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Supporting Information

Spectroscopic evidence of the C-N covalent bond formed between two interstellar molecules (ISM)：acrylonitrile and ammonia

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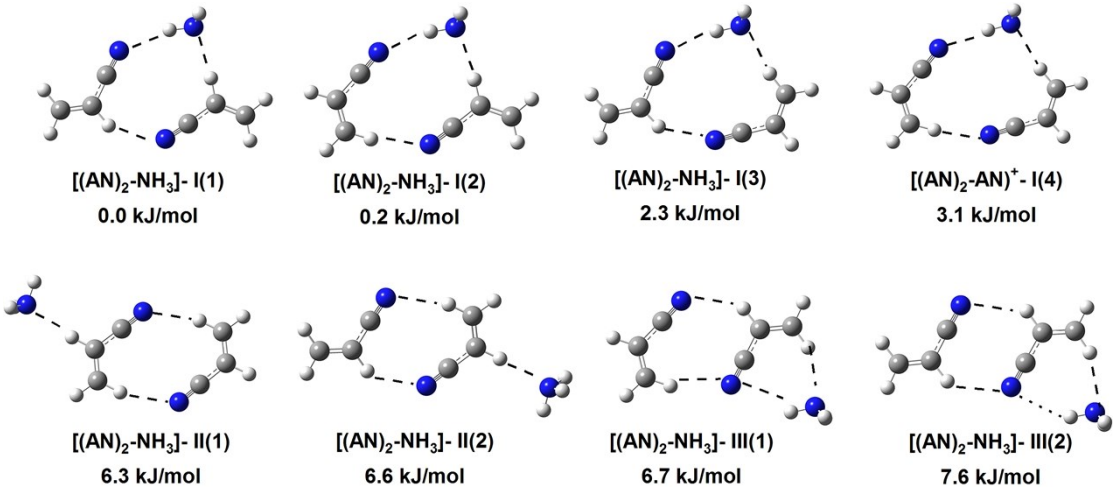


Figure S1. Representative geometric parameters of eight structures of $(AN)_2$-NH_3 predicted with B3LYP-6-311++g (d p) level.

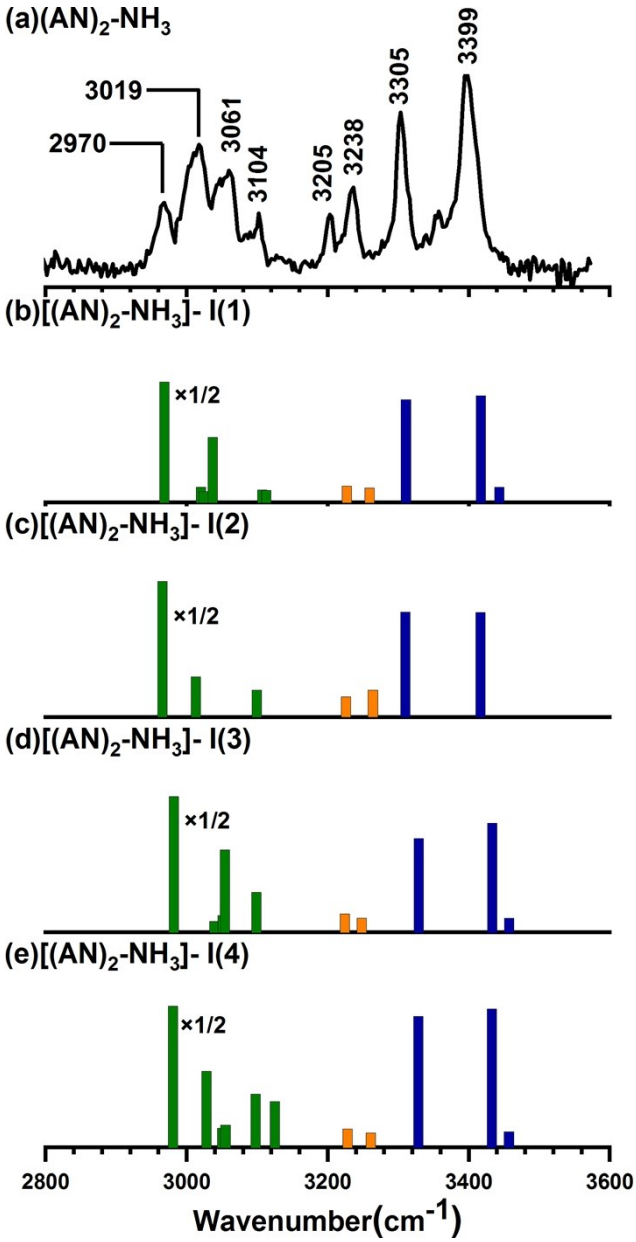


Figure S2. (a) Observed and (b)--(e) calculated IR spectra of $(AN)_2$-NH_3 clusters in the 2800–3600-cm^{-1} region. The calculated harmonic and anharmonic spectra of the first type stable structures [$(AN)_2$-NH_3]-I(1), -I(2) -I(3), and -I(4) were optimized under the method of B3LYP/6-311++(d, p). Calculated harmonic spectra are scaled by the factor of 0.96. The green, blue, and orange sticks represent the CH, NH, and anharmonic vibration modes, respectively.

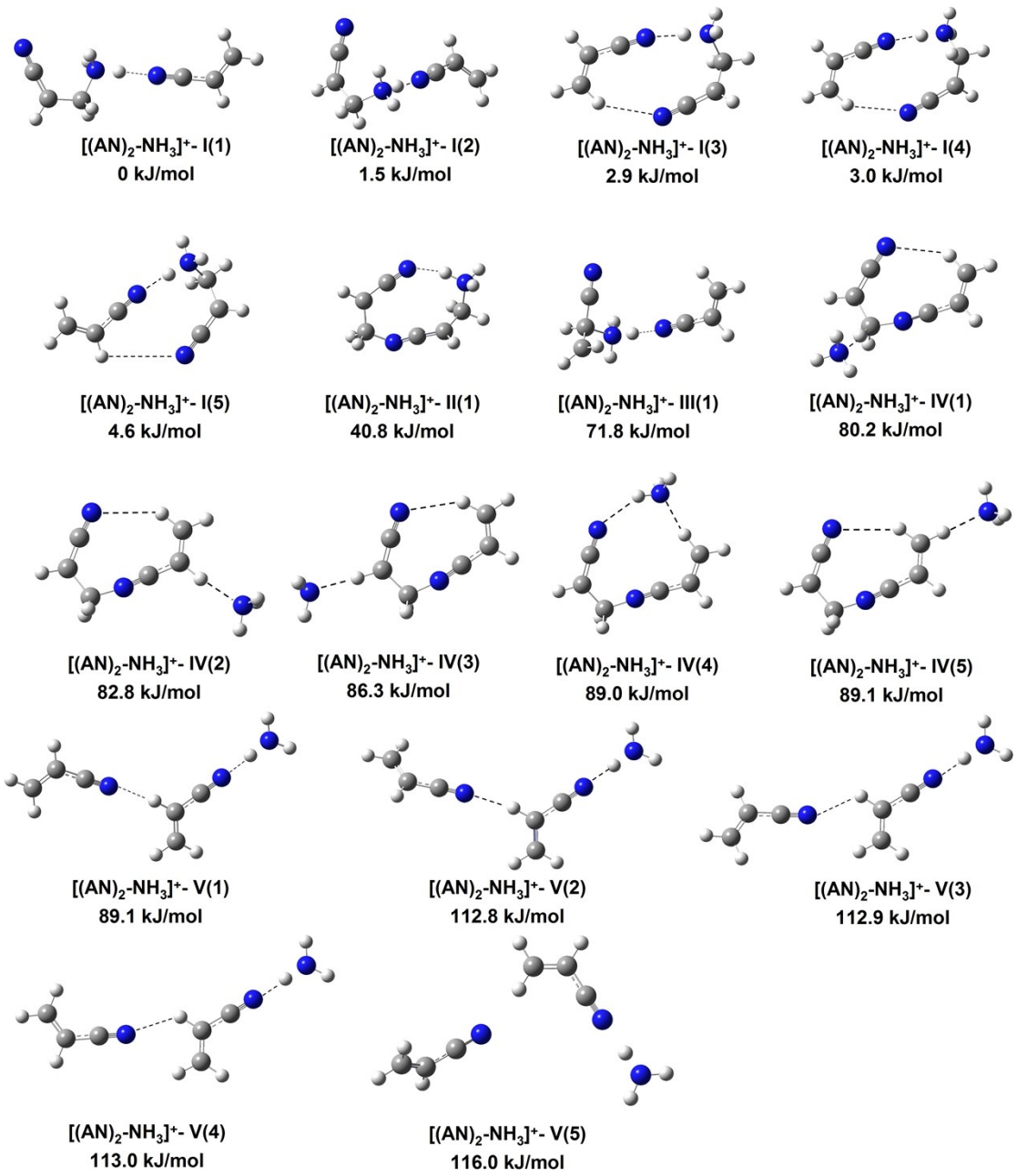


Figure S3. Seventeen isomers of $[(AN)_2\text{-}NH_3]^+$ have been found and divided into five categories according to their structural characteristics. Geometric and relative of seventeen structures of $[(AN)_2\text{-}NH_3]^+$predicted at B3LYP-6-311++g (d p) level.

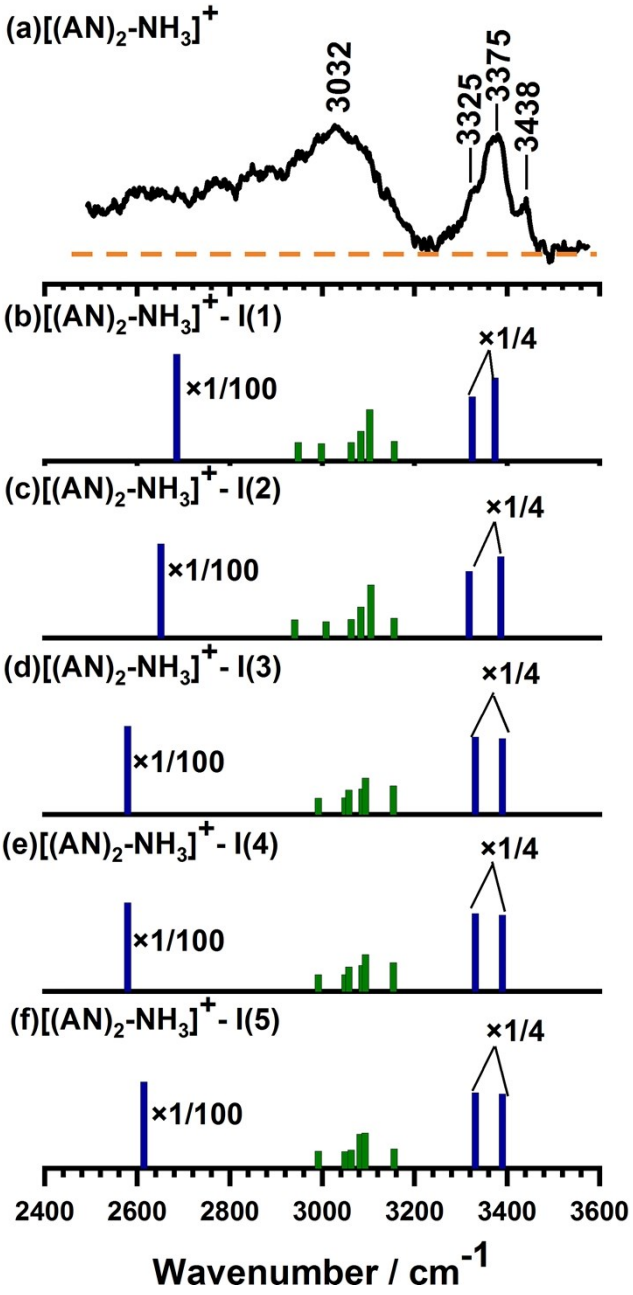
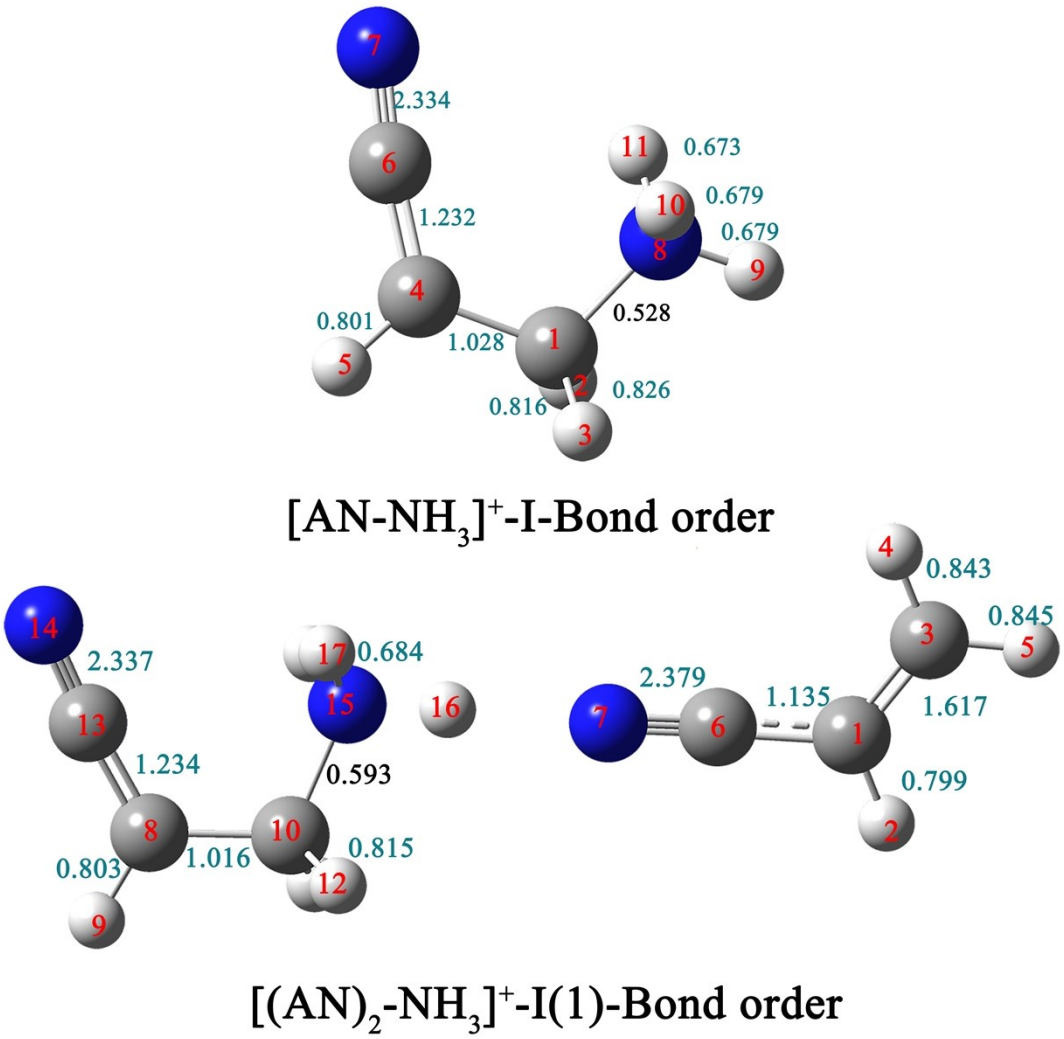


Figure S4. (a) observed spectra and (b)-(f) The calculated spectra of the first type stable structures, $[(AN)_2\text{-}NH_3]^+$-I(1), -I(2) -I(3), -I(4) and -I(5) were optimized under the method of B3LYP/6-311++(d, p) with the scaling factor of 0.97 in region of 2400-3600 cm^{-1}. The green and blue sticks represent the CH and NH vibration modes, respectively.

1



2

3 **Figure S5** The bond order of $(AN\text{-}NH_3)^+$- I and $(AN)_2\text{-}NH_3)^+$- I(1) were optimized under the basis set
4 of B3LYP/6-311++(d, p).

5

6

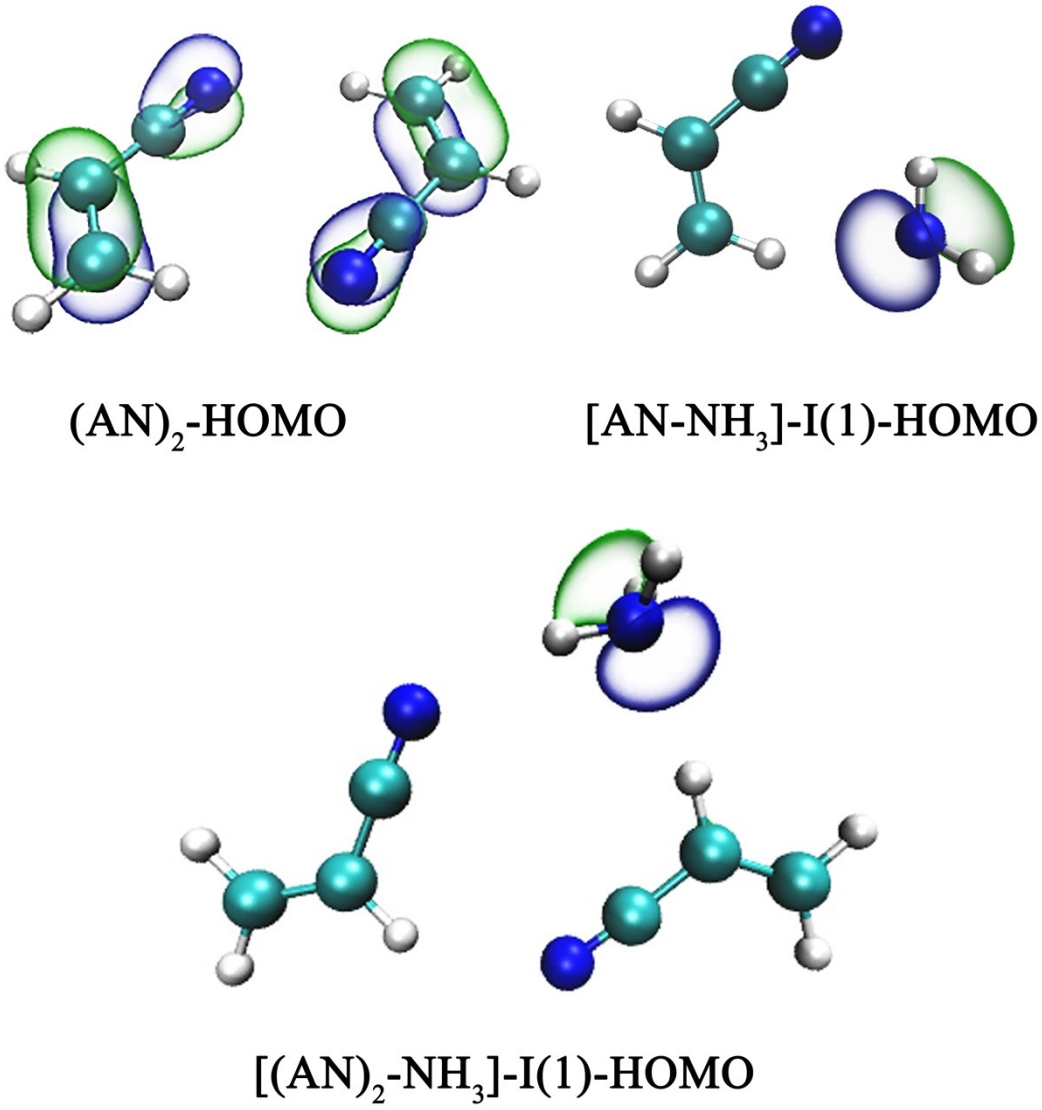


Figure S6. The HOMO orbitals of $(AN)_2$, $(AN\text{-}NH_3)$-I, and $[(AN)_2\text{-}NH_3]$-I(1) optimized under the method of B3LYP/6-311++(d, p).

Table S1. Observed and calculated harmonic and anharmonic vibrational wavenumbers and IR intensities of AN-NH_3.

Expt.	Calculations[b]				
	Modes[a]	**(AN-NH_3)-I**	**(AN-NH_3)-II**	**(AN-NH_3)-III**	**(AN-NH_3)-IV**
2976	ν_{CH2}[d]	2967 (3.0) [c]	2984 (1.2)	2974 (8)	2976 (8)
3021	anti-Sym ν_{CH2}	3007(38.1)	2992(121.8)	3006 (25.7)	3010 (0.3)
3058	ν_{CH}	3055 (2.9)	3036 (3.3)	3052 (1.4)	3028 (0.7)
3107	anti-sym ν_{CH2}	3114 (9.3)	3123 (1.8)	3107 (24.3)	3099 (1.1)
3211	$2\nu_4$(NH) [d]	3206 (0.8)	3209 (0.05)	3206 (0.1)	3212 (0.2)
3239	$2\nu_4$ (NH) [d]	3227 (1.0)	3269 (0.1)	3227 (0.9)	3238 (1.1)
3311	sym ν_{NH}	3345 (6.8)	3349 (1)	3349 (1)	3311 (20)
3404	anti-sym ν_{NH}	3456 (13.2)	3463 (6.6)	3464 (5.8)	3425 (34)
	anti-sym ν_{NH}	3466 (4.8)	3465 (6.3)	3464 (5.9)	3438 (1.3)

[a] approximate mode description for four structures AN-NH_3 [b] calculated by B3LYP-6-311++g(d, p); harmonic vibrational wavenumbers are scaled by the factor of 0.96 [c] The value in the parentheses is infrared intensity in km mol^{-1}. [d] anharmonic vibrational mode.

Table S2. Observed and calculated harmonic vibrational wavenumbers and IR intensities of (AN-NH_3)$^+$.

Expt.	Calculations[b]					
	Modes[a]	**[(AN)-NH_3]$^+$-I**	**[(AN)-NH_3]$^+$-II**	**[(AN)-NH_3]$^+$-III**	**[(AN)-NH_3]$^+$-IV**	**[(AN)-NH_3]$^+$-V**
3404	anti-sym ν_{NH}	3348 (110.3) [c]	3397 (110.9)	3445 (29.2)	3530 (148.6)	3367 (105.4)
3292	anti-sym ν_{NH}	3318 (110.8)	2522 (3000)	1974 (4.2)	3527 (161.1)	3352 (104.8)
3235	sym ν_{NH}	3252 (38.8)	3310 (83.2)	3332 (92.6)	3337 (425.5)	3268 (56.6)
3146	ν_{CH}	3090 (19.4)	2964 (9.1)	3067 (6.6)	3065 (8.2)	3058 (7.3)
3054	anti-sym ν_{CH}	3010 (1.0)	3146 (25.5)	3141 (3.2)	3141 (5.4)	3178 (5.9)
2940	sym ν_{CH}	2932 (1.2)		3046 (1.0)	3045 (1.5)	2984 (2.5)

[a] approximate mode description for five structures[(AN)-NH_3]$^+$ respectively. [b]calculated by B3LYP-6-311++g(d, p), harmonic vibrational wavenumbers are scaled by the factor of 0.97 [c] The value in the parentheses is infrared intensity in km mol^{-1}.

Table S3. Observed and calculated harmonic and anharmonic vibrational wavenumbers and IR intensities of $(AN)_2$-NH_3.

Expt.	Calculations[b]						
	Modes[a]	**$[(AN)_2$-$NH_3]$-I(1)**	**$[(AN)_2$-$NH_3]$-I(2)**	**$[(AN)_2$-$NH_3]$-I(3)**	**$[(AN)_2$-$NH_3]$-I(4)**	**$[(AN)_2$-$NH_3]$-II(1)**	**$[(AN)_2$-$NH_3]$-III(1)**
	anti-sym ν_{NH}	3442 (2.4)[c]	3443(2.3)	3457 (1.8)	3456 (2.5)	3465(6.1)	3467(4.7)
3399	anti-sym ν_{NH}	3416 (47.2)	3416 (51.3)	3433 (48.3)	3432 (62.6)	3464 (14.2)	3458 (14.2)
3305	sym ν_{NH}	3310 (45.2)	3309 (51.6)	3329 (40.8)	3328 (59.0)	3350 (1.4)	3345 (7.5)
3238	$2\nu_t$ NH[d]	3259 (2.2)	3264 (17.0)	3248 (2.0)	3261 (2.0)	3245 (0.9)	3263 (1.2)
3205	$2\nu_t$ NH[d]	3227 (3.3)	3226 (14.0)	3224 (2.0)	3228 (4.0)	3226 (1.0)	3230 (1.2)
3104	ν_{CH}	3112 (1.5)	3108 (10.1)	3098 (14.6)	3124 (17.3)	3125 (9.7)	3126 (5.5)
		3107 (0.8)	3106 (1.0)	3128 (0.9)	3097 (20.9)	3121 (5.9)	3115 (11.8)
3061	ν_{CH}	3036 (26.2)	3039 (3.2)	3050 (3.2)	3054 (5.8)	3055 (4.6)	3058 (6.6)
2970		2968 (107.2)	2965 (118.5)	3054 (35.8)	3050 (4.4)	2997 (118.5)	3056 (3.6)
3019	ν_{CH}	3023 (1.1)	3012 (22.8)	3039 (0.3)	3027 (32.0)	3029 (26.0)	3031 (17.3)
		3019(2.2)	3019 (2.2)	2981 (122.8)	2980 (128.0)	3028(8.6)	3011 (30.7)

[a] approximate mode description for six structures $(AN)_2$-NH_3 respectively. [b] calculated by B3LYP-6-311++g(d, p); harmonic vibrational wavenumbers are scaled by the factor of 0.96 [c] The value in the parentheses is infrared intensity in km mol^{-1}. [d] anharmonic vibrational mode.

Table S4. Observed and calculated harmonic vibrational wavenumbers and IR intensities of $[(AN)_2\text{-}NH_3]^+$.

		Calculations[b]				
Expt.	Modes [a]	**$[(AN)_2\text{-}NH_3]^+$-I(1)**	**$[(AN)_2\text{-}NH_3]^+$-II(1)**	**$[(AN)_2\text{-}NH_3]^+$-III(1)**	**$[(AN)_2\text{-}NH_3]^+$-IV(1)**	**$[(AN)_2\text{-}NH_3]^+$-V(1)**
3375	anti-sym ν_{NH}	3374 (80)[c]	3396 (16.5)	3386 (72)	3461 (15.7)	3509 (44.8)
3235	sym ν_{NH}	3324 (14)	3333 (20.1)	3319 (80)	3459 (16.3)	3391 (1220)
	anti-sym ν_{CH2}	3155 (1.1)	3089 (8.6)	3185 (2.2)	3357 (2.9)	3156 (0.5)
	ν_{CH}	3102 (11)	3079 (9.7)	3155 (1.2)	3152 (13.7)	3154 (0.3)
3032	ν_{CH}	3083 (4.2)	3049 (0.6)	3084 (4.3)	3108 (12.4)	3081 (10.2)
	sym ν_{CH2}	3062 (0.7)	2996 (4.9)	3064 (2.8)	3085 (15.6)	3062 (9.2)
	anti-sym ν_{CH2}	2997 (0.3)	2954 (11.3)	3062 (0.7)	3052 (6.0)	3060 (3.0)
	sym ν_{CH2}	2948 (0.7)	2921 (2)	2993 (1.0)	2958 (6.8)	3035 (13)
	shared proton	2685 (1500)	2962 (660)	2601 (3000)	2609 (1000)	2335 (3028)

[a] approximate mode description for five structures type $[(AN)_2\text{-}NH_3]^+$ respectively. [b]calculated by B3LYP-6-311++g(d, p), harmonic vibrational wavenumbers are scaled by the factor of 0.97 [c] The value in the parentheses is infrared intensity in km mol^{-1}.