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Supporting information

Two-dimensional IR Spectroscopy Reveals a Hidden Fermi Resonance Band in the Azido Stretch Spectrum of β-Azidoalanine

Jun Young Park,[a,b,†] Hyeok-Jun Kwon,[b,†] Saptarsi Mondal,[a,b] Hogyu Han,[*,b] Kyungwon Kwak,[*,a,b] and Minhaeng Cho[*,a,b]

[a]Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Korea University, Seoul 02841, Republic of Korea. E-mail: kkwak@korea.ac.kr; mcho@korea.ac.kr

[b]Department of Chemistry, Korea University, Seoul 02841, Republic of Korea. E-mail: hogyuhan@korea.ac.kr

Contents

I. Materials

Unlabeled & *β*-position of ^{15}N labeled azide compounds were synthesized according to the modified procedure of Brewer's methods.[1, 2]

Ala-N_3 (Ac-Ala(N_3)-NHMe): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (brs, 1H), 6.63 (d, J = 7.5 Hz, 1H), 4.61 (m, 1H), 3.72 (dd, J = 12.5, 5.0 Hz, 1H), 3.53 (dd, J = 12.5, 6.5 Hz, 1H) 2.84 (d, J = 5.0 Hz, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.55, 169.69, 52.24, 51.88, 26.43, 23.13;; HRMS (CI+) for, $C_6H_{11}N_5O_2$ (MH$^+$), calcd 185.1838, found 186.0996.

Ala-N^{15}NN (Ac-Ala(N^{15}NN)-NHMe): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (brs, 1H), 6.63 (d, J = 7.5 Hz, 1H), 4.62 (m, 1H), 3.73 (m, 1H), 3.53 (m, 1H), 2.84 (d, J = 4.5 Hz, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.55, 169.69, 52.24, 51.88, 26.43, 23.13; ^{15}N NMR (70 MHz, $CDCl_3$) δ 133.45; HRMS (CI+) for $C_6H_{11}N_4{}^{15}NO_2$ (MH$^+$), calcd 186.1772, found 187.0966.

II. Time-resolved IR pump-probe spectroscopy of aliphatic azide

$$\Delta OD = y_0 + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \sin\left\{\pi \frac{(t-\varphi)}{\omega}\right\}$$

Ala-N_3 shows an apparent beating feature by the excited-state decay kinetics measured at 2074 cm^{-1}. IR PP signal is fitted by the above equation to represent the Fermi resonance, [3-5] where φ is phase shift and ω is oscillation period, respectively.

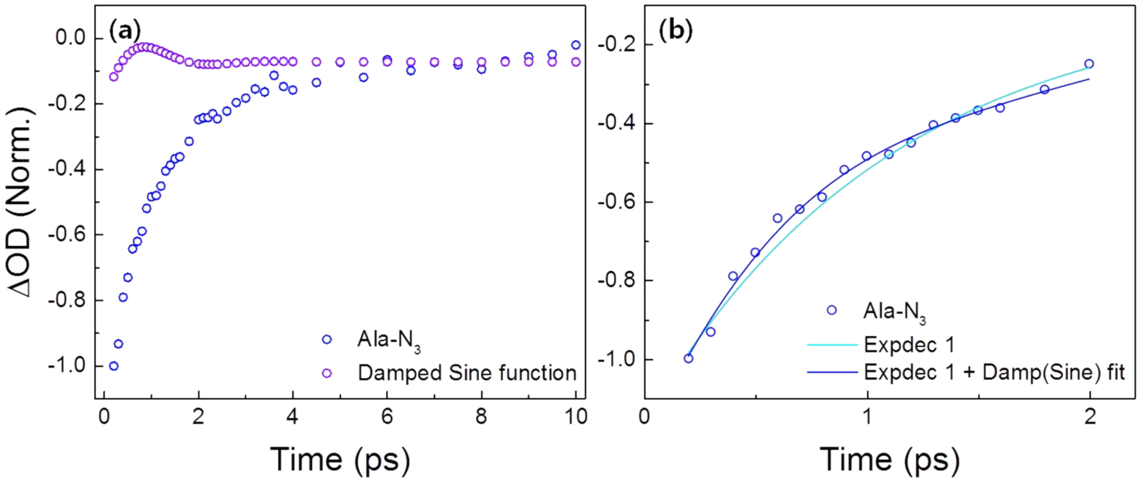


Figure S1. 1-2 transition decay of Ala-N_3 in DMF (a). It has mono-exponential decay component and a damped sine component. 1-2 transition decay of Ala-N_3 in DMF at early time within 2 ps (b). The smooth line for Ala-N_3 is fitting curves containing both mono-exponential decay (cyan) and mono-exponential decay and damped sine components (blue). Selected probe frequencies: 2074 cm^{-1} for Ala-N_3.

Table S1. Fitting results for IR pump-probe spectra from Figure 4.

	τ_1 (ps)	τ_2 (ps)	y_0 (a.u.)	R^2
Ala-N_3	1.11 ± 0.17		-0.0800 ± 0.00824	0.99
	1.26 ± 0.17 (0.87)[a]	0.8 (0.13)[a]	-0.0718 ± 0.00835	0.99
Ala-$N^{15}NN$	1.12 ± 0.17		-0.0684 ± 0.00741	0.99

[a] Relative amplitude ratios from damped sine function. τ_1 is vibrational lifetime, τ_2 is coherence lifetime, and y_0 is offset of a fitting curve.

III. FT-IR and fitting analysis of unlabeled and labeled azide in water

Figure S2 shows the FT-IR spectra of the unlabeled and labeled azide in water and their fitting using Voigt function/s. As a result of changing the solvent from DMF to water, the azido stretch mode gets shifted from 2103 cm^{-1} (Ala-N$_3$ in DMF) to 2118 cm^{-1} (Ala-N$_3$ in water), and its spectrum exhibits the extended wing toward the high-frequency side (figure S2-(a)) similar to the azide in DMF. This asymmetric lineshape can be explained with the overlap of two spectral components centered at 2118 and 2145 cm^{-1} obtained from the fitting using two Voigt functions with the ratio of the integrated area of 7.5:1 for the unlabeled azide (Table S2). Figure S2-(b) shows the FT-IR spectrum of Ala-N^{15}NN in water. This symmetric absorption band of labeled azide can be reliably fitted with a single Voigt function centered at 2076 cm^{-1}, which indicates the absence of the accidental Fermi resonance band. The FT-IR spectral analysis thus demonstrates that the vibrational properties of aliphatic azide remain unchanged in going from DMF to water.

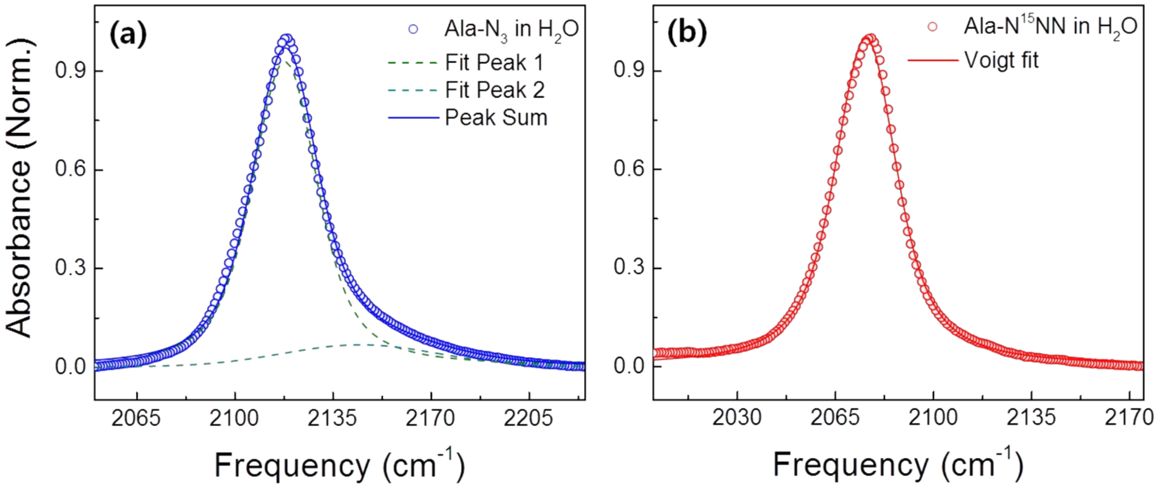


Figure S2. FT-IR spectra of unlabeled aliphatic azide (a) and ^{15}N labeled azide (b) in water. Dashed lines show the fitting of the band using Voigt function. The unlabeled azide requires two Voigt functions for a reliable fitting because of its asymmetric nature, whereas the labeled azide needs a single Voigt function for fitting.

Table S2. List of the fitting parameters of the Voigt fitting of the unlabeled and labeled azide in water along with the Adj. χ^2 for the fitting.

Water		Ala-N_3	Ala-$N^{15}NN$
Peak 1	ω_0 (cm^{-1})	2118	2076.0
	FWHM (cm^{-1})	27.7	26.5
	Area	34.7	37.2
Peak 2	ω_0 (cm^{-1})	2145	
	FWHM (cm^{-1})	65.2	
	Area	4.6	
Adj. χ^2		0.99	0.99

IV. Anharmonic frequency analysis

To find out the origin of the Fermi resonance band, the anharmonic frequency analysis has been performed for both unlabeled and labeled aliphatic azide using the Gaussian 16 quantum chemistry package. Both azides have been optimized at the B3LYP/6-311++G level of theory with very tight convergence criteria. The absence of any negative frequency indicates that the calculated geometries are at local minima. Subsequently, anharmonic frequencies have been computed at the same level. The harmonic and anharmonic frequency of the azide asymmetric stretch is found to be 2113.7 and 2035.4 cm^{-1}, respectively (mode 12 in table S3, S4, and figure S3). The maximum frequency range of ± 25.0 cm^{-1} from the azide asymmetric stretch, minimum cubic force constant (the third derivative of energy, $\left|k_{ijk}\right|$) of 1 cm^{-1}, and the minimum difference of the second-order perturbative energy (PT2) to the variational energy of 1 cm^{-1} are set as the threshold to find out the most suitable interactions to be considered as Fermi resonance.[5, 6]

Based on these criteria, it has been found that two combination bands consisting of modes 30 & 39 and modes 28 & 41 having k_{ijk} of 59.0 and -30.8 cm^{-1}, respectively, can participate in the Fermi resonance with the azide asymmetric stretch (Table S3). The normal modes 28, 30, 39, and 41 are described in detail in table S4 and figure S3. We have also shown the displacement vector (light blue) associated with the molecular vibration of those normal modes in figure S3. It is quite clear that none of the modes consist of isotope labeled N atom from the azide group. Those combination bands mainly consist of CH_2 twisting, chain C-H bend, and N-H bend vibrations, as depicted in figure S3. Hence, it can be concluded from this anharmonic frequency analysis that the ^{15}N substitution to middle N atom of the $-N_3$ stretch does not affect other near-resonant combination bands. The anharmonic frequency of the ^{15}N labeled azide has also been calculated, but Fermi resonance interaction could not be found, which met the criteria as mentioned above.

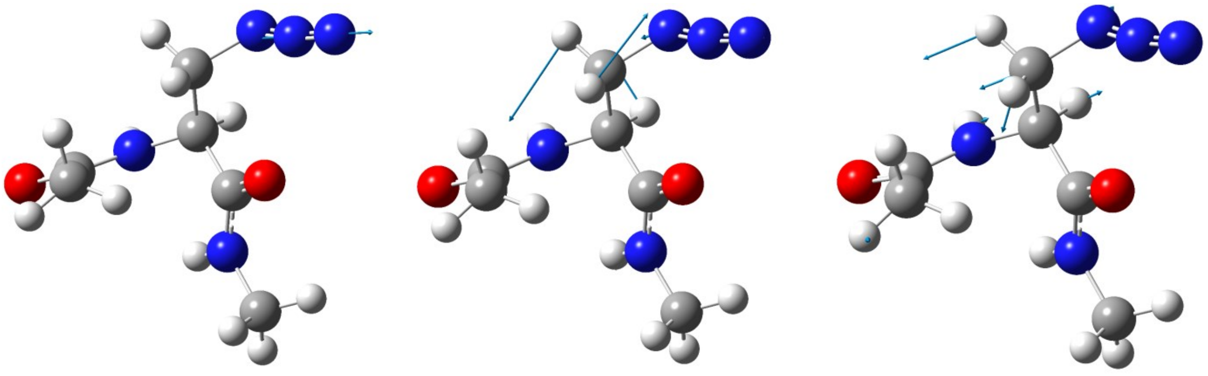
Table S3. List of possible combination bands of unlabeled aliphatic azide that can participate in the Fermi resonance with the azide asymmetric stretch (mode 12). The interactions associated with the frequency difference of maximum ± 25.0 cm^{-1} from the azide asymmetric stretch, minimum of cubic interaction force constant 1 cm^{-1}, and the minimum difference of the second-order perturbative energy (PT2) to the variational energy of more than 1 cm^{-1} are listed in the table as Fermi resonance interaction. All the three parameters are in cm^{-1}.

I	J+K	Freq. Diff.	Cubic int. force.	PT2-Variat.

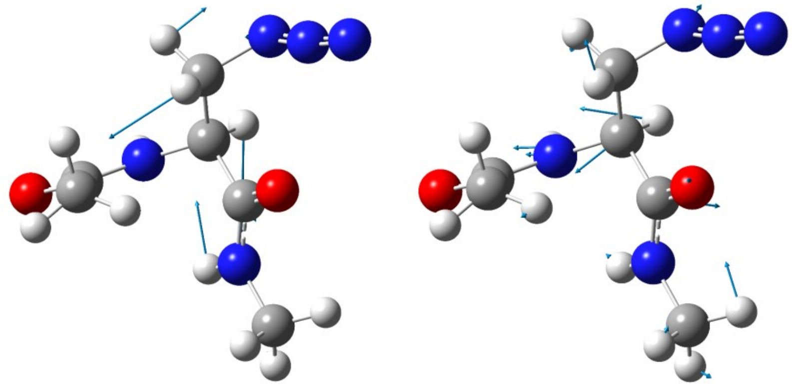
				const. (k_{ijk})	Diff.
12	39	30	-19.6	59.0	-25.061
	41	28	4.2	-30.8	196.227

Table S4. The detailed description of the normal modes of the near-resonant combination bands that can participate with the azide asymmetric stretch mode 12 along with their corresponding harmonic and anharmonic frequencies calculated at B3LYP/6-311++G level of theory.

Mode	Description	E(harm) /cm^{-1}	E(Anharm) /cm^{-1}
12	Azide asymmetric stretch	2113.7	2035.4
28	CH_2 twisting + chain C-H bend + N-H bend	1299.7	1266.3
30	N_3 sym. stretch + CH_2 twisting + chain C-H bend	1241.1	1215.8
39	CH_2 rocking + chain C-H bend	892.3	862.7
41	C-N stretch + CH_2 twisting + CH_3 bend + N-H bend + chain C-H bend	809.9	789.6



Mode 12: 2114 cm^{-1} **Mode 30:** 1241 cm^{-1} **Mode 39:** 892 cm^{-1}



Mode 28: 1300 cm^{-1} **Mode 41:** 810 cm^{-1}

Figure S3. Azide asymmetric stretch band and the detailed description of the normal modes of the near-resonant combination bands that can participate with the azide asymmetric stretch mode 12 along with their corresponding harmonic frequencies calculated at the

B3LYP/6-311++G level of theory. The displacement vector is shown in light blue for all the modes. None of them consists of isotope labeled N atom from the azide group.

V. Supporting References

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