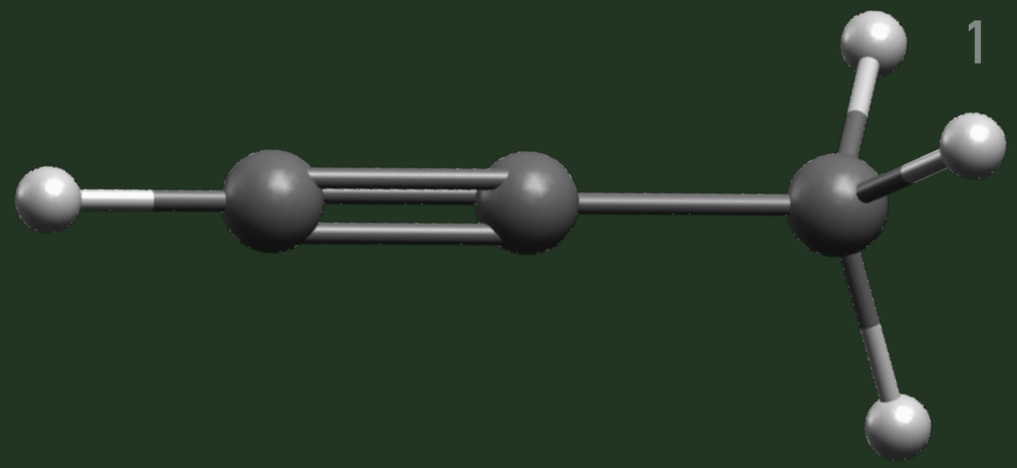

^{13}C MONO-SUBSTITUTED ISOTOPOLOGUES OF PROPYNE (H_3CCCH): INVESTIGATING THE ACETYLENIC CH STRETCH PERTURBATION

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Dongfeng Zhao - University of Science and Technology of China
Harold Linnartz - Universiteit Leiden

- Intramolecular vibrational relaxation (IVR)
  -the acetylenic CH stretch can be used to study non- and near-resonant perturbations - Kerstel *et al.* J.Chem.Phys., 100 (1994) 2588

- Chemical evolution in planetary atmospheres, circumstellar shells, planetary nebulae, and the interstellar medium
  -the close spacing of the *K*'-subbands and the relatively low dipole moment (μ=0.78 D) make propyne an ideal probe of gas temperature
  -observed ratio of ^{13}C:^{12}C gives insight into the fractionation history of astronomical objects

- Propyne is seen in both galactic and extragalactic sources

- The mono-substituted ^{13}C isotopologues are significantly less studied compared to the ^{12}C isotopologue

CCSD(T)/ANO1 VPT2 PREDICTIONS

➡ Taken from Doney *et al.* JPCA, 122 (2018) 582, with references therein

Harmonic and anharmonic (VPT2) frequencies (in cm^{-1}) of propyne with corresponding intensities (in km/mol) given in parenthesis. Experimental values are given below in italics.

Vibrational mode (State Symmetry)	$^{12}CH_3^{12}C^{12}CH$		$^{13}CH_3^{12}C^{12}CH$		$^{12}CH_3^{13}C^{12}CH$		$^{12}CH_3^{12}C^{13}CH$	
	ω	ν	ω	ν	ω	ν	ω	ν
$\nu_1(A_1)$ CH str.	3471.5	3337.3(46.2) *3335.0520* ☆	3471.5	3337.2(46.1) *3334.9720* ☆	3470.2	3333.0(34.3) *3325.0133* ☆	3454.3	3321.1(44.3) *3318.6667* ☆
$\nu_2(A_1)$ CH_3 sym. str.	3050.3	2938.8(9.5) *2940.9996* [21]	3047.0	2934.1(9.7) *2936.7668* [21]	3050.3	2938.5(9.6) *2940.7414* [21]	3050.3	2938.7(9.6) *2940.9564* [21]
$\nu_3(A_1)$ C≡C str.	2180.2	2138.0(3.1) *2137.87* [17]	2178.9	2136.7(3.1) *2143.37* [19]	2129.3	2092.0(4.2) *2190.72* [19]	2154.8	2113.3(3.1) *2166.74* [19]
$\nu_4(A_1)$ CH_3 sym. deform.	1414.3	1382.7(0.0) *1385.03* [31]	1403.8	1372.8(0.0) *1400.6* [19]	1414.3	1382.2(0.0)	1414.2	1382.6(0.0)
$\nu_5(A_1)$ C-C str.	935.3	924.2(0.5) *930.276 530* [18]	918.1	907.7(0.6) *946.58* [19]	931.8	920.3(0.6)	925.1	914.6(0.6)
$\nu_6(E)$ CH_3 asym. str.	3126.4	2976.8(7.3) *2980.860 2* [21]	3115.2	2967.0(7.2) *2990.5* [19]	3126.4	2976.4(7.2)	3126.4	2976.6(7.2)
$\nu_7(E)$ CH_3 degen. deform.	1486.6	1449.4(7.7) *1450.271* [31]	1485.0	1447.8(7.8) *1452.42* [19]	1486.3	1448.8(7.8)	1486.6	1449.4(7.8)
$\nu_8(E)$ CH_3 rocking	1057.0	1034.3(0.1) *1036.147 539* [18]	1048.6	1026.1(0.2) *1044.21* [19]	1053.2	1030.6(0.1)	1057.0	1034.3(0.1)
$\nu_9(E)$ H-C≡C bend	642.8	635.5(45.6) *638.569 14* [32]	642.8	635.4(45.5) *638.65* [19]	642.4	635.2(45.8)	638.4	631.3(45.4)
$\nu_{10}(E)$ C-C≡C bend	325.3	327.8(7.6) *330.938 56* [33]	324.9	327.5(7.6) *329.5* [19]	317.8	320.5(7.2)	323.4	326.0(7.4)

➡ Calculated using CFOUR

➡ ν_1 frequency is accounting for a Fermi resonance (*e.g.* $\nu_3+2\nu_9$)

➡ Taken from Doney *et al.* JPCA, 122 (2018) 582, with references therein

Harmonic and anharmonic (VPT2) frequencies (in cm^{-1}) of propyne with corresponding intensities (in km/mol) given in parenthesis. Experimental values are given below in italics.

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➡ Calculated using CFOUR

➡ ν_1 frequency is accounting for a Fermi resonance (*e.g.* $\nu_3+2\nu_9$)

- The normal isotopologue has a known Fermi resonance between ν_1 and $\nu_3+2\nu_9$
- For $H_3{}^{13}CCCH$ and $H_3CC^{13}CH$, the combination band $\nu_3+2\nu_9$ is predicted to have about 2% the intensity of the fundamental band
- For $H_3C^{13}CCH$, the combination bands $\nu_3+2\nu_9$ and $\nu_7+3\nu_9$ are predicted to have about 30% and 10%, respectively, the intensity of the fundamental band

CCSD(T)/ANO1 VPT2 PREDICTIONS

CCSD(T)/ANO1 vibration-rotation interaction constants (α_i, in cm^{-1}). Experimental values are given below in italics.

Mode	$^{12}CH_3^{12}C^{12}CH$		$^{13}CH_3^{12}C^{12}CH$		$^{12}CH_3^{13}C^{12}CH$		$^{12}CH_3^{12}C^{13}CH$	
	$\alpha_i^A \times 10^3$	α_i^B x10^3	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$
ν_1	0.035 *0.41*[4]	0.646 *0.665*[4]	0.035 *-0.2* ☆	0.622 *0.630* ☆	0.030 *101.0* ☆	0.640 *0.662* ☆	0.027 *-37.7* ☆	0.590 *0.625* ☆
ν_2	55.4 *38*[34]	0.077 *-0.084*[21]	54.8	0.061 *-0.113*[21]	55.4	0.077 *-0.080*[21]	55.4	0.073 *-0.148*[21]
ν_3	2.57 *6.6*[17]	1.48 *1.510*[21]	2.54	1.43	2.42	1.41	2.67	1.46
ν_4	-27.4	1.67 *0.40*[21]	-27.2	1.42	-27.4	1.67	-27.4	1.57
ν_5	6.01 *7.572*[15]	1.29 *1.260*[21]	6.04	1.25	6.03	1.29	5.90	1.20
ν_6	35.9 *17*[35]	0.064 *0.026*[21]	35.4	0.044	35.9	0.063	35.9	0.060
ν_7	39.7 *42.89*[31]	-0.887 *-0.26*[21]	39.6	-0.759	39.7	-0.891	39.7	-0.834
ν_8	-29.5 *-61.8*[17]	0.196 *0.141*[21]	-29.2	0.187	-29.3	0.194	-29.5	0.196
ν_9	0.652 *1.353*[36]	-0.187 *-0.18*[21]	0.651	-0.180	0.670	-0.186	0.652	-0.156
ν_{10}	1.29 *2.170*[33]	-0.821 *-0.78*[21]	1.42	-0.798	1.19	-0.787	1.30	-0.803

- Taken from Doney *et al.* JPCA, 122 (2018) 582, with references therein
- Calculated using CFOUR

CCSD(T)/ANO1 VPT2 PREDICTIONS

CCSD(T)/ANO1 vibration-rotation interaction constants (α_i, in cm^{-1}). Experimental values are given below in italics.

Mode	$^{12}CH_3^{12}C^{12}CH$		$^{13}CH_3^{12}C^{12}CH$		$^{12}CH_3^{13}C^{12}CH$		$^{12}CH_3^{12}C^{13}CH$	
	$\alpha_i^A \times 10^3$	α_i^B x10^3	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$
ν_1	0.035 *0.41*[4]	0.646 *0.665*[4]	0.035 *-0.2* ☆	0.622 *0.630* ☆	0.030 *101.0* ☆	0.640 *0.662* ☆	0.027 *-37.7* ☆	0.590 *0.625* ☆
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ν_6	35.9 *17*[35]	0.064 *0.026*[21]	35.4	0.044	35.9	0.063	35.9	0.060
ν_7	39.7 *42.89*[31]	-0.887 *-0.26*[21]	39.6	-0.759	39.7	-0.891	39.7	-0.834
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ν_9	0.652 *1.353*[36]	-0.187 *-0.18*[21]	0.651	-0.180	0.670	-0.186	0.652	-0.156
ν_{10}	1.29 *2.170*[33]	-0.821 *-0.78*[21]	1.42	-0.798	1.19	-0.787	1.30	-0.803

- Taken from Doney *et al.* JPCA, 122 (2018) 582, with references therein
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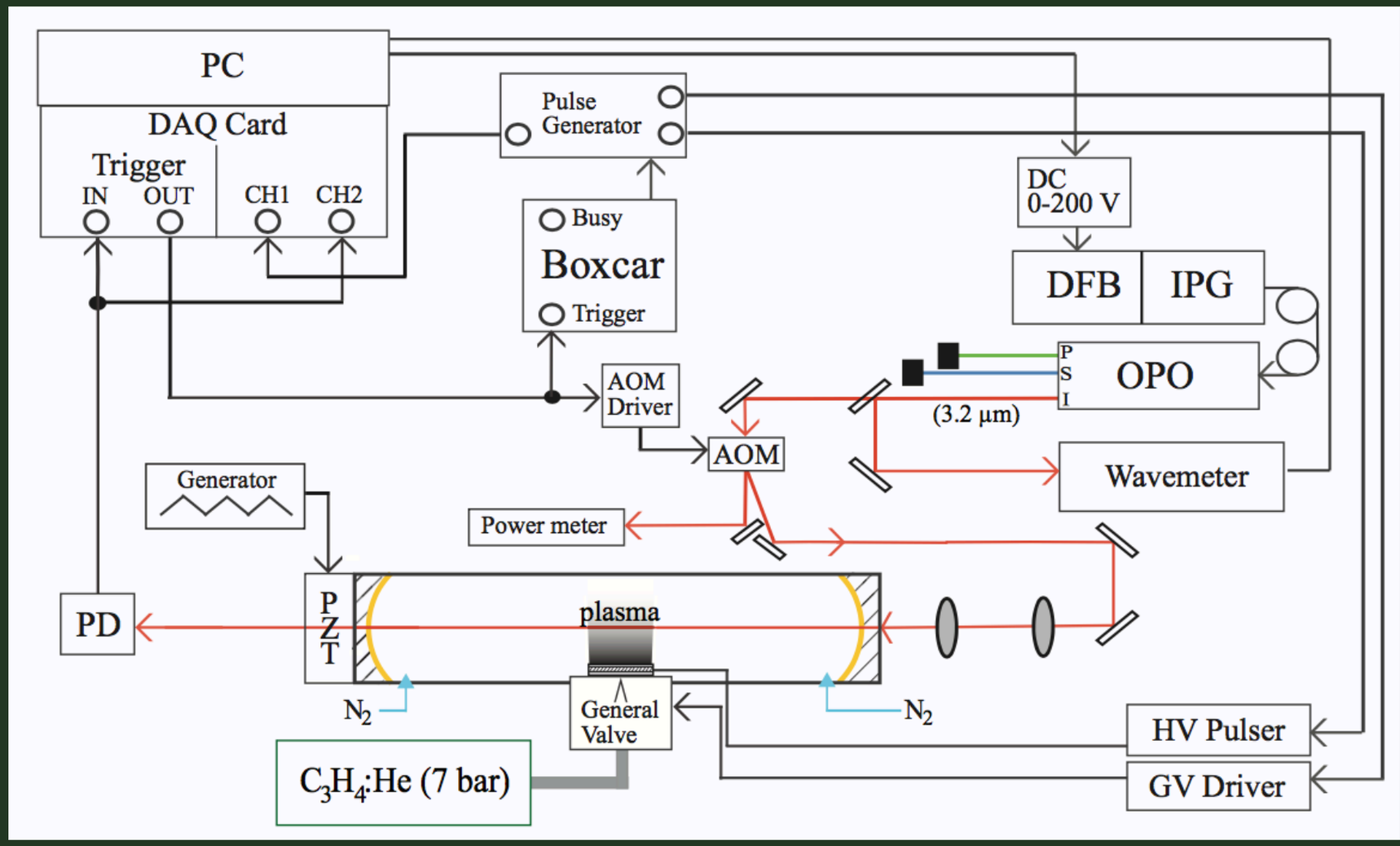
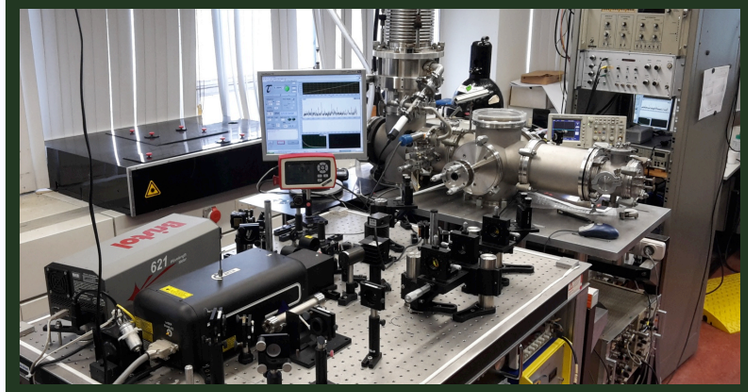
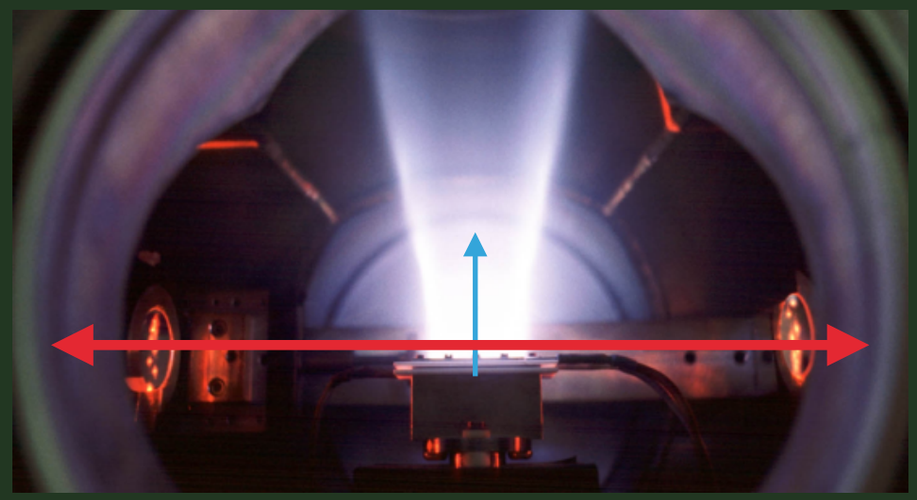
APPARATUS

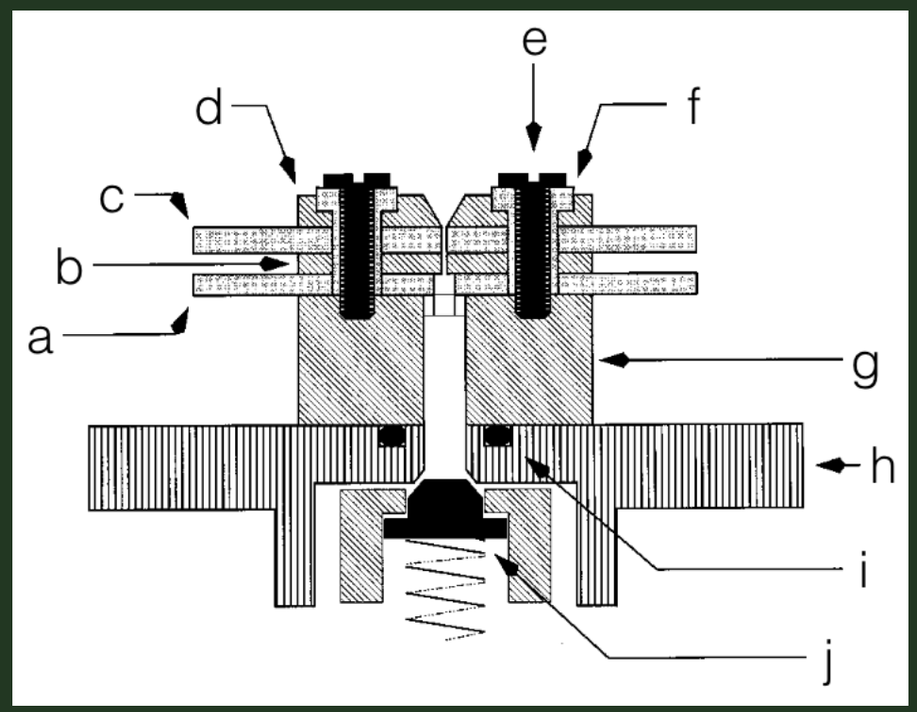




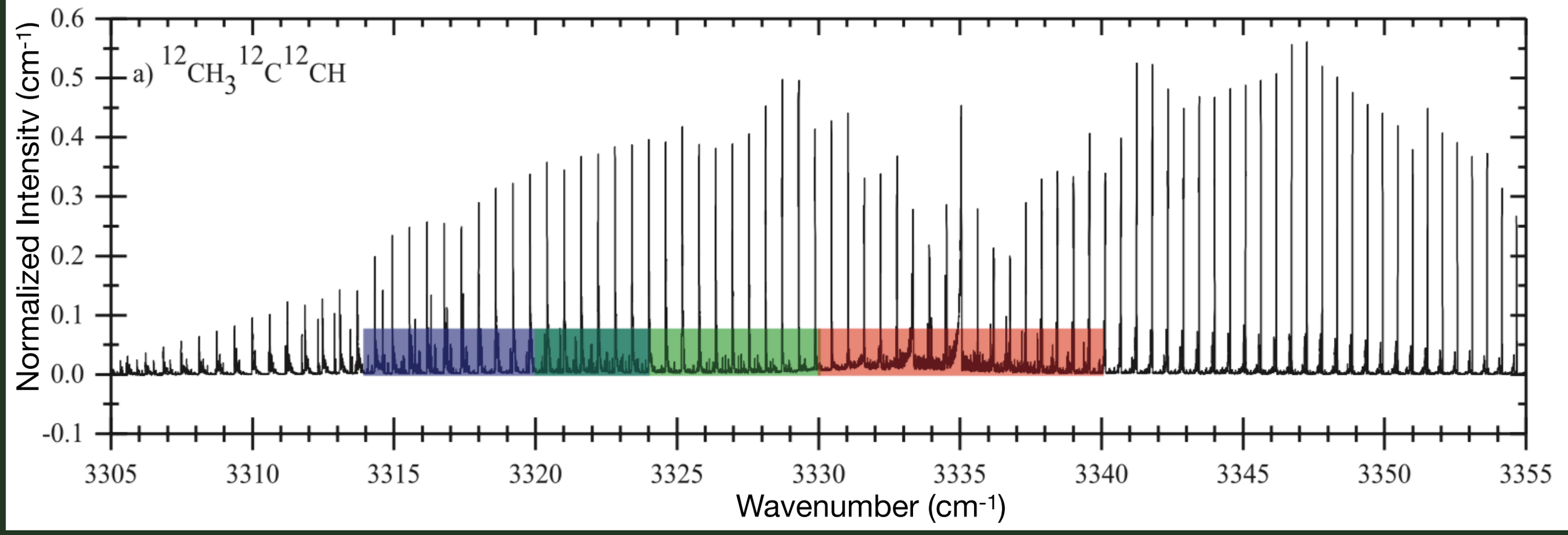
- Continuously tunable IR light from 2500 - 4100 cm^{-1}
- Quantum shot noise limited absorbance sensitivity
- Near-Doppler free absorption linewidths (≤60 MHz)

- 0.5% propyne in 1:1 Ar:He
  -contains a natural abundance (~ 1.1%) of the mono-substituted ^{13}C isotopologues of propyne
- Supersonic planar jet expansion
- Thin slit discharge nozzle (0.5x32mm)

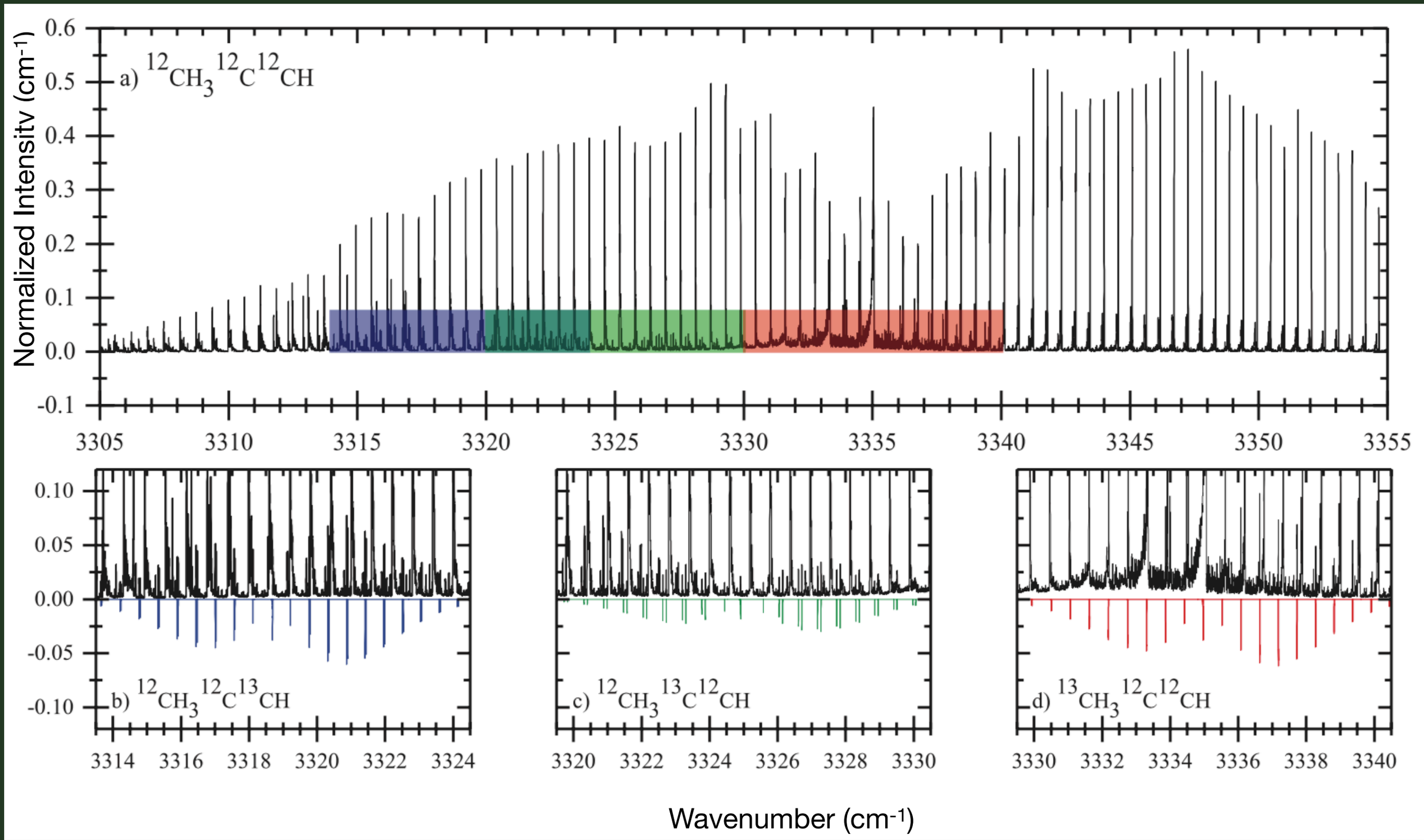




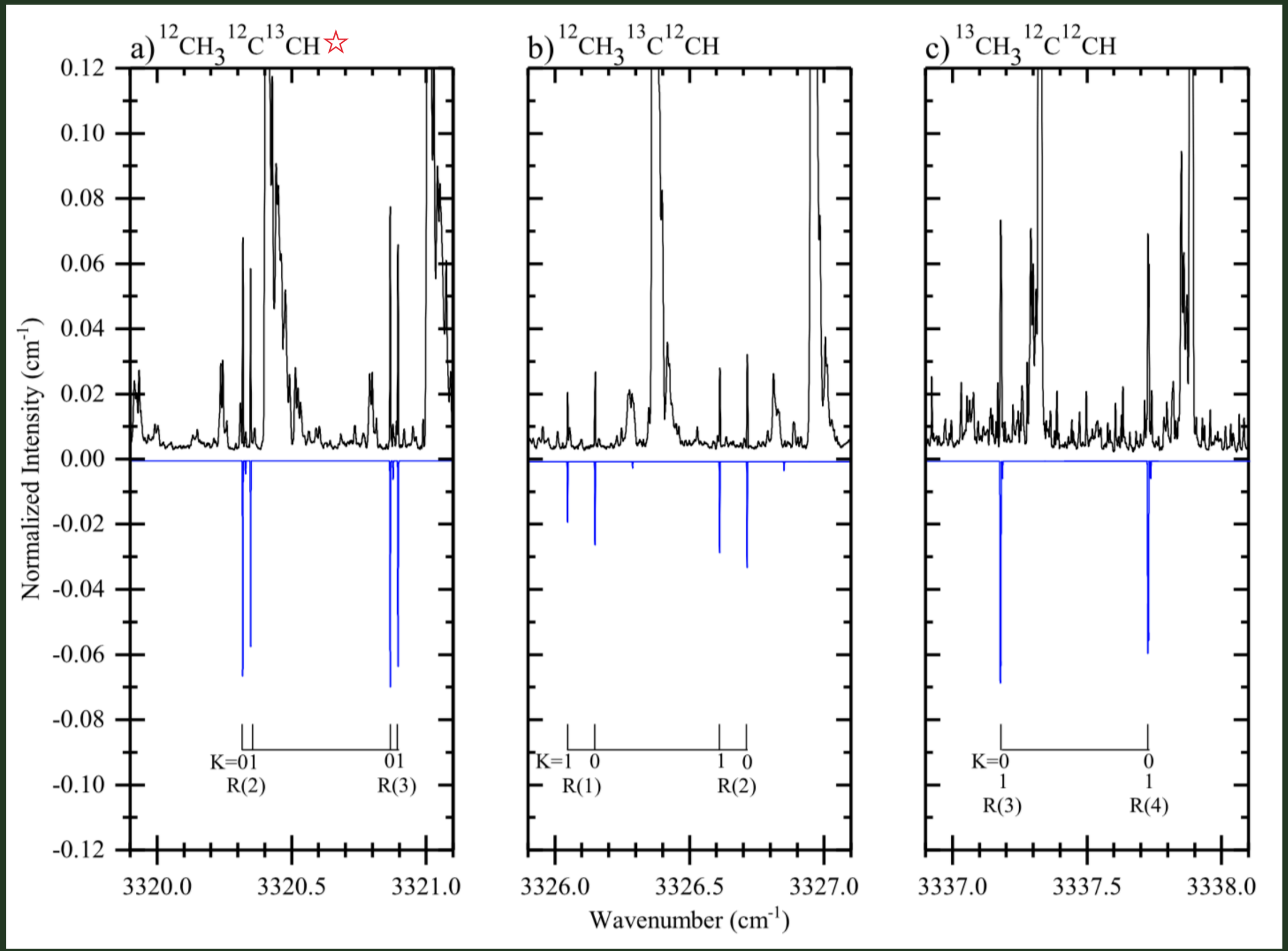
ACETYLENIC CH STRETCH

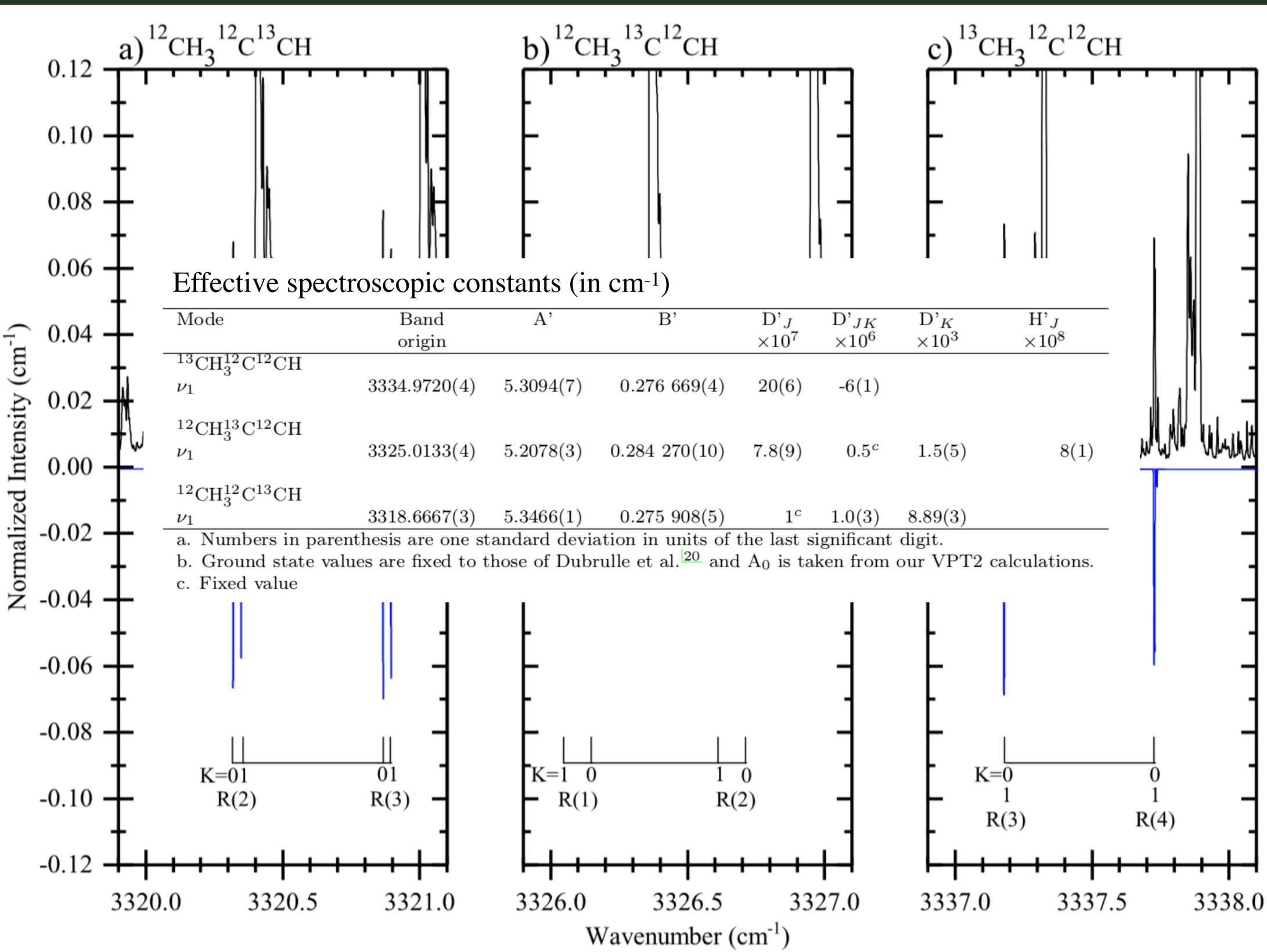


- Simulated spectra at 10K rotational temperature



K'-SUBBAND SHIFTS





Effective spectroscopic constants (in cm^{-1})

Mode	Band origin	A'	B'	D'$_J$ ×10^7	D'$_{JK}$ ×10^6	D'$_K$ ×10^3	H'$_J$ ×10^8
$^{13}CH_3^{12}C^{12}CH$							
ν_1	3334.9720(4)	5.3094(7)	0.276 669(4)	20(6)	-6(1)		
$^{12}CH_3^{13}C^{12}CH$							
ν_1	3325.0133(4)	5.2078(3)	0.284 270(10)	7.8(9)	0.5[c]	1.5(5)	8(1)
$^{12}CH_3^{12}C^{13}CH$							
ν_1	3318.6667(3)	5.3466(1)	0.275 908(5)	1[c]	1.0(3)	8.89(3)	

a. Numbers in parenthesis are one standard deviation in units of the last significant digit.
b. Ground state values are fixed to those of Dubrulle et al.[20] and A_0 is taken from our VPT2 calculations.
c. Fixed value

- CCSD(T)/ANO1 VPT2 calculations predict Fermi resonances, which are confirmed by experimental band origins - but the combination band intensities are too weak to be distinguishable in the experimental spectrum

- All isotopologues have small predicted values for $\alpha_1{}^A$ which could not be experimentally confirmed for two isotopologues ($H_3CC^{13}CH$ and $H_3C^{13}CCH$) - suggesting a "double crossing" type perturbation (likely the result of an interaction with at least one other (A_1+A_2) pair state) as determined for the normal isotopologue

- Based on the observed shift w.r.t. ^{13}C placement, the ν_1 and the main perturbing state involves vibrations that occur at opposite ends of the carbon chain

- The SLA group at Universiteit Leiden

- Funding:
  NWO
  NOVA
  Dutch Astrochemistry Network