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

Anharmonic coupling behind vibrational spectra of solvated ammonium: lighting up overtone states by Fermi resonance through tuning solvation environments

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Electronic Supplementary Information

The following information contains optimized coordinates and geometric parameters, Hamiltonian matrices of vibrational quantum states, and other properties relevant to Fermi resonance of ammonium-centered clusters, $NH_4^+...X_n$, where the attached species X include Ne, Ar, Kr, H_2O, and NH_3, and n = 1–5.

Table S1. Cartesian coordinates of $NH_4^+...X_n$ clusters optimized at the MP2/aug-cc-pVDZ level.

NH_4^+

N	0.00000000	0.00000000	0.00000000
H	-0.00000000	-0.00000000	1.02802758
H	-0.00000000	-0.96923370	-0.34267586
H	-0.83938100	0.48461685	-0.34267586
H	0.83938100	0.48461685	-0.34267586

$NH_4^+...Ne$

N	-0.00000000	-0.00000000	-1.51827062
H	-0.00000000	-0.00000000	-0.49054062
H	0.00000000	0.96804311	-1.86156959
H	0.83834993	-0.48402156	-1.86156959
H	-0.83834993	-0.48402156	-1.86156959
Ne	0.00000000	0.00000000	1.67031438

$NH_4^+...Ne_2$

N	0.00000000	0.00000000	1.17648232
H	0.00000000	0.83955600	0.58423132
H	0.00000000	-0.83955600	0.58423132
H	0.83785600	-0.00000000	1.77013732

H	-0.83785600	-0.00000000	1.77013732
Ne	0.00000000	2.61763200	-0.64720568
Ne	0.00000000	-2.61763200	-0.64720568

$NH_4^+...Ne_3$

N	0.00000000	0.00000000	0.76128627
H	0.00000000	0.96856175	0.41990729
H	-0.83879908	-0.48428087	0.41990729
H	0.83879908	-0.48428087	0.41990729
H	0.00000000	0.00000000	1.78783627
Ne	0.00000000	3.01731476	-0.27921867
Ne	2.61307124	-1.50865738	-0.27921867
Ne	-2.61307124	-1.50865738	-0.27921867

$NH_4^+...Ne_4$ I

N	0.00000000	0.00000000	0.00000000
H	-0.00000000	-0.00000000	1.02684459
H	-0.00000000	-0.96811836	-0.34228153
H	-0.83841510	0.48405918	-0.34228153
H	0.83841510	0.48405918	-0.34228153
Ne	-0.00000000	-0.00000000	3.19269099
Ne	-0.00000000	-3.01009793	-1.06423033
Ne	-2.60682127	1.50504896	-1.06423033
Ne	2.60682127	1.50504896	-1.06423033

$NH_4^+...Ne_4$ II

N	0.00000000	0.00000000	-1.24632114
H	0.00000000	0.96773899	-0.90283913
H	0.83808655	-0.48386949	-0.90283913
H	-0.83808655	-0.48386949	-0.90283913
H	-0.00000000	-0.00000000	-2.27263914
Ne	0.00000000	2.98219998	-0.12271811
Ne	2.58266094	-1.49109999	-0.12271811
Ne	-2.58266094	-1.49109999	-0.12271811
Ne	0.00000000	0.00000000	1.73869486

$NH_4^+...Ne_5$

N	-0.00000000	-0.00000000	0.51909187
H	-0.00000000	-0.00000000	1.54563687
H	0.00000000	0.96711902	0.17471887

H	-0.83754964	-0.48355951	0.17471887
H	0.83754964	-0.48355951	0.17471887
Ne	-0.00000000	-0.00000000	3.71089487
Ne	0.00000000	2.98242802	-0.60489014
Ne	-2.58285843	-1.49121401	-0.60489014
Ne	2.58285843	-1.49121401	-0.60489014
Ne	-0.00000000	-0.00000000	-2.46656813

NH_4^+...Ar

N	0.00000000	0.00000000	-2.13208379
H	0.00000000	0.00000000	-1.10185579
H	0.00000000	0.96770600	-2.47556579
H	0.83805798	-0.48385300	-2.47556579
H	-0.83805798	-0.48385300	-2.47556579
Ar	0.00000000	0.00000000	1.30295221

NH_4^+...Ar_2

N	0.00000000	0.00000000	1.52846289
H	0.00000000	0.84124800	0.93506389
H	0.00000000	-0.84124800	0.93506389
H	0.83733600	-0.00000000	2.12201989
H	-0.83733600	-0.00000000	2.12201989
Ar	0.00000000	2.80667700	-0.46703911
Ar	0.00000000	-2.80667700	-0.46703911

NH_4^+...Ar_3

N	-0.00000000	-0.00000000	0.96126285
H	0.00000000	0.97028428	0.61938583
H	-0.84029084	-0.48514214	0.61938583
H	0.84029084	-0.48514214	0.61938583
H	0.00000000	-0.00000000	1.98718285
Ar	0.00000000	3.25066727	-0.19581820
Ar	-2.81516044	-1.62533364	-0.19581820
Ar	2.81516044	-1.62533364	-0.19581820

NH_4^+...Ar_4 I

N	0.00000000	0.00000000	0.00000000
H	-0.00000000	-0.00000000	1.02834455
H	-0.00000000	-0.96953254	-0.34278152
H	-0.83963981	0.48476627	-0.34278152

H	0.83963981	0.48476627	-0.34278152
Ar	-0.00000000	-0.00000000	3.45597656
Ar	-0.00000000	-3.25832595	-1.15199219
Ar	-2.82179305	1.62916298	-1.15199219
Ar	2.82179305	1.62916298	-1.15199219

NH_4^+...Ar_4 II

N	-0.00000000	0.00000000	-1.38270455
H	0.00000000	0.96866218	-1.03732758
H	0.83888606	-0.48433109	-1.03732758
H	-0.83888606	-0.48433109	-1.03732758
H	-0.00000000	0.00000000	-2.40836655
Ar	0.00000000	3.29153921	-0.35082165
Ar	2.85055657	-1.64576960	-0.35082165
Ar	-2.85055657	-1.64576960	-0.35082165
Ar	0.00000000	0.00000000	1.89686945

NH_4^+...Ar_5

N	-0.00000000	-0.00000000	0.51930932
H	0.00000000	-0.00000000	1.54702632
H	0.00000000	0.96768516	0.17304538
H	-0.83803993	-0.48384258	0.17304538
H	0.83803993	-0.48384258	0.17304538
Ar	0.00000000	0.00000000	3.98006432
Ar	0.00000000	3.29562520	-0.51053747
Ar	-2.85409515	-1.64781260	-0.51053747
Ar	2.85409515	-1.64781260	-0.51053747
Ar	-0.00000000	-0.00000000	-2.76519168

NH_4^+...Kr

N	0.00000000	0.00000000	-2.69463000
H	0.00000000	0.00000000	-1.66271100
H	0.00000000	0.96757600	-3.03806100
H	-0.83794540	-0.48378800	-3.03806100
H	0.83794540	-0.48378800	-3.03806100
Kr	0.00000000	0.00000000	0.82331400

NH_4^+...Kr_2

N	0.00000000	0.00000000	1.78784537
H	0.00000000	0.84216000	1.19327137

H	0.00000000	-0.84216000	1.19327137
H	0.83724800	-0.00000000	2.38107237
H	-0.83724800	-0.00000000	2.38107237
Kr	0.00000000	2.86716000	-0.27310563
Kr	0.00000000	-2.86716000	-0.27310563

$NH_4^+...Kr_3$

N	0.00000000	0.00000000	1.09272549
H	0.00000000	0.97174499	0.74988949
H	-0.84155585	-0.48587250	0.74988949
H	0.84155585	-0.48587250	0.74988949
H	0.00000000	0.00000000	2.11825249
Kr	0.00000000	3.32831599	-0.11126852
Kr	-2.88240620	-1.66415800	-0.11126852
Kr	2.88240620	-1.66415800	-0.11126852

$NH_4^+...Kr_4$ I

N	0.00000000	0.00000000	0.00000000
H	-0.00000000	-0.00000000	1.02908760
H	-0.00000000	-0.97023309	-0.34302920
H	-0.84024650	0.48511654	-0.34302920
H	0.84024650	0.48511654	-0.34302920
Kr	-0.00000000	-0.00000000	3.54610036
Kr	-0.00000000	-3.34329549	-1.18203345
Kr	-2.89537882	1.67164774	-1.18203345
Kr	2.89537882	1.67164774	-1.18203345

$NH_4^+...Kr_4$ II

N	0.00000000	0.00000000	-1.45443621
H	0.00000000	0.96955900	-1.10849520
H	0.83966272	-0.48477950	-1.10849520
H	-0.83966272	-0.48477950	-1.10849520
H	-0.00000000	0.00000000	-2.47984421
Kr	0.00000000	3.40721999	-0.49624220
Kr	2.95073907	-1.70361000	-0.49624220
Kr	-2.95073907	-1.70361000	-0.49624220
Kr	-0.00000000	0.00000000	1.93279279

$NH_4^+...Kr_5$

N	-0.00000000	-0.00000000	0.50322406

H	-0.00000000	-0.00000000	1.53182706
H	0.00000000	0.96835719	0.15653811
H	-0.83862192	-0.48417859	0.15653811
H	0.83862192	-0.48417859	0.15653811
Kr	0.00000000	0.00000000	4.05491106
Kr	0.00000000	3.41542322	-0.44127275
Kr	-2.95784327	-1.70771161	-0.44127275
Kr	2.95784327	-1.70771161	-0.44127275
Kr	0.00000000	-0.00000000	-2.88453694

$NH_4^+...H_2O$

N	0.00001125	-1.34562722	0.00000000
H	-0.00291663	-0.28771642	0.00000000
H	-0.48126923	-1.69952281	0.83256600
H	-0.48126923	-1.69952281	-0.83256600
H	0.96400260	-1.69306699	0.00000000
O	0.00152189	1.36252936	0.00000000
H	-0.00540070	1.94949232	-0.76968500
H	-0.00540070	1.94949232	0.76968500

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

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

$NH_4^+...(H_2O)_3$ I

N	-0.00000000	-0.00000000	0.70329510
H	0.97320689	-0.14042202	0.36586914
H	-0.36499441	0.91303290	0.36586914
H	-0.60821248	-0.77261088	0.36586914
H	-0.00000000	-0.00000000	1.72476310
O	2.62862373	-0.38867328	-0.22500877

H	3.30392759	-0.98682625	0.12371327
H	3.08297980	0.12596289	-0.90625977
O	-0.97771093	2.47079157	-0.22500877
H	-0.79734719	3.35469835	0.12371327
H	-1.65057696	2.60695738	-0.90625977
O	-1.65091280	-2.08211829	-0.22500877
H	-1.43240284	-2.73292027	-0.90625977
H	-2.50658040	-2.36787209	0.12371327

$NH_4^+...(H_2O)_3$ II

N	0.00000000	0.00000000	-2.10272380
H	0.00000000	0.83613600	-1.47071780
H	0.00000000	-0.83613600	-1.47071780
H	-0.83296600	0.00000000	-2.69448180
H	0.83296600	0.00000000	-2.69448180
O	0.00000000	1.81150500	-0.08190580
H	0.00000000	2.76595500	0.06534420
H	0.00000000	1.39014500	0.79745720
O	0.00000000	-1.81150500	-0.08190580
H	0.00000000	-1.39014500	0.79745720
H	0.00000000	-2.76595500	0.06534420
O	0.00000000	0.00000000	2.14424820
H	-0.76444200	0.00000000	2.74018520
H	0.76444200	0.00000000	2.74018520

$NH_4^+...(H_2O)_3$ III

N	1.45622612	-1.27849002	0.00000000
H	0.39803512	-1.30433106	0.00000000
H	1.79556908	-0.29219001	0.00000000
H	1.81015715	-1.75769199	0.83049299
H	1.81015715	-1.75769199	-0.83049299
O	-1.22919488	-1.27660312	0.00000000
H	-1.84768486	-2.01796514	0.00000000
H	-1.77232591	-0.45616814	0.00000000
O	2.32155303	1.36913401	0.00000000
H	1.75106900	2.15009699	0.00000000
H	3.22375001	1.71785904	0.00000000
O	-2.50944497	1.13039584	0.00000000
H	-3.01279296	1.44206484	0.76512800

H	-3.01279296	1.44206484	-0.76512800

$NH_4^+...(H_2O)_4$ I

N	0.00000000	0.00000000	0.00000000
H	0.00415700	0.84415400	0.59769700
H	0.84415400	-0.00415700	-0.59769700
H	-0.00415700	-0.84415400	0.59769700
H	-0.84415400	0.00415700	-0.59769700
O	-0.00000000	2.33813000	1.64487200
H	-0.52474200	2.50808100	2.43896800
H	0.57913900	3.10835600	1.56564600
O	2.33813000	0.00000000	-1.64487200
H	2.50808100	0.52474200	-2.43896800
H	3.10835600	-0.57913900	-1.56564600
O	0.00000000	-2.33813000	1.64487200
H	0.52474200	-2.50808100	2.43896800
H	-0.57913900	-3.10835600	1.56564600
O	-2.33813000	-0.00000000	-1.64487200
H	-3.10835600	0.57913900	-1.56564600
H	-2.50808100	-0.52474200	-2.43896800

$NH_4^+...(H_2O)_4$ II

N	-0.85368588	1.13979800	0.00000000
H	-0.64075197	0.54950101	-0.82923002
H	-0.64075197	0.54950101	0.82923002
H	-0.28514489	2.00689200	0.00000000
H	-1.84446989	1.38549200	0.00000000
O	-0.18869207	-0.82399297	-1.82528609
H	-0.15999117	-0.99465996	-2.77511810
H	0.08977998	-1.64987498	-1.38961213
O	-0.18869207	-0.82399297	1.82528609
H	0.08977998	-1.64987498	1.38961213
H	-0.15999117	-0.99465996	2.77511810
O	0.52975912	-2.93795700	0.00000000
H	1.44558713	-3.25437400	0.00000000
H	-0.00133887	-3.74841100	0.00000000
O	0.62105911	3.55300300	0.00000000
H	0.94124619	4.04926499	0.76530386
H	0.94124619	4.04926499	-0.76530386

$NH_4^+...(H_2O)_4$ III

N	-1.00876714	-0.00108405	0.76519995
H	-0.14719606	-0.56490093	0.56790495
H	-0.88040726	0.97371098	0.43495201
H	-1.83035607	-0.42689014	0.29770191
H	-1.16936517	0.01348888	1.77344595
O	1.26891606	-1.42624073	0.25608394
H	1.42481519	-2.37588571	0.33068190
H	2.13692002	-1.02390860	0.03510499
O	-0.63257247	2.66967304	-0.09295290
H	-1.30357255	3.32574296	-0.32594189
H	0.21180948	3.12097016	-0.22781486
O	3.59043590	-0.09168039	-0.36142493
H	4.00554494	-0.15673029	-1.23255492
H	4.33129388	-0.02265532	0.25650409
O	-3.26295295	-1.15269429	-0.51454916
H	-4.13884794	-1.33990342	-0.15012720
H	-3.28988088	-1.50791125	-1.41351218

$NH_4^+...(H_2O)_4$ IV

N	-0.54677310	2.79444090	0.00000000
H	-0.32175999	2.20097793	0.83665205
H	-0.32175999	2.20097793	-0.83665205
H	-1.53530111	3.05154889	0.00000000
H	0.02194389	3.64287390	0.00000000
O	0.15694515	0.90059398	1.78597304
H	0.25570228	0.74292102	2.73292403
H	0.45641310	0.08961896	1.32412703
O	0.15694515	0.90059398	-1.78597304
H	0.45641310	0.08961896	-1.32412703
H	0.25570228	0.74292102	-2.73292403
O	0.89153693	-1.11211309	0.00000000
H	0.35734094	-1.94079609	0.00000000
H	1.81177993	-1.41117708	0.00000000
O	-0.68740205	-3.33676810	0.00000000
H	-0.87632815	-3.89479514	-0.76637162
H	-0.87632815	-3.89479514	0.76637162

$NH_4^+...NH_3$

N	-0.00000000	-0.00000000	-1.35274600
H	-0.00000000	-0.00000000	-0.23770700
H	-0.88611215	-0.36495796	-1.71419500
H	0.12699321	0.94987462	-1.71419500
H	0.75911894	-0.58491665	-1.71419500
N	-0.00000000	-0.00000000	1.36361100
H	-0.74695755	-0.57078192	1.76807900
H	-0.12083286	0.93227517	1.76807900
H	0.86779041	-0.36149326	1.76807900

$NH_4^+...(NH_3)_2$

N	-0.00045695	1.04979594	0.00000819
H	0.88559606	0.44992694	-0.00049480
H	-0.88654891	0.44974794	0.00049370
H	-0.00088732	1.65264254	-0.82608083
H	0.00028235	1.65262935	0.82610315
N	2.35755712	-0.51169395	-0.00002548
H	3.18277880	0.02002023	0.28630267
H	2.59156567	-0.89816166	-0.91725368
H	2.32272994	-1.31515533	0.63124768
N	-2.35712388	-0.51181718	0.00003789
H	-2.21364856	-1.48234443	-0.28751888
H	-3.07551964	-0.14771273	-0.63002953
H	-2.80618241	-0.56558650	0.91708631

$NH_4^+...(NH_3)_3$ I

N	-0.00000000	0.00000000	0.67906424
H	-0.30505556	0.95137991	0.34477725
H	-0.67139139	-0.73987582	0.34477725
H	0.97644695	-0.21150409	0.34477725
H	-0.00000000	0.00000000	1.70057424
N	-0.84227002	2.63030009	-0.21336074
H	-0.08187044	3.31295379	-0.23278174
H	-1.55967841	3.04426594	0.38555426
H	-1.23841567	2.64077271	-1.15536574
N	2.69904171	-0.58572281	-0.21336074
H	2.91003736	-1.58557501	-0.23278174
H	3.41625085	-0.17141185	0.38555426
H	2.90618409	-0.24788692	-1.15536574

N	-1.85677169	-2.04457728	-0.21336074
H	-1.66776842	-2.39288579	-1.15536574
H	-2.82816692	-1.72737878	-0.23278174
H	-1.85657244	-2.87285409	0.38555426

NH_4^+...$(NH_3)_3$ II

N	-2.19738579	-0.09911469	0.00000000
H	-1.60111424	0.78897979	0.00000000
H	-1.49456940	-0.91439674	0.00000000
H	-2.79371767	-0.13362811	0.82879000
H	-2.79371767	-0.13362811	-0.82879000
N	-0.31127017	1.96264048	0.00000000
H	0.56427111	1.42885297	0.00000000
H	-0.27492198	2.57933337	0.81358000
H	-0.27492198	2.57933337	-0.81358000
N	-0.11618464	-1.93329334	0.00000000
H	-0.02833110	-2.54490851	-0.81349900
H	-0.02833110	-2.54490851	0.81349900
H	0.71263591	-1.32554617	0.00000000
N	2.51455375	0.05507576	0.00000000
H	2.86516591	0.56869675	0.81198800
H	2.86516591	0.56869675	-0.81198800
H	3.05439424	-0.81403441	0.00000000

NH_4^+...$(NH_3)_3$ III

N	1.04110303	0.92900104	0.00277099
H	0.25613703	0.16318405	0.00275598
H	0.93706706	1.52466203	-0.82138902
H	0.93948902	1.52217405	0.82902498
H	2.01191103	0.49892903	0.00069902
N	-0.94080999	-0.96898094	0.00263997
H	-0.90696897	-1.58996996	-0.80849202
H	-1.88708398	-0.54747793	0.00069393
H	-0.90932301	-1.58768393	0.81561298
N	-3.77092197	0.26093809	-0.00257713
H	-4.01778994	0.83281407	-0.81212215
H	-4.02332699	0.82193410	0.81285785
H	-4.43569898	-0.51498191	-0.01003414
N	3.66132102	-0.21861399	-0.00272092

H	4.20945205	0.02870399	-0.82942391
H	3.65992401	-1.24039499	0.02435910
H	4.23136700	0.07169802	0.79466709

$NH_4^+...(NH_3)_4$ I

N	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.04400402
H	-0.00000000	-0.98429643	-0.34800134
H	-0.85242571	0.49214821	-0.34800134
H	0.85242571	0.49214821	-0.34800134
N	0.00000000	-0.00000000	2.96480160
H	-0.92249221	-0.17033956	3.36967771
H	0.31372772	0.88407147	3.36967771
H	0.60876449	-0.71373191	3.36967771
N	-0.00000000	-2.79524175	-0.98826720
H	-0.31372772	-2.88227212	-1.95673648
H	-0.60876449	-3.41487325	-0.45031300
H	0.92249221	-3.23374247	-0.96262823
N	-2.42075037	1.39762088	-0.98826720
H	-3.26174923	0.81796954	-0.96262823
H	-2.33925702	1.71283224	-1.95673648
H	-2.65298474	2.23464214	-0.45031300
N	2.42075037	1.39762088	-0.98826720
H	2.33925702	2.41577292	-0.96262823
H	2.65298474	1.16943988	-1.95673648
H	3.26174923	1.18023111	-0.45031300

$NH_4^+...(NH_3)_4$ II

N	1.22734223	0.01003530	0.86044286
H	0.63432519	0.85385925	0.64242277
H	0.61221724	-0.82354675	0.64869503
H	2.11114120	-0.00230176	0.29269581
H	1.47028529	0.01181246	1.85193585
N	-0.72982786	1.98616515	0.18535968
H	-1.52806286	1.38274809	-0.03733718
H	-0.57269793	2.57159602	-0.63640542
H	-1.04512183	2.62274825	0.91904060
N	-0.74383476	-1.94019785	0.21095929
H	-1.05185969	-2.56755874	0.95565940

H	-0.58031879	-2.53864497	-0.60017263
H	-1.55078279	-1.34989691	-0.02260975
N	-3.36997186	-0.03695003	-0.52053384
H	-3.52537892	0.47100283	-1.39426091
H	-3.93986282	0.44851006	0.17597512
H	-3.84449784	-0.93240707	-0.65887567
N	3.70795613	-0.02646087	-0.66705929
H	3.80436112	-0.84170496	-1.27552417
H	4.53563117	-0.03814875	-0.06763734
H	3.82897507	0.78379104	-1.27778242

NH_4^+...$(NH_3)_4$ III

N	1.19086500	0.01261112	0.85129484
H	0.15608105	-0.17448310	1.03776588
H	1.68504505	0.02159814	1.74502482
H	1.60112312	-0.74751774	0.25511675
H	1.32041079	0.94775819	0.39289792
N	-1.54006587	-0.49016647	1.38241694
H	-1.70767366	-1.45179054	1.68477686
H	-2.16876594	-0.33346653	0.57862999
H	-1.90428394	0.09180938	2.13933701
N	-3.53420908	-0.04323965	-0.99731692
H	-3.20872814	-0.00475150	-1.96434193
H	-4.08425425	0.80681023	-0.86197581
H	-4.21178093	-0.80736779	-0.97077195
N	2.34753934	-2.12853050	-0.77126742
H	3.10021925	-1.82147129	-1.39040443
H	1.66749440	-2.58938958	-1.37886143
H	2.75316052	-2.87573147	-0.20415651
N	1.56072841	2.63839331	-0.38241594
H	2.38855933	3.13047744	-0.04045093
H	0.77780130	3.26998313	-0.20269884
H	1.66158737	2.61405842	-1.39886794

Table S2. NH bond lengths of the central ammonium ion and NH...Rg bond distances in ammonium–rare gas clusters, $NH_4^+...Rg_n$, optimized at the MP2/aug-cc-pVDZ level.

Cluster	Free NH bond length (Å)	Bonded NH bond length (Å)	NH...Rg distance (Å)
NH_4^+	1.027	–	–
$NH_4^+...Ne$	1.027	1.028	2.161
$NH_4^+...Ne_2$	1.027	1.027	2.163
$NH_4^+...Ne_3$	1.027	1.027	2.165
$NH_4^+...Ne_4$ I	–	1.027	2.166
$NH_4^+...Ne_4$ II	1.026	1.027	2.160
$NH_4^+...Ne_5$	–	1.027	2.165
		1.027	2.161
$NH_4^+...Ar$	1.027	1.030	2.405
$NH_4^+...Ar_2$	1.026	1.029	2.414
$NH_4^+...Ar_3$	1.026	1.029	2.422
$NH_4^+...Ar_4$ I	–	1.028	2.428
$NH_4^+...Ar_4$ II	1.026	1.028	2.422
$NH_4^+...Ar_5$	–	1.028	2.433
		1.028	2.426
$NH_4^+...Kr$	1.027	1.032	2.486
$NH_4^+...Kr_2$	1.026	1.031	2.500
$NH_4^+...Kr_3$	1.026	1.030	2.509
$NH_4^+...Kr_4$ I	–	1.029	2.517
$NH_4^+...Kr_4$ II	1.025	1.029	2.513
$NH_4^+...Kr_5$	–	1.029	2.523
		1.029	2.519

Table S3. NH bond lengths of the central ammonium ion and NH...X hydrogen bond distances in $NH_4^+...(H_2O)_n$ and $NH_4^+...(NH_3)_n$ clusters optimized at the MP2/aug-cc-pVDZ level.

Cluster	Free NH bond length (Å)	H-bonded NH bond length (Å)	NH...X distance (Å)
$NH_4^+...H_2O$	1.025	1.058	1.650
$NH_4^+...(H_2O)_2$	1.023	1.046	1.716
$NH_4^+...(H_2O)_3$ I	1.021	1.039	1.775
$NH_4^+...(H_2O)_3$ II	1.022	1.048	1.697
$NH_4^+...(H_2O)_3$ III	1.022	1.059	1.627
		1.043	1.743
$NH_4^+...(H_2O)_4$ I	–	1.034	1.824
$NH_4^+...(H_2O)_4$ II	1.021	1.041	1.756
		1.037	1.792
$NH_4^+...(H_2O)_4$ III	1.021	1.048	1.687
		1.037	1.793
		1.037	1.800
$NH_4^+...(H_2O)_4$ IV	1.021	1.050	1.680
$NH_4^+...NH_3$	1.024	1.115	1.601
$NH_4^+...(NH_3)_2$	1.023	1.070	1.758
$NH_4^+...(NH_3)_3$ I	1.022	1.054	1.849
$NH_4^+...(NH_3)_3$ II	1.022	1.076	1.714
		1.070	1.744
$NH_4^+...(NH_3)_3$ III	1.022	1.097	1.648
		1.062	1.799
$NH_4^+...(NH_3)_4$ I	–	1.044	1.921
$NH_4^+...(NH_3)_4$ II	1.021	1.057	1.810
		1.054	1.831
		1.050	1.863
$NH_4^+...(NH_3)_4$ III	1.021	1.068	1.759
		1.050	1.876
		1.049	1.875

Table S4. Hamiltonian matrix elements (in cm^{-1}) of NH bending overtones and stretching fundamentals involved in Fermi resonance and the original IR intensities of corresponding vibrational quantum states (in km/mol) in the bare NH_4^+ ion.[a]

	Bending overtones															Stretching fundamentals				Original
	uu						ux						xx			s_{sym}	s_{asym}	s'_{asym}	s''_{asym}	IR int.
uu	**2875.0**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	0.0	69.7	-0.3	0.1	0.0	0.0
	0.0	**2877.0**	0.0	0.0	0.0	0.0	0.3	-0.7	-0.7	-1.0	-1.4	-1.4	0.0	0.0	0.0	-0.1	-19.4	-15.2	45.2	0.0
	0.0	0.0	**2877.0**	0.0	0.0	0.0	-0.5	-0.7	-1.0	1.2	0.8	-0.9	0.0	0.0	0.0	0.2	7.8	-49.2	-13.2	0.0
	0.0	0.0	0.0	**2877.0**	0.0	0.0	-1.8	0.7	-0.5	-1.0	0.3	-0.4	0.0	0.0	0.0	-0.4	-47.1	-1.9	-20.9	0.0
	0.0	0.0	0.0	0.0	**2878.0**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.7	-0.2	0.0	-0.1	-0.4	-1.0	0.0
	0.0	0.0	0.0	0.0	0.0	**2878.0**	0.1	0.0	0.0	0.0	0.0	0.0	0.0	-0.2	-1.6	-0.2	0.6	1.0	0.7	0.0
ux	0.0	0.3	-0.5	-1.8	0.0	0.1	**3108.5**	-0.2	0.5	0.3	-0.5	0.1	0.0	0.0	0.0	0.0	26.9	9.6	21.6	0.2
	0.0	-0.7	-0.7	0.7	0.0	0.0	-0.2	**3107.9**	0.3	-0.5	0.1	0.5	0.0	0.0	0.0	0.0	-8.7	19.8	-11.7	0.1
	0.0	-0.7	-1.0	-0.5	0.0	0.0	0.5	0.3	**3107.9**	-0.1	0.0	0.5	0.0	0.0	0.0	0.0	10.9	21.1	-1.0	0.1
	0.0	-1.0	1.2	-1.0	0.0	0.0	0.3	-0.5	-0.1	**3108.5**	0.5	0.0	0.0	0.0	0.0	0.0	28.7	-18.5	-12.0	0.2
	0.0	-1.4	0.8	0.3	0.0	0.0	-0.5	0.1	0.0	0.5	**3108.2**	0.3	0.0	0.0	0.0	0.0	5.5	-6.1	-30.1	0.2
	0.0	-1.4	-0.9	-0.4	0.0	0.0	0.1	0.5	0.5	0.0	0.3	**3108.2**	0.0	0.0	0.0	0.0	10.4	23.9	-15.0	0.2
xx	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**3339.5**	0.0	0.0	-14.1	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	1.7	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**3343.6**	0.0	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	-0.2	-1.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**3344.1**	0.4	0.0	0.0	0.0	0.0
s_{sym}	69.7	-0.1	0.2	-0.4	0.0	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	-14.1	0.0	0.4	**3209.3**	0.0	0.0	0.0	0.0
s_{asym}	-0.3	-19.4	7.8	-47.1	-0.1	0.6	26.9	-8.7	10.9	28.7	5.5	10.4	0.0	0.0	0.0	0.0	**3320.9**	0.0	0.0	200.9
s'_{asym}	0.1	-15.2	-49.2	-1.9	-0.4	1.0	9.6	19.8	21.1	-18.5	-6.1	23.9	0.0	0.0	0.0	0.0	0.0	**3320.9**	0.0	201.0
s''_{asym}	0.0	45.2	-13.2	-20.9	-1.0	0.7	21.6	-11.7	-1.0	-12.0	-30.1	-15.0	0.0	0.0	0.0	0.0	0.0	0.0	**3321.0**	201.0

[a] Notations for NH vibrational modes: u, umbrella; x, scissoring; s_b, H-bonded stretching; s_{sym}, totally symmetric stretching; s_{asym}, asymmetric stretching.

Table S5. The original frequencies (in cm^{-1}) of NH stretching fundamentals and bending overtones, the coupling constants (in cm^{-1}) between them, and the original IR intensities of stretching fundamentals (in km/mol) that involved in Fermi resonance in NH_4^+...Ar_n clusters.[a]

NH_4^+…Ar		uu						ux						xx			Original
C_{3v}		2913	2925	2925	2937	2939	2940	3153	3153	3167	3166	3166	3167	3395	3401	3400	IR int.
s_{sym}	3209	27.3	1.4	0.0	-60.5	0.1	-0.6	0.0	-0.6	1.7	-13.2	-12.7	-1.6	14.9	0.3	0.0	147
$s_{b,asym}$	3293	-54.5	0.6	-0.2	-6.7	0.2	-1.9	0.0	0.9	3.6	-28.7	-30.7	-4.0	-7.4	-0.1	0.0	324
$s_{f,asym}$	3340	2.0	-29.0	2.2	-0.7	-3.8	-40.2	-6.6	33.6	-0.8	23.6	-21.7	-0.6	0.6	0.0	0.0	188
$s'_{f,asym}$	3341	0.5	-2.0	-30.9	0.0	42.3	-3.6	32.3	6.6	-23.6	-0.7	1.0	-22.6	0.1	0.0	-0.1	188

NH_4^+…Ar_2		uu						ux						xx			Original
C_{2v}		2916	2926	2933	2933	2942	2950	3158	3159	3167	3168	3175	3175	3400	3406	3407	IR int.
s_{sym}	3209	-36.5	0.0	-38.9	0.0	0.0	42.5	0.0	0.0	-12.1	0.0	0.0	0.0	15.9	0.0	-0.9	75
$s_{b,asym}$	3265	0.0	53.5	0.0	0.0	0.0	0.0	23.2	0.0	0.0	0.0	0.0	-38.7	0.0	0.0	0.0	548
$s_{b,sym}/s_{f,sym}$	3318	44.6	0.0	6.7	0.0	0.0	25.4	0.0	0.0	-45.6	0.0	0.0	0.0	-4.7	0.0	0.3	265
$s_{f,asym}$	3346	0.0	0.0	0.0	0.0	52.1	0.0	0.0	-40.4	0.0	0.0	21.9	0.0	0.0	0.0	0.0	175

NH_4^+…Ar_3		uu						ux						xx			Original
C_{3v}		2927	2929	2930	2941	2941	2954	3168	3168	3168	3168	3180	3180	3406	3412	3412	IR int.
s_{sym}	3210	-56.5	0.0	0.4	-0.6	-0.3	40.0	1.3	-3.8	5.2	1.5	0.6	-0.9	16.4	0.3	0.0	30
$s_{b,asym}$	3277	0.7	10.5	37.4	-32.5	4.3	-1.7	-13.8	19.5	19.0	13.7	4.9	-30.8	-0.6	0.0	0.0	511
$s'_{b,asym}$	3278	0.7	-42.5	9.2	-5.0	-30.1	-0.5	18.0	13.3	13.5	-18.4	31.3	5.5	-0.4	0.0	-0.1	512
s_f	3338	-34.0	0.0	0.2	1.6	-0.3	-35.4	-9.4	31.2	-30.4	-9.3	0.1	0.4	2.3	0.0	0.0	207

Table S5. (continued)

NH_4^+…Ar_4 I		uu						ux						xx			Original
T_d		2937	2940	2941	2941	2941	2942	3176	3176	3176	3176	3177	3176	3411	3417	3417	IR int.
s_{sym}	3212	-69.6	0.7	4.9	-0.3	3.0	-3.0	-0.5	-0.4	0.3	-0.1	0.1	0.7	-16.8	0.0	0.0	0
$s_{b,asym}$	3285	-0.4	3.6	-11.9	33.6	-26.2	-24.0	8.0	-12.1	27.6	-18.5	10.9	25.4	0.3	0.0	0.0	480
$s'_{b,asym}$	3286	3.5	-4.0	-1.4	-14.9	24.0	-41.2	-35.5	-16.5	2.6	18.4	4.4	11.6	0.4	0.0	0.0	480
$s''_{b,asym}$	3287	0.7	31.1	17.5	-27.0	-27.5	-9.6	9.9	-14.0	18.8	16.3	19.7	-28.0	-0.2	0.0	0.0	480

NH_4^+…Ar_4 II		uu						ux						xx			Original
C_{3v}		2926	2928	2929	2934	2934	2941	3164	3164	3164	3164	3170	3170	3400	3406	3405	IR int.
s_{sym}	3216	60.6	0.0	-0.6	0.1	0.0	-34.5	0.1	-3.6	-5.1	-0.1	0.0	1.1	16.5	0.3	0.0	17
$s_{b,asym}$	3283	0.5	0.1	37.8	34.1	0.1	-2.3	0.1	-24.6	23.5	0.1	0.3	-30.0	0.7	0.3	0.0	480
$s'_{b,asym}$	3284	0.0	-45.3	0.1	0.0	28.6	0.0	21.5	0.1	-0.1	22.8	-32.0	-0.3	0.0	0.0	-0.3	480
s_f	3343	-29.9	0.0	0.5	-3.1	0.0	-38.6	0.5	-33.5	-32.7	-0.5	0.0	1.2	-2.7	0.0	0.0	194

NH_4^+…Ar_5		uu						ux						xx			Original
C_{3v}		2928	2933	2933	2935	2937	2937	3169	3169	3172	3171	3171	3172	3406	3412	3413	IR int.
s_{sym}	3220	54.4	0.0	-0.7	-44.4	0.6	-0.5	0.6	0.5	-0.5	1.6	-1.1	0.5	-16.9	0.3	0.0	1
$s_{b,asym}$	3291	-17.6	-19.6	13.0	-21.5	-16.2	-30.8	-11.3	-23.5	10.2	3.1	-33.9	-10.1	-0.4	0.2	-0.1	485
$s'_{b,asym}$	3291	6.2	-18.4	-25.8	8.7	32.4	-23.9	24.0	-19.0	-17.2	-22.0	-6.8	16.3	0.2	0.2	0.2	485
$s''_{b,asym}$	3295	-25.9	12.8	-16.5	-28.6	20.8	12.9	15.0	11.9	-12.8	32.5	-20.3	11.3	0.5	-0.1	0.1	506

[a] Notations for NH vibrational modes: u, umbrella; x, scissoring; s_{sym}, totally symmetric NH stretching; s_b, H-bonded NH stretching ($s_{b,sym}$ for symmetric and $s_{b,asym}$ for asymmetric); s_f, free NH stretching ($s_{f,sym}$ for symmetric and $s_{f,asym}$ for asymmetric).

Table S6. The original frequencies (in cm^{-1}) of NH stretching fundamentals and bending overtones, the coupling constants (in cm^{-1}) between them, and the original IR intensities of stretching fundamentals (in km/mol) that involved in Fermi resonance in NH_4^+...Ne_n clusters.[a]

NH_4^+…Ne		uu						ux						xx			Original
C_{3v}		2923	2927	2927	2931	2932	2933	3159	3159	3164	3164	3164	3164	3395	3400	3401	IR int.
s_{sym}	3242	-55.5	-1.0	0.1	43.4	0.0	-2.8	0.0	0.0	0.0	0.4	-0.4	0.0	16.1	0.0	0.4	2
$s_{b,asym}$	3329	-31.1	0.8	0.0	-39.5	0.0	1.5	0.0	0.4	0.6	-31.0	30.4	0.6	-0.7	0.0	0.0	283
$s_{f,asym}$	3334	0.0	-1.6	-25.5	-0.1	-42.6	-0.9	-29.7	0.6	-20.5	0.0	0.0	20.2	0.0	0.0	0.0	196
$s'_{f,asym}$	3334	0.7	-26.6	1.7	-2.7	0.9	-41.8	0.6	30.2	0.0	-20.5	-21.0	0.0	-0.1	0.0	0.0	196

NH_4^+…Ne_2		uu						ux						xx			Original
C_{2v}		2925	2930	2931	2933	2936	2939	3164	3164	3166	3167	3170	3170	3401	3406	3407	IR int.
s_{sym}	3242	55.6	0.0	32.8	0.0	0.0	-28.6	0.0	0.0	0.4	0.0	0.0	0.0	-16.2	0.0	0.4	3
$s_{b,asym}$	3329	0.0	-50.7	0.0	0.0	0.0	0.0	-21.5	0.0	0.0	0.0	0.0	36.8	0.0	0.0	0.0	309
$s_{b,sym}/s_{f,sym}$	3334	28.0	0.0	-13.3	0.0	0.0	39.1	0.0	0.0	-43.7	0.0	0.0	0.0	0.7	0.0	0.0	246
$s_{f,asym}$	3334	0.0	0.0	0.0	0.0	-49.4	0.0	0.0	35.9	0.0	0.0	-19.8	0.0	0.0	0.0	0.0	192

NH_4^+…Ne_3		uu						ux						xx			Original
C_{3v}		2931	2933	2934	2938	2938	2944	3170	3170	3170	3170	3175	3175	3406	3412	3412	IR int.
s_{sym}	3250	-64.2	1.4	-2.1	-0.7	0.5	29.5	0.1	0.1	0.0	-0.1	0.0	0.0	16.3	0.1	-0.3	3
$s_{b,asym}$	3334	-1.4	-10.0	37.0	-26.2	-19.7	-0.2	-18.0	-11.8	11.5	-17.8	28.3	-8.8	0.0	0.0	0.0	309
$s'_{b,asym}$	3334	-1.5	-37.3	-10.1	19.9	-26.8	-0.8	10.9	-18.7	17.6	12.8	-9.1	-28.8	0.1	0.0	0.0	246
s_f	3339	20.6	-1.4	0.5	0.4	-0.8	44.8	26.9	12.3	13.4	-26.5	0.0	-0.8	0.6	0.0	0.0	192

Table S6. (continued)

NH_4^+…Ne_4 I		uu						ux						xx			Original
T_d		2937	2940	2940	2941	2941	2941	3177	3177	3177	3177	3177	3177	3412	3417	3418	IR int.
s_{sym}	3254	71.2	-0.1	0.2	-0.1	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	-16.7	0.0	-0.4	0
$s_{b,asym}$	3339	-0.1	-0.2	0.0	-20.2	40.5	-24.2	5.3	-14.9	14.1	-33.6	-16.2	-3.7	0.0	0.0	0.0	480
$s'_{b,asym}$	3339	0.1	-0.1	-0.1	14.5	30.4	38.7	-30.9	-4.9	21.7	5.6	-2.6	19.3	0.0	0.0	0.0	480
$s''_{b,asym}$	3339	0.0	-0.1	-0.4	44.9	8.4	-23.4	21.5	-13.0	4.8	-1.3	19.4	28.7	0.0	0.0	0.0	480

NH_4^+…Ne_4 II		uu						ux						xx			Original
C_{3v}		2931	2933	2934	2937	2937	2941	3169	3169	3169	3169	3172	3172	3404	3410	3410	IR int.
s_{sym}	3253	-66.1	0.1	3.0	-0.8	0.1	25.7	0.0	0.0	0.0	0.0	0.0	0.0	-16.4	-0.1	0.3	17
$s_{b,asym}$	3337	0.1	37.0	0.1	1.4	34.7	0.1	21.1	4.7	4.5	-20.9	28.2	8.1	0.0	-0.3	-0.1	480
$s'_{b,asym}$	3337	1.8	-0.1	37.0	34.5	-1.5	0.8	-5.0	22.2	20.6	4.5	8.2	-28.6	0.1	-0.1	0.3	480
s_f	3343	18.1	0.0	-1.2	-0.8	-0.1	46.1	-8.9	28.2	-29.1	-9.0	-0.3	0.7	-0.6	0.0	0.0	194

NH_4^+…Ne_5		uu						ux						xx			Original
C_{3v}		2936	2939	2939	2940	2940	2941	3174	3175	3176	3175	3175	3176	3410	3416	3416	IR int.
s_{sym}	3257	69.3	0.0	0.1	-15.7	0.1	2.7	0.0	0.0	0.0	-0.1	0.2	0.0	-16.6	0.0	-0.4	0
$s_{b,asym}$	3340	-0.1	-21.5	2.0	-0.3	45.6	-1.1	28.8	4.9	21.3	1.6	1.9	-20.9	0.0	0.4	0.0	285
$s'_{b,asym}$	3340	0.4	-2.1	-24.0	10.4	1.1	43.0	5.0	-29.3	-2.3	24.3	18.3	1.2	0.2	0.0	-0.4	285
$s''_{b,asym}$	3342	-10.6	-0.3	-5.7	-48.1	-0.1	8.6	0.3	-2.8	4.9	-28.1	32.1	5.5	-0.2	0.0	0.0	298

[a] Notations for NH vibrational modes: u, umbrella; x, scissoring; s_{sym}, totally symmetric NH stretching; s_b, H-bonded NH stretching ($s_{b,sym}$ for symmetric and $s_{b,asym}$ for asymmetric); s_f, free NH stretching ($s_{f,sym}$ for symmetric and $s_{f,asym}$ for asymmetric).

Table S7. The original frequencies (in cm^{-1}) of NH stretching fundamentals and bending overtones, the coupling constants (in cm^{-1}) between them, and the original IR intensities of stretching fundamentals (in km/mol) that involved in Fermi resonance in NH_4^+...Kr_n clusters.[a]

NH_4^+…Kr		uu						ux						xx			Original
C_{3v}		2898	2920	2920	2939	2942	2942	3147	3147	3168	3168	3168	3168	3395	3400	3401	IR int.
s_{sym}	3158	7.6	0.0	0.0	-59.7	-0.2	0.0	0.0	0.0	13.9	-8.7	-8.7	-13.9	10.7	0.0	0.3	438
$s_{b,asym}$	3279	-60.4	0.0	0.0	10.9	0.1	0.0	0.0	0.0	19.4	-12.2	-12.2	-19.5	-10.7	0.0	-0.3	274
$s_{f,asym}$	3342	0.0	-26.7	-0.9	0.0	-2.2	-40.8	-24.5	17.1	-8.6	-18.0	18.3	-8.7	0.0	0.3	0.0	179
$s'_{f,asym}$	3343	-0.2	0.9	-26.8	0.2	-40.7	2.2	17.3	25.0	18.4	-8.8	9.0	18.7	-0.1	0.0	0.3	179

NH_4^+…Kr_2		uu						ux						xx			Original
C_{2v}		2900	2916	2927	2929	2943	2956	3151	3152	3165	3166	3179	3180	3401	3406	3407	IR int.
s_{sym}	3170	-24.8	0.0	-35.7	0.0	0.0	46.3	0.0	0.0	15.0	0.0	0.0	0.0	-12.5	0.0	1.7	198
$s_{b,asym}$	3204	0.0	51.7	0.0	0.0	0.0	0.0	-19.9	0.0	0.0	0.0	0.0	33.4	0.0	0.0	0.0	838
$s_{b,sym}/s_{f,sym}$	3314	-49.9	0.0	-16.3	0.0	0.0	-17.3	0.0	0.0	-39.0	0.0	0.0	0.0	-7.4	0.0	0.3	258
$s_{f,asym}$	3352	0.0	0.0	0.0	0.0	48.0	0.0	0.0	36.2	0.0	0.0	-19.5	0.0	0.0	0.0	0.0	160

NH_4^+…Kr_3		uu						ux						xx			Original
C_{3v}		2914	2917	2917	2938	2938	2958	3162	3162	3162	3162	3183	3183	3406	3411	3412	IR int.
s_{sym}	3181	48.9	0.2	0.0	0.0	0.0	-43.6	-5.9	1.8	-1.9	-5.9	0.0	0.0	13.4	0.0	0.4	75
$s_{b,asym}$	3229	0.0	-3.2	40.2	-29.5	10.0	0.0	14.2	13.5	13.8	-14.3	22.6	-14.9	0.0	-0.4	0.0	757
$s'_{b,asym}$	3230	-0.4	39.9	3.2	-10.0	-29.7	0.2	13.8	-14.5	-14.6	-14.1	15.2	23.0	-0.1	0.0	-0.4	757
s_f	3345	41.2	0.1	0.0	0.0	0.0	29.4	27.4	-8.7	8.7	27.4	0.0	0.1	4.6	0.0	0.1	195

Table S7. (continued)

NH_4^+…Kr_4 I		uu						ux						xx			Original
T_d		2929	2932	2932	2933	2933	2933	3172	3172	3172	3172	3172	3172	3411	3417	3416	IR int.
s_{sym}	3189	66.8	0.1	0.1	0.2	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	-13.9	0.3	0.0	0
$s_{b,asym}$	3250	-0.4	0.2	-0.4	46.2	8.5	-18.1	13.8	4.9	-27.0	0.7	1.8	24.2	0.2	0.0	0.0	693
$s'_{b,asym}$	3251	0.2	1.3	-0.2	-19.9	18.0	-42.7	12.4	27.0	-9.0	3.5	7.4	-23.4	-0.1	0.0	0.0	692
$s''_{b,asym}$	3252	0.1	1.4	0.2	0.5	-46.6	-19.7	-21.9	-0.6	-17.9	19.6	-17.7	-7.9	-0.1	0.0	0.0	692

NH_4^+…Kr_4 II		uu						ux						xx			Original
C_{3v}		2923	2926	2926	2928	2929	2931	3163	3162	3162	3162	3165	3165	3398	3404	3404	IR int.
s_{sym}	3188	63.0	0.3	2.9	-0.3	2.2	-24.1	-5.0	-0.8	0.1	-6.8	-2.3	-0.2	-14.9	0.0	0.0	23
$s_{b,asym}$	3247	-0.8	1.1	-29.4	-8.4	40.4	-5.1	-28.4	4.6	3.4	22.1	23.1	-5.8	-0.7	0.2	-0.2	612
$s'_{b,asym}$	3248	0.0	50.2	-2.8	-16.7	-6.0	1.0	-1.5	-14.8	-21.8	2.8	-6.7	-33.1	0.3	0.1	0.4	613
s_f	3344	-26.3	0.0	-2.0	0.1	-7.7	-41.4	-32.1	-2.5	2.7	-32.6	-7.4	-0.3	4.7	0.0	0.0	174

NH_4^+…Kr_5		uu						ux						xx			Original
C_{3v}		2913	2928	2928	2938	2941	2941	3161	3161	3174	3174	3174	3173	3404	3411	3410	IR int.
s_{sym}	3191	43.6	-0.7	-1.0	-53.2	-0.1	1.4	0.3	0.7	1.3	1.3	0.4	-1.9	15.6	-0.3	0.0	11
$s_{b,asym}$	3262	-25.9	-12.1	19.2	-21.5	2.0	-30.0	-7.7	-20.7	27.8	-3.3	23.8	-11.7	0.4	0.1	-0.2	552
$s'_{b,asym}$	3264	5.2	23.3	19.9	3.1	41.0	-5.1	26.7	-13.5	-20.1	-16.1	11.7	-12.3	0.0	-0.2	-0.2	562
$s''_{b,asym}$	3264	28.5	-14.0	15.5	19.9	-6.6	-28.9	-12.5	-17.7	-8.8	-21.4	-0.5	31.6	0.4	0.1	-0.2	548

[a] Notations for NH vibrational modes: u, umbrella; x, scissoring; s_{sym}, totally symmetric NH stretching; s_b, H-bonded NH stretching ($s_{b,sym}$ for symmetric and $s_{b,asym}$ for asymmetric); s_f, free NH stretching ($s_{f,sym}$ for symmetric and $s_{f,asym}$ for asymmetric).

Table S8. The original frequencies (in cm^{-1}) of NH stretching fundamentals and bending overtones, the coupling constants (in cm^{-1}) between them, and the original IR intensities of stretching fundamentals (in km/mol) that involved in Fermi resonance in $NH_4^+...(H_2O)_n$ clusters.[a]

$NH_4^+…H_2O$		uu						ux						xx			Original
		2793	2866	2893	2942	2970	2997	3075	3101	3150	3176	3178	3204	3362	3389	3412	IR int.
s_b	2659	21.9	1.1	0.0	30.5	0.0	31.9	0.0	0.0	13.0	0.0	0.0	-25.5	0.7	0.0	-7.4	1487
$s_{f,sym}$	3264	-62.4	-0.7	0.0	20.5	0.0	20.2	0.1	0.0	-17.5	0.0	0.0	18.0	-8.9	0.0	-4.5	88
$s_{f,asym}$	3352	0.0	0.0	-17.2	0.0	42.0	0.0	0.0	-31.9	0.0	14.6	-17.6	0.0	0.0	0.8	0.0	142
$s'_{f,asym}$	3353	0.7	-24.7	0.0	-27.2	0.0	31.5	31.8	0.0	20.2	0.0	0.0	14.1	0.3	0.0	0.7	145

$NH_4^+…(H_2O)_2$		uu						ux						xx			Original
		2850	2895	2941	2944	2990	3038	3136	3142	3183	3186	3231	3234	3425	3432	3434	IR int.
$s_{b,sym}$	2888	1.4	20.1	29.4	0.0	0.0	38.4	-9.1	-0.4	-24.7	-1.1	0.2	-6.9	-8.6	0.4	-0.1	892
$s_{b,asym}$	2889	21.6	42.0	9.0	0.0	-0.1	-22.9	-20.9	-1.0	-1.2	0.0	1.3	-30.7	1.8	1.0	-8.4	1404
$s_{f,sym}$	3316	-47.6	4.9	32.3	0.1	-0.1	-7.3	-8.8	-0.4	31.3	1.4	0.2	-3.6	-4.6	-0.2	2.5	128
$s_{f,asym}$	3373	0.0	0.0	0.0	-15.5	-42.0	0.0	-1.5	31.3	-0.5	10.6	13.6	0.6	0.0	0.5	0.1	107

$NH_4^+…(H_2O)_3$ I		uu						ux						xx			Original
		2930	2930	2931	2990	2990	3048	3196	3196	3196	3197	3254	3255	3460	3466	3465	IR int.
$s_{b,sym}$	3014	-36.9	0.2	0.6	-0.1	0.3	-43.1	-7.9	4.0	-3.6	-8.0	0.0	-0.2	10.8	0.2	0.0	204
$s_{b,asym}$	3033	-0.6	6.9	-38.6	34.8	-1.0	0.0	-20.0	8.4	8.4	20.4	-24.3	-8.4	0.0	1.6	4.3	1251
$s'_{b,asym}$	3033	0.2	38.8	6.7	1.5	34.7	0.2	8.1	20.3	20.1	-7.4	7.6	-24.4	0.0	4.2	-1.7	1251
s_f	3363	-43.7	-0.1	0.7	0.0	0.0	21.0	23.7	-0.6	0.6	23.7	0.0	0.0	2.2	0.0	0.0	105

Table S8. (continued)

$NH_4^+…(H_2O)_3$ II		uu						ux						xx			Original
		2759	2862	2890	2966	2995	3024	3060	3097	3163	3202	3191	3231	3363	3404	3440	IR int.
$s_{b,sym}$	2850	0.0	52.7	0.0	0.0	0.0	0.0	0.0	-21.5	0.0	0.0	-24.2	0.0	0.0	0.0	0.0	1025
$s_{b,asym}$	2885	-5.2	0.0	0.0	-21.8	0.0	-39.0	0.0	0.0	0.0	-23.0	0.0	0.0	4.5	0.0	5.6	997
$s_{f,sym}$	3327	-52.2	0.0	0.0	-35.2	0.0	6.6	0.0	0.0	0.0	30.2	0.0	0.0	6.8	0.0	1.4	167
$s_{f,asym}$	3387	0.0	0.0	0.0	0.0	-46.6	0.0	37.8	0.0	0.0	0.0	0.0	11.1	0.0	0.0	0.0	102

$NH_4^+…(H_2O)_3$ III		uu						ux						xx			Original
		2853	2910	2930	2970	2989	3006	3121	3159	3179	3218	3196	3237	3389	3431	3469	IR int.
s_b	2644	15.9	28.5	0.0	-29.1	0.0	-24.7	0.0	-15.1	0.0	-23.0	12.2	0.0	-1.5	0.0	-5.8	1765
s'_b	2958	-31.6	-32.0	0.0	2.3	0.0	-30.6	0.0	27.6	0.0	-6.4	-19.2	0.0	3.9	0.0	-6.6	933
$s_{f,sym}$	3332	43.5	-4.3	0.0	36.3	0.0	-6.3	0.0	12.5	0.0	-27.3	-1.1	0.0	-6.4	0.0	0.9	60
$s_{f,asym}$	3391	0.0	0.0	15.2	0.0	-43.9	0.0	-32.2	0.0	-11.4	0.0	0.0	11.8	0.0	0.1	0.0	97

$NH_4^+…(H_2O)_4$ I		uu						ux						xx			Original
		2988	2991	2992	2993	2993	2995	3241	3242	3243	3245	3243	3245	3491	3498	3498	IR int.
$s_{b,sym}$	3088	-51.4	-0.5	-0.9	31.2	1.4	4.7	0.1	3.9	0.0	-0.1	0.0	0.1	-11.2	-2.8	0.1	0
$s_{b,asym}$	3134	-0.7	48.1	-13.5	-0.6	-3.4	-1.2	2.2	-1.8	-17.4	-2.8	-7.9	33.4	0.0	0.0	-0.4	964
$s'_{b,asym}$	3134	-2.4	13.5	47.7	-3.2	0.3	5.6	-4.9	1.0	8.8	32.9	-17.5	3.6	0.0	0.0	0.9	964
$s''_{b,asym}$	3135	-1.1	-0.8	5.5	6.0	-22.3	-45.0	39.0	-0.2	1.1	5.3	-0.1	-1.5	0.0	0.0	-5.7	967

Table S8. (continued)

$NH_4^+…(H_2O)_4$ II		uu						ux						xx			Original
		2875	2914	2949	2956	2990	3023	3146	3166	3186	3208	3220	3241	3419	3443	3463	IR int.
$s_{b,sym}$	3013	-16.1	0.1	0.2	32.3	-8.3	37.1	-2.4	-0.1	0.0	-14.1	0.1	-11.4	6.9	0.0	6.6	462
$s_{b,asym}$	3006	0.0	31.3	37.4	-0.1	0.0	-0.2	0.1	-19.1	-20.7	0.0	18.0	0.1	0.0	-0.3	0.0	758
$s'_{b,asym}$	3073	40.2	0.0	0.1	22.1	-27.2	-19.4	30.2	0.1	0.0	-15.4	0.0	-22.3	-6.9	-0.1	1.2	1281
s_f	3371	32.8	0.0	0.0	-32.4	-11.7	19.8	-26.7	-0.1	0.1	-21.3	0.1	-4.8	-2.4	0.0	-0.6	116

$NH_4^+…(H_2O)_4$ III		uu						ux						xx			Original
		2910	2939	2969	2973	3002	3036	3169	3203	3198	3233	3231	3265	3428	3465	3496	IR int.
s_b	2847	9.3	-9.5	34.4	-27.1	-0.4	-24.5	5.3	-9.5	12.7	19.1	-9.1	13.5	-1.2	-1.5	-5.6	1340
s'_b	3060	40.1	-10.4	-7.7	-25.3	-8.2	30.8	15.1	-12.0	12.3	2.4	-10.6	8.9	6.4	-1.5	6.5	560
s''_b	3082	-11.0	-27.7	-19.6	-9.9	-27.8	-18.0	-12.4	-21.3	16.1	-9.9	-5.1	-24.5	-0.2	-2.7	-1.0	1120
s_f	3371	29.7	-0.7	-29.6	5.4	15.4	-18.2	-24.9	5.9	4.6	20.3	3.0	2.5	2.6	0.0	0.3	92

$NH_4^+…(H_2O)_4$ IV		uu						ux						xx			Original
		2749	2856	2888	2964	2997	3030	3053	3088	3160	3197	3192	3230	3359	3398	3433	IR int.
$s_{b,asym}$	2795	0.0	-53.3	-1.7	0.0	0.0	0.0	0.0	20.4	-0.4	0.0	22.3	0.0	0.0	-0.4	0.0	1068
$s_{b,sym}$	2840	4.6	0.1	0.0	-20.6	0.8	-37.5	-0.2	0.0	0.0	-22.4	0.0	-1.1	-3.7	0.0	3.9	1042
$s_{f,sym}$	3331	-53.1	0.0	0.0	35.8	2.0	-5.7	0.0	0.0	0.0	-30.2	0.0	-1.0	7.3	0.0	-2.0	139
$s_{f,asym}$	3393	-0.1	0.0	0.0	-2.1	46.3	2.1	-38.4	0.0	0.0	0.6	0.0	-11.2	0.0	0.0	0.1	96

[a] Notations for NH vibrational modes: u, umbrella; x, scissoring; s_{sym}, totally symmetric NH stretching; s_b, H-bonded NH stretching ($s_{b,sym}$ for symmetric and $s_{b,asym}$ for asymmetric); s_f, free NH stretching ($s_{f,sym}$ for symmetric and $s_{f,asym}$ for asymmetric).

Table S9. The original frequencies (in cm^{-1}) of NH stretching fundamentals and bending overtones, the coupling constants (in cm^{-1}) between them, and the original IR intensities of stretching fundamentals (in km/mol) that involved in Fermi resonance in $NH_4^+...(NH_3)_n$ clusters.[a]

$NH_4^+...(NH_3)_2$		uu						ux						xx			Original
		2860	2903	2944	2996	3037	3129	3146	3159	3188	3199	3281	3290	3434	3447	3456	IR int.
$s_{b,asym}$	2279	-1.3	-56.5	1.5	0.0	0.1	-0.9	-22.6	-1.1	1.2	0.1	-0.7	17.1	-0.3	0.0	-0.2	2917
$s_{b,sym}$	2374	1.7	2.0	8.6	0.1	0.0	-34.3	0.9	0.0	14.4	0.6	0.0	-0.1	1.4	0.0	0.1	1005
$s_{f,sym}$	3314	41.6	0.0	36.1	-0.1	0.0	4.0	-0.5	0.0	-29.0	-1.2	0.0	-0.3	-5.3	0.0	-3.8	74
$s_{f,asym}$	3380	0.0	-0.2	0.0	-0.1	-39.3	0.0	-1.2	29.1	0.0	-0.1	-11.4	-0.4	0.0	0.1	0.0	77

$NH_4^+...(NH_3)_3$		uu						ux						xx			Original
		2961	2962	2962	3036	3036	3109	3224	3223	3223	3224	3297	3297	3483	3489	3488	IR int.
$s_{b,asym}$	2684	-2.8	37.4	-3.5	13.4	32.9	1.6	1.9	19.1	-18.9	2.0	-0.7	18.9	-0.3	-0.4	0.3	1938
$s'_{b,asym}$	2684	-0.2	-3.6	-37.1	-32.3	12.9	-1.5	-18.0	1.6	-1.5	-18.3	17.8	0.2	0.2	0.2	0.4	1938
$s_{b,sym}$	2719	27.7	2.7	0.1	2.0	1.0	-35.6	-5.1	2.9	1.3	6.7	-0.7	0.8	4.3	0.1	0.0	285
s_f	3360	-40.3	-1.4	1.7	0.0	0.0	-15.8	-19.4	6.8	6.8	19.4	0.0	0.0	-3.1	-0.1	0.0	64

$NH_4^+...(NH_3)_4$		uu						ux						xx			Original
		3033	3035	3035	3034	3035	3036	3280	3280	3280	3280	3280	3280	3521	3528	3528	IR int.
$s_{b,sym}$	2885	51.4	-0.8	0.3	0.1	-0.2	-1.1	-0.2	0.3	-0.2	-0.1	-0.5	-0.4	6.4	0.0	-0.1	1
$s_{b,asym}$	2896	-0.8	8.1	20.4	7.3	-19.1	-37.9	-19.2	3.7	-21.0	8.9	9.5	9.7	0.0	0.0	0.0	1359
$s'_{b,asym}$	2896	-0.4	-33.8	18.8	-1.2	-25.2	15.3	-3.2	21.3	6.0	-21.1	7.8	9.0	0.0	0.0	0.0	1359
$s''_{b,asym}$	2895	1.0	33.8	14.6	-11.3	-19.1	22.6	-8.5	11.5	-8.2	-3.9	-21.8	-17.6	0.1	0.0	0.0	1358

[a] Notations for NH vibrational modes: u, umbrella; x, scissoring; s_b, H-bonded NH stretching ($s_{b,sym}$ for symmetric and $s_{b,asym}$ for asymmetric); s_f, free NH stretching ($s_{f,sym}$ for symmetric and $s_{f,asym}$ for asymmetric).