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Reinvestigation of the acetylenic C–H stretching fundamental of propyne via high resolution, optothermal infrared spectroscopy: Nonresonant perturbations to ν_1

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We present the high resolution spectrum of the ν_1 fundamental of propyne near 3335 cm^{-1} obtained using a very warm free jet expansion in our optothermal detection spectrometer. By using a high concentration sample expanded at low backing pressures we have been able to observe transitions for K values up to $K=6$. The additional data available allow us to reinvestigate this vibrational band. We find an unusual perturbation pattern in this band where the individual subbands (rovibrational transitions for a single K value) appear to be completely unperturbed at the level of precision of our data (7.5 MHz), but the subband origin orderings are perturbed through nonresonant interactions. Attempts to account for the subband ordering using a two-state anharmonic interaction are unsuccessful indicating that the perturbations are of multistate origin. This type of nonresonant perturbation to the subband origins of symmetric top molecules should be a common feature of symmetric tops with large A rotational constants. As a result of this investigation we conclude that the previously reported value of α^A , determined from a very cold expansion where only $K=0$ and $K=1$ were observed, is not a measure of the true (unperturbed) value of this constant. This conclusion is also supported by force field calculations presented here that use an empirical harmonic force field augmented by diagonal anharmonicities for the hydride stretches. These calculations, which reproduce measured values of α^A and α^B for lower energy bands quite successfully, also show that the previous determination of α^A is too large and must be dominated by perturbation contributions. We have also measured the weak Fermi resonant band $\nu_3 + 2\nu_9^0$ which acquires its intensity through interaction with ν_1 . Again we find an anomalous subband ordering like that observed in ν_1 .

I. INTRODUCTION

Molecular beam methods allow the measurement of fully resolved rovibrational spectra of relatively large polyatomics, permitting detailed investigations of the intramolecular dynamics of the vibrationally excited molecule. Vibrational and rotational cooling achieved in the free jet expansion provide great simplification of the spectrum due to the reduced numbers of populated ground state levels. For larger molecules, where the rotational constants are typically small (less than a wave number) this simplification is often necessary to fully resolve the rotational structure of the vibrational band. Recently there have been a number of studies of this type performed showing that these spectra are perturbed through very weak near-resonant couplings to the background vibrational states.¹ It is the study of these perturbations that provides information about the nature and rate of the intramolecular vibrational energy redistribution (IVR) process.

Here we report the reinvestigation of the acetylenic C–H stretch fundamental (ν_1) of propyne near 3335 cm^{-1} . The high resolution, molecular beam spectrum of propyne has been reported previously by McIlroy and Nesbitt.^{1(b)} However, due to the extreme rotational cooling only the

$K=0$ and $K=1$ states were observed, leading to the conclusion that ν_1 is unperturbed. Using very concentrated mixtures with weak expansion conditions, we have obtained a much warmer spectrum that includes up to $K=6$. The vibrational band shows an intriguing perturbation that affects only the K subband origins and not the J structure. Interestingly, $K=0$ and 1 are among the most perturbed subbands. This K subband origin perturbation appears in other symmetric top acetylenes that we have studied. In particular, a longer range perturbation is observed in the $2\nu_1$ band of propyne as well. The overtone spectrum also shows the weak J dependent coupling normally observed in large molecule spectra. The analysis of the near-resonant couplings in the first overtone are presented in a separate paper.² Here we focus on the nonresonant perturbations of the fundamental observed in the sparse spectrum of this small molecule.

II. EXPERIMENT

A detailed description of our spectrometer has been given previously.^{1(d),1(e)} Briefly, the output of a Burleigh FCL 20 color center laser makes about 50 crosses of a collimated cw molecular beam as it passes through a plane-parallel multipass. Downstream from the laser crossing region the molecular beam impinges on a semiconducting bolometer. When the laser is resonant with a rovibrational transition the bolometer measures an increase in the thermal content of the molecular beam.³

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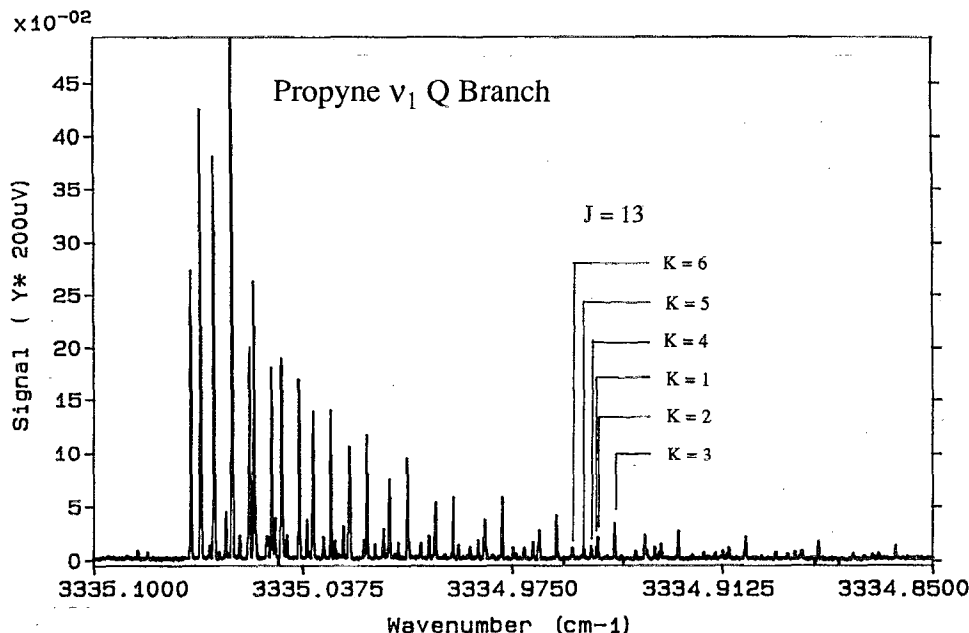


FIG. 1. The Q branch of the acetylenic C–H stretch fundamental of propyne is shown for J values up to $J=17$. The K structure is labeled for $J=13$. This pattern repeats for each J value in the Q branch. The spectrum is obtained using weak expansions of rather concentrated mixtures (10% propyne in He). The rotational temperature is about 50 K. The highest ground state observed in the Q branch ($J=21$, $K=6$) has a ground state energy of about 300 cm^{-1} . For especially strong spectra that are not too congested it is advantageous to use warm expansions so that a larger number of transitions can be measured.

The spectrum of propyne was obtained with slightly different expansion conditions than normally used. The mixtures used are much richer in propyne so that the rotational temperature can be raised from the typically very cold (5–10 K) values observed in more dilute samples. The molecular beam was formed by expanding a 10% mixture of propyne in He with a backing pressure of 3 atm through a $30\text{ }\mu\text{m}$ nozzle. The resulting rotational temperature for propyne is between 30–50 K. Using this rich mixture poses no problems in assigning the spectrum. The identity of the lines belonging to the fundamental is unambiguously determined by precise ground state combination differences ($\sigma=7.5\text{ MHz}$), thus ruling out transitions due to hot bands or clusters. The standard deviation of our combination differences is about a factor of 2 higher than we normally achieve.^{1(d)} This increase is most likely due to the fact that there were two water absorptions that caused gaps in the calibration etalon signal. The spectrum was pieced together across these regions using ground state combination differences.

III. RESULTS

The Q branch of the acetylenic C–H stretch fundamental is shown in Fig. 1. The Q branch has been assigned for $K=1$ –6 and for $J=1$ –21. The highest ground state level for which a transition is observed has an energy of 300 cm^{-1} demonstrating the high temperature of the expansion. All lines in the Q branch region shown can be assigned to ν_1 with the exception of the two small lines slightly to the blue of the origin of the Q branch. These lines are most likely due to the hot band transition out of ν_{10} (band origin 1.71

cm^{-1} to the red of ν_1) or possibly arise from a ^{13}C isotopomer. The first line in the Q branch is not the strongest due to saturation of the transition.

The $R(7)$ transition is shown in a more expanded scale in Fig. 2. This shows the position of the $K=0$ lines relative to those of higher K . The $K=1$ and $K=2$ lines are observed at nearly the same frequency. The separation of the $K=1$ and $K=2$ lines in $R(7)$ is mainly due to the D_{JK} term and so the splitting increases with J . The pattern observed for the different K transitions is preserved for each value of J .

The spectrum is first analyzed for each different K subband. The line positions are fit to the rigid rovibrator form

$$\nu = [\nu_{\text{subband}} + B'_{\text{eff}} J'(J'+1) + D_J J'^2(J'+1)^2] - [B''_{\text{eff}} J''(J''+1) + D_J J''^2(J''+1)^2]. \quad (1)$$

In this expression D_J is held at the reported ground state value⁴ in both the ground and excited state. The B_{eff} term includes D_{JK} ,

$$B_{\text{eff}} = B - D_{JK}K^2. \quad (2)$$

The ground state values, B'' and D''_{JK} , are also held fixed to the microwave determined values.⁴ The results for the subband origins and B'_{eff} values for $K=0$ –6 are given in Table I. The increase in B'_{eff} can be entirely accounted for by the effect of D_{JK} , as shown by the calculated values in Table I. The D'_{JK} value obtained is in good agreement with the ground state value.

Recently we have measured the $J=0 \rightarrow 1$ microwave transition in both the ground and ν_1 fundamental excited states of propyne by the method of infrared (IR)–

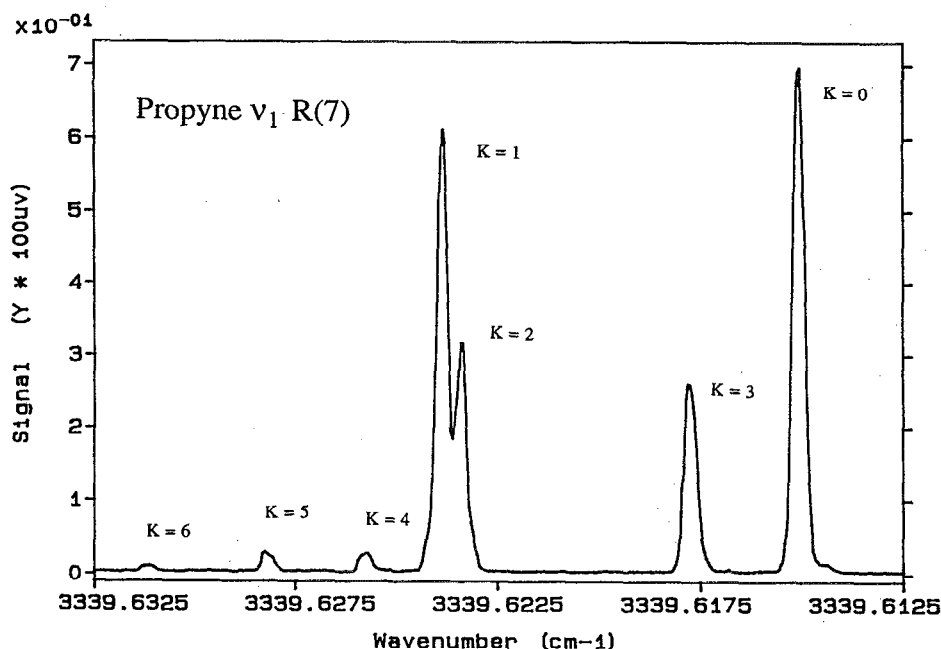


FIG. 2. The $R(7)$ transition of v_1 propyne is shown in detail. The K structure is obviously perturbed. This K subband ordering is observed for all measured J values. The splitting of the $K=1$ and $K=2$ transitions observed in $R(7)$ is not evident at lower J values. The shifting of these transitions appears to be due solely to D_{JK} .

microwave double resonance. These measurements yield the determination $-\Delta B = \alpha_1^B = 6.728(6) \times 10^{-4} \text{ cm}^{-1}$. This value is within the 2σ error estimate from the fit to the IR data, and shows that the upper state rotational constants predict the separation of these two rotational levels to an accuracy on the order of 200 kHz, demonstrating the regularity of the J rotational structure.

Although the rotational constants for the K subbands show no evidence of perturbation the subband origins show strong evidence of perturbation as can be seen by the results in Table I. The subband origins for an unperturbed parallel band of a symmetric top molecule should be monotonically spaced as $(\Delta A - \Delta B)K^2$ from the true band ori-

gin.⁵ We have previously observed anomalous K subband orderings in CF_3CCH .⁶ There we were able to deperturb the spectrum by considering a single anharmonically coupled state. However, in the case of CF_3CCH the perturber was very close in energy and only weakly coupled, permitting us to observe both components of the perturbation. In the present case of propyne we cannot identify the presence of the perturbing state (or states) as demonstrated by the lack of unassigned transitions in the full Q branch region of Fig. 1. The strength of the only unassigned lines in the spectrum establishes that the intensity of the perturber (or perturbors) cannot be more than 1% of the strongest observed transitions.

TABLE I. Spectroscopic constants for propyne v_1 .

B_1'	0.284 394 9(40) cm^{-1}		
α_1^B	0.000 665(4) cm^{-1}		
D_{JK}'	$5.424(6) \times 10^{-6} \text{ cm}^{-1}$		
K subband	Subband origin ^a (cm^{-1})	B_{eff}' (cm^{-1})	$B_{\text{eff}}'(\text{calc})^c$ (cm^{-1})
0	3 335.059 40(20)	0.284 394 1(44)	0.284 394 9 —(08)
1	3 335.068 03(22)	0.284 390 9(49)	0.284 389 5 +(14)
2	3 335.067 75(26)	0.284 375 2(54)	0.284 373 3 +(19)
3	3 335.062 51(30)	0.284 348 4(60)	0.284 346 2 +(22)
4	3 335.069 73(20)	0.284 304 3(42)	0.284 308 3 —(40)
5	3 335.072 25(71)	0.284 255 3(130)	0.284 259 6 —(43)
6	3 335.075 07(117)	0.284 203 7(193)	0.284 200 4 +(36)

All reported errors are 2σ in the last digits.

^aThe $K=0$ subband origin is fixed to the value reported by McIlroy and Nesbitt.

^b $B_{\text{eff}}' = B_1' - D_{JK}'K^2$.

^cCalculated values use the given values of B_1' and D_{JK}' . The (observed—calculated) value is given for the error in the last digits and can be compared to the 2σ errors reported for B_{eff}' .

IV. DISCUSSION

In what follows we attempt to deperturb the spectrum by carefully considering the vibrational couplings that can occur in C_{3v} symmetric top molecules. However, the deperturbation is hindered by the fact that we cannot identify the perturbations in the spectrum. This leads to correlations in the fits that result in rather large uncertainties in the parameters. Even with these uncertainties there are large questions on the physical reality of the size of some of these parameters. In order to check their validity, calculations of the spectroscopic parameters are performed from an empirical force field. The results show that, even for this very small molecule, the coupling process, which eventually leads to irreversible IVR in larger systems, is multistate and complex.

Propyne is a relatively small molecule. The full density of background states (all symmetries) at 3335 cm^{-1} is only about 2 states/ cm^{-1} .⁷ Since there are no A_2 modes in this C_{3v} molecule, A_2 states arise only from multiple excitations in the E symmetry degenerate modes and only come paired with an A_1 state. States that differ only in the direction (sign) of all the vibrational angular momenta (l_i) will have the same average energy. When the total vibrational angular momentum is $3N \pm 1$, these states form the two components of an E vibrational state. When the total vibrational angular momentum is $3N$, we expect a nearly degenerate A_1, A_2 pair. A_1 states, without a companion A_2 state, only arise from states that have zero vibrational angular momentum in each of the E modes.⁸

For nonrotating molecules, ν_1 can only couple, via anharmonic interactions, with other vibrational states of A_1 symmetry, which represent about one sixth of the total density of vibrational states.⁹ When the molecule rotates around the z -axis (the symmetry axis), Coriolis couplings can occur which mix A_1 and A_2 states.¹⁰ Because there are no A_2 modes, the z -axis Coriolis interaction only couples states arising from combination and overtone bands of E mode. Thus, ν_1 and $2\nu_1$ cannot Coriolis couple to A_2 states except to the extent the vibrational state has, via anharmonic interactions, a small mixture of a state with excitation in E modes. However, the two states that are in an $A_1 + A_2$ pair will exhibit a z -axis Coriolis interaction for $K > 0$. The coupling matrix element is given by $Ak\Sigma\xi l_i$, where A is the rotational constant and k the signed value for K .¹⁰ Given the large value for the A rotational constant, and the small splitting expected for the typical pair of $A_1 + A_2$ states, this will strongly mix the states allowing the ν_1 state to couple via anharmonic interactions to twice as many states. Further, the near resonant background states will tune very rapidly as a function of K .

Perpendicular (x, y axis) Coriolis interactions can couple the acetylenic C–H stretch to the manifold of E states.¹⁰ Such interactions will triple the density of available states for coupling to ν_1 . The fact that each individual K subband has an unperturbed J structure, with D'_{JK} close to D''_{JK} , rules out the possibility that we are observing perpendicular Coriolis coupling effects. The perpendicular Coriolis coupling is given by¹⁰

$$W_{\text{int}} = W_{\text{cor}}[J(J+1) \pm K(K \pm 1)]^{1/2}. \quad (3)$$

The lack of perturbation to the Q branch even at very high J values (out to $J=20$) indicates that the perpendicular Coriolis prefactor, W_{cor} , must be quite small. As discussed below, it is possible to put a lower limit on the interaction strength of the perturbing states. This lower limit, $\sim 0.1\text{ cm}^{-1}$ at the lowest J values, is much too large to go undetected in the high J region of the Q branch if an interaction according to Eq. (3) were operating. Perpendicular Coriolis couplings are ruled out as the cause of the K subband perturbations we observe. The lack of strong perpendicular Coriolis couplings is consistent with the results on a number of other terminal acetylenes.^{11–13}

The perturbation(s) responsible for the observed K subband perturbations must result from the anharmonic coupling between the A_1 and z -axis Coriolis mixed $A_1 + A_2$ pairs. A coupling to a single A_1 (all $l_i=0$ or no degenerate modes excited) state that does not occur in an $A_1 + A_2$ pair cannot explain the data. As discussed below, two crossings of ν_1 by the perturbing state are required to reproduce the subband ordering. This cannot be achieved unless the parallel Coriolis interaction is present. Couplings of A_1 vibrational states of propyne to these $A_1 + A_2$ pairs has been observed previously in the studies of Henfrey and Thrush of lower energy states.^{14–16} The discussion for ν_1 presented here is similar to these previous studies.

Due to the low density of states ($A_1 + A_2$ states have a density of about $0.7\text{ states/cm}^{-1}$) we attempted to account for the observed subband origins with coupling to a single $A_1 + A_2$ pair. Such a model accounted for a similarly perturbed K band structure in ν_1 of CF_3CCH .⁶ Before discussing our fits it would be helpful to determine which K subbands are most perturbed. In the previous report of McIlroy and Nesbitt the value of α^A was determined from the $K=0/K=1$ splitting to be -0.00879 cm^{-1} .^{1(b)} This value is an order of magnitude larger than α^B for ν_1 . Physically it is expected that the excitation of the C–H stretch along the symmetry axis will have a larger effect on α^B than α^A and this is found for CF_3CCH .⁶ This is confirmed with an estimate for α^A derived from a simple model force field (see below). Furthermore, such a large α^A value for propyne would allow K resolution even in the bulb spectrum and this is not observed.¹⁷ However, supporting the value of McIlroy and Nesbitt is the fact that the $K=0/K=1$ splitting in the overtone is nearly twice that of the fundamental.² Assuming this α^A value means that the higher K subbands are increasingly more perturbed. Our observation of the higher subband origins, however, suggests that the lower K subbands are most perturbed since for $K > 3$ the origins have the expected order and begin to show the “correct” relative spacings.

We will now evaluate whether a single perturbing state, with reasonable parameters, can explain the observed subband perturbations. For ν_1 the unperturbed subband origins ($J=0$) are given by

$$\nu_1 \text{ subbands} = \nu_1 + (A_1 - B_1)K^2. \quad (4)$$

TABLE II. Propyne ν_1 subband origin fits assuming an anharmonic interaction with an A_1+A_2 state pair.

Parameter	Model I (cm^{-1})	Model II (cm^{-1})
ν_1	3 335.066 47	3 335.065 90(6)
$\Delta A_1 - \Delta B_1$	0.000 239(33)	0.000 255(2)
$\delta\nu$	$142(20) \times W_{\text{anh}}^2$	$4\,310(1\,428) \times W_{\text{anh}}^2$
$(\delta A - \delta B)$	$287(180) \times W_{\text{anh}}^2$	$839(140) \times W_{\text{anh}}^2$
$A\zeta_{\text{eff}}$	$-881(539) \times W_{\text{anh}}^2$	$-3\,667(775) \times W_{\text{anh}}^2$
$\Delta\nu$...	$-8\,311(2\,800) \times W_{\text{anh}}^2$
K subband	$(\text{Obs} - \text{Calc}) \times 10^4 \text{ cm}^{-1}$	$(\text{Obs} - \text{Calc}) \times 10^4 \text{ cm}^{-1}$
0	-0.1	0.0
1	+6.0	0.0
2	-5.9	0.0
3	+0.1	0.0
4	-0.9	-0.2
5	0.0	+0.4
6	+0.9	-0.2

For an A_1+A_2 pair in the background density of states that interacts through a z -axis Coriolis interaction the subbands are

$$\nu_{A_1+A_2 \text{ subbands}} = \nu_b + (A_b - B_b)K^2 \pm A_b \zeta_{\text{eff}} K. \quad (5)$$

The last term in Eq. (5) is due to the Coriolis interaction and ζ_{eff} is

$$\zeta_{\text{eff}} = 2 \sum \zeta_i I_i. \quad (6)$$

We have neglected any splitting of the A_1+A_2 origins. Of particular interest when considering perturbations that tune relative to each other is the energy difference between the two states. For the K subbands this is

$$\Delta E_{\pm} = \delta\nu + (\delta A - \delta B)K^2 \pm A\zeta_{\text{eff}}K. \quad (7)$$

In Eq. (7) the symbol δ denotes the difference in the spectroscopic constants of the two interacting states. For example δA is simply the sum over the different α^A terms of the two states. When these two states are anharmonically coupled the positions of the K subbands can be found from

$$\nu[K] = \nu_1 + (\Delta A_1 - \Delta B_1)K^2 + (W_{\text{anh}}^2/2\Delta E_+) + (W_{\text{anh}}^2/2\Delta E_-), \quad (8)$$

with ΔE_+ being the upper state resulting from the parallel Coriolis interaction between the A_1+A_2 pair. The rotational terms ΔA_1 and ΔB_1 are the difference of the rotational constants of ν_1 and the ground state. Assumed in Eq. (8) is that second order perturbation theory is valid and this is insured by the failure to observe the perturbing states which requires that the extent of mixing be small.

In Table II the results for a fit of the observed subband origins to Eq. (8) are given. In this formula there is an exact correlation between ΔE and W_{anh}^2 , thus without observing a perturbing state we can only determine $\delta\nu$, $(\delta A - \delta B)$, and ζ_{eff} up to a factor of W_{anh}^2 , the anharmonic matrix element between the two states. The second fit presented in Table II adds an additional parameter that allows for a splitting of the A_1+A_2 pair at $K=0$ also. This can

TABLE III. Spectroscopic data for propyne ν_1 . Experimental and calculated values.

Mode	ω_e (cm^{-1}) ^a	α^B (cm^{-1}) ^a	α^A (cm^{-1})	ζ
(a) Experimental values				
ν_1 (A_1)	3467	0.000 665	...	
ν_2 (A_1)	3058	-0.000 084	0.038(5) ^b	
ν_3 (A_1)	2138	0.001 510	0.006 6(2) ^c	
ν_4 (A_1)	1429	0.000 40	...	
ν_5 (A_1)	930	0.001 260	0.007 572(8) ^d	
ν_6 (E)	3038	0.000 026	0.017 ^e	0.049 ^c
ν_7 (E)	1492	-0.000 26	0.042 89(3) ^f	-0.314 39(2) ^f
ν_8 (E)	1044	0.000 141	-0.061 8(1) ^c	0.399 7 ^b
ν_9 (E)	658	-0.000 18	0.001 353(3) ^g	0.996 89 ^g
ν_{10} (E)	328	-0.000 78	0.002 170(4) ^h	0.891 74 ^h
(b) Calculated values				
ν_1 (A_1)	3517	0.000 623	0.000 002	
ν_2 (A_1)	2918	0.000 306	0.067 5	
ν_3 (A_1)	2155	0.001 442	0.001 6	
ν_4 (A_1)	1358	0.000 923	0.000 22	
ν_5 (A_1)	928	0.000 964	0.006 4	
ν_6 (E)	3013	0.000 308	0.050 6	0.060 5
ν_7 (E)	1462	-0.000 649	0.018 0	-0.296 5
ν_8 (E)	1048	-0.000 013	-0.030 3	0.377 7
ν_9 (E)	638	-0.000 489	0.000 009	1.000 0
ν_{10} (E)	327	-0.001 076	0.003 6	0.887 0

^aReferences 1(b) and 1(c).

^bReference 20.

^cReference 16.

^dReference 25.

^eReference 17.

^fReference 14.

^gReference 26.

^hReference 27.

result from a direct coupling⁶ or from different long range anharmonic couplings of the A_1 and A_2 states to other background states.⁵ We note that the first model (degenerate at $K=0$) fits seven subbands to five parameters. In this fit ζ_{eff} and $(\delta A - \delta B)$ have a correlation of >0.9999 . For the second model, where an additional constant is included, there are numerous strong correlations between the parameters.

In the first fitting model the $K=1$ and $K=2$ subband origins are not very well fit; the residual is about three times the uncertainty in the $\nu_0(K)$ determined by the fits to the individual subbands. The second model with its additional parameter fits the data quite well, as expected. At this point the reasonableness of the fit parameters can be considered by examining the fit results with respect to the spectroscopic constants of propyne.

In order to explain the trend of the subband origins it is necessary that one of the two A_1+A_2 states crosses the ν_1 state twice. The first crossing must occur between $K=0$ and $K=1$ and come from higher energy. This crossing will push the $K=1$ subband origin to the blue and the $K=0$ origin to the red resulting in a large $K=0/K=1$ splitting, as observed in the spectrum. The state must then turn back to the blue and recross between $K=2$ and $K=3$, but closer to $K=3$. This second crossing will push the $K=3$ subband origin to the red as required. Such double crossings are possible for symmetric top molecules due to the addition of

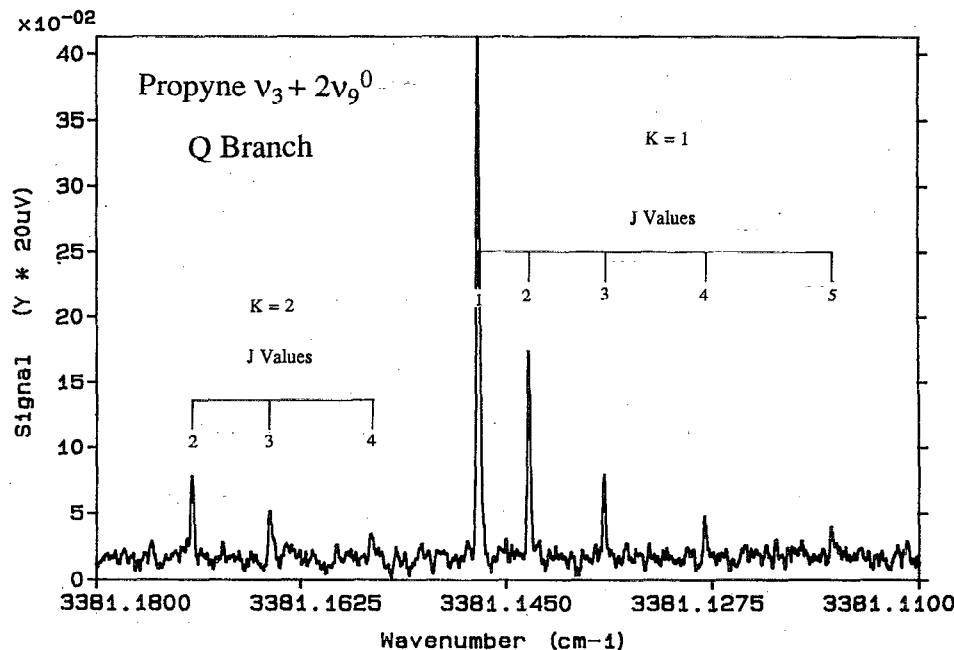


FIG. 3. The Q branch of $\nu_3 + 2\nu_9^0$, which acquires its intensity due to anharmonic resonance with ν_1 , is presented. The frequencies are only approximate and were determined from the laser grating drive reading ($\pm 1 \text{ cm}^{-1}$). Measurement of the R branch and P branch (up to $J' = 6$) shows that the $K = 0$ transitions fall at the same frequency as the $K = 1$ transitions, to within our experimental resolution (8 MHz). As observed for ν_1 , the K subband positions are perturbed by nonresonant interactions.

the parallel Coriolis term in Eq. (5). This behavior has been observed in the CF_3CCH fundamental.⁶ The fit to the first model represents this interaction scheme.

Already the fit to the first model cannot calculate the spectrum to the precision of the data. Further the parameters are unphysically large. Since the perturber is not observed in the spectrum at the 1% level, a lower limit to the anharmonic matrix element can be found. The closest approach of the perturber to a strong line occurs at $K = 0$ where the perturber is $(142 \text{ cm} \times W_{\text{anh}}^2)$ away. This would produce a relative intensity of the $K = 0$ lines of the perturber of $(142 \text{ cm} \times W_{\text{anh}})^{-2}$. Based on the signal to noise of the $K = 0$ lines we estimate that this intensity must be $< 1\%$, implying that $W_{\text{anh}} > 0.07 \text{ cm}^{-1}$. Using this value in the results given in Table II the value of $\delta(A - B)$ must be $> 1 \text{ cm}^{-1}$. This value must be made entirely from α^A and α^B terms. Table III contains a compilation of the experimental values for the spectroscopic constants. Based upon these constants, no state calculated within 100 cm^{-1} of ν_1 gives a $\delta(A - B)$ value $> 0.1 \text{ cm}^{-1}$. This failure of the model is easily seen by reference to Eq. (7) for the energy difference between ν_1 and the perturber. A crossing near $K = 1$ and a recrossing near $K = 3$, as required by this model, means that $4\delta(A - B)$ must be about equal to $A\xi_{\text{eff}}$. The ξ_i values are mostly near unity for propyne and A is very large ($A_0 = 5.308 \text{ cm}^{-1}$).⁴ Obviously the α values will not easily be able to add up to the A rotational constant.

A similar assessment of the second model, which allows a splitting of the $A_1 + A_2$ pair, leads to a similar conclusion. Again the closest approach to a strong line occurs at $K = 0$ which is $(152 \times W_{\text{anh}}^2)$ away, so $W_{\text{anh}} > 0.07 \text{ cm}^{-1}$. This time $\delta(A - B)$ must be $> 2 \text{ cm}^{-1}$. We conclude that

the interaction with a single $A_1 + A_2$ pair cannot explain the propyne ν_1 spectrum; the ν_1 state is perturbed by more than one state. Assuming that this perturbation is strongest at low K , as supported by the more regular spacing of the higher K subband origins, we can put a model independent lower limit on the couplings. The $K = 1$ subband origin is blue shifted by about 0.008 cm^{-1} . The fact that the perturbation is not observed at the 1% level for $K = 1$ means that $W_{\text{anh}} > 0.08 \text{ cm}^{-1}$.

The second model was quite successful at calculating the subband origins, albeit using a model of six parameters for seven observations. Still the fact that the ν_1 state must be perturbed by more than one state is suggested by the fit results. The added parameter, $\Delta\nu$, that gives the splitting between the $A_1 + A_2$ pair at $K = 0$ is actually larger than $\delta\nu$, the energy separation between ν_1 and the unperturbed origin of the $A_1 + A_2$ pair. The model requires one state approaching from above and crossing and another state approaching from below and crossing at a different K value, i.e., two states perturbing ν_1 ! The conclusion that more than one state is coupled for propyne is consistent with the careful analysis by Henfrey and Thrush of some lower frequency bands of propyne.¹⁴⁻¹⁶ These papers provide beautiful illustrations of the disrupting effects of $A_1 + A_2$ pairs on the K subbands of C_3O , symmetric tops. Molecules with large A values, like propyne, are especially susceptible to many state, nonresonant perturbations at different K values as the parallel Coriolis interacting $A_1 + A_2$ pairs tune through a state. For example, we have recently measured the ν_1 and $2\nu_1$ spectra of $\text{CD}_3\text{C}\equiv\text{CH}$ and find the same type of nonresonant perturbations to the K subband order-

ing. Further analysis of these spectra will be presented in a future publication.¹⁸

We have also measured the spectrum of the $\nu_3 + 2\nu_2$ parallel band near 3381 cm^{-1} . This band is an A_1 only state, all $l_i = 0$.¹⁹ This state is involved in a very long range, nonresonant anharmonic interaction with ν_1 . It is coupled to ν_1 with a 7 cm^{-1} anharmonic matrix element which gives it $\sim 2\%$ of the intensity of ν_1 .¹⁹ Accordingly, we have run the spectrum with a more dilute sample at higher stagnation pressures (5% propyne in He expanded at 6 atm) to achieve higher signal to noise in a colder beam. We observe transitions for $K=0, 1$, and 2. The Q branch is shown in Fig. 3. Again we find a perturbed K subband ordering without a J dependence due to nonresonant couplings to $A_1 + A_2$ pairs. The $K=0$ and $K=1$ subband origins are at the same frequency, based on the spectra from the R branch, with the $K=2$ subband origin lying 0.32 cm^{-1} to the blue. All three subbands have the same α^B value of $0.001\,08(2)\text{ cm}^{-1}$. The calculated value from Table III is $0.001\,15\text{ cm}^{-1}$ and is in very good agreement with the experimental value showing that the subbands are not perturbed for low J .

Apparently the ν_2 band of propyne, the symmetric methyl C-H stretch, also exhibits this nonresonant coupling. McIlroy and Nesbitt have determined an α^A of -0.055 cm^{-1} based on the $K=0/K=1$ splitting.^{1(b)} Physically it is expected that the symmetric C-H stretch will *decrease* the A rotational constant, not increase it as observed. The gas phase bulb spectrum of Thomas and Thompson, which includes the Q branch positions of the K subbands as high as $K=10$, supports this physical picture; the measured α^A is $+0.038\text{ cm}^{-1}$.²⁰ Force field calculations, presented below, also support a positive value for α^A with a calculated value of $+0.07\text{ cm}^{-1}$. The study of Henfrey and Thrush on ν_3 also reveals the same nonresonant K subband perturbation due to $A_1 + A_2$ pairs.¹⁶ The four A_1 , all $l_i = 0$, bands in the near infrared (from 2000 to 4000 cm^{-1}) exhibit this type of perturbation! As the energy increases, for example in $2\nu_1$, this type of perturbation is expected to be present and probably even more complex due to the increasing density of states.

V. FORCE FIELD CALCULATIONS

From the above discussion it is clear that it would be extremely helpful to have reasonable estimates for the size of vibration-rotation interaction constants in order to check the reasonableness of various perturbation schemes. These terms are related to the cubic anharmonic force field, and anharmonic force constants are known for only a handful of molecules. Traditionally, anharmonic force field calculations have been tedious and only done on relatively small molecules. Recently, Handy's group has developed a powerful program SPECTRO that evaluates via the perturbation theory expressions all the traditional spectroscopic constants that depend on the cubic and quartic force field.²¹ This program coupled with high quality *ab initio* force fields has recently had success in interpreting (and in some cases reinterpreting) experimental data for small molecules.²² Here we present the calculation of vibration-

rotation constants of propyne using a very simple force field. The agreement with experimental values is very encouraging, and suggests that this program can be used to flag constants that are badly contaminated by resonance contributions.

The force field we have used is based upon the empirical harmonic force field for propyne due to Duncan, McKean, and Nivellini.¹⁹ We use these harmonic force constants for the curvilinear internal coordinates. We add cubic and quartic diagonal force constants along the CH stretching modes, with values determined by the typical Morse parameters for methyl and acetylenic CH stretches.²³ The nonlinear transformation from curvilinear to rectilinear coordinates introduces many additional anharmonic terms in the rectilinear force field (which is used in the traditional perturbation theory expressions).²⁴

The calculated values of the vibration-rotational constants are also given in Table III. The agreement is respectable considering the simple force field used, generally within a factor of two for the α 's. The only values not well calculated are the smaller α 's, for example α_6^B and α_8^B . The errors here probably reflect the neglect of other sources of anharmonicity. We find that for the largest α 's this force field provides an adequate estimate. These results are very encouraging for the use of SPECTRO to help assign perturbations in other medium size molecules. For example, in our analysis of the CF_3CCH fundamental the rotational constants of a few perturbers were well determined in the deperturbation.⁶ However, a lack of experimental data prevented us from using this information in making assignments. Empirical force fields and SPECTRO may be a simple and accurate way of estimating this crucial information.

The SPECTRO results indicate that α_1^A for propyne should indeed be much smaller than α_1^B . The fact that α_1^B is very accurately calculated further supports this reduced α_1^A value. Assuming a small α_1^A value means that the low K subbands ($K=1-3$) are most affected by the perturbation. In fact, the $K=5-6$ subband energy difference provides an α_1^A of $-0.000\,41\text{ cm}^{-1}$, more in keeping with the SPECTRO results. We conclude that the $K=0/K=1$ splitting is strongly affected by the perturbation and does not provide the α^A value for ν_1 propyne. The fact that the $K=0-1$ splitting in $2\nu_1$ is nearly twice that of ν_1 must be accidental.

VI. CONCLUSIONS

The reinvestigation of the ν_1 spectrum of propyne using very warm molecular beam expansions and optothermal detection has shown that the $K=0/K=1$ spacing is artificially large due to a long range perturbation. The value for α_1^A reported previously by McIlroy and Nesbitt^{1(b)} based only on this splitting does not represent the unperturbed α^A value for this mode. This conclusion is supported by the experimental data which shows that the higher K subbands are spaced much more closely than predicted by the α^A based on the $K=0/K=1$ spacing. The further analysis of the spectrum is possible due to the increased information in the warmer spectrum. In general, thermal conditions in molecular beam spectra should be

chosen so that the largest number of transitions can be measured with sufficient signal to noise and without excessive spectral congestion.

Our conclusion is further supported by calculations of the rotational constants of propyne. The constants were calculated with using an empirical force field by the SPECTRO program developed by Handy's group.²¹ The good agreement between the calculated and measured values for the vibration-rotational constants of propyne indicate that this approach can be used on other molecules where a reasonable harmonic force field is known or can be estimated. The calculated value of α^4 is very small value, in agreement with our experimental observation.

Attempts to explain the K subband orderings in ν_1 propyne by an interaction with a single state were not successful. We conclude that at least two states perturb the spectrum. These interactions involve coupling matrix elements of greater than about 0.1 cm^{-1} . The mixing of these states is nonresonant in nature; the perturbing states are not observed at the 1% level in the spectrum. This nonresonant interaction which perturbs the K subband structure states will operate in all symmetric tops. It is especially important for molecules with large A values where the Coriolis term can provide many wavenumbers of tuning as a function of K .

When the spectrum of a medium-large molecule gets more complex due to an increase in the density of background states, as occurs in the overtone of propyne, the large number of very weak and local perturbations that are resonant dominate the appearance of the spectrum. The weak couplings provide insight into the vibrational energy redistribution process. However, in interpretations of the IVR process the nonresonant interactions observed in the propyne ν_1 fundamental must be considered as well.

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