

High-Resolution Infrared Spectra of the ν_1 Fundamental Bands of Mono-Substituted ^{13}C Propyne Isotopologues

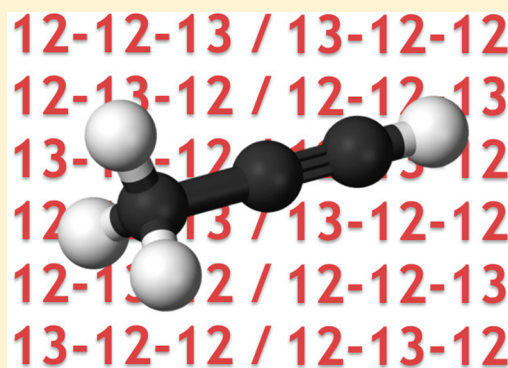
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Supporting Information

ABSTRACT: We present a combined experimental and *ab initio* study on the jet-cooled high-resolution infrared spectra of the ν_1 (acetylenic stretch) fundamental band for three isotopologues of propyne: $^{13}\text{CH}_3^{12}\text{C}\equiv^{12}\text{CH}$, $^{12}\text{CH}_3^{13}\text{C}\equiv^{12}\text{CH}$, and $^{12}\text{CH}_3^{12}\text{C}\equiv^{13}\text{CH}$. The experimental spectra are recorded in natural abundance using a continuous supersonic expansion of regular propyne diluted in argon and helium, in combination with continuous wave cavity ring-down spectroscopy (cw-CRDS). The fully rotationally resolved $K' = 0$ and 1 subbands of all three monosubstituted ^{13}C isotopologues have been measured near 3330 cm^{-1} , and their spectroscopic analysis is presented here for the first time. The assignment of the bands and perturbation analysis are assisted by high level *ab initio* calculations at the CCSD(T) level of theory, from which vibrational frequencies, rotational constants, and Fermi resonances are predicted for each isotopologue.



1. INTRODUCTION

Propyne, also known as methylacetylene ($\text{H}_3\text{CC}\equiv\text{CH}$), is a small unsaturated hydrocarbon of importance for studying intramolecular vibrational relaxation (IVR)^{1–8} and chemical evolution in the interstellar medium (ISM), planetary atmospheres, and circumstellar shells of evolved stars.^{9–13} In particular, propyne is an ideal probe of the interstellar medium's kinetic temperature, since with increasing K' the subbands have increasing excitation temperatures.¹⁴ Furthermore, the relatively low dipole moment ($\mu = 0.78\text{ D}$)¹⁵ suggests propyne is easily thermalized, relative to more polar molecules, and the narrow spacing between K' subbands of a given rotational transition, allows for simultaneous observation of multiple K-transitions.¹⁴ In addition, the presence of an acetylenic CH stretch, which with only one quanta of excitation falls into the range of high state density, makes propyne an ideal benchmark molecule to study non- and near-resonant perturbations.⁷

The normal isotopologue of propyne ($^{12}\text{CH}_3^{12}\text{C}^{12}\text{CH}$; hereafter referred to as I0) has been extensively studied spectroscopically in its electronic ground state (X^1A_1 ; Doney et al.¹⁶ and references therein). It is known that many of the vibrational modes of I0 are perturbed.^{4,5,7,17,18} Furthermore, non- or near-resonant anharmonic interactions play an important role in the IVR that is seen in propyne. The study of such perturbations provides insight into the nature of the IVR process. For example, the acetylenic stretch fundamental of the normal isotopologue does not exhibit any effects due to IVR, while its overtone modes do.⁷ However, the $1\nu_1$ acetylenic stretch fundamental is involved in a long-range Fermi

resonance with the dark state $\nu_3 + 2\nu_9$,^{4,19} as well as, a second “double crossing” type anharmonic perturbation.⁴ The Fermi resonance affects the observed band origin frequency and overall intensity, while the “double crossing” type perturbation affects the K' -subband origin order, and consequently can be quantified by the difference of the vibrationally excited and ground state A rotational constants (ΔA).

The monosubstituted ^{13}C isotopologues are significantly less spectroscopically studied compared to the normal isotopologue. There exist only two high-resolution studies for all three isotopologues ($^{13}\text{CH}^{12}\text{C}^{12}\text{CH}$, $^{12}\text{CH}^{13}\text{C}^{12}\text{CH}$, and $^{12}\text{CH}^{12}\text{C}^{13}\text{CH}$, hereafter referred to as I1, I2, and I3, respectively). One is the microwave measurement of the vibrational ground state constants (X^1A_1 ; B_0 , D_0 , and H_0),²⁰ and the other a mid-infrared (MIR) study of the ν_2 fundamental (at $\sim 2940\text{ cm}^{-1}$).²¹ Other vibrational modes of monosubstituted ^{13}C propyne have been measured at lower resolution; including all ten of the fundamental vibrational modes of I1, the ν_3 and ν_9 fundamentals of I2 and I3, two combination bands of I1, and the $2\nu_9$ overtone band of I1–I3.¹⁹ In a study by Duncan et al.,¹⁹ the Fermi resonance between ν_1 and $\nu_3 + 2\nu_9$ was reported for I1 and I2, and was inferred to occur for I3. However, observation of the “double crossing” perturbation requires high-resolution spectroscopic measurements to resolve the K -subband origin spacing.

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Table 1. Harmonic and Anharmonic (VPT2) Frequencies (in cm^{-1}) of Propyne with Corresponding Intensities (in km/mol) Given in Parentheses and Experimental Values Given in Italics

vibrational mode (state symmetry)	$^{12}\text{CH}^{12}\text{C}^{12}\text{CH}$ (I0) ^a		$^{13}\text{CH}^{12}\text{C}^{12}\text{CH}$ (I1)		$^{12}\text{CH}^{13}\text{C}^{12}\text{CH}$ (I2)		$^{12}\text{CH}^{12}\text{C}^{13}\text{CH}$ (I3)	
	ω	ν	ω	ν	ω	ν	ω	ν
$\nu_1(\text{A}_1)$ CH str.	3471.5	3337.3(46.2) 3335.0520 ^b	3471.5	3337.2(46.1) 3334.9720 ^b	3470.2	3333.0(34.3) 3325.0133 ^b	3454.3	3321.1(44.3) 3318.6667 ^b
$\nu_2(\text{A}_1)$ 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
$\nu_3(\text{A}_1)$ $\text{C}\equiv\text{C}$ 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
$\nu_4(\text{A}_1)$ 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)
$\nu_5(\text{A}_1)$ C–C str.	935.3	924.2(0.5) 930.276530 ¹⁸	918.1	907.7(0.6) 946.58 ¹⁹	931.8	920.3(0.6)	925.1	914.6(0.6)
$\nu_6(\text{E})$ CH_3 asym. str.	3126.4	2976.8(7.3) 2980.8602 ²¹	3115.2	2967.0(7.2) 2990.5 ¹⁹	3126.4	2976.4(7.2)	3126.4	2976.6(7.2)
$\nu_7(\text{E})$ 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)
$\nu_8(\text{E})$ CH_3 rocking	1057.0	1034.3(0.1) 1036.147539 ¹⁸	1048.6	1026.1(0.2) 1044.21 ¹⁹	1053.2	1030.6(0.1)	1057.0	1034.3(0.1)
$\nu_9(\text{E})$ H– $\text{C}\equiv\text{C}$ bend	642.8	635.5(45.6) 638.56914 ³²	642.8	635.4(45.5) 638.65 ¹⁹	642.4	635.2(45.8)	638.4	631.3(45.4)
$\nu_{10}(\text{E})$ C– $\text{C}\equiv\text{C}$ bend	325.3	327.8(7.6) 330.93856 ³³	324.9	327.5(7.6) 329.5 ¹⁹	317.8	320.5(7.2)	323.4	326.0(7.4)

^aDoney et al.¹⁶ ^bThis work.

In this contribution, we present a combined study on the *ab initio* calculations and experimental measurement of the three monosubstituted ^{13}C propyne isotopologues. The analysis of high-resolution experimental spectra of the ν_1 fundamental bands of all three isotopologues around 3330 cm^{-1} is supported by anharmonic calculations of the vibrational frequencies and vibration–rotation interaction constants. Anharmonic perturbations are dependent on the energy of the involved transitions, which is affected by the location of the ^{13}C in the molecule; the present study allows us to investigate the extent to which the three monosubstituted ^{13}C isotopologues exhibit similar perturbations as I0, such as those for the ν_1 fundamental. In section 2, the experimental and theoretical details are given. The results and their analysis are discussed in section 3.

2. METHODS

The experimental setup has been described in detail in Zhao et al.,²² and only details relevant to the current experiment are described here. A gas mixture of 0.5% propyne in 1:1 argon:helium is used as the precursor gas, which contains a natural abundance ($\sim 1.1\%$) of the monosubstituted ^{13}C isotopologues of propyne. Assuming similar intrinsic intensities between the different isotopologues, this comes with an expected reduction in S/N of about a factor 100 with respect to I0. The gas is supersonically expanded with about 0.5 bar backing pressure through a long ($0.05 \times 32\text{ mm}$) slit nozzle into a vacuum chamber with a stagnation pressure of $0.1 \times 10^{-2}\text{ mbar}$. The collimation along a well-defined absorption pathway, in combination with an effective adiabatic cooling, increases the detection sensitivity while simplifying the spectral complexity. For these conditions rotational temperatures of the order of 10–20 K are typically obtained, and are uniform along the laser beam axis due to the planar jet expansion.

The absorption spectrum is recorded using cw-CRDS, with the IR laser path intersecting the expansion roughly 1 cm downstream from the nozzle slit throat. The optical cavity is

comprised of two highly reflective plano-concave mirrors ($R \sim 99.98\%$, centered at 3300 cm^{-1}). Typical empty cavity ring-down times (τ_0) are about $7\text{ }\mu\text{s}$. For this experiment the optical cavity length (about 56 cm) is modulated over at least two free spectral ranges (FSRs) at $\sim 26\text{ Hz}$, using a piezo crystal stack mounted on the back of one of the cavity mirrors, to achieve resonance with the laser wavelength. The resulting spectrum is recorded in a series of $\sim 1.2\text{ cm}^{-1}$ parts that partially overlap to guarantee that spectra are merged correctly. The observed noise level is $\sim 5 \times 10^{-7}\text{ cm}^{-1}$ in the present experimental conditions. While the spectrum is recorded, the laser frequency is simultaneously measured using a wavelength meter (Bristol Instruments, 621A-IR). The frequency accuracy is independently calibrated by measuring known transitions of water (H_2O).²³ The resulting maximum frequency uncertainty of $\pm 0.002\text{ cm}^{-1}$ is dictated by the wavemeter.

All *ab initio* calculations are carried out at the CCSD(T) level of theory. The same method has recently been used to study I0, and has been described in detail in Doney et al.;¹⁶ only relevant details will be described here. Equilibrium geometries are determined using the large core–valence correlation-consistent quadruple- ζ basis set (cc-pCVQZ).^{24–26} While the vibrational frequencies and spectroscopic parameters are determined using the atomic natural orbital (ANO) basis set (with the primitive basis set (13s8p6d4f2g) for non-hydrogen atoms and (8s6p4d2f) for hydrogen) with the truncation [4s3p2d1f] for non-hydrogen atoms and [4s2p1d] for hydrogen (hereafter known as ANO1).^{25–27} Furthermore, only the valence electrons are considered in the correlation treatment, i.e., standard frozen-core (fc) calculations. At the (fc)-CCSD(T)/ANO1 optimized geometry, second-order vibrational perturbation (VPT2) theory calculations are determined from full cubic and the semidiagonal part of the quartic force fields obtained by numerical differentiation of analytic CCSD(T) second derivatives.^{28,29} All calculations are performed with the development version of the CFOUR program.³⁰

Table 2. CCSD(T)/ANO1 Vibration–Rotation Interaction Constants (α_i , in cm^{-1}) of Propyne ^{13}C -Isotopologues, with Experimental Values Given in Italics

mode	$^{12}\text{CH}^{12}\text{C}^{12}\text{CH}$ (I0) ^a		$^{13}\text{CH}^{12}\text{C}^{12}\text{CH}$ (I1)		$^{12}\text{CH}^{13}\text{C}^{12}\text{CH}$ (I2)		$^{12}\text{CH}^{12}\text{C}^{13}\text{CH}$ (I3)	
	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$	$\alpha_i^A \times 10^3$	$\alpha_i^B \times 10^3$
ν_1	0.035 <i>0.41⁴</i>	0.646 <i>0.665⁴</i>	0.035 <i>−0.2^b</i>	0.622 <i>0.630^b</i>	0.030 <i>101.0^b</i>	0.640 <i>0.662^b</i>	0.027 <i>−37.7^b</i>	0.590 <i>0.625^b</i>
ν_2	55.4 <i>38³⁴</i>	0.077 <i>−0.084²¹</i>	54.8	0.061 <i>−0.113²¹</i>	55.4	0.077 <i>−0.080²¹</i>	55.4	0.073 <i>−0.148²¹</i>
ν_3	2.57 <i>6.6¹⁷</i>	1.48 <i>1.510²¹</i>	2.54	1.43	2.42	1.41	2.67	1.46
ν_4	−27.4	1.67 <i>0.40²¹</i>	−27.2	1.42	−27.4	1.67	−27.4	1.57
ν_5	6.01 <i>7.572¹⁵</i>	1.29 <i>1.260²¹</i>	6.04	1.25	6.03	1.29	5.90	1.20
ν_6	35.9 <i>17³⁵</i>	0.064 <i>0.026²¹</i>	35.4	0.044	35.9	0.063	35.9	0.060
ν_7	39.7 <i>42.89³¹</i>	−0.887 <i>−0.26²¹</i>	39.6	−0.759	39.7	−0.891	39.7	−0.834
ν_8	−29.5 <i>−61.8¹⁷</i>	0.196 <i>0.141²¹</i>	−29.2	0.187	−29.3	0.194	−29.5	0.196
ν_9	0.652 <i>1.353³⁶</i>	−0.187 <i>−0.18²¹</i>	0.651	−0.180	0.670	−0.186	0.652	−0.156
ν_{10}	1.29 <i>2.170³³</i>	−0.8 ²¹ <i>−0.78²¹</i>	1.42	−0.798	1.19	−0.787	1.30	−0.803

^aDoney et al.¹⁶ ^bThis work.

3. RESULTS AND DISCUSSION

Calculation Results. Since spectroscopic information for monosubstituted ^{13}C propyne is limited, accurate theoretical vibrational frequencies and vibration–rotation interactions constants are needed to aid in assignment of new ro-vibrational bands. The CCSD(T)/ANO1 harmonic and anharmonic (VPT2) vibrational frequencies are given in Table 1. For modes for which high-resolution data have been reported (ν_1 – ν_{10} of I0 and ν_1 – ν_2 of I1–I3), the predicted frequencies are all within about 6 cm^{-1} of the experimental values, and for modes with only low-resolution data, the observed–calculated deviations (o–c) is much larger—on average about 20 cm^{-1} . On the basis of our previous study of I0, the expected uncertainties for the calculated vibrational frequencies are $\pm 10 \text{ cm}^{-1}$.¹⁶

For all four isotopologues, the VPT2 calculations predict the ν_1 state lying at a lower energy relative to the $\nu_3 + 2\nu_9$ state. With the exception of I2, this is consistent with the previous assignments by Duncan et al.¹⁹ We note that, for the CCSD(T)/ANO1 VPT2 calculations of the isotopologue $^{12}\text{CH}^{13}\text{C}^{13}\text{CH}$ (hereafter referred to as I4; see Supporting Information), the $\nu_3 + 2\nu_9$ state is predicted at a lower energy relative to the ν_1 state, with ν_1 at 3322.7 cm^{-1} (o–c = −1.6 cm^{-1}) and $\nu_3 + 2\nu_9$ at 3305.5 cm^{-1} (o–c = −11.5 cm^{-1}).¹⁹

Fermi resonances between ν_1 , $\nu_3 + 2\nu_9$, and $\nu_7 + 3\nu_9$ (the latter two of which are dark states) have to be addressed in order to accurately reproduce the observed experimental frequencies (see Supporting Information). For I0, I1, and I3, the interaction with $\nu_7 + 3\nu_9$ is negligible, and only the ν_1 and $\nu_3 + 2\nu_9$ interaction affects the band origins and intensities. In particular, for I0 and I1, the predicted Fermi coupling constant is $\sim 6.0 \text{ cm}^{-1}$, which is comparable to that determined by Duncan et al.¹⁹ and gives the $\nu_3 + 2\nu_9$ combination band about 1% the intensity of the ν_1 fundamental band. This shifts ν_1 from the pure anharmonic frequency at 3338.0 cm^{-1} , to 3337.3 cm^{-1}

for I0 and 3337.2 cm^{-1} for I1. The band origins accounting for the coupling are about −2 cm^{-1} off from the experimental values.¹⁹ Similarly, the Fermi resonance shifts the respective $\nu_3 + 2\nu_9$ combination bands from 3390.5 to 3391.2 cm^{-1} for I0, and from 3389.1 to 3389.9 cm^{-1} for I1. The combination bands are both observed by Duncan et al.¹⁹ with Q-branches at 3381.15 and 3379.8 cm^{-1} , for I0 and I1, respectively, and the resulting o–c of −10 cm^{-1} is within the accuracy of our calculations. For I3, the Fermi resonance is predicted to be only slightly stronger than for I0 or I1. The coupling constant is $\sim 5.4 \text{ cm}^{-1}$, which gives the $\nu_3 + 2\nu_9$ combination band about 2% the intensity of the ν_1 fundamental band, and shifts the ν_1 fundamental from 3322.0 to 3321.1 cm^{-1} and the $\nu_3 + 2\nu_9$ combination band from 3357.0 to 3358.3 cm^{-1} .

Because of the close band origins, the Fermi resonance between ν_1 and $\nu_3 + 2\nu_9$ in I2 is predicted to be the strongest among the three monosubstituted ^{13}C propyne isotopologues. In addition, unlike for the other three isotopologues, the second Fermi resonance between $\nu_3 + 2\nu_9$ and $\nu_7 + 3\nu_9$ also influences the $\nu_3 + 2\nu_9$ band origin and intensity. The predicted coupling constant is $\sim 5.9 \text{ cm}^{-1}$ between ν_1 and $\nu_3 + 2\nu_9$, while the Fermi resonance between $\nu_3 + 2\nu_9$ and $\nu_7 + 3\nu_9$ is weaker. The predicted coupling constant for the latter is only $\sim 1.4 \text{ cm}^{-1}$. These interactions shift the predicted frequencies of ν_1 , $\nu_3 + 2\nu_9$, and $\nu_7 + 3\nu_9$ from their pure anharmonic values at 3336.6, 3346.8, and 3343.5 cm^{-1} to 3333.0, 3345.7, and 3348.3 cm^{-1} , respectively. Moreover, the anharmonic interactions result in the two dark states borrowing intensity from ν_1 such that the intensity of $\nu_3 + 2\nu_9$ and $\nu_7 + 3\nu_9$ is about 30% and 10%, respectively, that of the fundamental. Consequently, the intrinsic intensity of the ν_1 fundamental of I2 is expected to be about 75% that of the ν_1 fundamental of either I1 or I3.

In addition to the anharmonic frequencies, we have also computed the VPT2 vibration–rotation interaction constants, α_i , and the results are given in Table 2. For all α_i^B , the predicted value shows a good agreement with the experimental value, as

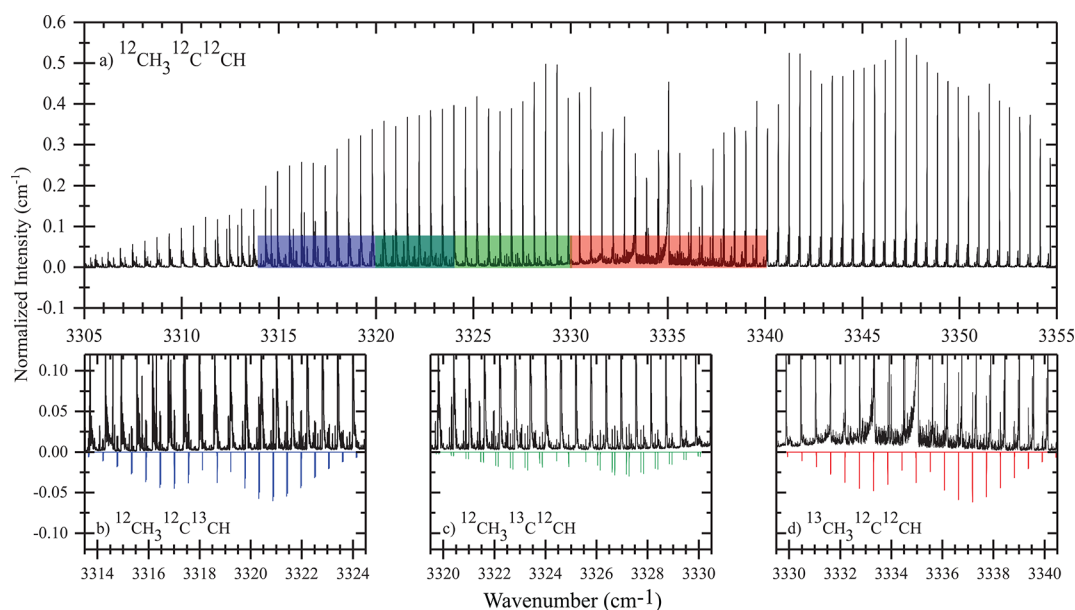


Figure 1. Experimental spectrum (in black) of propyne showing (a) the ν_1 band of $^{12}\text{CH}_3^{12}\text{C}^{12}\text{CH}$ (I0), (b) the ν_1 band of $^{12}\text{CH}_3^{12}\text{C}^{13}\text{CH}$ (I3) and its simulated spectrum (in blue), (c) the ν_1 band of $^{12}\text{CH}_3^{13}\text{C}^{12}\text{CH}$ (I2) and its simulated spectrum (in green), and (d) the ν_1 band of $^{13}\text{CH}_3^{12}\text{C}^{12}\text{CH}$ (I1) and its simulated spectrum (in red).

will be discussed in the next section. From previous studies, the calculated α^B are sufficiently accurate to estimate the rotational constant, B_v , of a given vibrational state to better than 0.01%.¹⁶ A similar agreement is seen for α_i^A , with the exception of α_1^A . The large o–c value for α_1^A is a result of perturbations, and is discussed in detail below.

Experimental Results. The cw-CRDS spectrum from 3305–3355 cm^{-1} (Figure 1a) is dominated by the ν_1 fundamental of I0, which is the parallel A_1 – A_1 transition with a Q-branch at 3335.0520 cm^{-1} . A closer look at the baseline shows that the region is actually a dense forest of weak rotational transitions, in which three additional A_1 – A_1 type transitions are clearly observed with rotational spacings of $\sim 0.28 \text{ cm}^{-1}$, consistent with propyne (Figure 1b–d).

Effective band origins and rotational constants for the upper states of each band are determined using the PGOPHER software,³⁷ and the standard unperturbed ro-vibrational Hamiltonian for a prolate symmetric top molecule, with the subband origins given by

$$\nu_{1,\text{subband}} = \nu_1 + (A - B)K^2 + BJ(J + 1) - D_J J^2(J + 1)^2 - D_{JK}J(J + 1)K^2 - D_K K^4 + (\text{higher order terms}) \quad (1)$$

where ν_1 is the band origin, A and B are the rotational constants, and D_J , D_{JK} , and D_K are the centrifugal distortion constants. Only transitions of the $K' = 0, 1$ and occasionally the $K' = 2$ subbands are observed, which consequently limits the perturbation analysis, as was demonstrated for the ν_1 fundamental band of I0.⁴ From the rotational profiles, the ro-vibrational transitions can be fit assuming a rotational temperature of 10 K and a Gaussian line width (FWHM) of 0.002 cm^{-1} .

Assignment of the energy levels is based on the band origin and rotational constant, B . The expected rotational constants are given by the general vibrational constant equations:

$$A_v = A_0 - \sum_i (v_i \alpha_i^A) \quad (2)$$

$$B_v = B_0 - \sum_i (v_i \alpha_i^B) \quad (3)$$

where B_0 is taken from the experimentally known ground state rotational constants (0.277300, 0.284942, and 0.276534 cm^{-1} , for I1, I2, and I3, respectively),²⁰ A_0 is taken from our VPT2 calculations, and α values are taken from Table 2.

Since a long-range Fermi resonance and a "double crossing" type perturbation are believed to affect the ν_1 state of the three isotopologues (I1–I3), similar to previous findings for I0, the K' subbands are initially fit separately. We use a least-squares analysis to determine tentative lower and upper state rotational constants, as well as the band origin. On the basis of these preliminary values, the bands are assigned to the ν_1 fundamental of I1 with a Q-branch at 3334.9720(4) cm^{-1} , the ν_1 fundamental of I2 with a Q-branch at 3325.0133(4) cm^{-1} , and the ν_1 fundamental of I3 with a Q-branch at 3318.6667(3) cm^{-1} .

A more rigorous analysis is performed by fixing the lower state constants to the respective ground state rotational constants known from microwave data for the three isotopologues,²⁰ and A_0 from our VPT2 calculations; again fitting the K' subbands separately. The resulting effective spectroscopic constants are given in Table 3, and confirm that the transitions belong to the same band despite the larger than expected K' spacing. The next step in the fitting routine is combining all K' -subbands in order to get an approximate value for A' ; the effective spectroscopic constants resulting from this overall fit are given in Table 4. The details of this latter fit are described below.

For I3, the Q-branch of the band at 3318.67 cm^{-1} is predominately obscured, and the band origin assignment relies on the observed Q1(1) and P- and R-branch transitions (Figure 1b). This band origin agrees with the band origin of the ν_1 fundamental band of I3 predicted by the VPT2 calculation. The band shows definite K structure throughout both the P- and R-branch, with the $K' = 1$ transitions consistently blueshifted by $\sim 0.03 \text{ cm}^{-1}$ relative to the $K' = 0$ transitions, and weak $K' = 2$

Table 3. Effective Spectroscopic Constants (in cm^{-1}) of Propyne Isotopologues for the Separate ν_1 K' -Subbands^a

K' -subband	subband origin	B'	$D'_J \times 10^6$	$H'_J \times 10^8$
¹³ CH ¹² C ¹² CH (I1) ^b				
0	3334.9718(4)	0.276 701(6)	0.5(3)	
1	3334.9731(5)	0.276 702(6)		
¹² CH ¹³ C ¹² CH (I2) ^b				
0	3325.0135(4)	0.284 240(6)	4.2(5)	2.4(5)
1	3324.9120(5)	0.284 246(10)	6(1)	6(2)
¹² CH ¹² C ¹³ CH (I3) ^b				
0	3318.6672(4)	0.275 894(8)		
1	3318.6951(4)	0.275 905(7)		

^aNumbers in parentheses are one standard deviation in units of the last significant digit. ^bGround state values are fixed to those of Dubrulle et al.²⁰ and A_0 is taken from our VPT2 calculations.

transitions red-shifted by $\sim 0.02 \text{ cm}^{-1}$ relative to the $K' = 1$ transitions (Figure 2a). A similar K' -subband ordering has been reported for the ν_1 fundamental of I0.^{4,21} A least-squares fit including all K -subbands, gives the rotational constants $B' = 0.275908(5) \text{ cm}^{-1}$ and $A' = 5.3466(1) \text{ cm}^{-1}$ (Table 4). The upper state B constant agrees with predicted $B_1 = 0.275943 \text{ cm}^{-1}$, confirming the assignment.

For I2, the full Q-branch of the band at 3325.01 cm^{-1} is clearly seen in the experimental spectrum (Figure 1c), and its band origin is consistent with the band origin of the ν_1 fundamental band of I2 predicted by the VPT2 calculation. Moreover, the intensity of the band is about half that of the ν_1 fundamental of I3, which is expected from the calculations. As with the I3 band, there is a large separation between the $K' = 0$ and 1 subbands, with the $K' = 1$ transitions red-shifted by 0.1 cm^{-1} relative to the $K' = 0$ transitions (Figure 2b). However, no $K' = 2$ transitions could be observed. A least-squares fit including both K -subbands, gives the rotational constants $B' = 0.284 270(10) \text{ cm}^{-1}$ and $A' = 5.2078(3) \text{ cm}^{-1}$ (Table 4). The low-resolution study had assigned this band as the $\nu_3 + 2\nu_9$ combination band, but while the predicted rotational constants are close ($B_1 = 0.284 292 \text{ cm}^{-1}$ and $B_{3+2\times 9} = 0.283 892 \text{ cm}^{-1}$), the o-c value assuming the band is ν_1 is an order of magnitude smaller compared to that assuming it is $\nu_3 + 2\nu_9$. This suggests that the band is in fact the I2 ν_1 fundamental.

For I1, the Q-branch of the band at 3334.97 cm^{-1} is almost entirely blended with the Q-branch of I0 (Figure 1d), but the Q1(1) and a sufficient number of P- and R-branch transitions are visible, allowing for accurate determination of the band origin. On the basis of the low-resolution study by Duncan et al.¹⁹ and the VPT2 calculations, this band can be assigned as the ν_1 fundamental of I1. Unlike with the previous two bands, at low- J'' ($J'' < 4$), no K structure can be observed (Figure 2c), but at higher J'' transitions the $K' = 0$ and $K' = 1$ transitions

begin to separate with the $K' = 0$ subband origin red-shifted relative to the $K' = 1$ subband origin. A least-squares fit of the two subbands together results in the rotational constants of $B' = 0.276 669(4) \text{ cm}^{-1}$ and $A' = 5.3094(7) \text{ cm}^{-1}$ (Table 4), which agree within their uncertainties with the VPT2 predicted values of $B_1 = 0.276 677 \text{ cm}^{-1}$ and $A_1 = 5.3092 \text{ cm}^{-1}$, fully in line with the assignment presented here.

While the observed band origins of all three ν_1 bands are consistent with those predicted by assuming a Fermi resonance with $\nu_3 + 2\nu_9$, no transitions belonging to the combination band for any of the isotopologues could be observed. In the case of I1 and I3, at natural abundances, based on the relative intensities of the ν_1 bands, the intensity of the $\nu_3 + 2\nu_9$ transitions is expected to be comparable to the baseline noise. Conversely, the $\nu_3 + 2\nu_9$ band of I2 could be detectable. However, it falls in a particularly congested portion of our experimental spectrum (around the ν_1 fundamental band origin of I0).

Perturbation Analysis. From the VPT2 calculations it is found that $A_1 \sim A_0$, as such at 10 K it is expected that almost no K structure is discernible, particularly at low- J'' . Given the good overall agreement between experimental and calculated α_i^B , the deviation between experimental and calculated α_i^A , and the unexpected K' -subband spacing, is likely a result of perturbations. In the case of I0, the inversion of the $K' = 0$ and 1 subband origins, and the larger than expected α_1^A (based on the $K' = 0$ and 1 subband transitions) were determined to be a result of anharmonic coupling of the ν_1 state with at least two z -axis Coriolis mixed ($A_1 + A_2$) states, one of which crosses the ν_1 state twice (i.e., a “double crossing” type perturbation).⁴

For I3, while B' agrees with that expected from the VPT2 calculations for ν_1 , A' differs by about 3 orders of magnitude, similar to that seen for ν_1 of I0.^{4,21} The inclusion of a Fermi resonance with $\nu_3 + 2\nu_9$ in the fit, does affect the overall position of the ν_1 band, but it does not resolve the large difference between the calculated and observed α^A . As determined for I0, the perturbations responsible for the observed K -subband perturbations in I3 likely result from a “double crossing” type perturbation, where the more prominent component of the “double crossing” intersects between the $K' = 0$ and 1 subbands, pushing the $K' = 1$ subband origin to the blue and the $K' = 0$ to the red.

Similar to I3, the experimental α^A of I2 differs by 4 orders of magnitude from the calculated value, and cannot be explained solely with the inclusion of a Fermi resonance with $\nu_3 + 2\nu_9$. This suggests that a similar perturbation as seen in the ν_1 fundamental of I0 and I3 affects the K' -subband order in the ν_1 fundamental of I2. However, the observed shift for I2 is significantly larger, and results in a K' -subband order reversed from that observed for I0 and I3. As such it is likely that the

Table 4. Effective Spectroscopic Constants (in cm^{-1}) of Propyne Isotopologues for the ν_1 Bands^a

mode	band origin	A'	B'	$D'_J \times 10^7$	$D'_{JK} \times 10^6$	$D'_K \times 10^3$	$H'_J \times 10^8$
¹³ CH ¹² C ¹² CH (I1)							
ν_1	3334.9720(4)	5.3094(7)	0.276 669(4)	20(6)	−6(1)		
¹² CH ¹³ C ¹² CH (I2)							
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 ¹² C ¹³ CH (I3)							
ν_1	3318.6667(3)	5.3466(1)	0.275 908(5)	1 ^c	1.0(3)	8.89(3)	

^aNumbers in parentheses are one standard deviation in units of the last significant digit. ^bGround state values are fixed to those of Dubrulle et al.,²⁰ and A_0 is taken from our VPT2 calculations. ^cFixed value

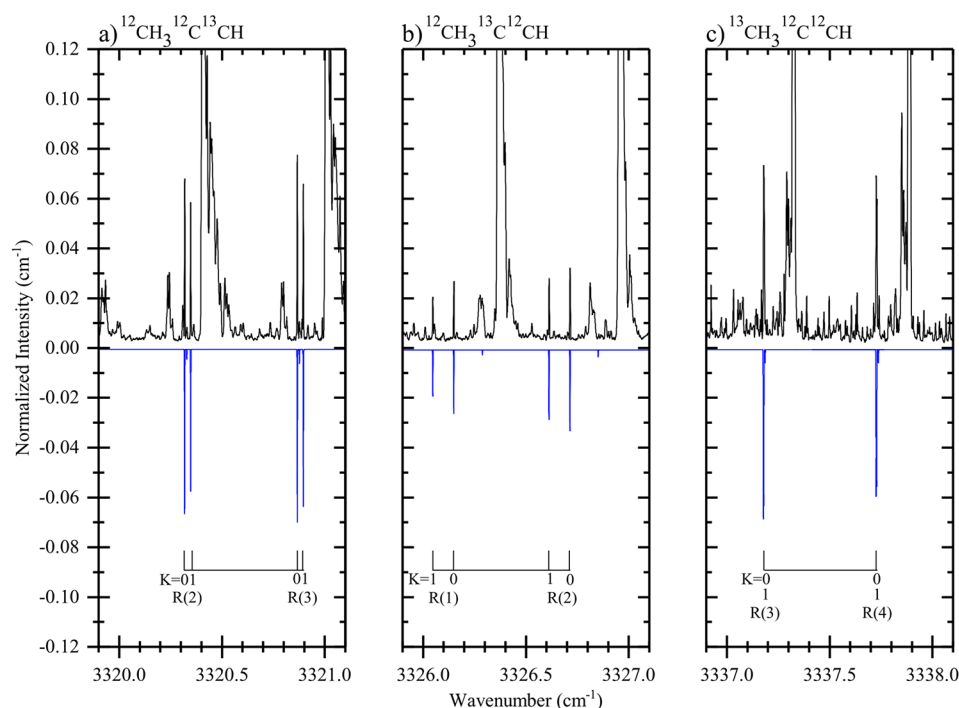


Figure 2. Experimental (in black) and simulated (in blue) spectra of (a) the R(2) and R(3) transitions of the ν_1 band of $^{12}\text{CH}_3^{12}\text{C}^{13}\text{CH}$ (I3), (b) the R(1) and R(2) transitions of the ν_1 band of $^{12}\text{CH}_3^{13}\text{C}^{12}\text{CH}$ (I2), and (c) the R(3) and R(4) transitions of the ν_1 band of $^{13}\text{CH}_3^{12}\text{C}^{12}\text{CH}$ (I1). The K structure in parts a and b is clearly perturbed, and that in part b shows a reverse in K -subband ordering compared to parts a and c. The same K -subband ordering is seen for all measured J values.

“double crossing” type perturbation intersects between the $K' = 1$ and 2 subbands, pushing the $K' = 1$ subband origin further to the red, resulting in a splitting larger than expected.

Interestingly, the ν_1 fundamental of I1 shows no sign of the “double crossing” type perturbation that is seen in the other isotopologues. However, in order to accurately reproduce the K splitting at $J'' \geq 4$, we had to use $D'_{JK} = -6 \times 10^{-5} \text{ cm}^{-1}$. The opposite sign of D_{JK} between the ground and excited state suggests that a perpendicular Coriolis interaction could also be involved, which is not seen in the ν_1 band of I0.⁴

For all of the bands, there is no noticeable perturbation in the J structure, which rules out close Fermi resonances or Coriolis interactions. Furthermore, the observed line shapes are clearly Gaussian, with no detectable Lorentzian character, which is expected for a prominent interaction with background states.⁷ As such, like the $1\nu_1$ state of I0, the $1\nu_1$ states of the monosubstituted ^{13}C propyne isotopologues do not seem to exhibit any effects due to IVR.

4. CONCLUSIONS

The jet-cooled spectrum of the ν_1 (acetylenic stretch) fundamental band and high level *ab initio* of all three monosubstituted ^{13}C propyne isotopologues is presented for the first time. The fundamental frequencies and spectroscopic constants determined here offer an accurate guide for spectroscopic searches of the ro-vibrational bands of monosubstituted ^{13}C propyne in either the laboratory or astronomical spectra.

The CCSD(T)/ANO1 VPT2 calculations predict small values for α^A for I1–I3, which could not be experimentally confirmed for two of the isotopologues (I2 and I3). All three isotopologues presented in this study show similar perturbations in the ν_1 fundamental, as seen for I0. Moreover, the

location of the ^{13}C in the $\text{C}-\text{C}\equiv\text{C}$ frame greatly influences the effects of these perturbations, with the strongest effects occurring when the ^{13}C is part of the triple bond. From the *ab initio* calculations, it is clear that the isotopic position heavily influences the impact of the long-range Fermi resonance with $\nu_3 + 2\nu_9$. In particular, since ν_1 , ν_3 , and ν_9 are all vibrations of the $\text{C}\equiv\text{C}$ bond, I0 and I1 are barely affected, but the ν_1 fundamental of I2, where the ^{13}C is on the middle C, loses about a third of its intensity to the dark state.

Even more drastic is the affect of the ^{13}C position on the “double crossing” type perturbation. As shown for the normal ^{13}C isotopologue, the value for α^A determined from the jet-cooled spectrum is not the deperturbed value, and a complete perturbation analysis requires room-temperature spectra where higher order K' -subbands can also be observed.⁴ Comparison of the observed $K' = 0$ and 1 spacing of I2 and I3 with that of I0, for which a complete perturbation analysis has been reported by Kerstel et al.,⁴ gives insight into the observed perturbations, and shows that in all except the I1 isotopologue a “double crossing” type perturbation is present, likely the result of an interaction with at least one other (A_1+A_2) pair state. Furthermore, from the $K' = 0$ and 1 band origin order we are able to conclude that while the crossing for I0 and I3 is between the $K' = 0$ and 1 subbands, for I2 the crossing is likely between the $K' = 1$ and 2 subbands. This is due to the fact that the $K' = 0$ and 1 band origin order for I2 is reversed compared to I0 and I3. Despite all the accurate info available from this work, it is not possible to identify the perturbing state. However, it is clear that the inclusion of the ^{13}C changes the energy spacing between ν_1 and the main perturbing state such that they are closest when the ^{13}C is on the middle or acetylenic C (I2 and I3, respectively), but when the ^{13}C is on the aliphatic C (I1) the two states are sufficiently separated that no

noticeable perturbation occurs. If the main perturber state was a vibrational state involving the acetylenic CH bond, then its frequency would shift similar to ν_1 upon ^{13}C addition, and there would not be the drastic difference in perturbations observed between the three isotopes. This hints that the ν_1 and the main perturbing state involve vibrations that occur at opposite ends of the carbon chain.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b10721.

Harmonic and anharmonic (VPT2) frequencies (in cm^{-1}) of $^{12}\text{CH}^{13}\text{C}^{13}\text{CH}$ (I4), observed line positions assigned to the ν_1 fundamental of each monosubstituted ^{13}C propyne isotopologue, and Fermi resonant contributors, where on the basis of known interactions in the components of the $\nu_3 + 2\nu_9$ combination band, nine states are considered when evaluating the Fermi interactions/perturbations of the ν_1 fundamental band (PDF)

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Notes

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