAPbX_3$, was modeled by gas-phase clusters of solvated methylammonium ions. Comparisons between experimental spectra of perovskite and simulated spectra of cluster models are given below. Results of different solvent types (halide anion *vs.* hydrogen halide molecule) and different halogen species are shown.

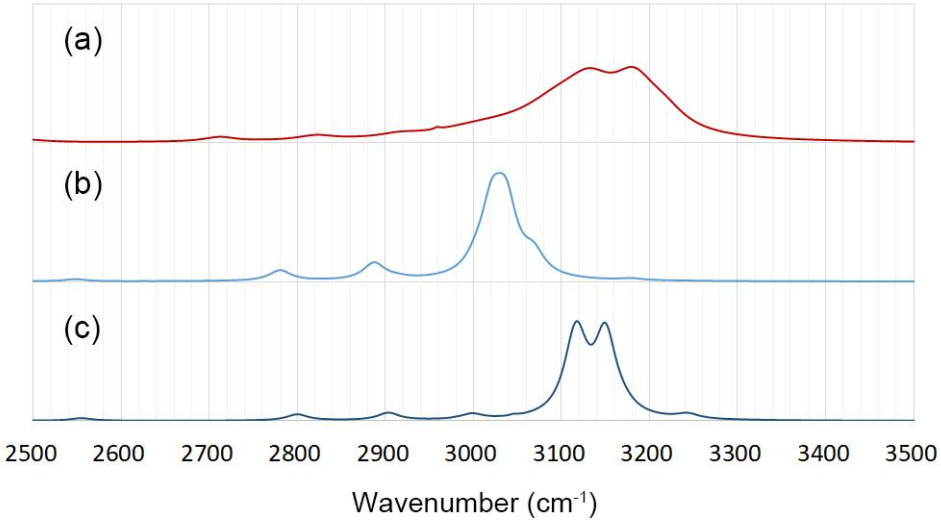

Figure S3. Comparison of IR spectra in the NH stretching region: (a) experimental spectrum of perovskite $MAPbI_3$ from Ref. 4, (b) simulated spectrum of cluster model $MA–H^+...(I^-)_3$, and (c) simulated spectrum of cluster model $MA–H^+...(HI)_3$.

[4] T. Glaser, C. Müller, M. Sendner, C. Krekeler, O. E. Semonin, T. D. Hull, O. Yaffe, J. S. Owen, W. Kowalsky, A. Pucci and R. Lovrinčić, Infrared spectroscopic study of vibrational modes in methylammonium lead halide perovskites, *J. Phys. Chem. Lett.*, 2015, **6**, 2913−2918.

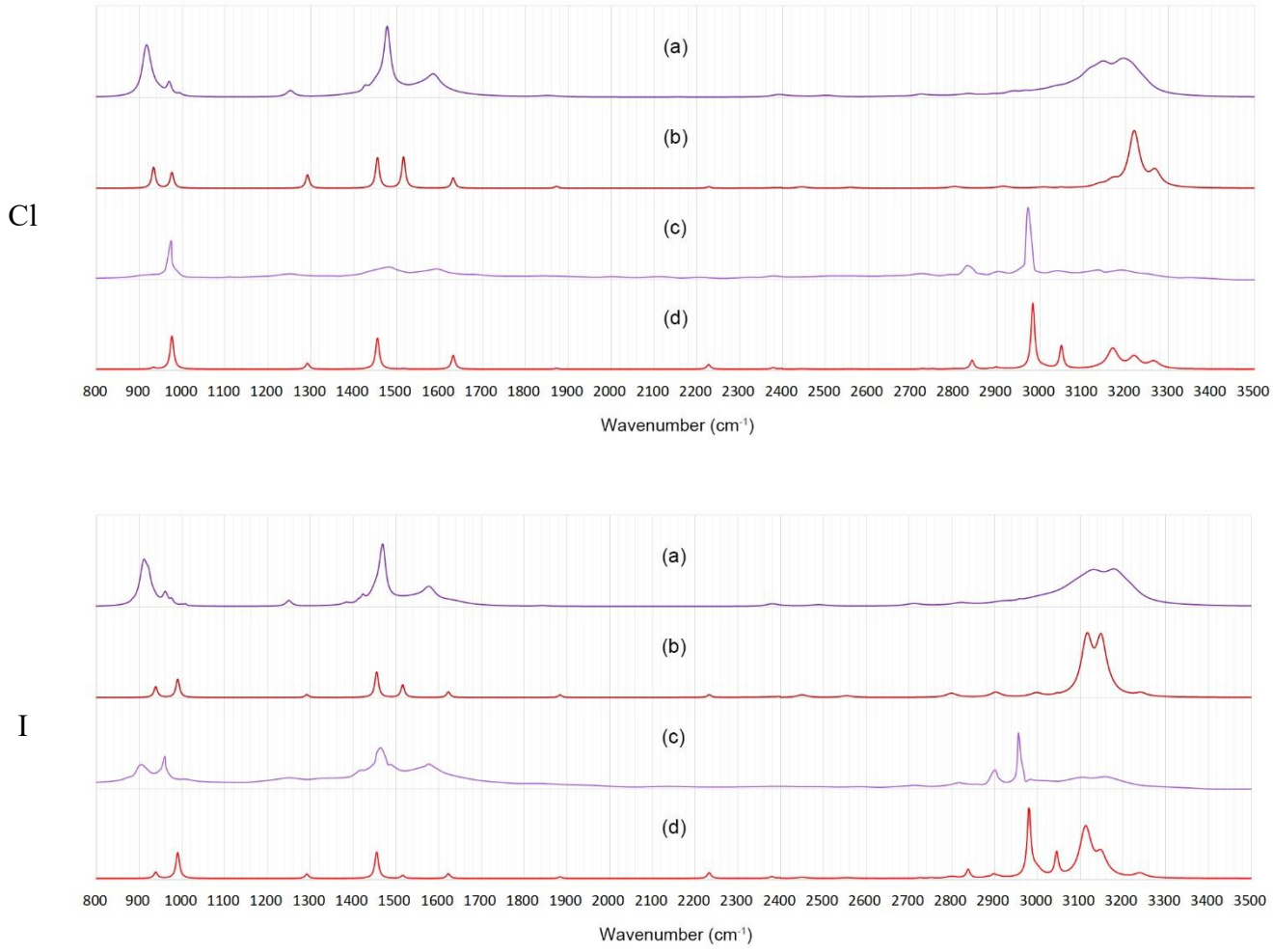

Figure S4. Comparison between experimental spectra of perovskite and simulated spectra of gas-phase model clusters with different halogen elements: (a) experimental IR spectrum of $MAPbX_3$ perovskite from Ref. 4, (b) simulated IR spectrum of $MA–H^+...(HX)_3$, (c) experimental Raman spectrum of $MAPbX_3$ perovskite from Ref. 5, and (d) simulated Raman spectrum of $MA–H^+...(HX)_3$.

[5] R. G. Niemann, A. G. Kontos, D. Palles, E. I. Kamitsos, A. Kaltzoglou, F. Brivio, P. Falaras and P. J. Cameron, Halogen effects on ordering and bonding of $CH_3NH_3^+$ in $CH_3NH_3PbX_3$ (X = Cl, Br, I) hybrid perovskites: A vibrational spectroscopic study, *J. Phys. Chem. C*, 2016, **120**, 2509−2519.

D. Cartesian coordinates of model clusters

Table S1. Cartesian coordinates of solvated methylammonium species optimized at the MP2/aug-cc-pVDZ level.

$CH_3NH_3^+...Ar_3$

N	0.00000000	0.00000000	0.40576196
H	0.00000000	0.95848077	0.03440498
H	-0.83006869	-0.47924038	0.03440498
H	0.83006869	-0.47924038	0.03440498
C	0.00000000	0.00000000	1.91276496
H	-0.90129996	0.52036577	2.25470597
H	0.00000000	-1.04073155	2.25470597
H	0.90129996	0.52036577	2.25470597
Ar	0.00000000	3.36478478	-0.39230095
Ar	-2.91398910	-1.68239239	-0.39230095
Ar	2.91398910	-1.68239239	-0.39230095

$CH_3NH_3^+...Kr_3$

N	0.00000000	0.00000000	0.60974872
H	0.00000000	0.95979042	0.23917972
H	0.83120288	-0.47989521	0.23917972
H	-0.83120288	-0.47989521	0.23917972
C	0.00000000	0.00000000	2.11470472
H	0.00000000	-1.04051575	2.45768572
H	0.90111307	0.52025787	2.45768572
H	-0.90111307	0.52025787	2.45768572
Kr	0.00000000	3.43658199	-0.23191728
Kr	-2.97616731	-1.71829100	-0.23191728
Kr	2.97616731	-1.71829100	-0.23191728

$CH_3NH_3^+...(N_2)_3$

N	0.00000000	0.00000000	0.50049310
H	0.00000000	0.96184402	0.13288410
H	-0.83298135	-0.48092201	0.13288410
H	0.83298135	-0.48092201	0.13288410
C	0.00000000	0.00000000	2.00395110
H	0.00000000	-1.03944899	2.35010910
H	0.90018923	0.51972449	2.35010910
H	-0.90018923	0.51972449	2.35010910
N	0.00000000	2.99937902	-0.39080590
N	0.00000000	4.08619302	-0.70329590

N	-2.59753842	-1.49968951	-0.39080590
N	-3.53874696	-2.04309651	-0.70329590
N	2.59753842	-1.49968951	-0.39080590
N	3.53874696	-2.04309651	-0.70329590

$CH_3NH_3^+...(CO)_3$

N	0.00000000	0.00000000	0.53962603
H	0.00000000	0.96588014	0.17377401
H	-0.83647673	-0.48294007	0.17377401
H	0.83647673	-0.48294007	0.17377401
C	0.00000000	0.00000000	2.03963103
H	0.00000000	-1.03852781	2.38915006
H	0.89939147	0.51926391	2.38915006
H	-0.89939147	0.51926391	2.38915006
C	0.00000000	3.05412012	-0.38004304
O	0.00000000	4.15317111	-0.70263207
C	-2.64494561	-1.52706006	-0.38004304
O	-3.59675169	-2.07658556	-0.70263207
C	2.64494561	-1.52706006	-0.38004304
O	3.59675169	-2.07658556	-0.70263207

$CH_3NH_3^+...(H_2O)_3$

N	0.00000000	0.00000000	0.25224110
H	0.12501171	0.96330656	-0.10845584
H	0.77174209	-0.58991660	-0.10845584
H	-0.89675381	-0.37338996	-0.10845584
C	0.00000000	0.00000000	1.74626310
H	0.97047116	0.36510470	2.10096314
H	-0.16904564	-1.02300503	2.10096314
H	-0.80142552	0.65790033	2.10096314
O	0.30075976	2.70147235	-0.57184073
H	0.93368957	3.35659750	-0.24692968
H	-0.20480413	3.16767476	-1.25193872
O	2.18916380	-1.61120176	-0.57184073
H	2.84568888	-1.40647180	-1.25193872
H	2.44005392	-2.48689764	-0.24692968
O	-2.48992356	-1.09027058	-0.57184073
H	-3.37374350	-0.86969986	-0.24692968
H	-2.64088475	-1.76120296	-1.25193872

$CH_3NH_3^+...(CH_3OH)_3$

N	0.00000000	0.00000000	1.26002610
H	0.41088269	0.87319110	0.87065608
H	-0.96164702	-0.08076070	0.87065608
H	0.55076433	-0.79243040	0.87065608
C	0.00000000	0.00000000	2.75053810
H	1.03289770	0.07700933	3.10937407
H	-0.58314089	0.85601098	3.10937407
H	-0.44975681	-0.93302031	3.10937407
O	1.00506288	2.16171438	-0.16979196
H	1.68282097	2.83354077	-0.01141698
C	0.06162597	2.67638863	-1.14719493
H	-0.71886317	1.91150489	-1.25198690
H	-0.39184788	3.61530410	-0.79972793
H	0.55565977	2.83111303	-2.11653095
O	-2.37463101	-0.21044720	-0.16979196
H	-3.29532877	0.04059532	-0.01141698
C	-2.34863353	-1.28482466	-1.14719493
H	-2.72964568	-0.93434104	-2.11653095
H	-1.29598021	-1.57830621	-1.25198690
H	-2.93502125	-2.14700226	-0.79972793
O	1.36956813	-1.95126717	-0.16979196
H	1.61250780	-2.87413609	-0.01141698
C	2.28700756	-1.39156397	-1.14719493
H	2.17398592	-1.89677199	-2.11653095
H	2.01484338	-0.33319868	-1.25198690
H	3.32686913	-1.46830183	-0.79972793

$CH_3NH_3^+...(NH_3)_3$

N	0.00000000	0.00000000	0.25834090
H	0.00181060	0.98670581	-0.09792310
H	-0.85541760	-0.49178488	-0.09792310
H	0.85360700	-0.49492093	-0.09792310
C	0.00000000	0.00000000	1.74737090
H	-0.89997752	0.51094962	2.11030590
H	0.00749341	-1.03487820	2.11030590
H	0.89248411	0.52392858	2.11030590
N	0.01140315	2.79984478	-0.57794610
H	-0.52434089	3.40199573	0.05053790
H	-0.38246106	2.96166623	-1.50698710
H	0.94802409	3.20772154	-0.60784810

N	-2.43043828	-1.39004698	-0.57794610
H	-2.68404428	-2.15509039	0.05053790
H	-2.37364766	-1.81205411	-1.50698710
H	-3.25198039	-0.78284782	-0.60784810
N	2.41903513	-1.40979780	-0.57794610
H	2.30395629	-2.42487372	-0.60784810
H	3.20838517	-1.24690533	0.05053790
H	2.75610872	-1.14961212	-1.50698710

$CH_3NH_3^+...(HCl)_3$

N	0.00000000	0.00000000	0.32849881
H	-0.07161297	0.96230858	-0.03662619
H	-0.79757719	-0.54317294	-0.03662619
H	0.86919017	-0.41913564	-0.03662619
C	0.00000000	0.00000000	1.83003981
H	0.05547212	-1.03802539	2.17637981
H	0.87122030	0.56705296	2.17637981
H	-0.92669242	0.47097243	2.17637981
Cl	-0.05266536	3.28097334	-0.31700219
H	-0.97822321	3.55329251	-1.17729319
Cl	-2.81507358	-1.68609621	-0.31700219
H	-2.58812997	-2.62381241	-1.17729319
Cl	2.86773894	-1.59487713	-0.31700219
H	3.56635319	-0.92948010	-1.17729319

$CH_3NH_3^+...(HBr)_3$

N	0.00000000	0.00000000	0.60175139
H	0.89104392	-0.37233892	0.23468039
H	-0.12306699	0.95783613	0.23468039
H	-0.76797693	-0.58549721	0.23468039
C	0.00000000	0.00000000	2.10144739
H	-0.96769001	0.37920147	2.44879239
H	0.15544690	-1.02764487	2.44879239
H	0.81224311	0.64844340	2.44879239
Br	3.14623276	-1.20889309	-0.20354661
H	2.85024383	-2.21661928	-1.16632261
Br	-0.52618426	3.32916404	-0.20354661
H	0.49452669	3.57669320	-1.16632261
Br	-2.62004851	-2.12027095	-0.20354661
H	-3.34477052	-1.36007393	-1.16632261

$CH_3NH_3^+...(HI)_3$

N	0.00000000	0.00000000	0.90761446
H	-0.01587807	0.96627048	0.53598745
H	-0.82887575	-0.49688606	0.53598745
H	0.84475382	-0.46938443	0.53598745
C	0.00000000	0.00000000	2.40455246
H	-0.01413168	-1.03898254	2.75325947
H	0.90685112	0.50725288	2.75325947
H	-0.89271944	0.53172966	2.75325947
I	-0.07790542	3.46621591	-0.16868957
H	-1.22404506	3.21050863	-1.27557357
I	-2.96287833	-1.80057603	-0.16868957
H	-2.16835950	-2.66530843	-1.27557357
I	3.04078375	-1.66563989	-0.16868957
H	3.39240456	-0.54520020	-1.27557357

E. Anharmonic coupling constants of model clusters

Table S2. Original peak positions of vibrational quantum states and the anharmonic coupling constants between relevant states (both in cm^{-1}) involved in Fermi resonance associated with NH modes in MA–H^+...X_3 clusters.[a]

			rr/rr'/r'r'										$ru_N/r'u_N$				$rx_N/r'x_N$								u_Nu_N	u_Nx_N		x_Nx_N			IR[b]
MA–H^+			1863	1865	1878	2216	2228	2229	2240	2585	2586	2589	2472	2472	2826	2826	2557	2556	2920	2920	2556	2557	2920	2920	3058	3153	3153	3250	3254	3255	
	s_{sN}	3227	0	0	-87	0	0	0	-86	0	0	39	0	0	0	0	0	-1	-1	3	-1	0	3	0	47	0	0	-26	0	0	58
	s_{aN}	3302	-20	28	0	0	17	24	0	-6	9	0	51	58	-42	-28	29	31	-26	-15	-31	30	16	-26	0	2	12	0	5	-20	132
	$s_{aN'}$	3302	28	20	0	0	-24	17	0	9	6	0	58	-50	-28	41	-30	29	15	-26	-29	-31	26	15	0	-11	2	0	-21	-5	132
MA–H^+...Ar_3			1893	1894	1906	2239	2251	2252	2263	2600	2601	2604	2492	2493	2841	2841	2582	2580	2937	2937	2580	2582	2937	2937	3071	3169	3169	3268	3272	3273	
	s_{sN}	3225	0	0	-80	0	0	0	-86	0	0	-43	0	0	0	0	0	0	-2	2	0	0	-2	-2	-46	0	0	26	0	0	93
	s_{aN}	3292	-30	5	0	0	28	4	0	11	-2	0	-57	-47	-13	-50	1	-41	19	-25	-41	-2	-25	-19	0	7	-10	0	19	-8	366
	$s_{aN'}$	3292	5	31	0	0	-4	28	0	-2	-12	0	-47	57	-51	14	42	1	25	19	1	-42	19	-25	0	-10	-7	1	-8	-19	366
MA–H^+...Kr_3			1900	1902	1913	2245	2256	2257	2269	2604	2605	2608	2495	2495	2842	2842	2584	2583	2938	2938	2583	2584	2938	2938	3069	3167	3167	3265	3269	3270	
	s_{sN}	3206	0	0	78	0	0	0	85	0	0	-43	0	0	0	0	0	0	-1	-2	0	0	2	-1	-45	0	0	25	0	1	106
	s_{aN}	3268	-29	0	0	0	27	0	0	11	0	0	33	-64	16	49	-31	-26	31	-3	-26	32	-3	-32	0	11	1	0	20	0	488
	$s_{aN'}$	3269	0	30	0	0	0	28	0	0	11	0	65	33	-50	16	-26	32	-3	-32	32	26	-32	3	0	-1	12	1	0	-20	488
MA–H^+...$(N_2)_3$			1941	1942	1953	2276	2287	2288	2299	2625	2625	2628	2535	2535	2875	2875	2627	2626	2970	2971	2626	2627	2970	2970	3112	3211	3211	3310	3314	3315	
	s_{sN}	3200	0	0	72	0	0	0	86	0	0	49	0	0	0	0	0	1	-2	-1	1	0	1	-2	46	0	0	-25	0	-1	158
	s_{aN}	3256	-25	-9	0	0	26	-10	0	12	5	0	68	12	-10	54	-35	-18	-4	-34	18	-34	-33	4	0	12	-5	0	-20	-1	555
	$s_{aN'}$	3257	9	-26	0	0	-10	-26	0	-5	12	0	-12	69	55	11	-19	35	34	-4	-35	-18	-4	-34	0	5	12	-1	-1	20	555
MA–H^+...$(CO)_3$			1969	1970	1980	2299	2310	2310	2321	2643	2643	2646	2557	2557	2893	2893	2646	2646	2985	2985	2646	2646	2985	2985	3132	3227	3227	3321	3326	3327	
	s_{sN}	3132	0	0	-65	0	0	0	83	0	0	52	0	0	0	0	-1	-1	0	-2	-1	1	2	0	43	0	0	-23	0	0	185
	s_{aN}	3180	24	0	0	0	26	0	0	-13	0	0	52	39	1	-56	25	-26	34	-4	27	26	-3	-35	0	11	-1	0	-18	-1	682
	$s_{aN'}$	3180	0	-25	0	0	0	-27	0	0	-13	0	39	-53	57	1	27	26	-3	-35	-26	27	-35	4	0	2	12	-1	-1	18	682

Table S2. (continued)

		rr/rr'/r'r'										$ru_N/r'u_N$				$rx_N/r'x_N$								u_Nu_N	u_Nx_N		x_Nx_N			IR[b]
$MA–H^+...(H_2O)_3$		2015	2016	2025	2341	2350	2351	2361	2679	2680	2682	2605	2605	2939	2939	2689	2689	3024	3024	2689	2689	3024	3024	3186	3274	3274	3362	3366	3367	
	s_{sN} 3076	0	0	-55	0	0	0	79	0	0	-56	0	0	0	1	2	4	-2	3	4	-2	3	2	42	0	0	-22	0	0	290
	s_{aN} 3103	-9	18	0	0	-12	-21	0	-7	-11	0	33	49	-52	24	-30	14	-10	-35	-14	-30	34	-10	0	11	-7	0	16	-7	942
	$s_{aN'}$ 3103	18	9	0	0	21	-12	0	11	-7	0	-49	32	-24	-52	15	31	-35	11	-30	15	-11	-34	0	6	12	0	8	16	941
$MA–H^+...(CH_3OH)_3$		2018	2018	2028	2327	2337	2338	2348	2649	2649	2652	2647	2647	2964	2964	2696	2696	3014	3015	2696	2696	3015	3014	3267	3320	3320	3374	3378	3378	
	s_{sN} 3005	0	-1	55	0	0	-1	76	0	0	-52	1	1	-1	-1	-4	1	-3	1	-3	-5	1	5	38	0	-1	-21	0	0	698
	s_{aN} 3008	-11	-16	-2	0	13	-17	-2	6	8	1	12	56	-50	-18	-10	-33	33	15	-33	10	-15	32	-1	-5	-12	0	-9	13	860
	$s_{aN'}$ 3008	-16	11	1	0	16	13	1	8	-6	-1	-55	12	-18	49	-33	10	-15	32	10	32	-32	-14	1	-11	5	0	-13	-9	860
$MA–H^+...(NH_3)_3$		2078	2079	2088	2408	2416	2416	2423	2751	2751	2754	2661	2661	3003	3003	2735	2736	3075	3075	2736	2735	3075	3075	3242	3317	3317	3393	3397	3398	
	s_{aN}/s_{sN} 2811	-1	-11	22	0	3	-15	-40	-3	9	36	-28	25	45	-2	-20	13	30	2	-12	-15	-1	28	21	-4	-5	-9	0	10	1134
	$s_{aN'}$ 2806	-13	0	-5	0	19	2	9	-11	-2	-8	-34	-30	9	55	14	23	6	-35	-23	13	35	6	-4	-7	4	2	12	2	1525
	s_{sN}/s_{aN} 2815	-1	8	29	0	1	12	-53	0	-7	47	16	-24	-33	10	12	-5	-20	-6	7	19	7	-23	27	2	5	-12	2	-7	832

[a] Notations of states: s_{sN} and s_{aN}, symmetric and asymmetric N–H stretching; r and r′, $CH_3–NH_3$ rocking; u_N, NH_3 umbrella; x_N, H–N–H scissoring.

[b] The original IR intensities (in km mol^{-1}) of the NH stretching modes.