

Ultrafast Infrared Spectroscopy Study of Azides with β -isotope labeling: Comparing with Aliphatic Azides and Aromatic Azides

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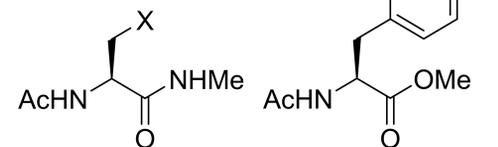
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❖ Abstract

Azides can be used as infrared (IR) probes of the local environment and molecular structural changes. The dynamics reported by a site-specific IR probe is limited to its vibrational lifetime, restricting the utility of azide probes due to short vibrational lifetimes. Moreover, the vibrational bands of azide probes are often accompanied by complex line shapes that arise from Fermi resonance. If these limitations could be overcome, their strikingly large molecular extinction coefficients would make azide groups very attractive as IR probes. We have synthesized primary and aromatic azides, and performed Fourier transform infrared (FTIR) and nonlinear infrared experiments (IR pump-probe and 2D-IR) to determine changes in azide stretch vibrational modes associated with isotope labeling, with the hope of avoiding Fermi resonance and increasing vibrational lifetime.

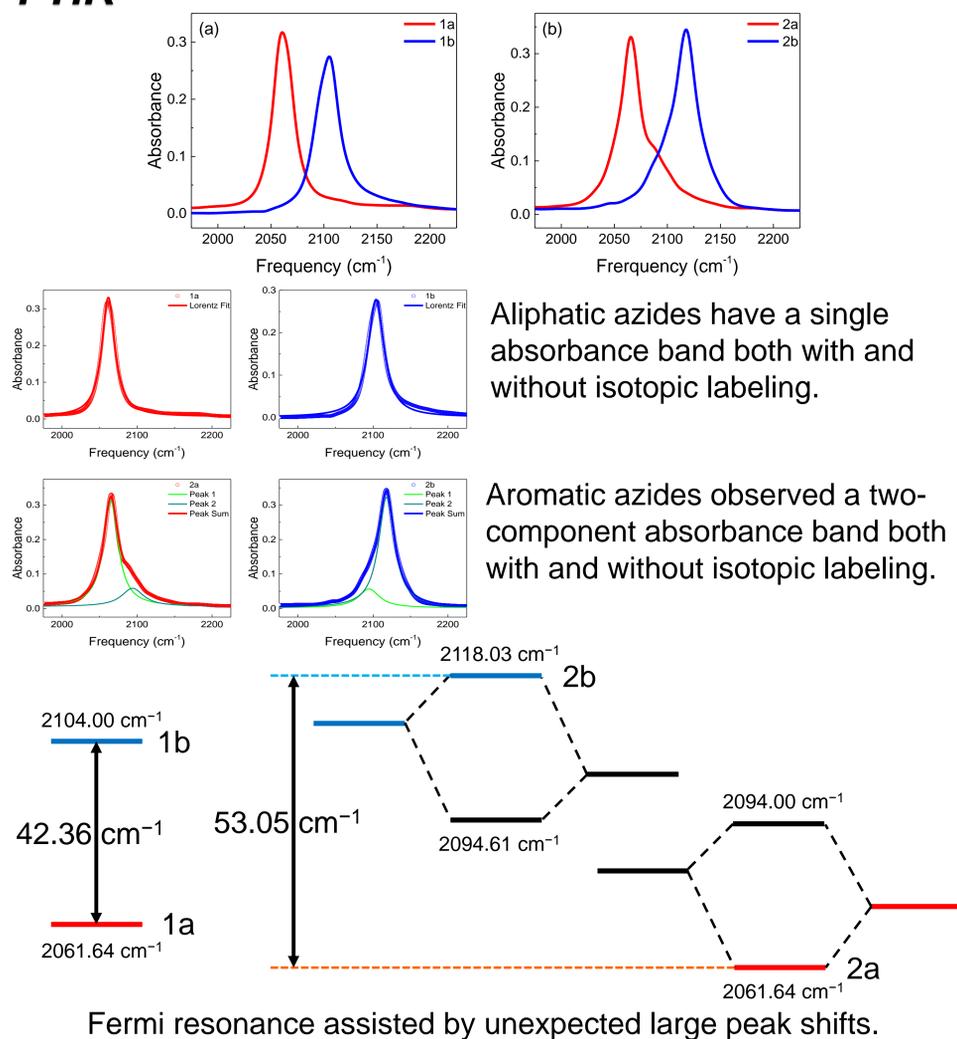
X = N¹⁵NN or N₃



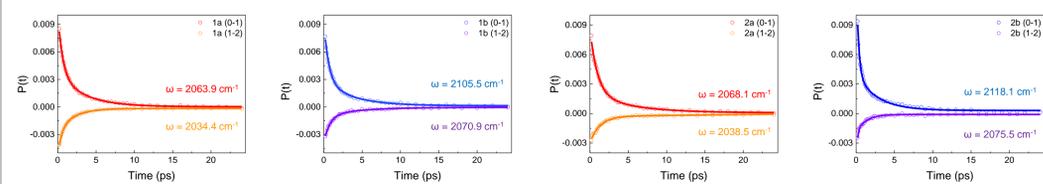
1a Ac-Ala(N¹⁵NN)-NHMe
1b Ac-Ala(N₃)-NHMe
2a Ac-p-N¹⁵NN-Phe-OMe
2b Ac-p-N₃-Phe-OMe

❖ Results of experimental data

- FTIR



- IR pump-probe spectroscopy

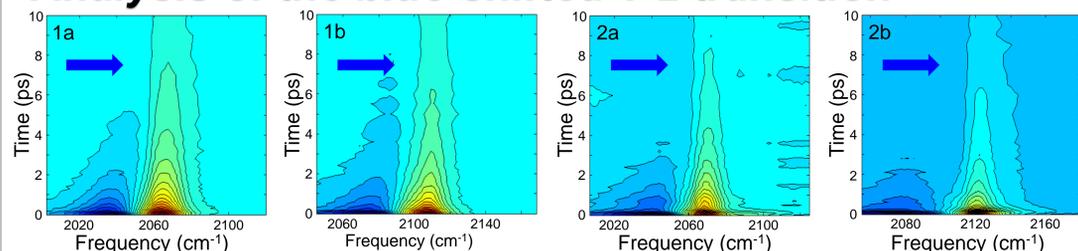


	1a	1b	2a	2b
ω_0 (cm ⁻¹)	2061.64	2104.00	2064.98	2118.03
FWHM (cm ⁻¹)	21.25	25.90	23.86	25.88
ϵ (cm ⁻¹ M ⁻¹)	633.6	548.7	661.8	689.2
D (10 ⁻² Debye ²)	9.84	9.66	11.3	10.2
T ₁ (ps)	0.63±0.03 (0.74)	0.63±0.04 (0.75)	0.97±0.08 (0.72)	0.31±0.03 (0.79)
	3.79±0.24 (0.26)	3.75±0.37 (0.25)	5.35±1.42 (0.28)	2.42±0.24 (0.21)

- Mid-N atom selectively isotopic labeling did not significantly affect the increase in vibrational lifetime.

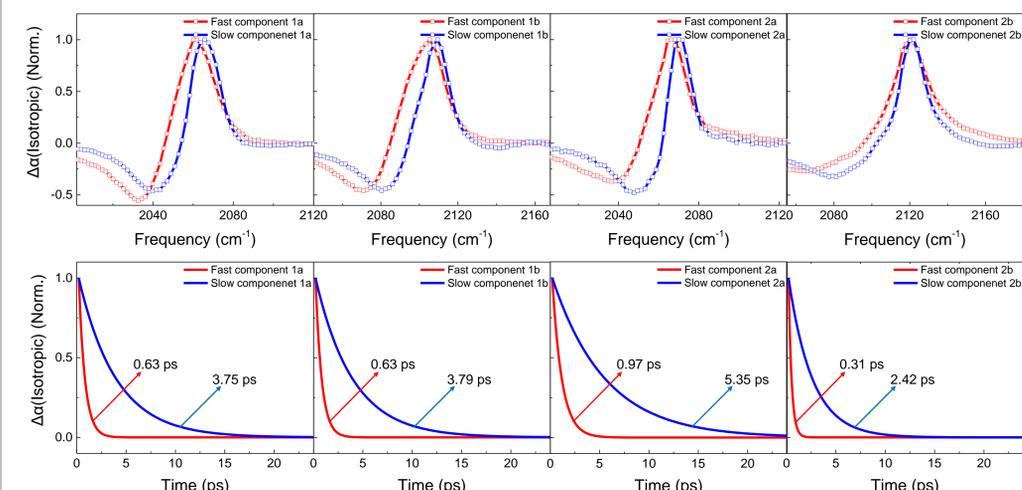
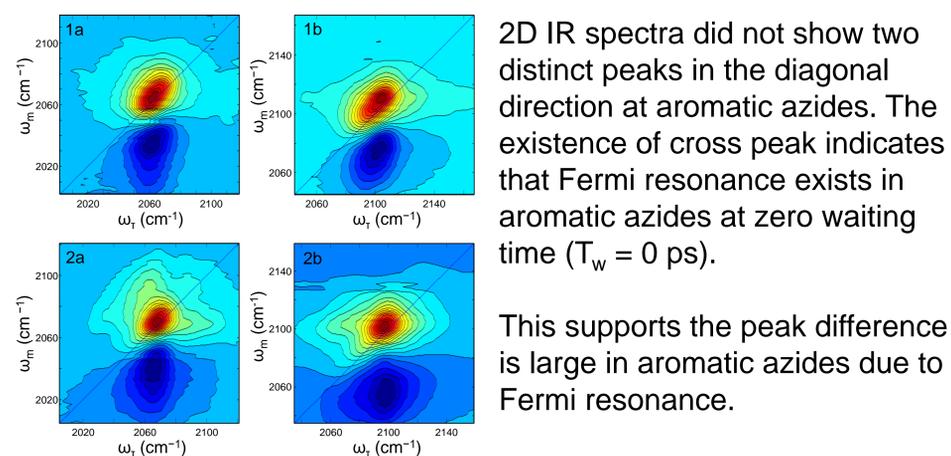
- Azide derivatives vibrational lifetimes of isotopic labeling and azide structure follow a nonmonotonic trend.

- Analysis of the blue-shifted 1-2 transition



All azide derivatives show a blue-shift over time in the 1-2 transition region about 10 cm⁻¹.

- 2D IR spectroscopy



The fast component assigned as the combination band, and the slow-component as the azide stretch band.

❖ Conclusion

In FT-IR measurements of aromatic azides, our results show that the addition of a single neutron to the middle atom of azides does not remove the Fermi resonance. We measured 2D-IR spectra in order to check for Fermi resonance. The existence of cross peak at zero waiting time indicates that Fermi resonance exists in the aromatic azide. We can assign Fermi resonance assisted by unexpected large peak shifts. Isotopic labeling on vibrational lifetimes does not show a uniform trend for the four azide derivatives. All azide derivatives' 1-2 transition frequencies show blue-shifts over time. We found that the azide stretches overlap with combination modes, by time-resolved IR-PP spectra.