Supporting Information for

"Identifying and Modulating Accidental Fermi Resonance: 2D IR and DFT Study of 4-Azido-L-Phenylalanine"

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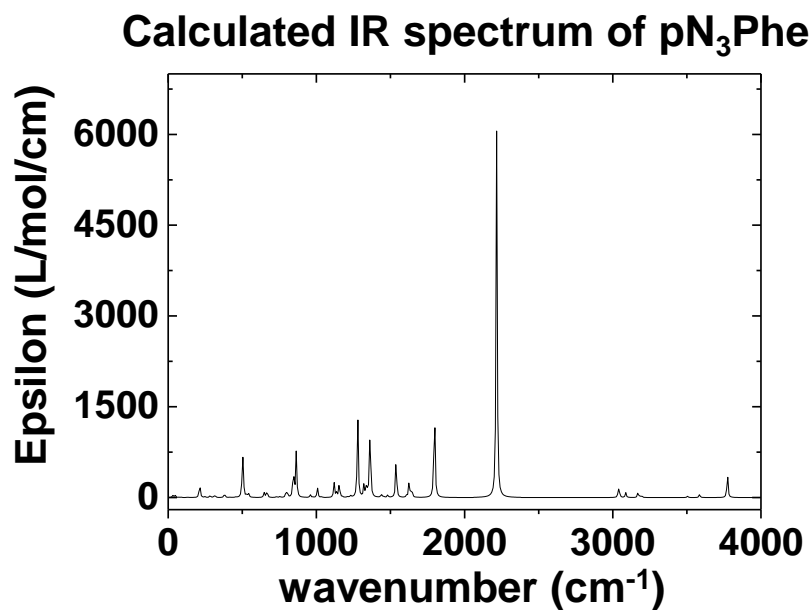
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1. Calculated IR Spectra of pN₃Phe

Calculated IR spectrum of pN$_3$Phe

Figure S1. Calculated IR spectrum of pN₃Phe in isopropanol using B3LYP/6-311++G(df, pd) basis in Gaussian.

Figure S1 shows the calculated IR spectrum (harmonic frequency) of pN₃Phe in isopropanol using B3LYP/6-311++G(df, pd) basis in Gaussian. Only one vibration peak is found in the window of azide asymmetric stretching vibration (2000 cm^{-1}-2300 cm^{-1}).
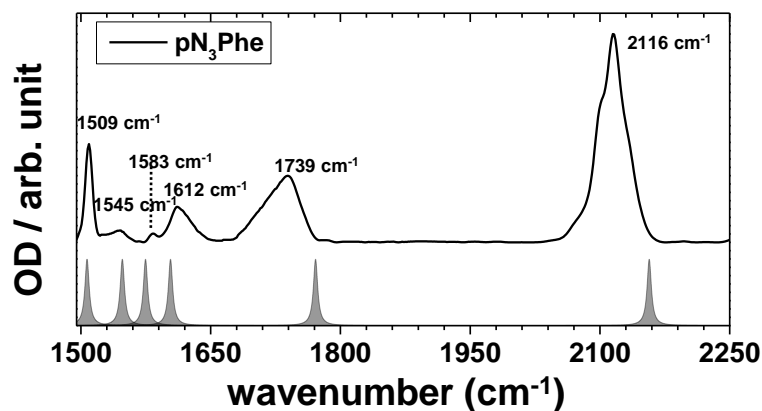
Figure S2. FTIR spectrum of pN$_3$Phe in isopropanol (black line). The calculated bands are plotted with Lorentzian distribution function centered at the anharmonic frequencies of corresponding normal modes with a FWHM of 6 cm^{-1} (gray peaks). The intensities of calculated bands are normalized.

Figure S2 shows the FTIR spectrum of pN$_3$Phe in isopropanol and the calculated anharmonic frequencies of corresponding bands. Because of the influence of solvent, we only plot the region from 1495 cm^{-1} to 2250 cm^{-1}. The absorption of solvent is subtracted from the spectrum. The spectrum is baseline corrected and smoothed. The calculated bands are normalized and plotted with Lorentzian distribution function centered at the anharmonic frequencies of corresponding normal modes with a FWHM of 6 cm^{-1}.

Table S1. Normal Modes of pN₃Phe in Isopropanol

assignment	υ (harm)	υ (anharm)
N$_3$ asymmetric stretch	2116	2157
carbonyl stretch	1739	1771
Kekulé ring vibration (four H-substitude C atoms)	1612	1604
Kekulé ring vibration (the other two C atoms)	1583	1575
Amide II vibration of the carbamate	1545	1548
ring CCC bend	1509	1507

2. Mulliken Charge Distribution
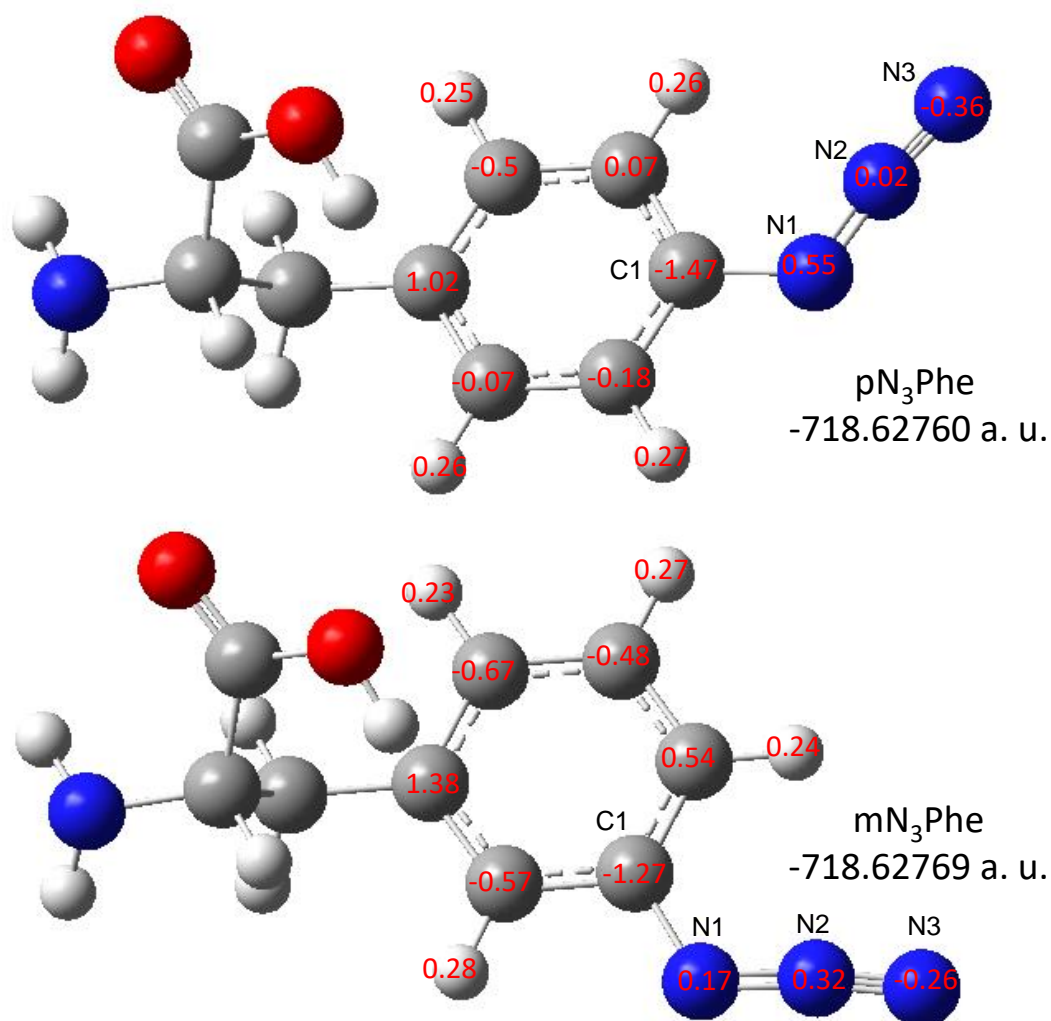
Figure S3. Mulliken charge distributions and relative energies of pN₃Phe and mN₃Phe calculated by Gaussian 09.

3. Anharmonic Frequency Calculations

Table S2. Calculated Anharmonic Frequencies and Cubic Force Constants of pN₃Phe in H₂O

mode	υ (cm^{-1})	κ_{ijk} (cm^{-1})	mode	υ (cm^{-1})	κ_{ijk} (cm^{-1})
11	2171.2				
40 20	2168.3	13.2	44 19	2177.6	-1.0
40 21	2171.2	-13.0	46 16	2179.1	-2.1
41 21	2151.5	22.1	47 16	2161.7	-4.7
42 21	2147.4	11.5	63 11	2172.4	4.2

Table S3. Normal Modes Involved in FRs of mN₃Phe in Isopropanol

mode	assignment	υ (harm)	υ (anharm)
11	N₃ asymmetric stretch	2217.8	2166.4
16	ring breath + N₃ bending	1517.7	1481.2
20	N₃ symmetric stretch + C–N stretch + Kekulé ring vibration	1361.5	1314.3
41	ring breath + N–H swing + C–H out of plane	857.8	875.2
47	Kekulé ring vibration + N₃ bending	687.6	678.9

4. Comparison of calculated IR spectra of pN$_3$Phe, pN^{15}NNPhe, mN$_3$Phe
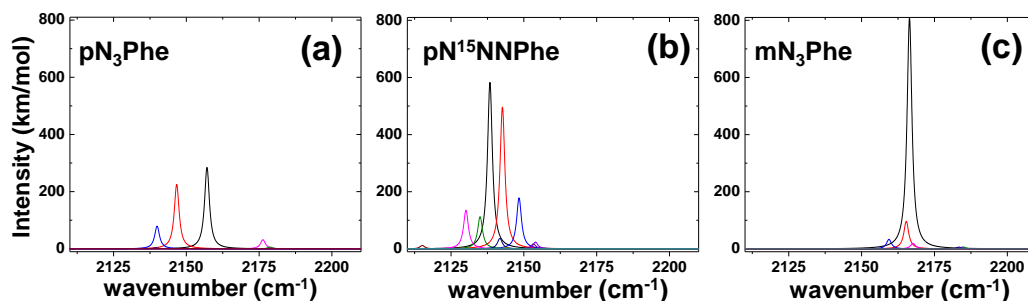

Figure S4. Calculated spectra of (a) pN$_3$Phe (b) pN^{15}NNPhe (c) mN$_3$Phe in azide asymmetric stretch region. The overtone or combination bands (colored) that located within 25 cm^{-1} of the azide asymmetric stretching vibration with intensity larger than 1 km/mol and azide asymmetric stretching band (black) are plotted. The calculated lineshape is convoluted with a Lorentzian function with FWHM of 2 cm^{-1}.

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It should be noted that first-principles calculations using Gaussian 09 give inaccurate intensity results of anharmonic modes in the presences of Fermi resonances because it was missing ad hoc equations to treat all cases of resonances in intensity equations and variational correction to the transition moments. The spectra only supply the frequency distribution as a reference.