Vibrational spectroscopy of protonated amine–water clusters: Tuning Fermi resonance and lighting up dark states

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Electronic Supplementary Information

The following information contains the procedure for calculating localized normal mode (LNM), the discussion on rotation-vibration couplings and simulated rotational profiles, calculated geometric parameters, harmonic vibrational frequencies, Hamiltonian matrices of vibrational quantum states, and other properties relevant to Fermi resonance of the simplest ammonium ion (NH_4^+) and methylated ammonium ions (protonated amines, including MA–H^+, DMA–H^+ and TMA–H^+), their hydrogen-bonded clusters with one water molecule, and their argon-tagged clusters.

Procedure for calculating localized normal mode (LNM)

In many large molecular systems, the vibrational normal modes are delocalized over the whole molecule. If we are interested in specific characteristics of a fragment in the system, the interpretation using normal mode analysis becomes rather complicated – There will be many modes contributing to the vibrations of that fragment, and we have to include all of them which contain a large portion of motions concerning other parts of the system. However, in many cases, the IR spectra show the characteristics of that fragment only, indicating that there should be a better way than the conventional normal modes to present the vibrational properties.

A natural answer to the above situation is to constrain the vibrational modes into the target fragment. Many methods have been proposed for this purpose. For example, in the partial Hessian vibrational analysis (PHVA) proposed by Head, the partial Hessian matrix was diagonalized to obtain the vibrations for adsorbates on surfaces.[1] This method would be one of the simplest ways to constrain vibrational modes vectors into a specific region, and many researchers have applied PHVA to different systems.[2,3]

To differentiate the conventional normal mode and the projected vibrational mode, we used the term "global normal mode" (GNM) for the original normal mode analysis across the whole molecular system, and "localized normal mode" (LNM) utilizing the concept of PHVA. We divided the Hessian matrix into several sub-matrices corresponding to different fragments and diagonalized them individually, resulting in LNMs as the eigenvector matrices. We then chose some of the vectors from LNMs, scanned the reduced-dimensional PES, and performed anharmonic vibrational analysis using the DVR algorithm. Note that the vector space spanned by LNM coordinates is exactly the same as the calculation along GNM coordinates if all LNMs/GNMs are included. The major difference between the two approaches occurs when we disregard some modes in the reduced-dimensional vibrational analysis; the choice of LNM or GNM will result in different loss of the information about the exact PES. Clearly, it is non-trivial to determine which method is better in any specific case. Nevertheless, as we have found only negligible vibrational coupling between CH_3 and NH_2/NH groups in neutral MA/DMA,[4,5] we believe that the current choice of LNMs is good enough in this study.

Rotation-vibration coupling and rotational profile in vibrational spectra

According to the characteristics of rotation-vibration coupling, the rotational profile of a vibrational transition can be seen when (i) there is a component of dipole derivative perpendicular to one rotational axis, and (ii) the rotational constant is not small (moment of inertia is not large) about that axis.

We have simulated the rotational profiles of these cluster systems using the PGOPHER program,[6] finding that the 3400 cm^{-1} band of $NH_4^+...H_2O$ shown in **Fig. 8(b)** would bear certain features attributed to the rotation-vibration coupling for free NH stretching modes. This mode satisfies criteria (i), and (ii) the corresponding rotational constant about the N–O axis is as large as 126 GHz. As the size of the amine moiety increases to $CH_3NH_3^+$ ($MA–H^+$), the bulky methyl group reduces the rotational constant to 24 GHz, and those fine structures almost disappear. The simulated

rotational profiles at different proposed temperatures are shown in **Fig. S1**. However, the current experimental resolution was not enough to resolve the rotational profile in either case.

For comparison, it is seen in Dopfer's work that the NH_4^+...Ar cluster did show a clear rotational profile.[7] The corresponding rotational constant is 180 GHz therein. All NH_4^+...Rg clusters have similar rotational constants about the N–Rg axis, and thus similar rotation-vibration coupling features are expected for their free NH stretching modes. Summarizing these findings, it is not the size of molecule/cluster alone that determines the effect of vibrational angular momentum, but the criteria (i) and (ii) mentioned above that decide its significance.

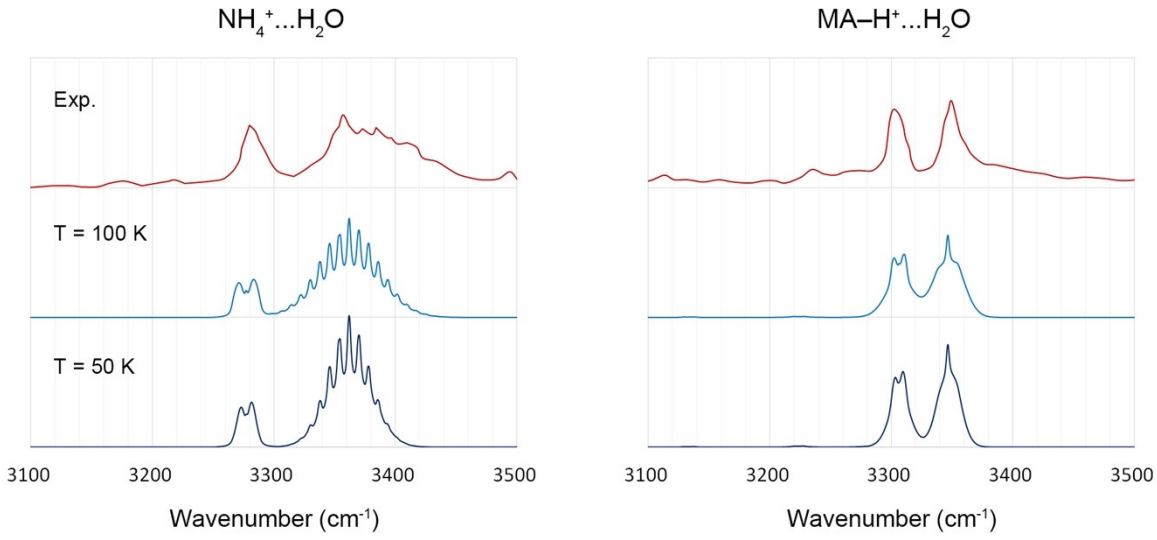

Figure S1. Simulated vibrational spectra with rotational profiles in the free NH stretching region of NH_4^+...H_2O and MA–H^+...H_2O. The experimental spectra (with Ar tagging and cooling) are shown for comparison.

References

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[6] PGOPHER, A Program for Simulating Rotational, Vibrational and Electronic Spectra, C. M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk

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Table S1. Cartesian coordinates of bare ammonium ions and ammonium–water 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

$NH_4^+...H_2O$

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

$NH_4^+...H_2O...Ar$ (type 1)

N	-3.10534360	-0.56825989	0.00000000
H	-2.24402878	0.04966401	0.00000000
H	-3.95280514	0.00763386	0.00000000
H	-3.11116951	-1.16292084	0.83432800
H	-3.11116951	-1.16292084	-0.83432800
O	-0.91318354	0.99988929	0.00000000
H	-0.88130467	1.96705355	0.00000000
H	0.01155044	0.70959874	0.00000000
Ar	2.35176671	-0.24607797	0.00000000

$Ar...NH_4^+...H_2O$ (type 2)

N	0.95283989	1.18513924	0.00000000
H	1.70488899	0.44390451	0.00000000
H	1.04153662	1.77341105	0.83392900
H	0.02403586	0.74834207	0.00000000
H	1.04153662	1.77341105	-0.83392900
O	2.88792265	-0.72061710	0.00000000
H	3.84631888	-0.58541737	0.00000000
H	2.76551313	-1.68071029	0.00000000

Ar	-2.23317169	-0.27799883	0.00000000

MA–H^+

N	0.00000000	0.00000000	0.70996389
H	0.00000000	0.95585690	1.08653789
H	0.82779636	-0.47792845	1.08653789
H	-0.82779636	-0.47792845	1.08653789
C	0.00000000	0.00000000	-0.80128311
H	0.90200503	0.52077284	-1.14055411
H	-0.90200503	0.52077284	-1.14055411
H	0.00000000	-1.04154569	-1.14055411

MA–H^+...H_2O

N	-0.68167544	0.67362437	0.00000000
H	0.33730608	0.42232717	0.00000000
H	-0.86809300	1.25489240	0.82389900
H	-0.86809300	1.25489240	-0.82389900
C	-1.53598156	-0.56416168	0.00000000
H	-1.29642947	-1.14286315	-0.89873000
H	-1.29642947	-1.14286315	0.89873000
H	-2.59122864	-0.27026469	0.00000000
O	1.94113114	-0.14869611	0.00000000
H	2.52076790	-0.25847630	-0.76737500
H	2.52076790	-0.25847630	0.76737500

MA–H^+...H_2O...Ar (type1)

N	2.23691321	-0.12902004	0.00000000
H	1.58600223	0.69519198	0.00000000
H	2.84101320	-0.05930707	-0.82556679
H	2.84101320	-0.05930707	0.82556679
C	1.46345217	-1.41843102	0.00000000
H	0.83834119	-1.43999799	0.89942926
H	0.83834119	-1.43999799	-0.89942926
H	2.16739415	-2.25766604	0.00000000
O	0.43698327	1.93512401	0.00000000
H	0.58480829	2.89147001	0.00000000
H	-0.52432774	1.82401304	0.00000000
Ar	-2.17264380	-0.34564392	0.00000000

Ar...MA–H^+...H_2O (type 2)

N	0.81190208	0.56984420	0.59375306
H	1.53559111	-0.15405278	0.36809707
H	-0.11164389	0.12341213	0.56664819
H	0.96568314	0.88723230	1.55624102
C	0.87927292	1.71410310	-0.37827206
H	1.87667990	2.16219818	-0.31328619
H	0.70744386	1.31522699	-1.38403000
H	0.10896690	2.44844208	-0.11844606
O	2.75537713	-1.23998575	-0.13981493
H	2.63051414	-2.06518081	-0.62993283
H	3.67819416	-1.26115066	0.15121900
Ar	-2.46629991	-0.43387608	-0.05359055

DMA–H^+

N	0.00000000	0.00000000	0.54707770
H	-0.81934300	0.00000000	1.16690170
H	0.81934300	0.00000000	1.16690170
C	0.00000000	1.25799800	-0.27843930
H	-0.90122500	1.25457300	-0.90292130
H	0.00000000	2.12378500	0.39480470
H	0.90122500	1.25457300	-0.90292130
C	0.00000000	-1.25799800	-0.27843930
H	0.00000000	-2.12378500	0.39480470
H	-0.90122500	-1.25457300	-0.90292130
H	0.90122500	-1.25457300	-0.90292130

DMA–H^+...H_2O

N	0.50380605	0.00661606	-0.43578517
H	-0.53534996	-0.00839293	-0.33150121
H	0.70280609	0.02268002	-1.44199416
C	1.07069402	-1.24578591	0.16020891
H	0.81292097	-1.26104887	1.22624190
H	0.63339504	-2.11201793	-0.35109408
H	2.16012502	-1.23743192	0.03365596
C	1.03738502	1.25530409	0.19781081
H	0.58537404	2.12475907	-0.29470525
H	0.76669297	1.23790413	1.26039680
H	2.12780102	1.27421308	0.08132685
O	-2.22525798	-0.00879491	0.06107971

H	-2.75200399	-0.73946190	0.41505772
H	-2.87481396	0.66573508	-0.18364434

DMA–H^+...H_2O...Ar (type 1)

N	-1.67700309	0.06844853	0.00000000
H	-1.01141598	0.87410338	0.00000000
H	-2.62027519	0.47216563	0.00000000
C	-1.48578588	-0.73191121	1.25226300
H	-0.46749556	-1.13803695	1.24267700
H	-1.62392926	-0.07284520	2.11776800
H	-2.22012012	-1.54652023	1.26796500
C	-1.48578588	-0.73191121	-1.25226300
H	-1.62392926	-0.07284520	-2.11776800
H	-0.46749556	-1.13803695	-1.24267700
H	-2.22012012	-1.54652023	-1.26796500
O	0.12262784	2.17987236	0.00000000
H	-0.05081570	3.13195235	0.00000000
H	1.08684480	2.10027253	0.00000000
Ar	2.21145452	-0.56660407	0.00000000

Ar...DMA–H^+...H_2O (type 2)

N	-0.64604209	0.21433302	0.01258612
H	-1.53011209	-0.33741699	-0.04090992
H	0.13381792	-0.44949796	-0.04623995
C	-0.58849409	0.92013290	1.33194918
H	-1.45329410	1.59131288	1.39772726
H	-0.62481207	0.17443083	2.13544712
H	0.34533390	1.49294592	1.38495322
C	-0.57729513	1.14640613	-1.15719280
H	-0.61868013	0.55859422	-2.08237585
H	-1.43266514	1.83070211	-1.10010072
H	0.36260687	1.70923914	-1.10469776
O	-3.10820207	-1.07274101	-0.08070197
H	-3.43229805	-1.77393207	0.50234297
H	-3.78503508	-0.99307496	-0.76774395
Ar	2.68987692	-0.50671892	-0.04274599

TMA–H^+

N	0.00000000	0.00000000	0.34833471

H	0.00000000	0.00000000	1.37644971
C	0.00000000	1.43229675	-0.10485722
H	-0.90147400	1.92509873	0.28008880
H	0.90147400	1.92509873	0.28008880
H	0.00000000	1.43807680	-1.20263122
C	-1.24040537	-0.71614837	-0.10485722
H	-1.21644740	-1.74324875	0.28008880
H	-2.11792140	-0.18184998	0.28008880
H	-1.24541104	-0.71903840	-1.20263122
C	1.24040537	-0.71614837	-0.10485722
H	2.11792140	-0.18184998	0.28008880
H	1.21644740	-1.74324875	0.28008880
H	1.24541104	-0.71903840	-1.20263122

TMA–H^+...H_2O

N	-0.37803599	-0.00343359	0.00000000
H	0.66369784	-0.02396082	0.00000000
C	-0.84588481	-0.70460013	1.23633000
H	-0.48760839	-1.74149309	1.21220700
H	-0.43920576	-0.18412472	2.11243600
H	-1.94376779	-0.68349309	1.25579800
C	-0.84588481	-0.70460013	-1.23633000
H	-0.43920576	-0.18412472	-2.11243600
H	-0.48760839	-1.74149309	-1.21220700
H	-1.94376779	-0.68349309	-1.25579800
C	-0.79780839	1.43277225	0.00000000
H	-0.39988722	1.91733151	0.90071700
H	-0.39988722	1.91733151	-0.90071700
H	-1.89521805	1.47634531	0.00000000
O	2.41727367	-0.01869610	0.00000000
H	3.00850539	0.74742628	0.00000000
H	3.00948382	-0.78408000	0.00000000

TMA–H^+...H_2O...Ar

N	-0.17023941	1.26152844	0.00000000
H	0.66169570	0.63384174	0.00000000
C	-0.96241817	0.97489975	1.23637600
H	-1.29569147	-0.06958557	1.20740700

H	-0.32308826	1.14451134	2.11182400
H	-1.82854978	1.64986414	1.26043500
C	-0.96241817	0.97489975	-1.23637600
H	-0.32308826	1.14451134	-2.11182400
H	-1.29569147	-0.06958557	-1.20740700
H	-1.82854978	1.64986414	-1.26043500
C	0.34329475	2.66697229	0.00000000
H	0.95151829	2.82057580	0.90031200
H	0.95151829	2.82057580	-0.90031200
H	-0.51425237	3.35310713	0.00000000
O	2.13423204	-0.31229917	0.00000000
H	3.05990070	-0.03035380	0.00000000
H	2.16917816	-1.27924532	0.00000000
Ar	-0.37654615	-2.65561209	0.00000000

Table S2. Selected geometric parameters related to NH and OH bonds of bare ammonium ions and ammonium–water clusters optimized at the MP2/aug-cc-pVDZ level.

Ammonium ion	NH_4^+	$MA–H^+$	$DMA–H^+$	$TMA–H^+$
Free NH bond length (Å) [a]	1.027	1.027	1.027	1.028
NC bond length (Å)	–	1.511	1.505	1.502
Ammonium–water cluster	$NH_4^+...H_2O$	$MA–H^+...H_2O$	$DMA–H^+...H_2O$	$TMA–H^+...H_2O$
Free NH bond length (Å) [a]	1.025	1.025	1.026	–
H-bonded NH bond length (Å)	1.058	1.050	1.044	1.042
NC bond length (Å)	–	1.504	1.498	1.496
NH...O distance (Å)	1.650	1.702	1.735	1.753
OH bond length (Å)	0.968	0.968	0.968	0.968
NH...O angle (°)	179.7	174.2	172.6	178.7
Ammonium–water–argon cluster (type 1)	$NH_4^+...H_2O...Ar$	$MA–H^+...H_2O...Ar$	$DMA–H^+...H_2O...Ar$	$TMA–H^+...H_2O...Ar$
Free NH bond length (Å) [a]	1.025	1.025	1.026	–
H-bonded NH bond length (Å)	1.060	1.050	1.045	1.042
NC bond length (Å)	–	1.504	1.498	1.496
NH...O distance (Å)	1.636	1.690	1.729	1.750
OH bond length (Å)	0.968, 0.969 [b]	0.968	0.968	0.968
OH...Ar distance (Å)	2.528	2.725	2.894	2.894
NH...O angle (°)	179.8	175.5	178.6	175.7
OH...Ar angle (°)	175.4	133.8	117.6	116.3
Argon–ammonium–water cluster (type 2)	$Ar...NH_4^+...H_2O$	$Ar...MA–H^+...H_2O$	$Ar...DMA–H^+...H_2O$	$Ar...TMA–H^+...H_2O$
Free NH bond length (Å)	1.024, 1.026 [b]	1.025, 1.026 [b]	1.026	–
H-bonded NH bond length (Å)	1.056	1.048	1.043	–
NC bond length (Å)	–	1.503	1.497	–
NH...O distance (Å)	1.660	1.710	1.741	–
OH bond length (Å)	0.968	0.968	0.968	–
NH...Ar distance (Å)	2.480	2.498	2.557	–
NH...O angle (°)	180.0	174.2	172.8	–
NH...Ar angle (°)	179.3	162.2	140.8	–

[a] All free NH bonds in each species have the same value of bond length to the third decimal place.

[b] The bond pointing toward Ar is slightly elongated.

Table S3. Selected harmonic vibrational frequencies (in cm^{-1}) related to NH and OH vibrational modes of bare ammonium ions and ammonium–water clusters calculated at the MP2/aug-cc-pVDZ level.[a]

Ammonium ion [b]	NH_4^+	MA–H^+	DMA–H^+	TMA–H^+
Free NH stretching	3391 (t)	3376 (d)	3358	3305
	3242	3272	3295	
NH_2 bending	1649 (d)	1595 (d)	1586	1361 (d) [c]
		1227 (d)	1357	
			1334	
			1221	
NH_3 umbrella	1401 (t)	1455	–	–
Ammonium–water cluster	$NH_4^+...H_2O$	MA–$H^+...H_2O$	DMA–$H^+...H_2O$	TMA–$H^+...H_2O$
Free NH stretching	3420	3395	3343	–
	3418	3329		
	3307			
H-bonded NH stretching	2819	2949	3027	3060
NH_2 bending	1683	1646	1610	1484 [c]
	1659	1606	1474	1455 [c]
		1241	1355	
		1233	1226	
NH_3 umbrella	1460	1480	–	–
	1434			
	1359			
OH stretching	3734	3735	3736	3737
	3623	3624	3624	3624
OH_2 bending	1573	1570	1570	1572

Table S3 (continued)

Ammonium–water–argon cluster (type 1)	$NH_4^+...H_2O...Ar$	$MA–H^+...H_2O...Ar$	$DMA–H^+...H_2O...Ar$	$TMA–H^+...H_2O...Ar$
Free NH stretching	3421	3398	3340	–
	3419	3329		
	3307			
H-bonded NH stretching	2786	2937	3020	3058
NH_2 bending	1684	1614	1631	1479 [c]
	1659	1612	1449	1455 [c]
		1241	1352	
		1239	1227	
NH_3 umbrella	1462	1502	–	–
	1435			
	1357			
OH stretching	3724	3738	3739	3739
	3612	3624	3625	3625
OH_2 bending	1573	1565	1566	1570
Argon–ammonium–water cluster (type 2)	$Ar...NH_4^+...H_2O$	$Ar...MA–H^+...H_2O$	$Ar...DMA–H^+...H_2O$	$Ar...TMA–H^+...H_2O$
Free NH stretching	3422	3391	3343	–
	3401	3323		
	3299			
H-bonded NH stretching	2848	2968	3040	–
NH_2 bending	1687	1645	1607	–
	1666	1608	1471	
		1243	1362	
		1236	1227	
NH_3 umbrella	1455	1480	–	–
	1439			
	1366			
OH stretching	3736	3736	3737	–
	3624	3624	3625	
OH_2 bending	1573	1570	1569	–

[a] Frequency scaled by 0.959; only modes most relevant to NH/OH vibrations above 1000 cm^{-1} are listed.

[b] (d) and (t) denote doubly and triply degenerate, respectively.

[c] C–N–H bending mode.

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

(a) TMA–H^+

	Bending overtones bb / bb' / b'b'			Str. fund. s	Original IR int.
bb/	**2807.3**	0.0	0.0	0.0	0.5
bb'/	0.0	**2813.9**	0.0	0.1	0.5
b'b'	0.0	0.0	**2830.2**	137.0	0.0
s	0.0	0.1	137.0	**3253.0**	64.6

(b) TMA–H^+...H_2O

	Bending overtones b_2b_2	b_1b_2	b_1b_1	Str. fund. s	Original IR int.
b_2b_2	**2965.9**	0.0	0.9	74.8	0.3
b_1b_2	0.0	**3000.3**	0.0	0.0	0.4
b_1b_1	0.9	0.0	**3052.2**	89.7	0.2
s	74.8	0.0	89.7	**3018.8**	885.8

(c) TMA–H^+...H_2O...Ar

	Bending overtones b_2b_2	b_1b_2	b_1b_1	Str. fund. s	Original IR int.
b_2b_2	**2966.6**	0.0	0.9	-73.6	0.3
b_1b_2	0.0	**2994.7**	0.0	0.0	0.3
b_1b_1	0.9	0.0	**3040.5**	-89.7	0.1
s	-73.6	0.0	-89.7	**3016.0**	849.5

[a] Notations for NH vibrational modes: b: C–N–H bending, s: N–H stretching; see **Fig. 3**.

Table S5. Hamiltonian matrix elements (in cm^{-1}) between NH bending overtones and stretching fundamentals involved in Fermi resonance and original IR intensities of vibrational quantum states (in km/mol) in DMA–H^+ ion and clusters.[a]

(a) DMA–H^+

	Bending overtones								Stretch. fund.		Original
	rw	tt	tw	ww	rx	tx	wx	xx	s_{sym}	s_{anti}	IR int.
rw	**2736.7**	0.0	0.0	0.0	0.0	3.6	0.0	0.0	0.0	0.0	0.0
tt	0.0	**2816.2**	0.0	-1.0	0.0	0.0	0.0	-1.0	-45.4	0.0	0.0
tw	0.0	0.0	**2868.0**	0.0	3.7	0.0	0.0	0.0	0.0	77.0	0.1
ww	0.0	-1.0	0.0	**2917.1**	0.0	0.0	0.0	-0.6	69.1	0.0	0.1
rx	0.0	0.0	3.7	0.0	**2931.0**	0.0	0.0	0.0	0.0	53.7	0.0
tx	3.6	0.0	0.0	0.0	0.0	**3045.4**	0.0	0.0	0.0	0.0	0.0
wx	0.0	0.0	0.0	0.0	0.0	0.0	**3092.7**	0.0	0.0	0.0	0.5
xx	0.0	-1.0	0.0	-0.6	0.0	0.0	0.0	**3280.2**	-24.8	0.0	0.2
s_{sym}	0.0	-45.4	0.0	69.1	0.0	0.0	0.0	-24.8	**3239.8**	0.0	64.7
s_{anti}	0.0	0.0	77.0	0.0	53.7	0.0	0.0	0.0	0.0	**3284.9**	95.4

(b) DMA–H^+...H_2O

	Bending overtones								Stretch. fund.		Original
	rw	tt	rx	tw	ww	tx	wx	xx	s_b	s_f	IR int.
rw	**2824.4**	0.0	-4.0	-0.3	1.1	-1.7	10.6	0.4	-1.8	4.3	0.0
tt	0.0	**2885.5**	-2.5	0.7	-0.3	1.6	-0.3	1.0	-9.9	-71.6	0.1
rx	-4.0	-2.5	**2951.8**	1.6	-2.3	0.6	-1.4	-11.9	-36.6	42.1	0.0
tw	-0.3	0.7	1.6	**2976.3**	-1.8	4.7	-1.4	0.8	-13.8	35.6	0.0
ww	1.1	-0.3	-2.3	-1.8	**3084.9**	-0.2	7.5	-0.1	71.0	4.7	0.1
tx	-1.7	1.6	0.6	4.7	-0.2	**3093.5**	-0.7	-1.7	-2.5	2.2	0.1
wx	10.6	-0.3	-1.4	-1.4	7.5	-0.7	**3195.3**	6.8	10.2	-2.9	0.3
xx	0.4	1.0	-11.9	0.8	-0.1	-1.7	6.8	**3315.4**	18.4	9.6	0.5
s_b	-1.8	-9.9	-36.6	-13.8	71.0	-2.5	10.2	18.4	**2954.4**	3.0	967.9
s_f	4.3	-71.6	42.1	35.6	4.7	2.2	-2.9	9.6	3.0	**3280.5**	72.9

Table S5. (continued)

(c) DMA–H^+...H_2O...Ar (type 1)

	Bending overtones								Stretch. fund.		Original
	rw	tt	rx	tw	ww	tx	wx	xx	s_b	s_f	IR int.
rw	**2835.9**	0.0	0.0	0.0	0.0	2.4	-11.9	0.0	0.0	0.0	0.0
tt	0.0	**2885.0**	1.9	1.2	0.6	0.0	0.0	-1.3	12.1	63.6	0.1
rx	0.0	1.9	**2956.6**	2.5	-2.3	0.0	0.0	-14.2	-40.7	41.8	0.0
tw	0.0	1.2	2.5	**2972.3**	-0.3	0.0	0.0	0.4	-19.9	46.8	0.0
ww	0.0	0.6	-2.3	-0.3	**3056.9**	0.0	0.0	0.1	62.1	12.0	0.0
tx	2.4	0.0	0.0	0.0	0.0	**3097.5**	0.2	0.0	0.0	0.0	0.1
wx	-11.9	0.0	0.0	0.0	0.0	0.2	**3195.6**	0.0	0.0	0.0	0.4
xx	0.0	-1.3	-14.2	0.4	0.1	0.0	0.0	**3323.7**	24.1	7.1	0.4
s_b	0.0	12.1	-40.7	-19.9	62.1	0.0	0.0	24.1	**2937.7**	2.9	967.0
s_f	0.0	63.6	41.8	46.8	12.0	0.0	0.0	7.1	2.9	**3280.9**	72.4

(d) Ar...DMA–H^+...H_2O (type 2)

	Bending overtones								Stretch. fund.		Original
	rw	tt	rx	tw	ww	tx	wx	xx	s_b	s_f	IR int.
rw	**2823.9**	-0.1	-4.4	-0.3	1.2	1.8	-9.9	-0.5	-2.1	5.0	0.0
tt	-0.1	**2899.7**	-2.5	0.6	-0.4	-1.8	0.3	-1.0	-9.9	-71.4	0.1
rx	-4.4	-2.5	**2952.8**	1.8	-2.3	-0.7	1.6	11.0	-37.6	42.6	0.0
tw	-0.3	0.6	1.8	**2980.8**	-1.8	-5.2	1.6	-0.8	-14.9	37.6	0.0
ww	1.2	-0.4	-2.3	-1.8	**3079.2**	0.2	-8.2	0.0	70.7	6.0	0.1
tx	1.8	-1.8	-0.7	-5.2	0.2	**3099.4**	-0.7	-1.9	3.0	-2.5	0.1
wx	-9.9	0.3	1.6	1.6	-8.2	-0.7	**3191.0**	7.5	-11.3	3.2	0.3
xx	-0.5	-1.0	11.0	-0.8	0.0	-1.9	7.5	**3312.3**	-20.1	-9.5	0.5
s_b	-2.1	-9.9	-37.6	-14.9	70.7	3.0	-11.3	-20.1	**2972.9**	3.2	962.2
s_f	5.0	-71.4	42.6	37.6	6.0	-2.5	3.2	-9.5	3.2	**3290.9**	136.2

[a] Notations for NH vibrational modes: r: rocking, t: twisting, w: wagging, x: scissoring, s_b: H-bonded stretching, s_f: free stretching; see **Fig. 5**. "rw" means one vibrational quantum in rocking and one in wagging; "tt" means two vibrational quanta in twisting mode.

Table S6. Hamiltonian matrix elements (in cm^{-1}) between NH bending overtones and stretching fundamentals involved in Fermi resonance and original IR intensities of vibrational quantum states (in km/mol) in MA–H^+ ion and clusters.[a]

(a) MA–H^+

	Bending overtones												Stretching fundamentals			Original
	wu	tu	tx'	wx	wx	tx	uu	ux'	ux	x'x'	x'x	xx	s_{sym}	s_{asym}	s'_{asym}	IR int.
wu	**2821.2**	0.0	0.0	0.3	0.0	-0.4	-0.1	3.6	2.6	0.0	0.0	0.1	0.2	45.3	26.7	0.0
tu	0.0	**2821.3**	0.3	-0.1	0.2	-0.1	0.0	-2.6	3.6	0.0	0.1	0.0	0.0	26.7	-44.8	0.0
tx'	0.0	0.3	**2914.0**	0.0	0.0	0.1	0.0	0.0	0.0	0.5	-0.2	-0.1	-0.5	1.3	-1.7	0.0
wx	0.3	-0.1	0.0	**2914.2**	0.0	0.0	0.5	0.1	0.0	-5.7	0.1	-0.2	5.8	1.9	1.2	0.1
wx	0.0	0.2	0.0	0.0	**2916.0**	0.0	0.0	-0.2	0.2	-0.1	-5.8	-1.2	0.1	18.8	-43.8	0.0
tx	-0.4	-0.1	0.1	0.0	0.0	**2916.0**	0.0	-0.1	-0.2	-0.2	-1.2	5.7	0.3	-44.3	-18.8	0.0
uu	-0.1	0.0	0.0	0.5	0.0	0.0	**3055.9**	0.1	-0.1	-0.5	0.0	0.0	-48.1	0.0	0.2	0.1
ux'	3.6	-2.6	0.0	0.1	-0.2	-0.1	0.1	**3152.5**	0.1	-0.2	-0.5	0.2	-0.2	5.7	12.3	0.2
ux	2.6	3.6	0.0	0.0	0.2	-0.2	-0.1	0.1	**3152.5**	0.1	0.4	0.3	0.0	12.7	-5.1	0.2
x'x'	0.0	0.0	0.5	-5.7	-0.1	-0.2	-0.5	-0.2	0.1	**3248.2**	0.0	0.0	25.9	0.0	-0.2	0.3
x'x	0.0	0.1	-0.2	0.1	-5.8	-1.2	0.0	-0.5	0.4	0.0	**3252.2**	0.0	0.0	3.7	-19.2	0.1
xx	0.1	0.0	-0.1	-0.2	-1.2	5.7	0.0	0.2	0.3	0.0	0.0	**3252.9**	0.0	19.2	3.7	0.1
s_{sym}	0.2	0.0	-0.5	5.8	0.1	0.3	-48.1	-0.2	0.0	25.9	0.0	0.0	**3227.3**	0.1	-0.5	58.1
s_{asym}	45.3	26.7	1.3	1.9	18.8	-44.3	0.0	5.7	12.7	0.0	3.7	19.2	0.1	**3302.6**	0.0	131.7
s'_{asym}	26.7	-44.8	-1.7	1.2	-43.8	-18.8	0.2	12.3	-5.1	-0.2	-19.2	3.7	-0.5	0.0	**3302.6**	131.6

Table S6. (continued)

(b) MA–H^+...H_2O

	Bending overtones												Stretching fundamentals			Original
	wu	tu	wx'	tx'	wx	tx	uu	ux'	ux	x'x'	x'x	xx	s_b	$s_{f,sym}$	$s_{f,asym}$	IR int.
wu	**2847.7**	0.0	-0.7	0.0	0.0	0.1	0.7	-5.9	0.0	0.1	0.0	0.0	32.7	-35.0	0.0	0.0
tu	0.0	**2860.3**	0.0	-1.3	0.0	0.0	0.0	0.0	2.9	0.0	0.1	0.0	0.0	0.0	54.0	0.0
wx'	-0.7	0.0	**2927.1**	0.0	0.0	0.2	0.5	-0.7	0.0	-7.1	0.0	0.2	24.4	-26.1	0.0	0.1
tx'	0.0	-1.3	0.0	**2937.8**	-0.1	0.0	0.0	0.0	-0.1	0.0	2.5	0.0	0.0	0.0	-29.0	0.0
wx	0.0	0.0	0.0	-0.1	**2973.9**	0.0	0.0	0.0	-0.3	0.0	-5.2	0.0	0.0	0.0	34.8	0.0
tx	0.1	0.0	0.2	0.0	0.0	**2985.9**	0.1	0.1	0.0	0.2	0.0	-3.4	-29.8	20.2	0.0	0.0
uu	0.7	0.0	0.5	0.0	0.0	0.1	**3099.7**	1.0	0.0	-0.5	0.0	-0.4	30.5	29.8	0.0	0.0
ux'	-5.9	0.0	-0.7	0.0	0.0	0.1	1.0	**3181.3**	0.0	-1.5	0.0	0.3	-10.1	14.8	0.0	0.4
ux	0.0	2.9	0.0	-0.1	-0.3	0.0	0.0	0.0	**3227.6**	0.0	-0.4	0.0	0.0	0.0	3.8	0.1
x'x'	0.1	0.0	-7.1	0.0	0.0	0.2	-0.5	-1.5	0.0	**3263.6**	0.0	0.4	-0.6	-21.2	0.0	0.2
x'x	0.0	0.1	0.0	2.5	-5.2	0.0	0.0	0.0	-0.4	0.0	**3313.3**	0.0	0.0	0.0	15.7	0.0
xx	0.0	0.0	0.2	0.0	0.0	-3.4	-0.4	0.3	0.0	0.4	0.0	**3357.9**	-23.6	-0.2	0.0	0.3
s_b	32.7	0.0	24.4	0.0	0.0	-29.8	30.5	-10.1	0.0	-0.6	0.0	-23.6	**2845.5**	6.1	0.0	1163.7
$s_{f,sym}$	-35.0	0.0	-26.1	0.0	0.0	20.2	29.8	14.8	0.0	-21.2	0.0	-0.2	6.1	**3274.1**	0.0	88.4
$s_{f,asym}$	0.0	54.0	0.0	-29.0	34.8	0.0	0.0	0.0	3.8	0.0	15.7	0.0	0.0	0.0	**3324.7**	94.8

Table S6. (continued)

(c) MA–H^+...H_2O...Ar (type 1)

	Bending overtones												Stretching fundamentals			Original
	wu	tu	tx'	wx'	wx	tx	uu	ux'	ux	x'x'	xx	x'x	s_b	$s_{f,sym}$	$s_{f,asym}$	IR int.
wu	**2874.3**	0.0	0.0	1.9	0.0	0.9	1.2	7.8	0.0	0.0	0.1	0.0	-29.1	28.3	-0.1	0.0
tu	0.0	**2880.8**	1.7	0.0	-0.1	0.0	0.0	0.0	4.8	0.0	0.0	-0.2	0.1	-0.1	-56.4	0.0
tx'	0.0	1.7	**2950.8**	0.0	-1.6	0.0	0.0	0.0	-0.2	-0.1	0.0	-2.8	-0.3	0.3	12.8	0.0
wx'	1.9	0.0	0.0	**2948.6**	0.0	0.7	0.5	1.6	0.0	-9.4	-1.7	0.0	-22.4	20.5	0.0	0.2
wx	0.0	-0.1	-1.6	0.0	**2946.3**	0.0	0.0	0.0	-0.8	0.0	-0.1	7.8	-0.3	0.3	-43.1	0.0
tx	0.9	0.0	0.0	0.7	0.0	**2950.2**	0.0	0.9	0.0	-1.6	-6.8	-0.1	-37.6	31.4	0.2	0.0
uu	1.2	0.0	0.0	0.5	0.0	0.0	**3141.3**	3.2	0.0	-0.6	-0.1	0.0	-31.2	-30.8	0.0	0.1
ux'	7.8	0.0	0.0	1.6	0.0	0.9	3.2	**3216.6**	0.0	-2.8	-1.0	0.0	-25.6	15.5	0.0	0.3
ux	0.0	4.8	-0.2	0.0	-0.8	0.0	0.0	0.0	**3212.5**	0.0	0.0	-2.5	0.1	0.0	-1.0	0.1
x'x'	0.0	0.0	-0.1	-9.4	0.0	-1.6	-0.6	-2.8	0.0	**3289.2**	3.4	0.0	14.3	15.2	0.0	0.3
xx	0.1	0.0	0.0	-1.7	-0.1	-6.8	-0.1	-1.0	0.0	3.4	**3288.2**	0.0	-8.6	2.7	-0.1	0.3
x'x	0.0	-0.2	-2.8	0.0	7.8	-0.1	0.0	0.0	-2.5	0.0	0.0	**3291.7**	-0.1	0.0	15.0	0.1
s_b	-29.1	0.1	-0.3	-22.4	-0.3	-37.6	-31.2	-25.6	0.1	14.3	-8.6	-0.1	**2831.7**	6.0	0.0	1158.2
$s_{f,sym}$	28.3	-0.1	0.3	20.5	0.3	31.4	-30.8	15.5	0.0	15.2	2.7	0.0	6.0	**3274.3**	0.0	90.1
$s_{f,asym}$	-0.1	-56.4	12.8	0.0	-43.1	0.2	0.0	0.0	-1.0	0.0	-0.1	15.0	0.0	0.0	**3326.9**	95.3

Table S6. (continued)

(d) Ar...MA–H^+...H_2O (type 2)

	Bending overtones												Stretching fundamentals			Original
	wu	tu	wx'	tx'	wx	tx	uu	ux'	ux	x'x'	xx'	xx	s_b	$s_{f,sym}$	$s_{f,asym}$	IR int.
wu	**2851.7**	0.7	-0.5	0.2	0.3	0.0	-0.7	5.8	-1.4	-0.1	0.0	0.1	33.1	-34.2	11.3	0.0
tu	0.7	**2863.2**	-0.2	0.9	-0.2	-0.1	0.4	-1.3	-2.9	0.0	-0.1	0.0	-6.2	9.0	53.7	0.0
wx'	-0.5	-0.2	**2934.0**	-0.8	0.1	0.2	-0.5	0.9	0.0	6.9	-1.2	-0.2	24.1	-25.6	-1.5	0.1
tx'	0.2	0.9	-0.8	**2943.1**	0.0	0.1	-0.1	0.3	-0.1	1.7	2.4	0.0	3.1	-2.1	29.3	0.0
wx	0.3	-0.2	0.1	0.0	**2977.1**	0.7	-0.1	0.0	-0.3	0.0	-5.2	1.8	-1.3	-1.6	-35.1	0.0
tx	0.0	-0.1	0.2	0.1	0.7	**2988.1**	-0.1	-0.2	0.3	-0.2	1.2	3.3	-30.6	21.2	3.6	0.0
uu	-0.7	0.4	-0.5	-0.1	-0.1	-0.1	**3100.7**	0.6	0.2	-0.5	0.0	-0.4	-30.5	-30.3	0.8	0.0
ux'	5.8	-1.3	0.9	0.3	0.0	-0.2	0.6	**3183.6**	0.0	-1.1	0.0	0.4	10.5	-14.3	-0.2	0.5
ux	-1.4	-2.9	0.0	-0.1	-0.3	0.3	0.2	0.0	**3227.8**	0.1	-0.1	-0.2	-1.7	0.6	-4.2	0.2
x'x'	-0.1	0.0	6.9	1.7	0.0	-0.2	-0.5	-1.1	0.1	**3269.4**	-0.1	0.4	0.9	21.0	-2.4	0.2
x'x	0.0	-0.1	-1.2	2.4	-5.2	1.2	0.0	0.0	-0.1	-0.1	**3315.8**	0.0	1.9	-2.7	-15.8	0.0
xx	0.1	0.0	-0.2	0.0	1.8	3.3	-0.4	0.4	-0.2	0.4	0.0	**3357.6**	23.5	0.5	1.8	0.2
s_b	33.1	-6.2	24.1	3.1	-1.3	-30.6	-30.5	10.5	-1.7	0.9	1.9	23.5	**2870.7**	6.1	-0.3	1122.3
$s_{f,sym}$	-34.2	9.0	-25.6	-2.1	-1.6	21.2	-30.3	-14.3	0.6	21.0	-2.7	0.5	6.1	**3274.0**	-0.8	144.0
$s_{f,asym}$	11.3	53.7	-1.5	29.3	-35.1	3.6	0.8	-0.2	-4.2	-2.4	-15.8	1.8	-0.3	-0.8	**3324.0**	165.8

[a] Notations for NH vibrational modes: t: twisting, w: wagging, u: umbrella, x: scissoring, s_b: H-bonded stretching, $s_{f,sym}$: symmetric free stretching, $s_{f,asym}$: asymmetric free stretching; see **Fig. 7**.

Table S7. Hamiltonian matrix elements (in cm^{-1}) between NH bending overtones and stretching fundamentals involved in Fermi resonance and original IR intensities of vibrational quantum states (in km/mol) in NH_4^+ ion and clusters.[a]

(a) NH_4^+

	Bending overtones												Stretching fundamentals				Original
	uu/uu'/uu"/u'u"/u'u'/u"u"						ux/ut/u't/u'x/u"t/u"x						xx/xt/tt			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
uu'/	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
uu"/	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
u'u"/	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
u'u'/	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
u"u"	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
ut/	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
u't/	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
u'x/	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
u"t/	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
u"x/	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
xt/	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
tt	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

Table S7. (continued)

(b) NH_4^+...H_2O

	Bending overtones												Stretching fundamentals					Original
	uu	uu'	uu"	u'u'	u'u"	u"u"	ux	ut	u'x	u't	u"x	u"t	xx	xt	tt	s_b	$s_{f,sym}$	$s_{f,asym}$	$s'_{f,asym}$	IR int.
uu	**2793.0**	0.1	0.0	-0.3	0.0	-0.3	0.0	0.0	1.3	0.0	0.0	-1.3	-0.3	0.0	-0.5	21.9	-62.4	0.0	0.7	0.3
uu'	0.1	**2866.2**	0.0	0.0	0.0	-0.1	-0.3	0.0	-0.4	0.0	0.0	-0.4	0.9	0.0	-0.9	1.1	-0.7	0.0	-24.7	0.0
uu"	0.0	0.0	**2893.2**	0.0	-0.2	0.0	0.0	5.0	0.0	-0.3	0.0	0.0	0.0	-0.8	0.0	0.0	0.0	-17.2	0.0	0.0
u'u'	-0.3	0.0	0.0	**2941.7**	0.0	0.5	-0.8	0.0	-1.4	0.0	0.0	-0.8	0.9	0.0	1.1	30.5	20.5	0.0	-27.2	0.0
u'u"	0.0	0.0	-0.2	0.0	**2969.8**	0.0	0.0	-1.0	0.0	-3.9	-1.4	0.0	0.0	0.1	0.0	0.0	0.0	42.0	0.0	0.0
u"u"	-0.3	-0.1	0.0	0.5	0.0	**2996.9**	1.0	0.0	0.8	0.0	0.0	-6.3	1.1	0.0	0.6	31.9	20.2	0.0	31.5	0.0
ux	0.0	-0.3	0.0	-0.8	0.0	1.0	**3075.4**	0.0	0.9	0.0	0.0	0.4	-0.4	0.0	0.2	0.0	0.1	0.0	31.8	0.1
ut	0.0	0.0	5.0	0.0	-1.0	0.0	0.0	**3100.8**	0.0	-0.6	0.4	0.0	0.0	-0.2	0.0	0.0	0.0	-31.9	0.0	0.1
u'x	1.3	-0.4	0.0	-1.4	0.0	0.8	0.9	0.0	**3149.9**	0.0	0.0	0.7	1.8	0.0	0.1	13.0	-17.5	0.0	20.2	0.5
u't	0.0	0.0	-0.3	0.0	-3.9	0.0	0.0	-0.6	0.0	**3175.8**	0.7	0.0	0.0	-1.0	0.0	0.0	0.0	14.6	0.0	0.1
u"x	0.0	0.0	0.0	0.0	-1.4	0.0	0.0	0.4	0.0	0.7	**3178.3**	0.0	0.0	-3.8	0.0	0.0	0.0	-17.6	0.0	0.0
u"t	-1.3	-0.4	0.0	-0.8	0.0	-6.3	0.4	0.0	0.7	0.0	0.0	**3203.5**	0.2	0.0	5.3	-25.5	18.0	0.0	14.1	0.2
xx	-0.3	0.9	0.0	0.9	0.0	1.1	-0.4	0.0	1.8	0.0	0.0	0.2	**3361.7**	0.0	0.4	0.7	-8.9	0.0	0.3	0.1
xt	0.0	0.0	-0.8	0.0	0.1	0.0	0.0	-0.2	0.0	-1.0	-3.8	0.0	0.0	**3389.0**	0.0	0.0	0.0	0.8	0.0	0.0
tt	-0.5	-0.9	0.0	1.1	0.0	0.6	0.2	0.0	0.1	0.0	0.0	5.3	0.4	0.0	**3412.1**	-7.4	-4.5	0.0	0.7	0.0
s_b	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	**2659.5**	10.9	0.0	0.0	1528.8
$s_{f,sym}$	-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	10.9	**3264.2**	0.0	0.0	91.2
$s_{f,asym}$	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	0.0	0.0	**3352.2**	0.0	145.4
$s'_{f,asym}$	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	0.0	0.0	0.0	**3353.2**	142.2

Table S7. (continued)

(c) NH_4^+...H_2O...Ar (type 1)

	Bending overtones												Stretching fundamentals					Original
	uu	uu'	uu"	u'u'	u'u"	u"u"	ut	ux	u't	u'x	u"t	u"x	tt	tx	xx	s_b	$s_{f,sym}$	$s_{f,asym}$	$s'_{f,asym}$	IR int.
uu	**2786.5**	-0.1	0.0	-0.3	0.0	-0.3	0.0	0.1	-1.3	0.0	0.0	1.3	0.3	0.0	0.5	-23.1	-62.6	-0.4	-0.3	0.4
uu'	-0.1	**2864.0**	0.1	0.0	0.2	0.1	0.2	0.0	-0.2	-0.3	0.3	-0.2	0.4	0.8	-0.4	0.5	0.3	-0.6	-24.3	0.0
uu"	0.0	0.1	**2892.1**	0.0	0.1	-0.1	0.0	-5.2	0.2	-0.1	0.0	0.1	-0.7	0.4	0.7	-0.7	-0.3	17.0	-0.2	0.0
u'u'	-0.3	0.0	0.0	**2943.5**	0.0	0.5	-0.4	-0.6	1.6	0.0	0.0	0.8	-0.9	0.0	-1.1	-29.4	20.7	24.5	12.3	0.0
u'u"	0.0	0.2	0.1	0.0	**2973.2**	0.0	1.0	-0.5	-0.1	4.0	1.5	0.0	0.0	0.1	0.0	0.0	0.0	19.0	-37.2	0.0
u"u"	-0.3	0.1	-0.1	0.5	0.0	**3001.8**	0.5	0.8	-0.7	0.0	0.0	6.5	-1.1	0.0	-0.6	-31.2	20.5	-28.0	-14.3	0.0
ut	0.0	0.2	0.0	-0.4	1.0	0.5	**3071.6**	0.0	-0.5	-0.3	0.7	-0.2	0.2	0.3	-0.1	0.0	0.0	-0.6	-31.7	0.1
ux	0.1	0.0	-5.2	-0.6	-0.5	0.8	0.0	**3098.7**	-0.3	0.2	-0.2	-0.6	0.2	-0.1	-0.3	0.0	-0.1	-32.2	0.3	0.1
u't	-1.3	-0.2	0.2	1.6	-0.1	-0.7	-0.5	-0.3	**3150.4**	0.0	0.0	0.6	1.8	0.1	0.1	11.8	17.4	17.2	9.1	0.6
u'x	0.0	-0.3	-0.1	0.0	4.0	0.0	-0.3	0.2	0.0	**3178.2**	0.6	0.1	0.0	1.1	0.1	0.1	0.0	-6.4	13.1	0.1
u"t	0.0	0.3	0.0	0.0	1.5	0.0	0.7	-0.2	0.0	0.6	**3180.1**	-0.1	-0.1	3.9	0.0	0.0	0.1	7.9	-16.5	0.0
u"x	1.3	-0.2	0.1	0.8	0.0	6.5	-0.2	-0.6	0.6	0.1	-0.1	**3206.8**	0.2	-0.1	5.4	-25.1	-17.7	12.5	6.2	0.3
tt	0.3	0.4	-0.7	-0.9	0.0	-1.1	0.2	0.2	1.8	0.0	-0.1	0.2	**3360.5**	0.0	0.4	1.5	9.1	0.2	0.2	0.1
tx	0.0	0.8	0.4	0.0	0.1	0.0	0.3	-0.1	0.1	1.1	3.9	-0.1	0.0	**3389.4**	0.0	0.0	-0.1	0.4	-0.4	0.0
xx	0.5	-0.4	0.7	-1.1	0.0	-0.6	-0.1	-0.3	0.1	0.1	0.0	5.4	0.4	0.0	**3414.7**	-7.2	4.4	0.9	0.3	0.1
s_b	-23.1	0.5	-0.7	-29.4	0.0	-31.2	0.0	0.0	11.8	0.1	0.0	-25.1	1.5	0.0	-7.2	**2612.7**	-11.0	0.0	0.0	1614.3
$s_{f,sym}$	-62.6	0.3	-0.3	20.7	0.0	20.5	0.0	-0.1	17.4	0.0	0.1	-17.7	9.1	-0.1	4.4	-11.0	**3265.1**	0.4	0.0	86.1
$s_{f,asym}$	-0.4	-0.6	17.0	24.5	19.0	-28.0	-0.6	-32.2	17.2	-6.4	7.9	12.5	0.2	0.4	0.9	0.0	0.4	**3354.0**	0.0	139.0
$s'_{f,asym}$	-0.3	-24.3	-0.2	12.3	-37.2	-14.3	-31.7	0.3	9.1	13.1	-16.5	6.2	0.2	-0.4	0.3	0.0	0.0	0.0	**3354.9**	141.8

Table S7. (continued)

(d) Ar...NH_4^+...H_2O (type 2)

	Bending overtones												Stretching fundamentals					Original
	uu	uu'	uu"	u'u'	u'u"	u"u"	ut	ux	u't	u'x	u"t	u"x	tt	tx	xx	s_b	$s_{f,sym}$	$s_{f,asym}$	$s'_{f,asym}$	IR int.
uu	**2804.6**	0.0	0.2	-0.3	0.0	-0.3	0.0	-0.7	-1.3	0.0	0.0	1.3	-0.4	0.0	-0.6	21.1	61.3	7.6	0.0	0.4
uu'	0.0	**2876.5**	0.0	0.0	0.0	0.0	0.3	0.0	0.0	-0.9	0.4	0.0	0.0	-0.8	0.0	0.0	0.0	0.0	-24.1	0.0
uu"	0.2	0.0	**2894.1**	0.0	0.0	-0.4	0.0	-4.6	0.4	0.0	0.0	-0.5	0.8	0.0	-0.7	-1.7	-3.8	18.7	0.0	0.1
u'u'	-0.3	0.0	0.0	**2949.8**	0.0	0.7	0.0	-0.6	1.2	0.0	0.0	1.0	1.0	0.0	1.2	31.5	-23.8	24.6	0.0	0.0
u'u"	0.0	0.0	0.0	0.0	**2969.2**	0.0	1.2	0.0	0.0	3.4	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-41.5	0.0
u"u"	-0.3	0.0	-0.4	0.7	0.0	**2987.6**	0.0	1.0	-0.8	0.0	0.0	5.7	1.1	0.0	0.5	32.4	-15.2	-34.4	0.0	0.0
ut	0.0	0.3	0.0	0.0	1.2	0.0	**3087.1**	0.0	0.0	-0.3	0.9	0.0	0.0	-0.9	0.0	0.0	0.0	0.0	-31.0	0.1
ux	-0.7	0.0	-4.6	-0.6	0.0	1.0	0.0	**3109.5**	-0.3	0.0	0.0	-0.5	-0.3	0.0	-0.8	1.5	4.8	-31.7	0.0	0.1
u't	-1.3	0.0	0.4	1.2	0.0	-0.8	0.0	-0.3	**3159.8**	0.0	0.0	0.5	-1.3	0.0	-0.1	-13.7	-19.6	17.1	0.0	0.6
u'x	0.0	-0.9	0.0	0.0	3.4	0.0	-0.3	0.0	0.0	**3183.1**	0.5	0.0	0.0	-0.8	0.0	0.0	0.0	0.0	14.6	0.1
u"t	0.0	0.4	0.0	0.0	1.2	0.0	0.9	0.0	0.0	0.5	**3179.1**	0.0	0.0	-3.2	0.0	0.0	0.0	0.0	-18.0	0.0
u"x	1.3	0.0	-0.5	1.0	0.0	5.7	0.0	-0.5	0.5	0.0	0.0	**3201.4**	-0.2	0.0	-4.6	25.9	16.2	17.5	0.0	0.3
tt	-0.4	0.0	0.8	1.0	0.0	1.1	0.0	-0.3	-1.3	0.0	0.0	-0.2	**3372.2**	0.0	0.4	0.2	8.8	0.6	0.0	0.1
tx	0.0	-0.8	0.0	0.0	0.0	0.0	-0.9	0.0	0.0	-0.8	-3.2	0.0	0.0	**3397.2**	0.0	0.0	0.0	0.0	0.4	0.0
xx	-0.6	0.0	-0.7	1.2	0.0	0.5	0.0	-0.8	-0.1	0.0	0.0	-4.6	0.4	0.0	**3418.1**	-7.4	4.4	-0.7	0.0	0.0
s_b	21.1	0.0	-1.7	31.5	0.0	32.4	0.0	1.5	-13.7	0.0	0.0	25.9	0.2	0.0	-7.4	**2699.2**	-10.7	-1.3	0.0	1425.8
$s_{f,sym}$	61.3	0.0	-3.8	-23.8	0.0	-15.2	0.0	4.8	-19.6	0.0	0.0	16.2	8.8	0.0	4.4	-10.7	**3258.5**	1.9	0.0	142.9
$s_{f,asym}$	7.6	0.0	18.7	24.6	0.0	-34.4	0.0	-31.7	17.1	0.0	0.0	17.5	0.6	0.0	-0.7	-1.3	1.9	**3337.4**	0.0	269.7
$s'_{f,asym}$	0.0	-24.1	0.0	0.0	-41.5	0.0	-31.0	0.0	0.0	14.6	-18.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	**3356.6**	136.9

[a] Notations for NH vibrational modes: u: umbrella, x: scissoring, t: twisting, s_b: H-bonded stretching, $s_{f,sym}$: symmetric free stretching, $s_{f,asym}$: asymmetric free stretching; see **Fig. 9**.