"Infrared spectra of mass-selected Br^--$(NH_3)_n$ and I^--$(NH_3)_n$ clusters"

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Table 1. Data for Br^-, NH_3 and Br^--NH_3 at MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels. Listed are optimized internal coordinates (r in Å, θ in degrees), harmonic vibrational frequencies (ω in cm^{-1}, intensities in km/mol in brackets), zpe (in kcal/mol), electronic energies (E in au), dissociation energy (D_0 in cm^{-1}), and enthalpy change for association reaction at 298K ($\Delta H^{298}_{0\rightarrow 1}$ in kcal/mol). H_b refers to H-bonded hydrogen atoms and H_t to terminal hydrogen atoms.

	MP2/aug-cc-pVDZ	MP2/aug-cc-pVTZ	Vibrational mode description
		Br^--NH_3	
$r(Br^-H_b)$	2.569	2.484	
$r(N-H_b)$	1.033	1.028	
$r(N-H_t)$	1.022	1.014	
$\theta(Br^-H_b-N)$	167.2	168.7	
$\theta(H_b-N-H_t)$	103.9	104.4	
$\theta(H_t-N-H_t)$	104.7	105.1	
$\omega_1(a')$	3533 (62)	3543 (46)	free sym. NH stretch
$\omega_2(a')$	3361 (310)	3339 (418)	IHB NH stretch
$\omega_3(a')$	1638 (18)	1656 (20)	NH_3 bend
$\omega_4(a')$	1171 (95)	1169 (91)	NH_3 umbrella
$\omega_5(a')$	293 (48)	312 (49)	intermol. bend
$\omega_6(a')$	126 (8)	138 (8)	intermol. stretch
$\omega_7(a'')$	3604 (0*)	3617 (1)	free asym. NH stretch
$\omega_8(a'')$	1670 (1)	1691 (0*)	NH_3 bend
$\omega_9(a'')$	228 (20)	236 (17)	intermol. bend
zpe	22.3	22.4	
E_{MP2}	-2629.027164	-2629.249189	
E_{MP2}(BSSE)	-2629.025012	-2629.246904	
D_0	2112	2270	
$\Delta H^{298}_{0\rightarrow 1}$	-6.5	-7.0	
		NH_3	
$r(N-H)$ [a]	1.020(+8)	1.012(0)	
$\theta(H-N-H)$ [a]	106.3(-4)	106.8(+1)	
$\omega_1(a_1)$	3480 (5)	3503 (3)	sym. NH str.
$\omega_2(a_1)$	1045 (131)	1037 (139)	NH_3 umbrella
$\omega_3(e)$	3635 (5)	3650 (8)	sym. NH str.
$\omega_4(e)$	1649 (13)	1669 (14)	NH_3 bend
zpe	21.6	21.7	
E_{MP2}	-56.404890	-56.460541	
		Br^-	
E_{MP2}	-2572.609288	-2572.774831	

[a] Numbers in parentheses are differences (last significant figure) between these calculated values and experimental values taken from reference [44].

* These modes have intensities below 0.5 km/mol, but are IR active.

Table 2. Data for $Br^-(NH_3)_2$ isomers calculated at the MP2/aug-cc-pVDZ level. The structures are depicted in Figure 5 of the paper. Listed are internal coordinates (***r*** in Å, ***θ*** in degrees), zero-point-energies (zpe in kcal/mol), energy differences ($\Delta E_{BSSE/Corr}$ in kcal/mol), and enthalpy change for the association at 298K ($\Delta H^{298}_{1\rightarrow 2}$ in kcal/mol). H_b refers to H-bonded hydrogen atoms, H_t to terminal hydrogen atoms, and H_{ba} to hydrogen atoms engaged in an ammonia-ammonia H-bond.

	C $_1$	***C*** $_{2h}$	***C*** $_{2v}$
$r(Br^-H_b)$	2.675 *D*	2.583	2.585
	2.528 *A*		
$r(N-H_b)$	1.030 *D*	1.032	1.032
	1.033 *A*		
$r(N-H_{ba})$	1.024		
$r(H_{ba}\cdots N)$	2.479		
$r(N-H_t)$	1.022 *D*	1.022	1.022
	1.022 *A*		
$\theta(Br^-H_b-N)$	159.7 *D*	167.3	166.9
	172.3 *A*		
$\theta(H_b-N-H_t)$	104.5 *D*	104.1	104.1
$\theta(N-H_{ba}-N)$	135.2		
$\theta(H_t-N-H_t)$	105.2 *A*	104.8	104.8
$\theta(H_b-Br^-H_b)$	59.7	180.0	175.7
zpe	45.4	44.7	44.7
E_{MP2}	-2685.446444	-2685.444313	-2685.444246
D_0	2000		
ΔE_{MP2}	0.0	1.34	1.38
$\Delta E_{BSSE/corr}$	0.0	0.2	0.2
$\Delta H^{298}_{1\rightarrow 2}$	-5.8	-	-

Table 3. MP2/aug-cc-pVDZ harmonic vibrational frequencies (in cm^{-1}) for structures of Br^--$(NH_3)_2$ depicted in Figure 5 of the paper. Also listed are mode symmetries and intensities in km/mol (in brackets).

	C_1	C_{2h}	C_{2v}
ω_1	3608 *a* (1)	3540 a_g (0)	3540 a_1 (0)
ω_2	3597 *a* (10)	3383 a_g(0)	3383 a_1 (30)
ω_3	3535 *a* (95)	1639 a_g (0)	1639 a_1 (17)
ω_4	3531 *a* (21)	1167 a_g (0)	1164 a_1 (58)
ω_5	3403 *a* (148)	290 a_g (0)	287 a_1 (17)
ω_6	3348 *a* (314)	112 a_g (0)	112 a_1 (0*)
ω_7	1690 *a* (10)	3607 a_u (0*)	5 a_1 (0*)
ω_8	1664 *a* (17)	1669 a_u (2)	3607 a_2 (0*)
ω_9	1645 *a* (14)	223 a_u (39)	1671 a_2 (0*)
ω_{10}	1640 *a* (13)	15 a_u (77)	222 a_2 (0*)
ω_{11}	1176 *a* (55)	6 a_u (1)	17*i* a_2
ω_{12}	1164 *a* (111)	3606 b_g (0)	3607 b_1 (0*)
ω_{13}	375 *a* (98)	1671 b_g (0)	1669 b_1 (2)
ω_{14}	301 *a* (7)	223 b_g (0)	223 b_1 (39)
ω_{15}	261 *a* (25)	3539 b_u (141)	10 b_1 (38)
ω_{16}	236 *a* (29)	3376 b_u (561)	3539 b_2 (141)
ω_{17}	209 *a* (15)	1639 b_u (36)	3377 b_2 (523)
ω_{18}	142 *a* (8)	1162 b_u (198)	1639 b_2 (19)
ω_{19}	126 *a* (17)	285 b_u (96)	1164 b_2 (142)
ω_{20}	85 *a* (5)	133 b_u (16)	132 b_2 (16)
ω_{21}	23 *a* (43)	3*i* b_u	286 b_2 (79)

* These modes have intensities below 0.5 km/mol, but are IR active.

Table 4. MP2/aug-cc-pVDZ data for the $Br^-(NH_3)_3$ structures depicted in Figure 7 of the paper. Provided are internal coordinates (r in Å, θ in degrees), zero point energies (zpe in kcal/mol), energy differences ($\Delta E_{BSSE/Corr}$ in kcal/mol), and enthalpy change for the association reaction at 298K ($\Delta H^{298}_{2\rightarrow3}$ in kcal/mol). H_b refers to H-bonded hydrogen atoms, H_t to terminal hydrogen atoms, and H_{ba} to hydrogen atoms engaged in an ammonia-ammonia H-bond.

	C_3	C_1	C_s	C_{3h}
$r(Br^-H_b)$	2.639	2.498 *A* 2.736 *D1* 2.650 *D2*	2.517 *B* 4.500 *S* (H_{ba})	2.587
$r(N-H_b)$	1.030	1.033 *A* 1.028 *D1* 1.030 *D2*	1.032 *B*	1.031
$r(N-H_{ba})$	1.025	1.024 *D1* 1.024 *D2*	1.027 *S*	
$r(H_{ba}\cdots N)$	2.391	2.579 *D1* 2.588 *D2*	2.297	
$r(N-H_t)$	1.021	1.022 *A* 1.023 *D1* 1.022 *D2*	1.021 *B*,*S*	1.022
$\theta(Br^-H_b-N)$	159.5	179.6 *A* 153.7 *D1* 160.7 *D2*	175.038 *B*	167.9
$\theta(H_b-N-H_t)$	105.6	104.8 *A* 103.4 *D1* 104.9 *D2*	104.8 *B* 105.3 *S*	104.2
$\theta(N-H_{ba}-N)^c$	137.1	139.5 *D1* 138.8 *D2*	167.5 *S*	
$\theta(H_t-N-H_t)$		105.1 *A*	105.3	104.8
$\theta(H_b-Br^-H_b)$	61.4	61.9 *A-D1* 62.8 *D1-D2* 62.3 *D2-A*	77.8	120.0
zpe	69.2	68.5	68.5	67.2
E_{MP2}	-2741.868327	-2741.859607	-2741.864096	-2741.861104
D_0	2144			
ΔE_{MP2}	0.0	5.47	2.65	4.53
$\Delta E_{BSSE/Corr}$	0.0	0.6	1.3	1.1
$\Delta H^{298}_{2\rightarrow3}$	-6.7	-5.6	-4.9	

Table 5. MP2/aug-cc-pVDZ harmonic vibrational frequencies (in cm^{-1}) for structures of $Br^-(NH_3)_3$ depicted in Figure 7 of the paper. Also listed are mode symmetries and intensities in km/mol (in brackets).

	C_3	C_1	C_s	C_{3h}
ω_1	3599 *a* (5)	3605 *a* (0*)	3612 *a′* (1)	3545 *a′*
ω_2	3522 *a* (176)	3598 *a* (8)	3591 *a′* (20)	3394 *a′*
ω_3	3391 *a* (225)	3586 *a* (8)	3541 *a′* (93)	1640 *a′*
ω_4	1697 *a* (14)	3542 *a* (72)	3404 *a′* (81)	1158 *a′*
ω_5	1648 *a* (16)	3533 *a* (74)	3360 *a′* (328)	286 *a′*
ω_6	1165 *a* (88)	3531 *a* (5)	1695 *a′* (11)	112 *a′*
ω_7	449 *a* (78)	3423 *a* (63)	1671 *a′* (1)	3608 *a″*
ω_8	337 *a* (37)	3400 *a* (135)	1637 *a′* (4)	1670 *a″*
ω_9	247 *a* (13)	3337 *a* (312)	1178 *a′* (36	219 *a″*
ω_{10}	159 *a* (0*)	1684 *a* (2)	1165 *a′* (212	31 *a″*
ω_{11}	99 *a* (11)	1676 *a* (22)	365 *a′* (23)	4*i* *a″*
ω_{12}	3599 *e* (16)	1668 *a* (2)	301 *a′* (91)	3543 *e′*
ω_{13}	3518 *e* (12)	1659 *a* (5)	223 *a′* (16)	3388 *e′*
ω_{14}	3388 *e* (111)	1645 *a* (5)	149 *a'* (3)	1640 *e′*
ω_{15}	1675 *e* (39)	1638 *a* (29)	133 *a'* (10)	1161 *e′*
ω_{16}	1640 *e* (1)	1201 *a* (104)	81 *a'* (29)	284 *e′*
ω_{17}	1176 *e* (62)	1179 *a* (7)	36 *a'* (3)	128 *e′*
ω_{18}	354 *e* (45)	1159 *a* (198)	21 *a'* (9)	8*i* *e′*
ω_{19}	285 *e* (29)	393 *a* (125)	3612 *a″* (0*)	3608 *e″*
ω_{20}	199 *e* (59)	318 *a* (20)	3540 *a″* (52)	1671 *e″*
ω_{21}	124 *e* (0*)	302 *a* (89)	3517 *a″* (132)	220 *e″*
ω_{22}	92 *e* (4)	273 *a* (40)	3352 *a″* (330)	26 *e″*
ω_{23}		247 *a* (8)	1669 *a″* (0*)	
ω_{24}		222 *a* (4)	1658 *a″* (6)	
ω_{25}		204 *a* (23	1636 *a″* (25)	
ω_{26}		186 *a* (16)	1162 *a″* (5)	
ω_{27}		147 *a* (9)	472 *a″* (88)	
ω_{28}		126 *a* (12)	319 *a″* (6)	
ω_{29}		124 *a* (10)	287 *a″* (16)	
ω_{30}		102 *a* (7)	220 *a″* (8)	
ω_{31}		83 *a* (2)	138 *a"* (12	
ω_{32}		62 *a* (0*)	119 *a"* (0*)	
ω_{33}		54 *a* (5)	55 *a"* (13)	

* These modes have intensities below 0.5 km/mol, but are IR active.