

Electronic supplementary information (ESI)

Growth mechanism of aromatic prebiotic molecules: insights from different processes of ion-molecule reactions in benzonitrile-ammonia and benzonitrile-methylamine clusters

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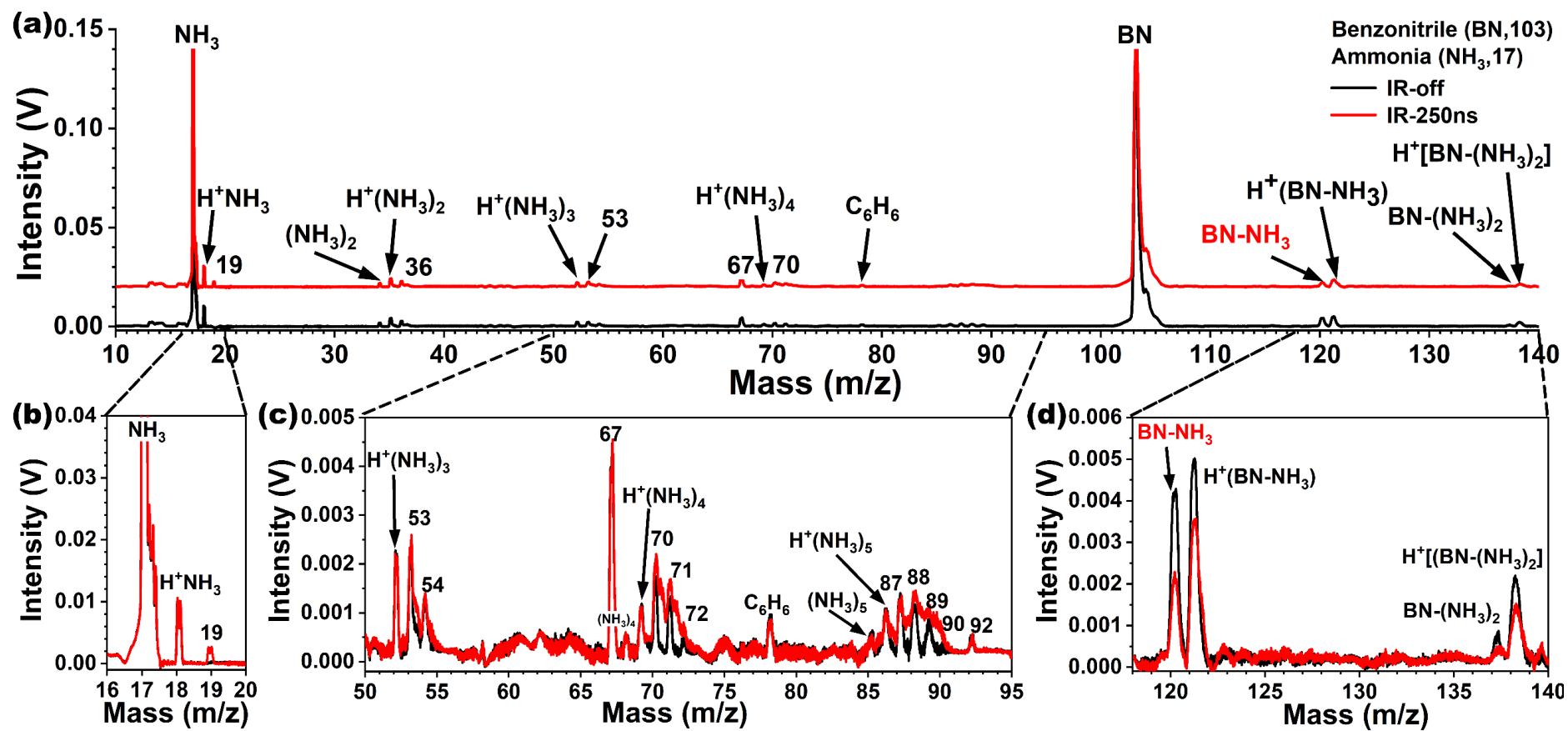


Fig. S1 (a-d) Mass spectra of the BN-NH_3 clusters with IR laser off (black curve) and on (red curve). IR laser at 3324 cm^{-1} is introduced 250 ns after the VUV ionization, when measure the mass spectra of the BN-NH_3 .

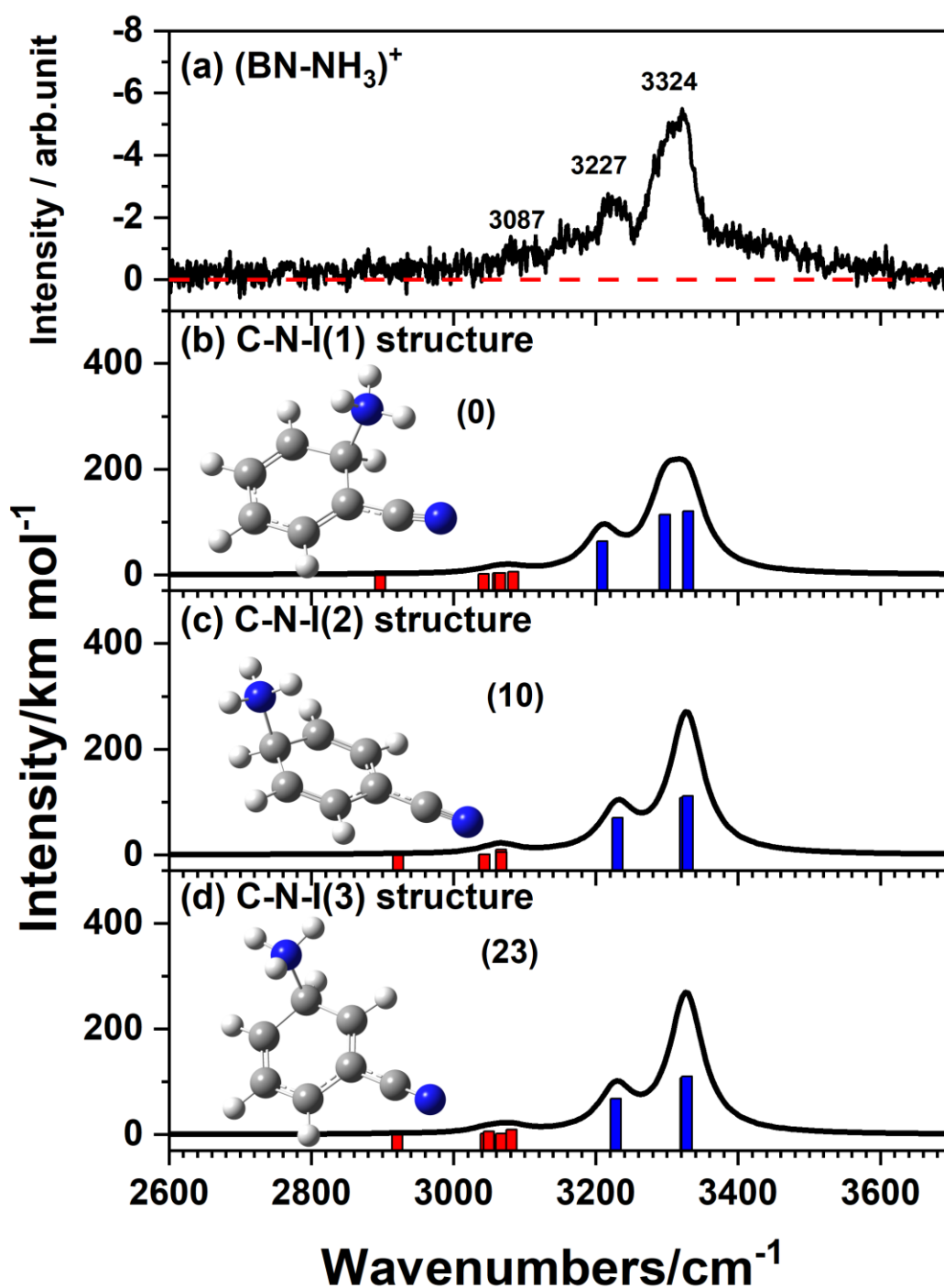


Fig. S2 (a) The observed spectrum of the cationic BN-NH₃ and (b-d) the computed spectra of C-N-I type structures. Calculated spectra of the three stable C-N-I type structures of (BN-NH₃)⁺ were optimized under the method of M06-2X-D3/6-311++G(d,p) with a scaling factor of 0.950, and the resulting stick spectra were convoluted by a Lorentzian line shape function with a width of 30 cm⁻¹ (fwhm). The predicted structures and relative energy at the zero point vibrational level (the number in parentheses in kJ mol⁻¹) of the cluster are also shown. The red and blue sticks represent the CH vibration modes and NH vibration modes, respectively.

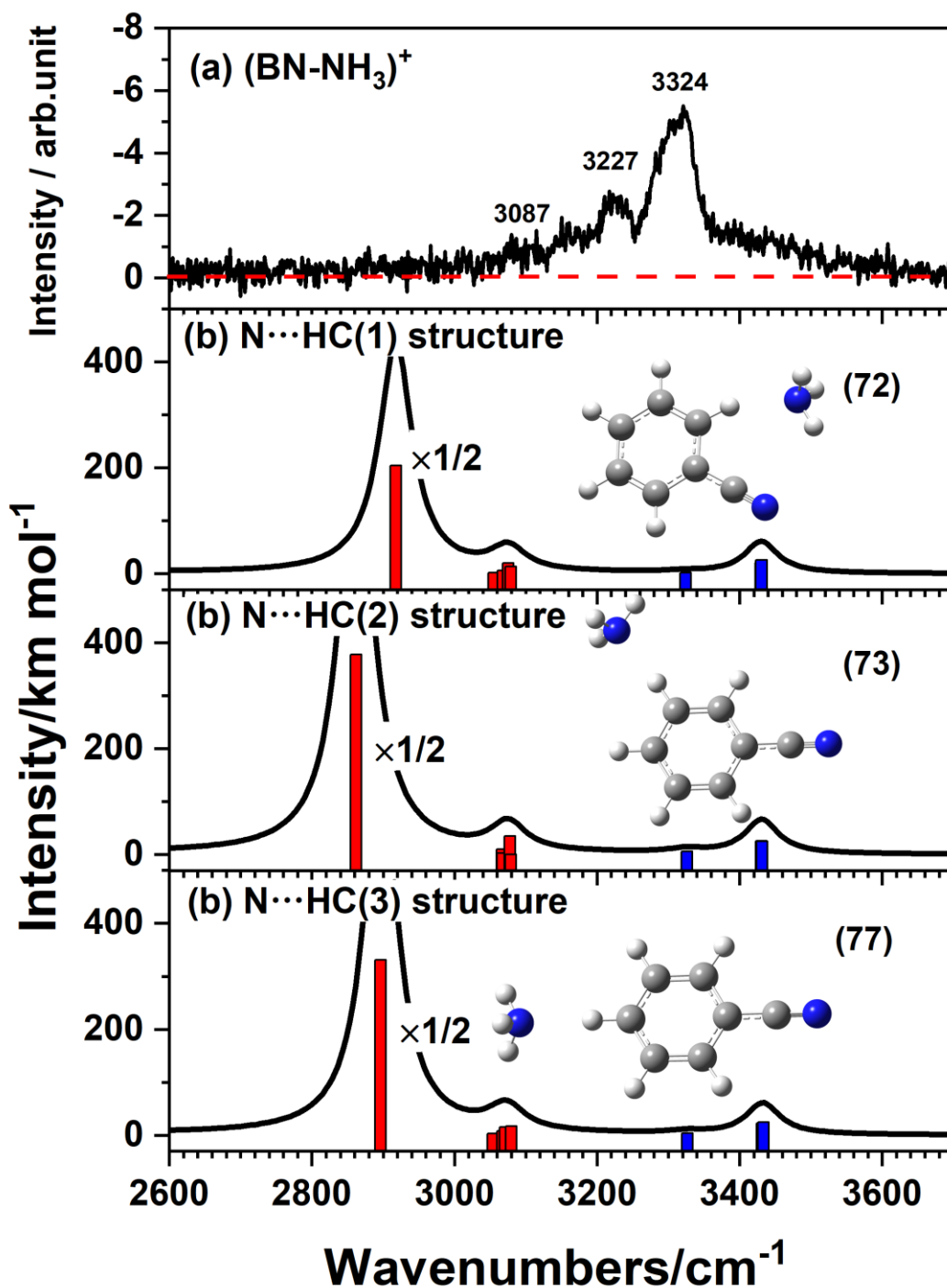


Fig. S3 (a) The observed spectrum of the cationic BN-NH_3 and (b-d) the computed spectra of $\text{N}\cdots\text{HC}$ type structures. Calculated spectra of the three stable $\text{N}\cdots\text{HC}$ type structures of $(\text{BN-NH}_3)^+$ were optimized under the method of M06-2X-D3/6-311++G(d,p) with a scaling factor of 0.950, and the resulting stick spectra were convoluted by a Lorentzian line shape function with a width of 30 cm^{-1} (fwhm). The predicted structures and relative energy at the zero point vibrational level (the number in parentheses in kJ mol^{-1}) of the cluster are also shown. The red and blue sticks represent the CH vibration modes and NH vibration modes, respectively.

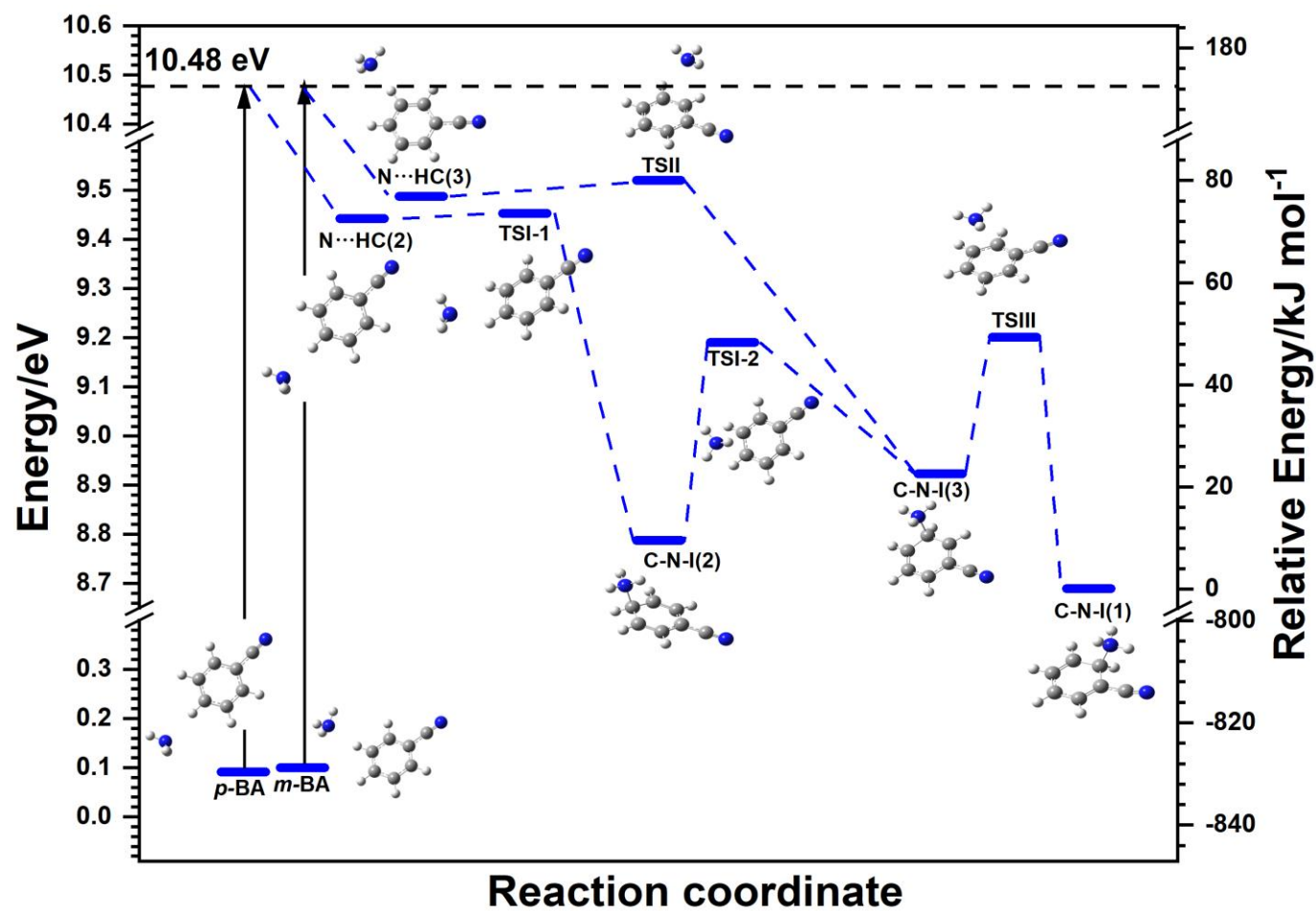


Fig. S4 Energy diagram for the isomerization reaction of $(\text{BN-NH}_3)^+$ after ionization from stable neutral $m\text{-BA}$ and $p\text{-BA}$ structures, The energies in the diagram were calculated at the M06-2X-D3/6-311++G(d,p) level. The relative energy of C-N-I(1) is set to 0 kJ mol^{-1} as the reference point.

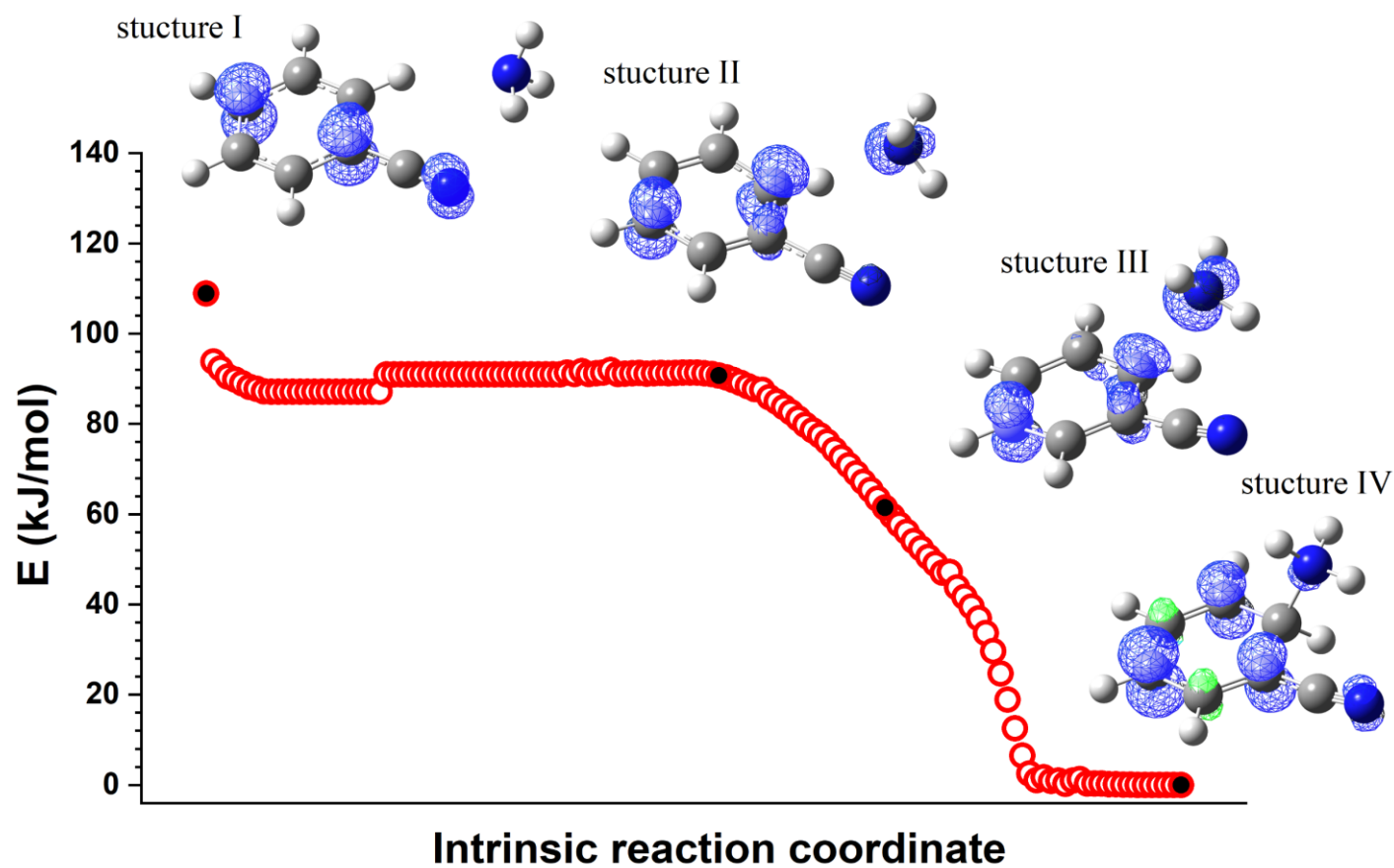


Fig. S5 The potential energy curves along the intrinsic reaction coordinate (IRC) of vertically ionized C-N-I type structure of $(\text{BN-NH}_3)^+$. The geometries of C-N-I(1) structure is same as that in Fig. 2(b). The spin density plots (isoval= 0.01) of the vertically ionized and stable structures are also shown in the figure. The blue and green grids represent positive and negative spin density, respectively. The charge distribution at the black marks is depicted in the vicinity spin density plot.

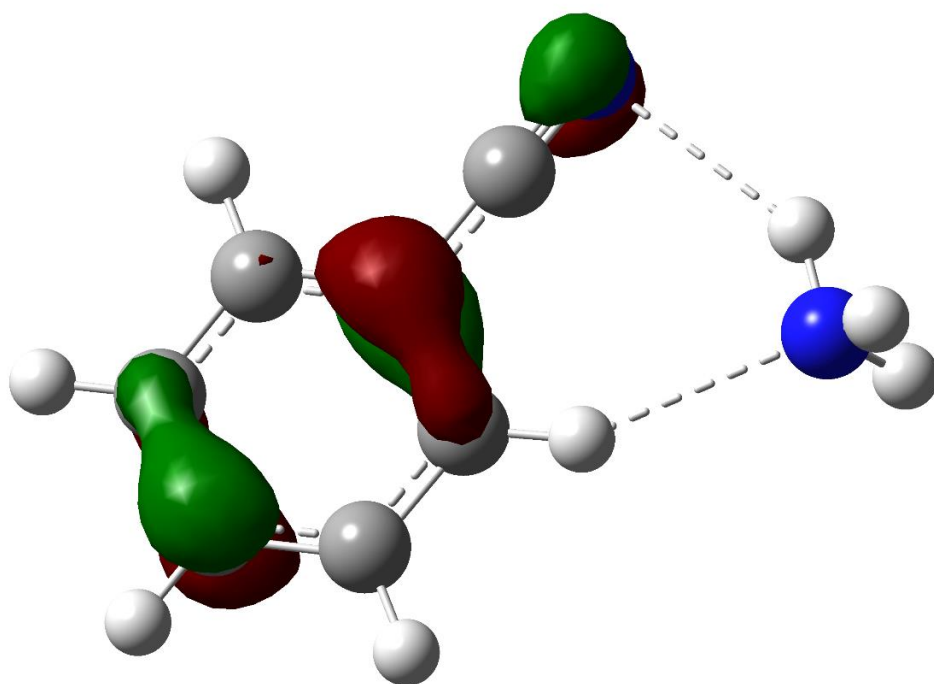


Fig. S6 The HOMO orbitals (isoval= 0.08) of BN-NH₃ optimized under the method of M06-2X-D3/6-311++G(d,p) .

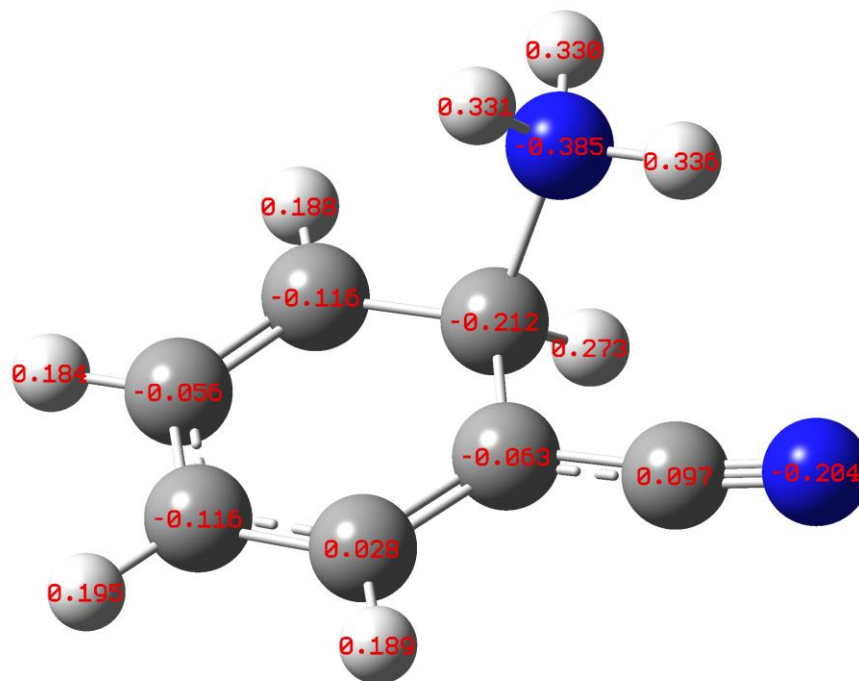


Fig. S7 The Mulliken charge distribution for the C-N-I type structure of (BN-NH₃)⁺. The geometries of C-N-I(1) structure is same as that in Fig. 2(b). Charge Distribution (the numerical unit on atoms is in a.u.) were optimized under the method of M06-2X-D3/6-311++G(d,p).

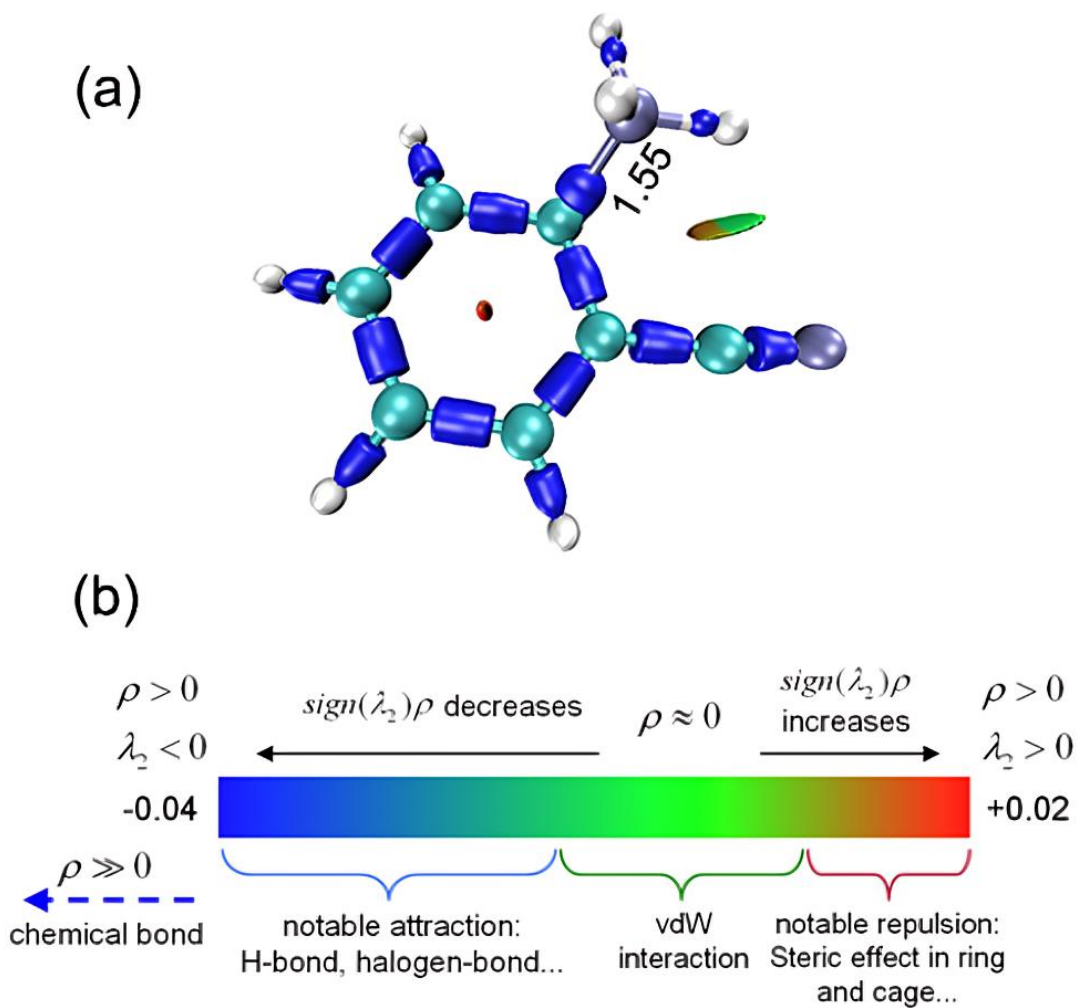


Fig. S8 (a) Isosurface map (Isovalue=1.0) of C-N-I(1) structure for $(\text{BN-NH}_3)^+$. (b) The coloring method for mapping the $\text{sign}(\lambda_2)\rho$ onto the isosurface. Similar to RDG analysis, the $\text{sign}(\lambda_2)\rho$ function differentiates the strength and characteristics of distinct regions by projecting them with various colors onto the isosurface of IRI. Here, $\text{sign}(\lambda_2)$ represents the second largest eigenvalue (λ_2) of the electron density (ρ) Hessian matrix and can be utilized to distinguish attractive and repulsive interactions.

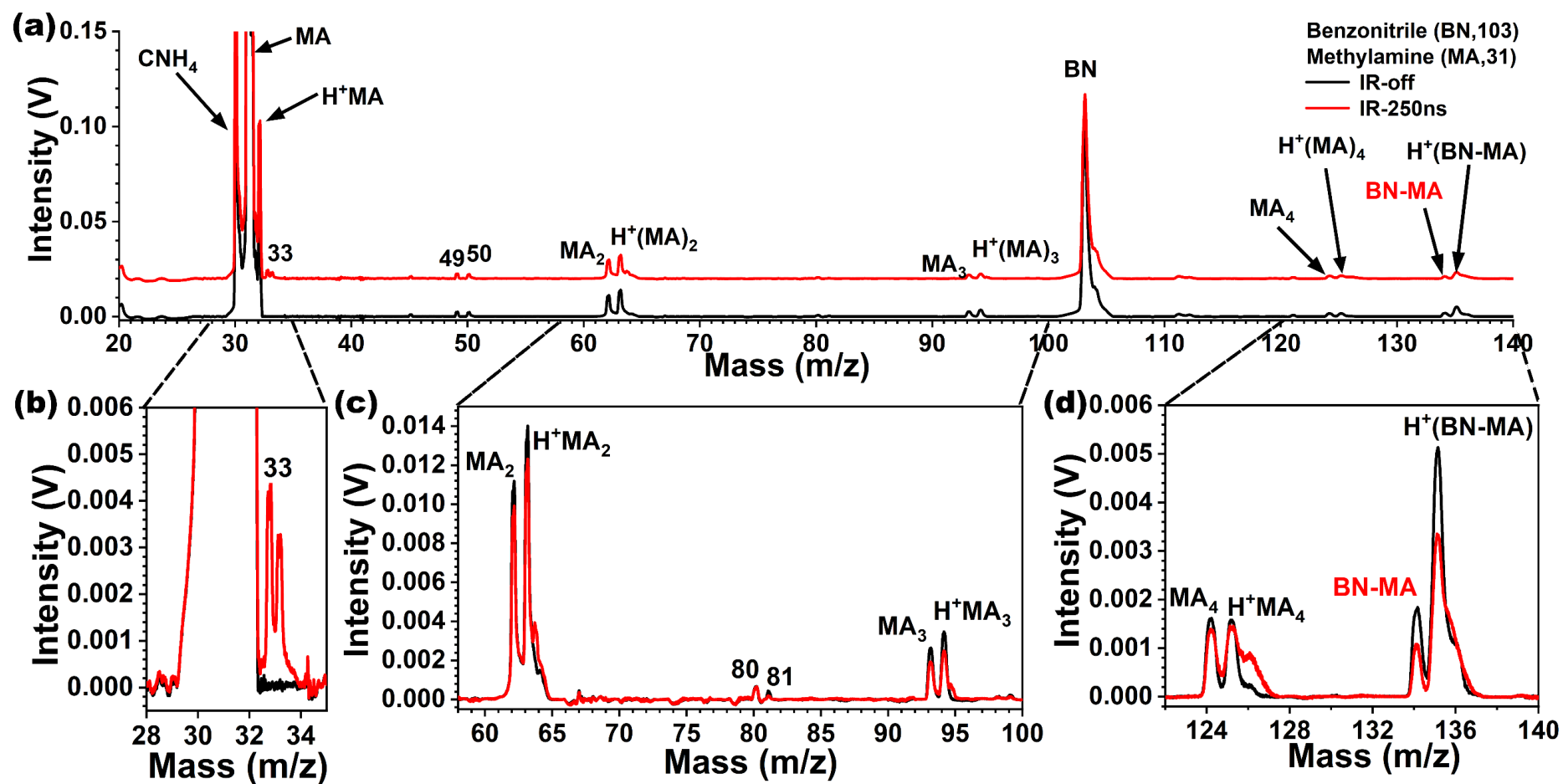


Fig. S9 (a-d) Mass spectra of the BN-MA clusters with IR laser off (black curve) and on (red curve). IR laser at 3374 cm^{-1} is introduced 250 ns after the VUV ionization, when measure the mass spectra of the BN-MA.

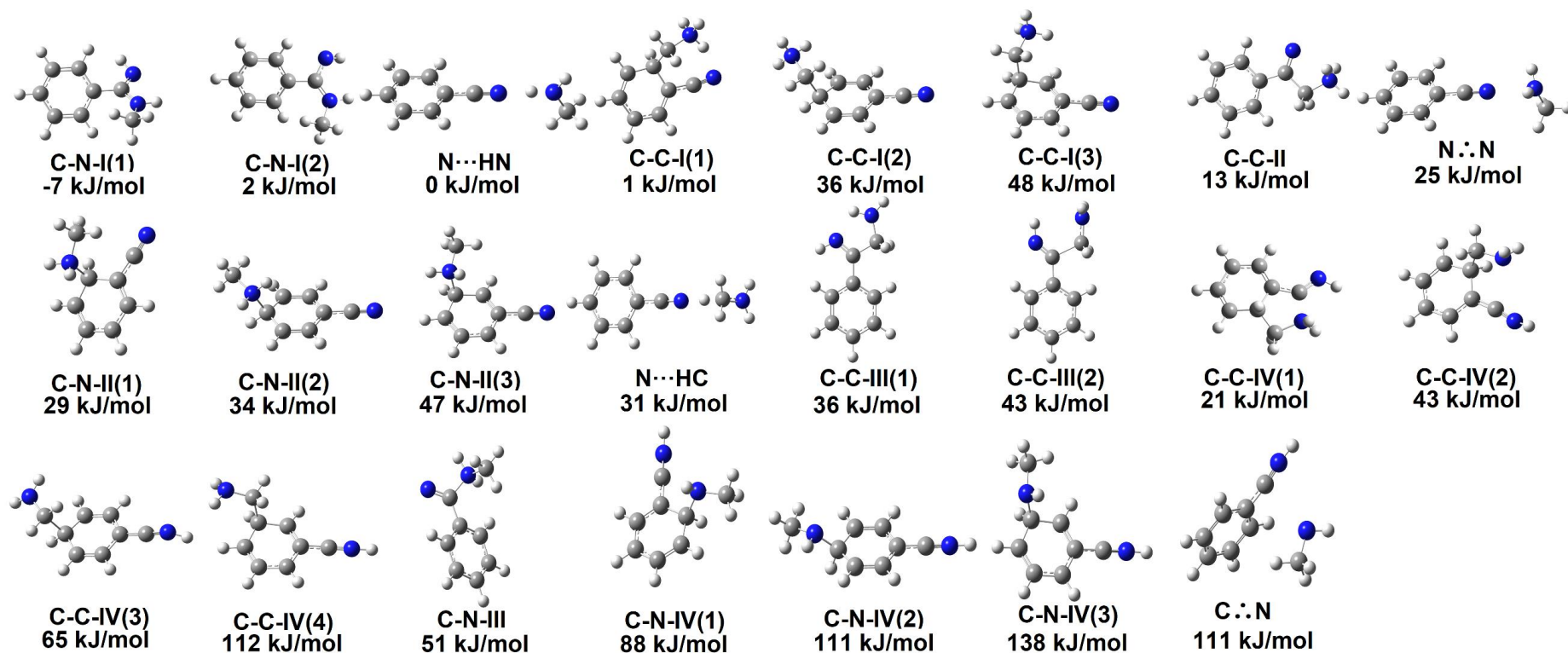


Fig. S10 Twenty-three isomers of $(\text{BN-MA})^+$ have been found and divided into twelve categories according to their structural characteristics. Geometric and relative of twenty-three structures of $(\text{BN-MA})^+$ predicted at M06-2X-D3/6-311++G(d,p) level. The structure categories and their relative zero-point energies are labeled below each structure.

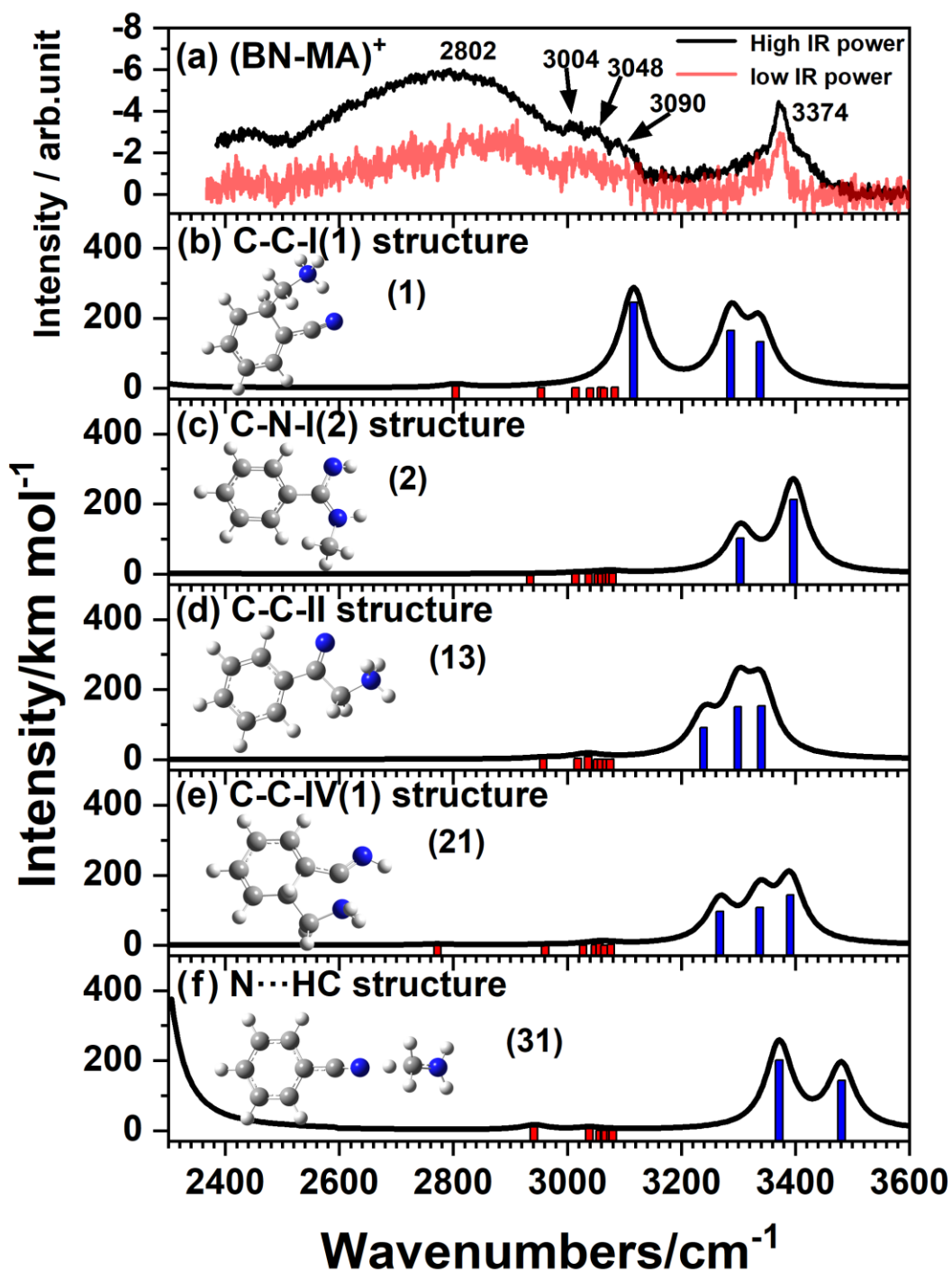


Fig. S11 (a) The other types of structures of $(\text{BN-MA})^+$ and (b-f) the corresponding calculated spectra I. Calculated spectra were optimized under the method of M06-2X-D3/6-311++G(d,p) with a scaling factor of 0.950, and the resulting stick spectra were convoluted by a Lorentzian line shape function with a width of 30 cm^{-1} (fwhm). The predicted structures and relative energy at the zero point vibrational level (the number in parentheses in kJ mol^{-1}) of the cluster are also shown. The red and blue sticks represent the CH vibration modes and NH vibration modes, respectively.

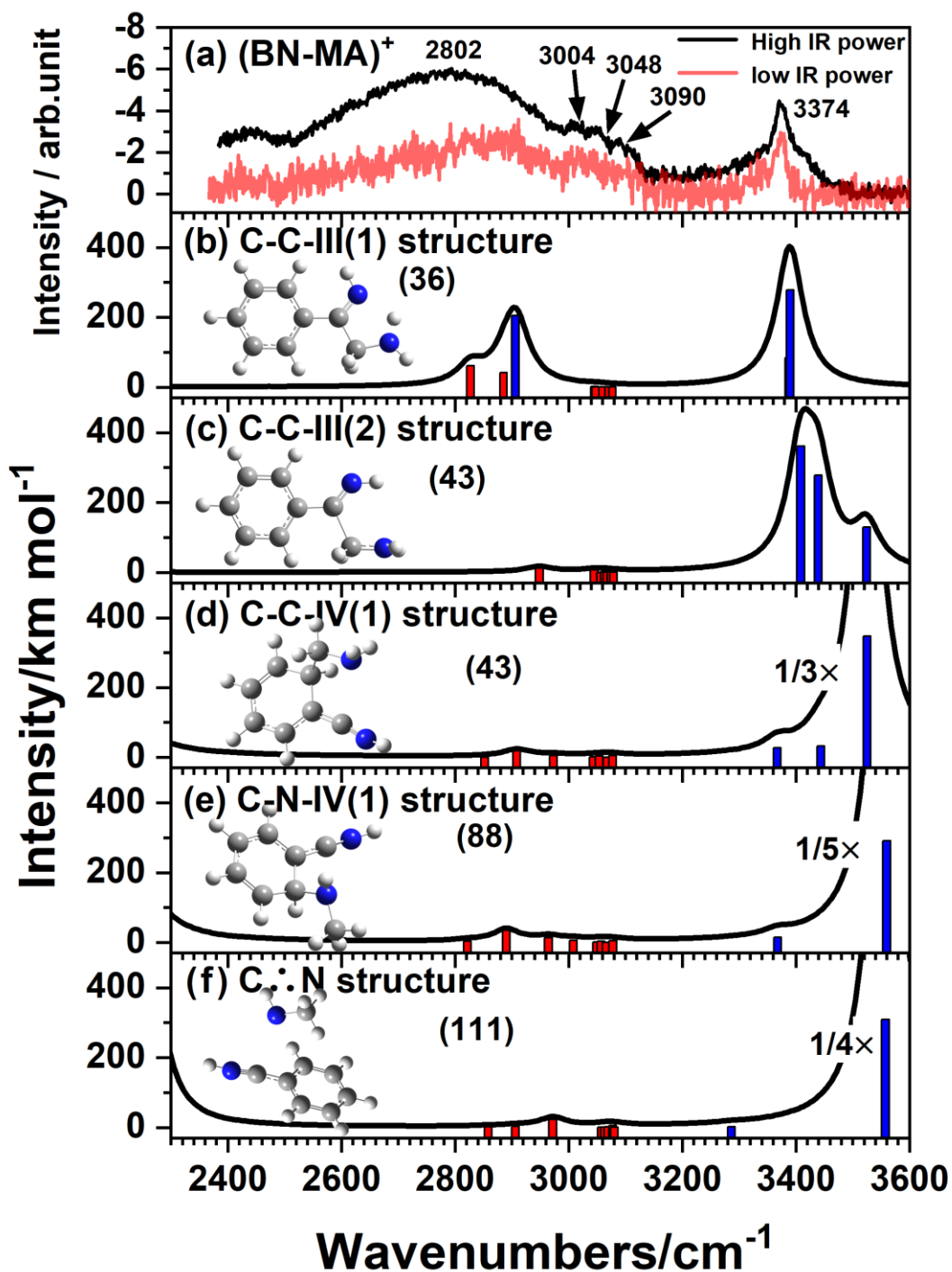


Fig. S12 (a) The other types of structures of $(\text{BN-MA})^+$ and (b-f) the corresponding calculated spectra II. Calculated spectra were optimized under the method of M06-2X-D3/6-311++G(d,p) with a scaling factor of 0.950, and the resulting stick spectra were convoluted by a Lorentzian line shape function with a width of 30 cm^{-1} (fwhm). The predicted structures and relative energy at the zero point vibrational level (the number in parentheses in kJ mol^{-1}) of the cluster are also shown. The red and blue sticks represent the CH vibration modes and NH vibration modes, respectively.

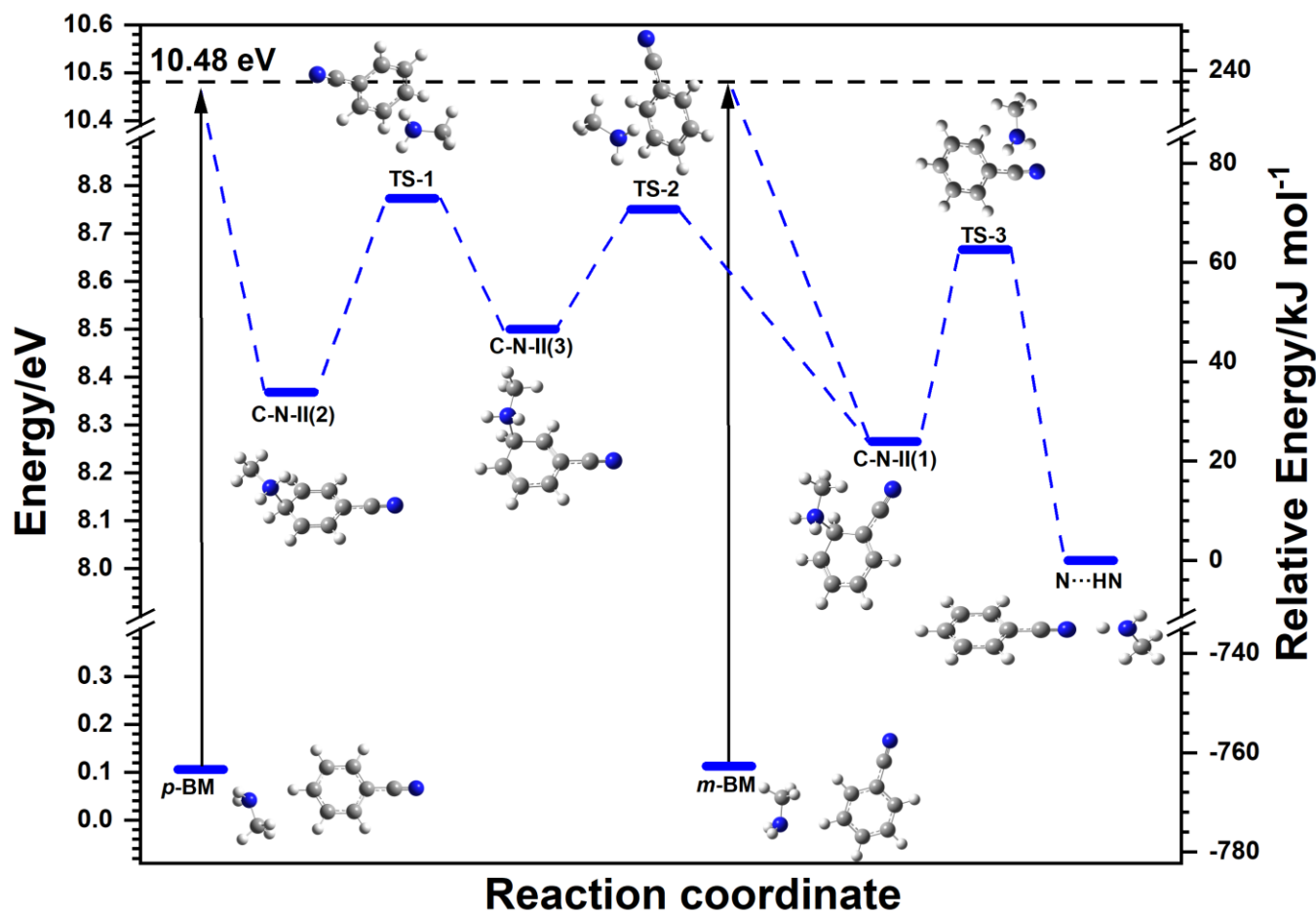


Fig. S13 Energy diagram for the isomerization reaction of $(\text{BN-MA})^+$ after ionization from stable neutral $m\text{-BA}$ and $p\text{-BA}$ structures, The energies in the diagram were calculated at the M06-2X-D3/6-311++G(d,p) level. The relative energy of $\text{N}\cdots\text{HN}$ is set to 0 kJ mol^{-1} as the reference point.

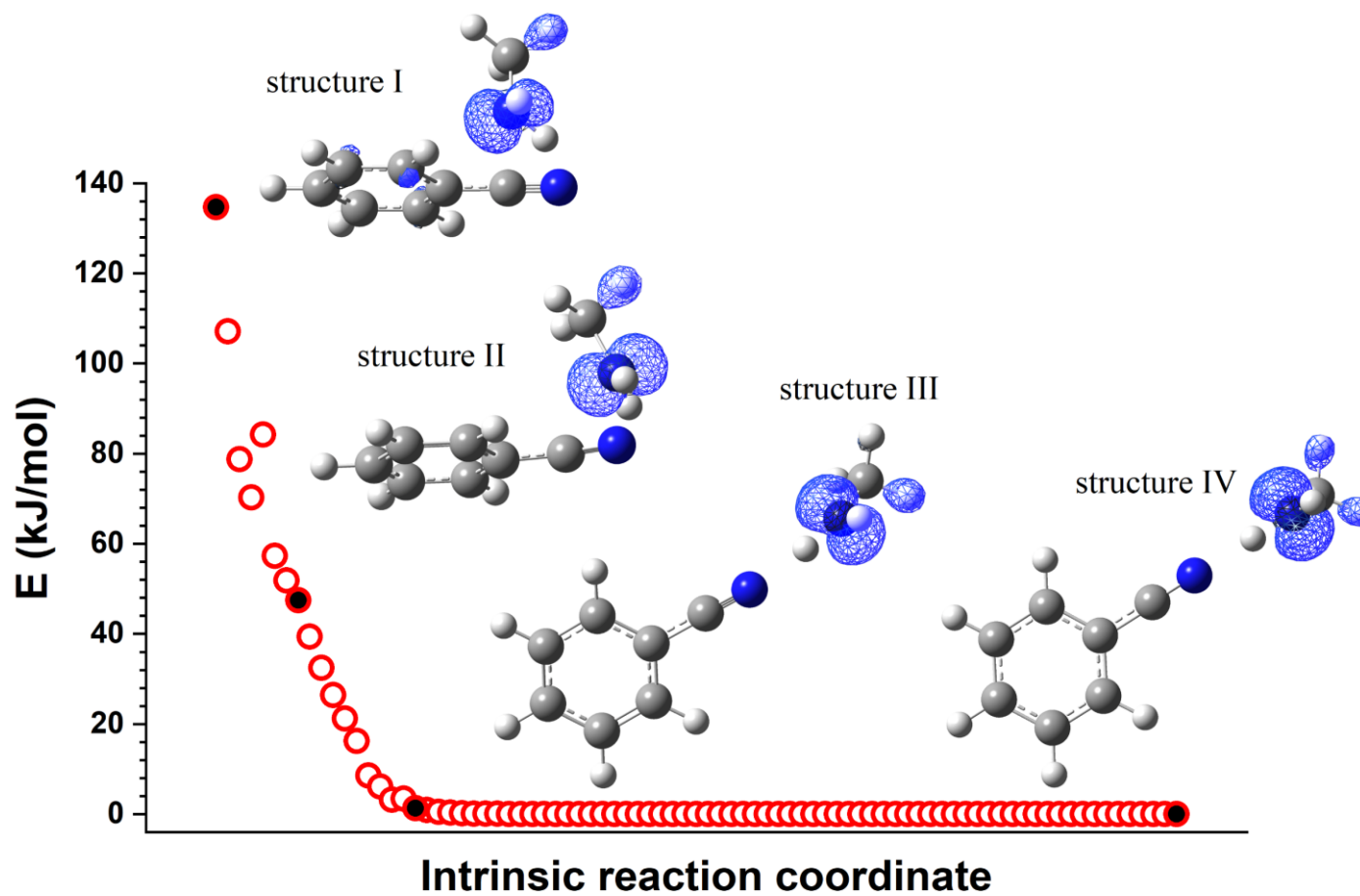


Fig. S14 The potential energy curves along the intrinsic reaction coordinate (IRC) of vertically ionized N...HN type structure of (BN-MA)⁺. The geometries of N...HN structure is same as that in Fig. 4(c). The spin density plots (isoval= 0.01) of the vertically ionized and stable structures are also shown in the figure. The blue and green grids represent positive and negative spin density, respectively. The charge distribution at the black marks is depicted in the vicinity spin density plot.

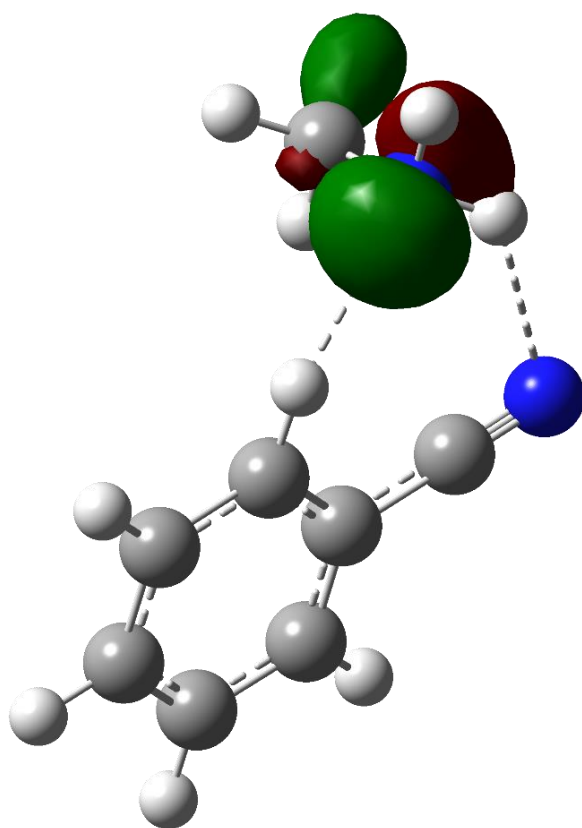


Fig. S15 The HOMO orbitals (isoval= 0.08) of BN-MA optimized under the method of M06-2X-D3/6-311++G(d,p) .

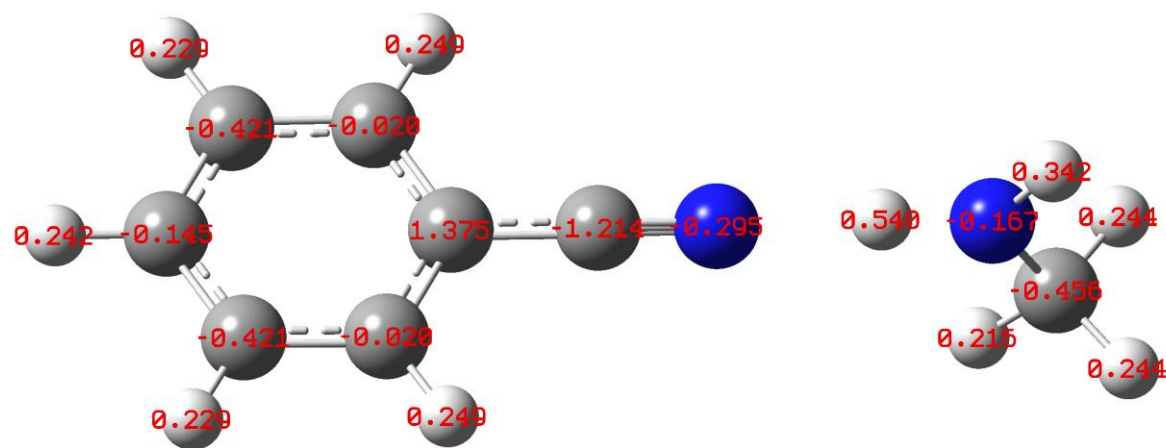


Fig. S16 The Mulliken charge distribution for the N...HN type structure of (BN-MA)⁺. The geometries of N...HN structure is same as that in Fig. 4(c). Charge Distribution (the numerical unit on atoms is in a.u.) were optimized under the method of M06-2X-D3/6-311++G(d,p).

Table S1 Calculated harmonic vibrational wavenumbers and IR intensities of BN-NH₃.

Experiment	Calculation ^a	Assignments
Bands (cm ⁻¹)	o-BA	Modes
3422	3459(11.0) ^b 3446(31.0)	anti-sym ν_{NH}
3324	3332(8.5)	sym ν_{NH}
3115	3072(5.6)	sym ν_{CH}
3098	3064(7.2)	anti-sym ν_{CH}
3075	3030(55.7)	anti-sym ν_{CH} (H-bond)
3044		
3010	2983(1.1) ^c	overtone of bend ν_{CH}

Note. ^a calculated by M06-2X-D3/6-311++G(d,p), harmonic vibrational wavenumbers are scaled by the factor of 0.95. ^b value in the parentheses is IR intensity in km mol⁻¹. ^c anharmonic vibrational wavenumbers and IR intensities.

Table S2 Mullikan charge in the BN moiety calculated for various (BN-NH₃)⁺

Methods	Mullikan charge in the BN moiety
M06-2X-D3/6-311++G(d,p)	0.116
B3LYP-D3(BJ) /6-311++G(d,p)	0.135
CAM-B3LYP-D3(BJ)/6-311++g(d,p)	0.145
WB97XD/6-311++g(d,p)	0.087
MP2/6-311++g(d,p)	0.109

Table S3 Calculated harmonic vibrational wavenumbers and IR intensities of BN-MA.

Experiment	Calculation ^a	Assignments
Bands (cm ⁻¹)	o-BM	Modes
3409	3442(12.3) ^b	anti-sym ν_{NH}
3349	3364(4.4)	sym ν_{NH}
3100	3065(6.8)	anti-sym ν_{CH} of BN
3074	3025(53.4)	anti-sym ν_{CH} (H-bond)
2986	2978(23.0)	anti-sym ν_{CH} of MA
2959	2949(28.9)	anti-sym ν_{CH} of MA
2898	2882(59.2)	sym ν_{CH} of MA
2821	2811(0.9) ^c	combination of bend ν_{CH}
2789	2770(3.5) ^c	combination of bend ν_{CH}

Note. ^a calculated by M06-2X-D3/6-311++G(d,p), harmonic vibrational wavenumbers are scaled by the factor of 0.95. ^b value in the parentheses is IR intensity in km mol⁻¹. ^c anharmonic vibrational wavenumbers and IR intensities.