Overtone spectra of C–H oscillators in cold molecules

M. W. Crofton[a] and C. G. Stevens
Lawrence Livermore National Laboratory, Livermore, California 94550
D. Klenerman,[b] J. H. Gutow, and R. N. Zare
Department of Chemistry, Stanford University, Stanford, California 94305

(Received 21 July 1988; accepted 8 September 1988)

The C–H stretch overtone spectra of methane (5–0), ethylene (5–0 and 6–0), ethane (5–0 and 6–0), propyne (4–0 and 5–0 acetylenic and 5–0 methyl C–H stretches), allene (5–0), propane (5–0 and 6–0), cyclopropane (5–0 and 6–0), dimethyl ether (5–0), and isobutane (5–0) have been recorded at temperatures between 143 and 189 K, depending on the molecule. A comparison is made to the spectra obtained at room temperature, with the goal of improved understanding of the band shapes. The temperature dependence of most of the observed bands is found to be significantly less than that expected for "simple" bands. For these small to medium size hydrocarbons, the temperature independence of the overtone bands is found to correlate loosely with the density of states and with the degree of saturation. Other factors are important determinants of spectral widths and temperature independence as well, such as conformational inequivalence of the C–H oscillators, and the number and positions of the oscillators. It is concluded that the vast majority of hydrocarbon C–H stretch high overtone bands have upper states which are extensively mixed with other states. This is the case even for most of the relatively small hydrocarbons. This mixing produces a broadening effect and greatly increases the transition density, thereby diluting the oscillator strength of the rovibrational transitions from that of the zero-order approximation. The Fermi resonance type of interaction appears to be of greater importance than the Coriolis type in determining the appearance of the high overtone bands.

INTRODUCTION

The concept of a local mode has grown out of studies of the overtone spectra of C–H oscillators at room temperature.[1,2] This is based on the simple picture that the high frequency C–H oscillators are largely uncoupled from the other vibrational modes of the molecule. However, closer inspection of the C–H overtone bands reveals less structure, in many cases, than one might expect from an uncoupled oscillator. Moreover, the widths (up to 300 cm^{-1}) are often surprisingly large, especially for the larger molecules, and many of the broad bands can be well described by Lorentzian functions. One important question concerning the nature and dynamics of isolated highly vibrationally excited molecules is how to interpret this behavior: in particular, there is controversy[3-9] over the broadening mechanism, namely, how much of this arises from normal rotational and vibrational congestion (hot bands and combination bands arising from excited states) and how much of this arises from coupling to nearby levels which distribute the C–H oscillator strength, often called homogeneous broadening.[10] In keeping with this usage of the term, any contribution to the overtone width that also would be present at absolute zero will be here classified as homogeneous.

In order to distinguish between inhomogeneous and homogeneous broadening, it is necessary to record spectra at low temperature to reduce the number of levels which are thermally populated, and thereby reduce the inhomogeneous contribution to the spectrum. Unfortunately, no general method has been developed to perform overtone spectroscopy on jet-cooled molecules because of the weakness of the transitions. Nevertheless, water, hydrogen peroxide, tetramethyldioxetane (TMD), and benzene have been studied by this means. Water was studied by means of bolometric detection,[11] H_2O_2 and tetramethyldioxetane (TMD) by observing the products of a unimolecular decomposition,[12-14] and benzene by laser labeling spectroscopy.[15] Another system, methane and trideuteromethane, has been studied at 77 K using bulk cooling and photoacoustic detection.[16] This method is limited to those few molecules with sufficient vapor pressure at low temperatures. The method used in this study is similar but uses higher temperature baths for all molecules, except CH_4.

Most of our knowledge concerning the relaxation of C–H overtones has been deduced from room temperature spectra and theoretical modeling. Quack and co-workers have studied molecules containing a lone C–H oscillator.[17-21] The strong coupling between the C–H stretch and the C–H bend results in a Fermi resonance polyad structure. For the larger molecules the bands are often broadened. The overtone linewidths of molecules containing multiple C–H oscillators are generally even greater. The theoretical work of Sibert, Reinhardt, Hynes, and co-workers[3,22-24] on molecules containing more than one C–H oscillator suggests that a Fermi resonance polyad structure is responsible for much of the width in the higher overtones of benzene as well as other such molecules. The recent experiments on benzene by Page, Shen, and Lee[15] have shown a dramatic temperature

---

[a] Present address: Department of Chemistry, University of California, Berkeley, Berkeley, California 94720.

[b] Present address: British Petroleum Research Center, Chertsey Road, Sunbury-on-Thames, Middlesex TW167LN, United Kingdom.

0021-9606/88/247100-12$02.10

dependence of the 3–0 C–H stretch overtone band and indicate that the upper state is already well approximated as a local mode. Unfortunately, they were not able to observe any higher overtones and therefore could not address the validity of the broad Fermi resonance polyad structure theory.[3]

As we have already mentioned, hydrogen peroxide,[12,13] water,[11] methane,[16] and TMD[14] have been studied at low temperatures. Hydrogen peroxide, water, and methane, all small molecules, show dramatic changes on cooling, an indication that the width is at least primarily caused by inhomogeneous broadening. In contrast, TMD, $(CH_3)_2COCO(CH_3)_2$, a far larger molecule, shows more subtle changes on cooling, which indicates that the dominant contribution to the width of the overtone features is homogeneous, although there is some inhomogeneous contribution.

Ammonia has been studied[25] at dry ice temperature using microwave-optical double resonance (MODR). The spectrum was found to consist of hybrid bands with significant Coriolis interactions present as well as frequent, patternless interactions with background dark vibrational states. In this molecule the optically bright states of the 5–0 and 6–0 N–H stretch overtones are mixed with virtually all background states that lie within a few wave numbers in zero-order approximation.

McDonald's group has studied[26–28] the fluorescence emitted from a wide range of jet-cooled molecules on a microsecond time scale after pulsed excitation of the stretching fundamental. For most of the large molecules very little of the fluorescence yield comes from the initially excited state, presumably because of extensive coupling to background states and intramolecular vibrational relaxation (IVR). Their experiments show a remarkable correlation between the symmetry-adjusted rovibronic density of states and the "dilution factor," a quantity which is roughly the ratio between the resonance fluorescence obtained and the resonance fluorescence expected in the absence of any state mixing. The results of Nesbitt and Leone[29] on the infrared fluorescence of low overtones of hydrocarbons, also show a low resonance fluorescence rate for the larger molecules.

We present here the C–H overtone spectra of methane (5–0), ethylene (5–0 and 6–0), ethane (5–0 and 6–0), propyne (4–0 and 5–0 acetylenic C–H and 5–0 methyl C–H stretches), allene (5–0), propane (5–0 and 6–0), cyclopropane (5–0 and 6–0), dimethyl ether (5–0), and isobutane (5–0) taken at temperatures between 77 and 189 K, depending on the molecule. A comparison is made to spectra obtained at room temperature, 298 K. These molecules are intended to constitute a survey of small through medium size hydrocarbons.

EXPERIMENTAL METHOD

The spectra were recorded using laser photoacoustic spectroscopy. As already mentioned, the method is similar to that of Scherer *et al.*[16] and is limited to gases which have a high vapor pressure at low temperature. The Stanford experimental apparatus has been described previously.[30] The low temperature photoacoustic cell is shown in Fig. 1. It was constructed entirely from glass and designed to be of small volume to maximize the signal to noise ratio. The vacuum jacket was evacuated and sealed off at the end of the construction phase. An attempt was made, without success, to observe the spectra of medium size molecules at liquid nitrogen temperature using the technique of Messer and De Lucia.[31] A second attempt will be made using a photoacoustic cell of modified design.

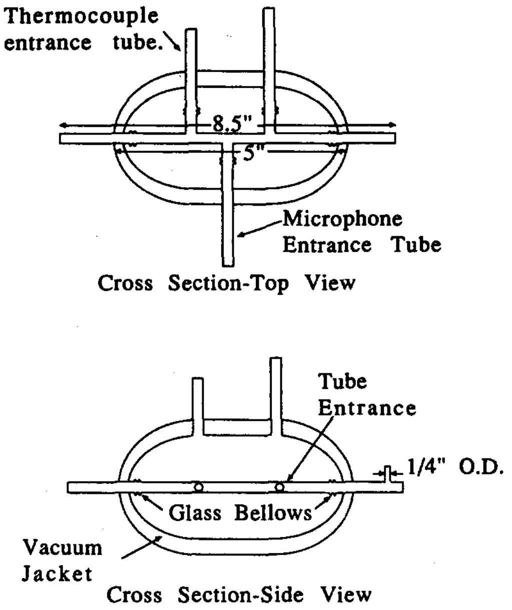

FIG. 1. Cooled photoacoustic cell. All tubing is 3/8 in. o.d. and 1/4 in. i.d. unless otherwise stated. The bottom cross section is a view from the side on which the microphone enters.

A variety of standard cold baths was employed: liquid nitrogen (77 K), *n*-pentane (143 K), *t*-butyl methyl ether (165 K), acetone (178 K), and ethyl acetate (189 K). Approximately 10 Torr of each sample gas was used. In order to maintain a high signal to noise ratio the gases were buffered in about 500 Torr of helium. The spectral resolution of the lasers is approximately 1 cm^{-1}.

The spectra were digitized together with optogalvanic lines from a neon lamp for absolute frequency calibration and etalon fringes of 3.25 cm^{-1} free spectral range for relative calibration. The intracavity power level was also monitored and digitized for ratioing of the spectrum. The microphone signal (BL-1785[16] from Knowles Electronics) and power reference signals were recorded at a time constant of 0.3 seconds and the scan rate was typically 25 cm^{-1}/min. The scanning between fringes is linear to within about 20%.

The cold baths were made *in situ* by simply adding the appropriate solvent to the cell jacket and more slowly adding liquid nitrogen. The bath was stirred by means of a magnetic stirring bar inside the jacket and an outside stirrer. The temperature of the gas inside the center tube was monitored with a thermocouple during the scans to ensure that it remained reasonably constant. The contribution to the microphone signal by warmer gas near the windows is expected to be minor. The stability of the baths varied; ethyl acetate produced a constant temperature for more than 30 min while *n*-pentane lasted less than 15 min.

The base lines of the spectra sometimes varied for the 298 K and low temperature scans as well as scan-to-scan. In each case, a number of scans was taken until some degree of confidence could be established in the reliability of the data. Still, it is possible that not all of the spectra are completely reliable, since some systematic errors may exist. The spectra are ratioed to the intracavity power as measured by an intracavity Brewster window reflection. As Smith *et al.*[32] have pointed out, this reflection is caused by nonidealities and does not necessarily give the proper base line. Furthermore, there are fringes associated with this reflection with an amplitude of about 15% of the reflected power and a free spectral range of about 10 cm. We observed similar fringes on the beam transmitted through the cavity high reflector, but of 3 or 4 times lower amplitude. Because of these fringes, we smoothed the power spectrum (recorded at a 0.3 s time constant) before ratioing. As a result, any sharp structure in the final spectra looks virtually identical to that observed by the BL-1785 microphone, but the spectrum has been corrected for the gently sloping gain curve of the dye laser. Since the scans are usually less than 500 cm^{-1} we have not considered the influence of window nonidealities on the base line. In spectra which we have taken and ratioed to the extracavity transmitted power, the results have been virtually identical, except that the base line (in the absence of correction for the high reflector transmittance curve) becomes very obviously sloped. A correction for the high reflector transmittance curve obviously would introduce some error in itself.

RESULTS AND DISCUSSION

Most of the spectra are displayed with room temperature and low temperature scans overlaid. To accomplish this, the scans at the two temperatures are normalized to have the same minimum and maximum points. For all molecules the density of vibrational states, at the energy at which the spectra were recorded, is indicated. The state densities were calculated using the Whitten–Rabinovitch method[33] assuming a harmonic approximation for each vibration, including torsions. No consideration was given to symmetry, in particular, to nuclear spin statistics and to the point group of the molecule.

We have assumed in the discussion to follow that for simple bands of the molecules studied we can expect the full-width half-maximum (FWHM) and the difference between maxima of P and R branch contours to show a $T^{1/2}$ dependence on absolute temperature, provided that the hot band contributions are small. It is not difficult to show, by means of simple calculations, that this is a reasonable approximation under the experimental conditions and given the experimental accuracy. The intensities of the hot bands depend exponentially on the temperature. In cases where the hot bands contribute significant intensity, such as propyne, allene, and ethane, the temperature dependence of the overall bandwidth may deviate considerably from a $T^{1/2}$ relation.

Methane

Methane and its isotopomers have been the subject of numerous overtone studies (see Refs. 16 and 34–41, and citations contained therein). The 4–0 and 5–0 C–H stretch overtones were observed for the first time in the 1930's.[34] The only band involving more than two quanta of stretch to be given a rotational assignment is the $3\nu_3$ band.[40,41] All of the others have a high density of transitions and complicated structure. In spite of the fact that the linewidths appear to be Doppler limited[16] (as long as the pressure is not too high), there are many overlapping transitions at room temperature, for example, in the 6–0 band. Since methane has a 10 Torr vapor pressure at liquid nitrogen temperature, it is not difficult to obtain the spectrum at this temperature. As we have already mentioned, Scherer, Lehmann, and Klemperer[16] have recently recorded the fifth C–H stretch overtone of methane at high resolution using the photoacoustic technique. Their spectrum shows a dramatic reduction in congestion at this temperature, but is still very dense. A rotational assignment has not yet appeared. We have used the same method to record the spectrum of the fourth (5–0) overtone at a resolution of about 1 cm^{-1}. This overtone has been assigned an upper state of $4\nu_1 + \nu_3$ (F_2 symmetry). The state $5\nu_1$ (A_1) is predicted to be nearly degenerate[36,37] with $4\nu_1 + \nu_3$, but because of its symmetry the transition $5\nu_1 \leftarrow 0$ is electric dipole forbidden. Therefore, to a first approximation this transition will have no intensity. These two states comprise the four local mode levels having five quanta in one C–H oscillator and zero quanta in the others.[39,42] In the absence of mixing with nearby states, one would expect a simple band structure somewhat similar in appearance to the ν_3 fundamental.[42,43] This is not the case as one immediately sees from the observed room temperature spectrum shown in Fig. 2(a). Such a phenomenon is, of course, typical of overtone spectra in general—the bands are usually much more complex than expected in the absence of any resonant interaction between energy levels.

The spectrum of the $4\nu_1 + \nu_3$ band at liquid nitrogen temperature is shown in Fig. 2(b). By smoothing the band shape we can obtain very approximate full-width half-maximum (FWHM) values of 180 ± 15 cm^{-1} at room temperature and 130 ± 15 cm^{-1} at 77 K. In the absence of any level mixing we would expect the FWHM to be approximately proportional to $T^{1/2}$, where T is the absolute temperature (K). Since the reduction is only a factor of 1.4 rather than 2, there must be some interaction involved which broadens the overall band.

A close look at the low temperature spectrum in Fig. 2(b) reveals several series of lines which seem to be associated with the most prominent lines (Q branches). We have tentatively identified four different bands in the region 13 750–13 790 cm^{-1}; the frequencies of their Q branch maxima are 13 753, 13 755, 13 782, and 13 788 cm^{-1}. Additional weaker bands are present also—there is another Q branch at $\approx$13 880 cm^{-1}, for example. A more detailed analysis of these bands, together with tentative rotational assignments for some of them, has been made.[43] Admittedly, some of the assignments mentioned are quite tenuous. The presence of numerous contributing vibrational bands, however, is not in doubt. There are eight or so distinct features which we suspect may be the Q branches of eight different bands. The overall shape of the $4\nu_1 + \nu_3$ band suggests that

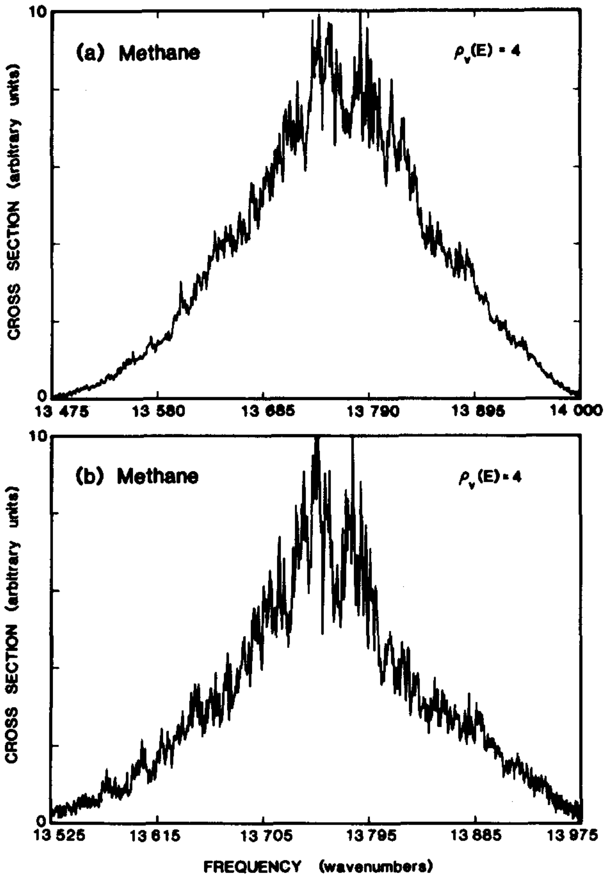

FIG. 2. Methane 5←0 overtone photoacoustic spectra: (a) room temperature, (b) 77 K.

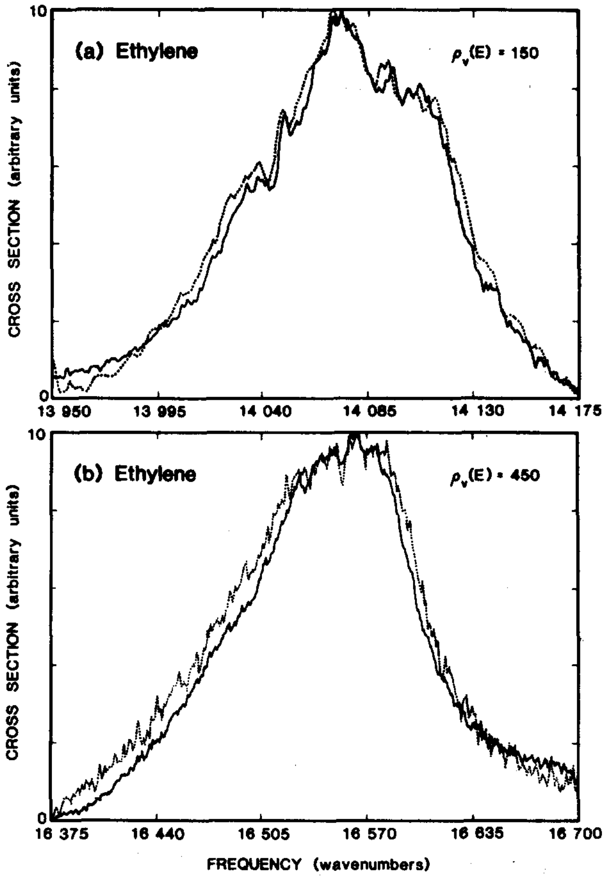

FIG. 3. Ethylene overtone photoacoustic spectra. Dotted line taken at room temperature, solid line at 143 K: (a) 5←0 transition, (b) 6←0 transition.

there are many more "subbands" than this contributing to its appearance. The sharp structure is superimposed on a gently sloping continuum which is of similar appearance at room and liquid nitrogen temperatures. The explanation of this presumably is that a significant fraction of the background vibrational states borrow intensity from the $4\nu_1 + \nu_3$ state by a resonant mixing process. The features assignable to the zero-order state contribute about 10% of the total integrated band intensity; thus the original state's oscillator strength seems to be reduced by an order of magnitude. Given the density of vibrational states at this energy ($4/\mathrm{cm}^{-1}$), we would suggest that at least 10% of all levels contribute significantly to the band in order for it to appear as shown. The wings of the band are extensive, not unlike those expected for a Lorentzian line shape. With similar coupling strengths and a higher density of levels, it is not difficult to imagine the band profile approaching that of a true Lorentzian line shape. This is the case for the band profiles of many large molecules; the most celebrated example is that of benzene. One further observation deserves to be noted here; in spite of the well-documented importance of C–H stretch–bend Fermi resonance in overtone spectra of molecules containing a single C–H oscillator,[17–21] the states ($3\nu_1 + \nu_3 + 2\nu_4$ and $4\nu_1 + 2\nu_4$) containing two quanta of the ν_4 bending mode do not occupy a prominent place in the spectrum here. They evidently appear with little intensity more than 100 cm^{-1} to the blue of the $4\nu_1 + \nu_3$ band center.

Ethylene (C_2H_4)

The 5–0 and 6–0 C–H stretch overtone bands of ethylene are shown in Figs. 3(a) and 3(b), with scans at 298 and 143 K overlaid. The 5–0 band is certainly more sharply structured, although both bands contract by ≈10% upon cooling. The $T^{1/2}$ rule would have predicted a 31% reduction. The 6–0 band is broader, however, with a room temperature width of 136 ± 5 cm^{-1} as compared to 102 ± 4 cm^{-1}. The hot band contribution to the intensity should be only ≈5%; therefore, most of the 10% contraction is probably caused by the rotational state distribution of the ground state. It is obvious, at any rate, that the FWHM of even the 5–0 band is considerably greater than could be expected for any simple band type. Homogeneous broadening or gray state congestion is evidently an important determinant of the appearance of the 5–0 and 6–0 bands. The fact that a temperature dependence is easily observed, together with the obvious structure of the bands, indicates that the number of vibrational components with strong intensity is limited.

Jasinski has studied the fifth overtone of ethene and deuterated ethenes.[44] The FWHM tends to decrease as the number of deuterium atoms in the molecule is increased. C_2D_3H has a FWHM of 92 cm^{-1}. The widths for the three isotopes with the chemical formula $C_2D_2H_2$ are significantly larger when the hydrogens are on different carbon atoms. This suggests the existence of an interaction between these C–H oscillators which produces a splitting of some 20 cm^{-1}. Initial observations of the fourth overtones of these same isotopic species cast doubt upon this interpretation, however, since transethylene-1,2-d_2 was found to have a low FWHM and a large temperature dependence.[43] In contrast, the corresponding band of ethylene-1,1-d_2 is surprisingly broad. Jasinski[44] also observes a shift to the blue of 50 cm^{-1} for a C–H oscillator having a deuterium bonded to the same carbon atom. The blue shift is explained as the result of an interaction between the C–H and C–D oscillators with a common carbon atom. The interaction is between the states $|6,0\rangle$ and $|5,1\rangle$, where $|x, y\rangle$ denotes x stretching quanta in the C–H oscillator and y stretching quanta in the C–D oscillator. All of this suggests that coupling between equivalent C–H oscillators is important in determining the position and width of the features in the ethene spectrum. Quantitative prediction of the FWHM for the various isotopes in each overtone level, however, requires a more detailed understanding of each molecule.

Ethane (C_2H_6)

The 5–0 and 6–0 stretching overtones of ethane are shown in Figs. 4(a) and 4(b). The FWHM values for these bands at the two temperatures are listed in Table I. These widths are much larger than those expected for simple bands. Both bands are approaching a Lorentzian profile, with no apparent structure. There is a slight asymmetry in the band shapes, however, in that the blue shoulders extend further than their red counterparts. Both bands contract by $\approx 10\%$ upon cooling to 143 K. Nearly all of the contraction in width in each case results from reduction of the red shoulder. It is very possible, if not likely, that much of this arises from decreased torsional and other hot band intensities. Their combined intensities should be $\approx 40\%$ that of the "fundamental." It seems likely that the gray state congestion in these bands is quite extensive. As in the case of ethene and many other molecules, however, it is quite possible that the large FWHM of these bands owes significantly to an interaction between C–H oscillators on adjacent carbon atoms. Observation of the spectra of CH_3CD_3 should clear up this point.

Methyl acetylene (propyne—C_3H_4)

The spectra of the $n\nu_1$ bands ($n = 1$–7) of propyne have been recorded by Berry and co-workers[45] with resolution limited by the combined effects of Doppler and pressure broadening. These bands, with the exception of $4\nu_1$ and $5\nu_1$, show resolved rotational structure. This is highly unusual for a molecule with such a high vibrational density of states of 7×10^3 and 6×10^5/cm^{-1} at $n = 4$ and 7, respectively. The experiments of McDonald's group[26–28] have also shown that propyne is an unusual molecule. They have suggested that both anharmonic and rotational coupling matrix elements are smaller for terminal ≡C–H stretches of acetylene derivatives than for other C–H stretches at a given state density, at least for fundamentals. This seems reasonable in view of the relatively isolated nature of the ≡C–H bond in the substituted acetylenes. In addition, the stretching and bending frequencies of C–H oscillators in most molecules occur with approximately a 2:1 ratio. The Fermi resonance interaction between $|v_s = n, v_b = 0\rangle$ and $|v_s = n-1, v_b = 2\rangle$ is thought to be of nearly universal importance in the overtone spectra of many hydrocarbons. In contrast, the ratio of the stretch (ν_1) and bend (ν_9) frequencies of the ≡C–H bond in propyne is about 5:1.[46]

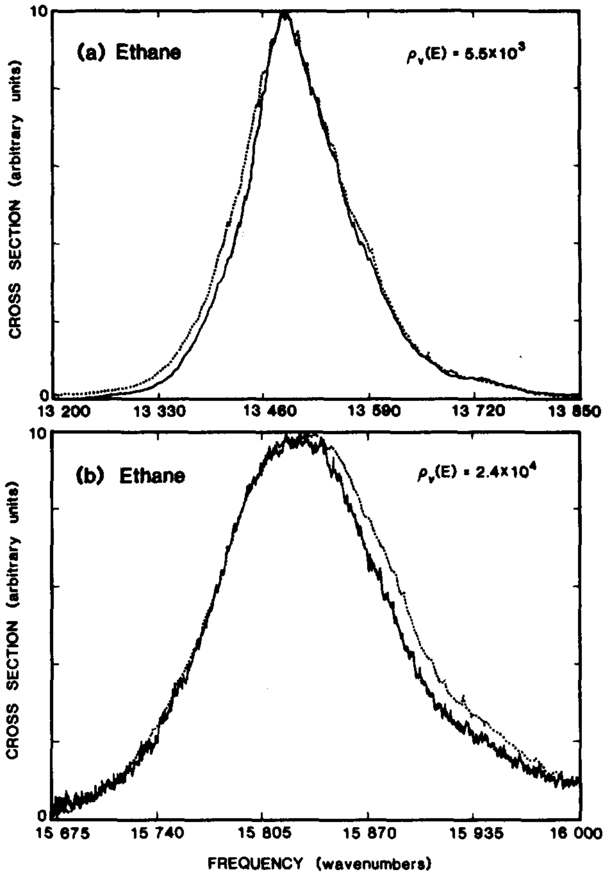

FIG. 4. Ethane overtone photacoustic spectra. Dotted line taken at room temperature, solid line at 143 K: (a) 5←0 transition, (b) 6←0 transition.

We have recorded the $4\nu_1$ and $5\nu_1$ bands as well as the 5–0 stretching overtone of the methyl group. They were obtained at the usual pressure of 10 Torr hydrocarbon and 500 Torr He buffer at 298 and 189 K. The $4\nu_1$ spectrum is displayed in Fig. 5(a). From the molecular symmetry, the $4\nu_1$ band type must be parallel. The rotational constants are $A = 5.29$ cm^{-1} and $B = C = 0.285$ cm^{-1} in the ground state.[47] We therefore expect to see (at our resolution of ≈ 1 cm^{-1}) a rather sharp Q branch and a separation between the maxima of the P and R branch contours of ≈ 22 cm^{-1} at room temperature. The FWHM, of course, will be somewhat larger. In addition, we expect to see a hot band $4\nu_1 + \nu_{10} \leftarrow \nu_{10}$ with an intensity about 40% that of the $4\nu_1 \leftarrow 0$ transition. Because of the difference in origins of the $4\nu_1$ and hot bands, some apparent broadening may result. Because the hot band intensity will show an exponential dependence with temperature, hot bands lead to a deviation from the $T^{1/2}$ rule. The highest frequency band in Fig. 5(a), with a Q branch maximum ($Q_{\max}$) at 12 764.3 cm^{-1},[45] is very close in appearance to the above description. In the high resolution spectrum of Berry (see Fig. 11 of Ref. 45), this

TABLE I. Summary of the data collected in this work. Some band center and full-width half-maximum data from Ref. 51 are also included.

Compound	Temperature	FWHM (cm^{-1})	FWHM (% change)	$\rho_v(E)$ (cm)	Transition	Peak (cm^{-1})
Methane	RT (room temp.)	180 ± 15		4	$4\nu_1 + \nu_3 \leftarrow 0$	13 770[a]
	77 K	130 ± 15	28 ± 5			
Ethylene	RT	102 ± 4		150	$5 \leftarrow 0$	14 082[b]
	143 K	94 ± 3	8 ± 2			
	RT	136 ± 5 (145 ± 5[c])		450	$6 \leftarrow 0$	16 550[a]
	143 K	120 ± 5	12 ± 4			
Ethane	RT	140 ± 3		5.5×10^3	$5 \leftarrow 0$	13 488[a]
	143 K	126 ± 3	10 ± 2			
	RT	130 ± 3		2.4×10^4	$6 \leftarrow 0$	15 824[a]
	143 K	118 ± 3	9 ± 2			
Propyne	RT	Not measured[d]		7×10^3	$3\nu_1 + \nu_3 + \nu_5 \leftarrow 0(HF_{RR})$	12 764[e]
	189 K		20 ± 5[d]			
	RT	46 ± 5		7×10^3	$4\nu_1 \leftarrow 0(S)$	12 713[e]
	189 K	40 ± 5	13 ± 4			
	RT	66 ± 5		1.1×10^4	$5 \leftarrow 0$(methyl)	13 570[a]
	189 K	54 ± 5	18 ± 3			
Allene	RT	56 ± 2		1.2×10^4	$5 \leftarrow 0$	13 976[a]
	189 K	50 ± 2	12 ± 3			
Propane	RT	Not measured[f]		2.0×10^6	$5 \leftarrow 0$	13 429[b,f]
	189 K		2 ± 2			
	RT	147 ± 15[c]		1.5×10^7	$6 \leftarrow 0$	15 562[c]
		101 ± 7[c]				15 746[c]
		123 ± 11[c]				15 845[c]
	165 K	Not measured[f]	3 ± 2			
Cyclopropane	RT	86 ± 4[c]		5.0×10^4	$5 \leftarrow 0$	$14\,059 \pm 5$[c]
	178 K	80 ± 5	8 ± 4			
	RT	95 ± 4[c]		2.0×10^5	$6 \leftarrow 0$	$16\,504 \pm 3$[a]
	178 K	95 ± 5	<5			
Dimethyl ether	RT	175 ± 10		2.2×10^5	$5 \leftarrow 0$	13 659[a]
	189 K	175 ± 10	<3			
Isobutane	RT	107 ± 6		2.6×10^9	$5 \leftarrow 0$	$13\,460 \pm 6$[a]
	189 K	103 ± 6	4 ± 4			

[a] Estimated band center—this should be within a few wave numbers of the band origin.

[b] Band maximum.

[c] Taken from Ref. 51 which estimated centers and widths (FWHM) for overlapping bands by fitting the features to overlapping Lorentzian profiles.

[d] Measured the change in separation of *P* and *R* branch maxima.

[e] *Q* branch maximum.

[f] We do not present width or band center data for these overlapping bands because we do not know what shape to fit the bands with.

band is rotationally resolved, with none of the K structure visible in the *P* and *R* branches. Hereafter we will refer to this band as HF_{RR}, for "high frequency rotationally resolved." In our low temperature scan of this band, the hot band intensity is reduced relative to the "fundamental" and the band contracts noticeably. Also, the separation between *P* branch and *R* branch maxima is reduced by $20 \pm 5\%$. The expected reduction according to $T^{1/2}$ is 20% if one neglects the hot band contribution to the spectrum.

The intense band with $Q_{\max}$ at $\approx 12\,713\ cm^{-1}$ (band *S*) is not rotationally resolved and has a quite different appearance. Compared to the *P* and *R* branch contours, the central *Q* branch is relatively much less intense. Whereas the separation between fundamental and first hot band *Q* branches in the previous case was $10\ cm^{-1}$, here it is only $6\ cm^{-1}$. Two explanations immediately come to mind for the fact that band *S* is not rotationally resolved in Berry's spectrum: (1) this band has larger absolute values of $(A'-A'') - (B'-B'')$, thereby more strongly splitting out the *K* structure, and (2) for whatever reason band *S* has its line density increased by gray state congestion. Other explanations are possible too. It appears from an inspection of bands HF_{RR} and *S* that HF_{RR} has a value of $B'-B''$ which is a negative number of larger absolute magnitude than that of band *S*. If so, this lends support to the idea that the *K* structure may be more strongly split in band *S* than in band HF_{RR}. In the absence of extensive vibrational level mixing, however, the temperature dependent shape of band *S* will vary in a similar fashion to band HF_{RR}. Figure 5(a) shows that the red shoulder of band *S* is reduced dramatically at low temperature (as we would expect since the hot bands contribute the most on this side) but the blue shoulder shows little change at the two temperatures. The contraction visible on the lower edge of the blue shoulder can be attributed at least in part to the reduction in the red shoulder of the overlapping band HF_{RR}. We believe that this indicates the appearance of transitions in band *S* which result from a mixing of states. This is supported by the relative weakness of the fundamental and hot band *Q* branches in band *S* as compared to band HF_{RR}. Normalized to their respective integrated band intensities, the *Q* branches in *S* are about six times weaker than the corresponding ones in HF_{RR}. This can be explained, as in the case

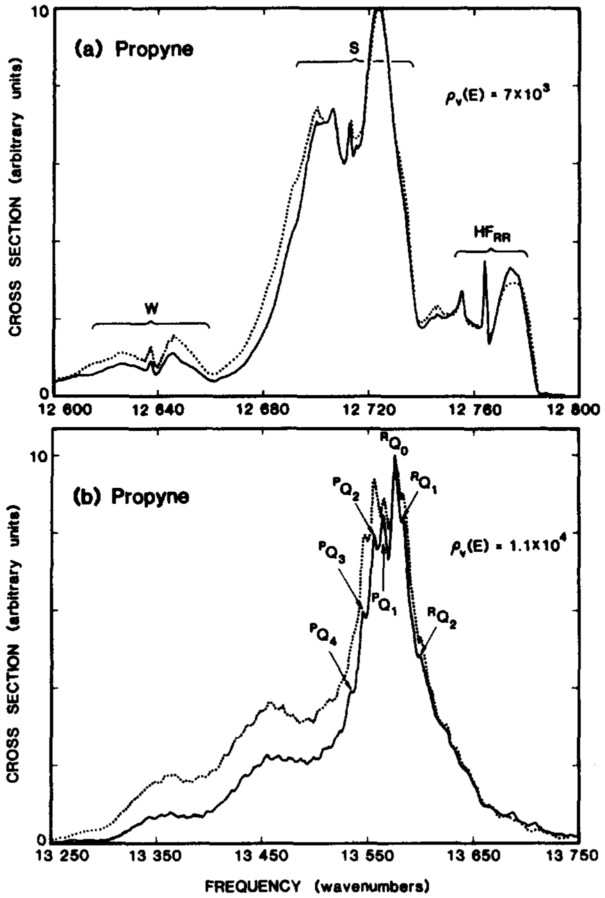

FIG. 5. Propyne overtone photacoustic spectra. Dotted line taken at room temperature, solid line at 189 K: (a) 4←0 acetylenic band, (b) 5←0 methyl band.

of the methane 5–0 band, by gray state congestion. The oscillator strength of the zero-order state is reduced by mixing with some of the bath states. Because the coupling matrix elements are small, the band is not broadened appreciably, but the prominence of any band features that would be present in the absence of mixing is greatly reduced.

Berry[45] has assigned band HF_{RR} to $4\nu_1$ and band S to the combination band $3\nu_1 + \nu_3 + \nu_5$, where ν_3 and ν_5 are the C≡C and C–C stretching modes, respectively.[46] This is incorrect; we assign them the opposite way, i.e., band HF_{RR} is $3\nu_1 + \nu_3 + \nu_5$ and band S ($Q_{\max}$ at 12 713 cm^{-1}) is $4\nu_1$. Our assignment is supported by the spectrum of methyl-d_3-acetylene, which we shall discuss in detail elsewhere.[48] It is also expected from the fact that, in the absence of strong, multilevel mixing, the integrated intensity of the pure overtone is always at least as great as any interacting combination band. The intensities of the combination bands are assumed to derive, as a first order of approximation, from mixing with the pure overtone state. Our assignment is surprising, since it implies that it is the combination band which has an upper state that is not so well mixed as that of the pure C–H stretch overtone (pure only in zero-order approximation). It would seem natural to suppose that the $3\nu_1 + \nu_3 + \nu_5$ state would be more strongly coupled to other modes of the molecule than would the $4\nu_1$ state. An analysis similar to that of Hutchinson[49] on the $5\nu_1$ band of cyanoacetylene should explain this result.

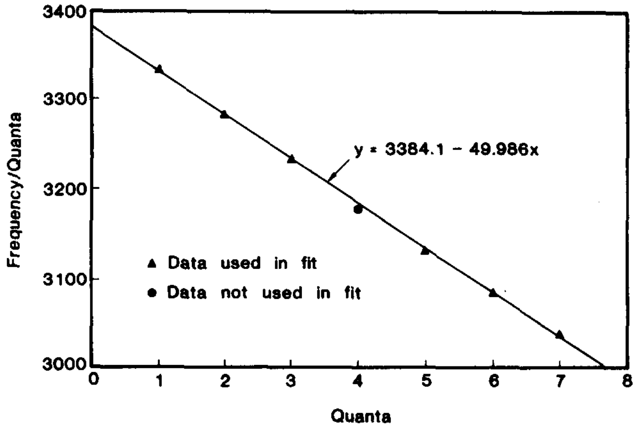

FIG. 6. Birge–Sponer plot for the propyne ν_1 overtone manifold. The point plotted for $4\nu_1$ is shown for comparison and was not used in determination of the best fit line.

The weakest band in Fig. 5(a) (band W), with $Q_{\max} = 12\,638$ cm^{-1}, is contracted at the lower temperature. While we do not know whether this band would show any rotational resolution under Berry's experimental conditions (because it is not shown in Fig. 11 of Ref. 45), this and the degree of prominence of the Q branch suggest that it would. It may be the combination band $3\nu_1 + \nu_2$, which is shifted by Fermi-resonance interaction with $3\nu_1 + 2\nu_7$.

The Fermi resonance between $4\nu_1$ and $3\nu_1 + \nu_3 + \nu_5$ results in a significant shift from the zero-order frequencies. A Birge–Sponer plot (Fig. 6) places the unperturbed $4\nu_1$ position at $\approx 12\,736$ cm^{-1}. The perturbed energies are given by[42]

$$E_{\pm} = \bar{E}_{12} \pm \tfrac{1}{2}[4|W_{12}|^2 + \delta^2]^{1/2}, \tag{1}$$

where the subscripts are defined as $1 \equiv |v_1 = 3, v_3 = v_5 = 1\rangle$ and $2 \equiv |v_1 = 4\rangle$, W_{12} is the off-diagonal energy matrix element, δ is the zero-order separation between the states, and $\bar{E}_{12}$ is the average of the zero-order energies. We have neglected to consider any matrix elements involving band W. From Fig. 6 and the measured frequency of the perturbed $4\nu_1$ band (12 713 cm^{-1}), we obtain $\delta \approx 6$ cm^{-1}, corresponding to $E_1^0 = 12\,742$ cm^{-1}. From Eq. (1) we calculate $|W_{12}| = 25$ cm^{-1}. As a check we calculate the relative intensities of the perturbed bands from the relations[38]

$$a = \left(\frac{\Gamma + \delta}{2\Gamma}\right)^{1/2}, \tag{2a}$$

$$b = \left(\frac{\Gamma - \delta}{2\Gamma}\right)^{1/2}, \tag{2b}$$

and

$$I_{\text{rel}} = \frac{b^2}{a^2}, \tag{2c}$$

where $\Gamma = (4W_{12}^2 + \delta^2)^{1/2}$, I_{rel} is the ratio of intensities, and a,b are the coefficients in the linear combinations of unperturbed state basis functions in the perturbed wave functions ($a^2 + b^2 = 1$). We obtain $I_{\text{rel}} = 1.3{:}1$ instead of the experimentally observed 3:1. While this is very poor agreement, a shift of just 10 cm^{-1} in the zero-order frequencies gives a completely different result. The observed intensity ratio is reproduced with the parameters $E_1^0 = 12\,751$, $E_2^0 = 12\,726$, and $|W_{12}| = 22$ cm^{-1}.

The fourth overtone of the propyne methyl group C–H stretch is shown in Fig. 5(b), also with room temperature and 189 K scans overlaid. This band is more complex that $4\nu_1$. In the local mode limit there are now three independent oscillators. The linear basis functions for each oscillator can be combined to form A_1 and E symmetry states, consistent with the C_{3v} point group of the molecule. By analogy with other molecules, the degeneracy of the A_1 and E local mode states will remain a near degeneracy after interactions have been considered. Bands involving the A_1 state will be of parallel type only, whereas E states will be associated with perpendicular type bands. Thus we expect the band in Fig. 5(b) to involve both types. Since the bond dipole approximation gives the ratio of A_1 to E intensity as $\cos^2\theta{:}\sin^2\theta$, where θ is the angle between the symmetry axis and a C–H bond, the perpendicular component is probably larger. This conclusion is consistent with the appearance of the band. Assignments for the sharp structural features of the band are shown in this figure. The value of $A'(1-\zeta)-B'$ is found to be ≈ 5.0 cm^{-1} from the nearly constant spacing of the Q branch subbands, suggesting a small value for the Coriolis coefficient ζ. The contraction of the band at the lower temperature is considerable, and not inconsistent with the $T^{1/2}$ rule. It is especially large on the low frequency side. This may not be entirely real, however, as a series of "identical" scans produced differing magnitudes of contraction on the red shoulder. Nevertheless, the temperature dependence is certainly larger than that for the methyl groups of alkanes. It is interesting to note that the greater temperature dependence and absence of a large broadening as compared with a fundamental band of perpendicular type, is occurring for a methyl group without C–H oscillators on an adjacent carbon atom. There remains a definite possibility that the structured band in Fig. 5(b) is simple and can be rotationally resolved, just as some of the $n\nu_1$ bands.

The two lower frequency bands seen in Fig. 5(b) are more mysterious. They are nearly structureless and appear to be broader (suggesting highly mixed upper states). We tentatively assign these to $|\nu_s = 4, \nu_4 = \nu_8 = 1\rangle$ and $|\nu_s = 4, \nu_4 = \nu_7 = 1\rangle$, where the latter applies to the higher frequency band. The structured, most intense band in Fig. 5(b) is, of course, assigned to $|\nu_s = 5\rangle$. Here ν_s is the C–H methyl stretch.

Allene (C_3H_4)

The fourth C–H stetching overtone (Fig. 7) of allene resembles the corresponding methyl group overtone in propyne. The FWHM values are virtually identical and allene also suggests a predominantly perpendicular band type with a similar spacing between Q branch components. However, the Q branch features are less distinct in the allene spectrum. The red shoulder contracts considerably when the temperature is lowered to 189 K, but the blue shoulder is fairly independent of this. At least part of the contraction in the blue shoulder can be attributed to a reduction in the red shoulder of the weak, overlapping band which appears at $\approx 14\,025$ cm^{-1}. It seems, then, that the allene overtone band contains a greater temperature independent component than does that of propyne. Evidently the upper states of allene are more highly mixed than that of propyne. The identity of the weak 14 025 cm^{-1} peak is very uncertain. There is a possibility that it represents a combination band whose upper state involves one quantum each in ν_2 and ν_7 and four quanta in one C–H oscillator.

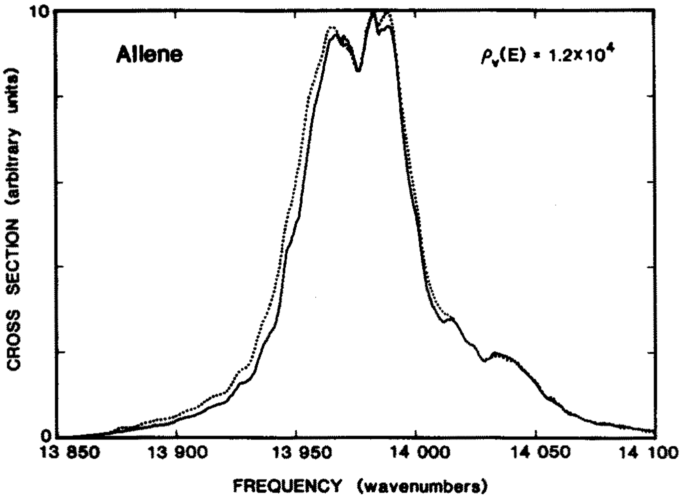

FIG. 7. 5←0 allene photoacoustic spectra. Dotted line taken at room temperature, solid line at 189 K.

Propane (C_3H_8)

The 5–0 and 6–0 bands of propane are displayed in Figs. 8(a) and 8(b), respectively. There was a tendency for the propane spectra to be noisy, with more pronounced etalon effects. It was not clear whether this was due to chance or some characteristic of the molecule. The 5–0 band has two very broad humps which correspond roughly to the methyl group C–H stretch for the larger peak and the methylene group C–H stretch for the smaller. Such an assignment agrees with the rule that the integrated intensity of simple bands is proportional to the number of equivalent C–H oscillators.[50] It also agrees with an estimate of the relative positions of methyl and methylene C–H oscillators based on the fundamental. Because of the hindered rotation of the methyl groups, there exist conformations in which the methyl C–H oscillators are no longer all equivalent. The equilibrium structure conformation of propane, which predominates at room temperature, has a plane of symmetry containing the carbon atoms and one hydrogen from each methyl group.[51] The more intense peak in Fig. 8(a) is obviously asymmetric and is probably composed of two peaks corresponding to conformationally inequivalent methyl C–H oscillators. The FWHM expected for a simple band of propane would be less than 50 cm^{-1}. The width which is observed for the more intense peak in the figure is ≈ 200 cm^{-1}. There may be some very subtle changes in the spectrum upon cooling to 189 K, but if they exist they are comparable to the experimental error.

In Fig. 8(b), one can see that the most intense peak of 6–0 is composed primarily of two components separated by

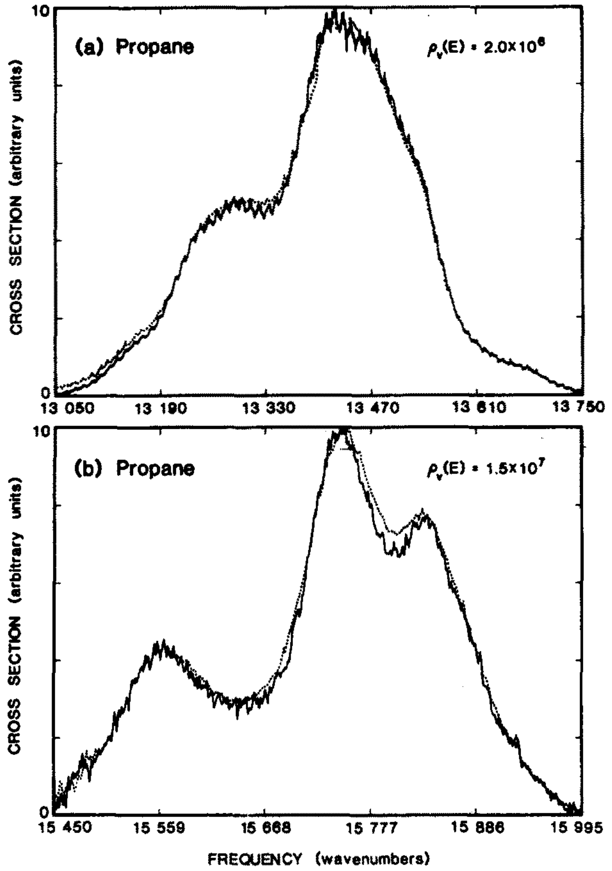

FIG. 8. Propane overtone photacoustic spectra. Dotted line taken at room temperature: (a) 5←0 transition, solid line at 189 K. (b) 6←0 transition, solid line at 165 K.

about 75 cm^{-1}, each having approximately Lorentzian profiles with widths of about 100 cm^{-1}. The same is probably true for the 5–0 band as well, except that the two components are not split so widely. These components presumably result from the conformational inequivalence,[51] with a splitting proportional to the number of stretching quanta in the upper state. The change in relative intensities of the two components upon cooling is very small and would indicate that these transitions originate from the same lower state levels. The low temperature spectrum shows a stronger dip between these two intense peaks and a slightly wider separation of the maxima. This can probably be ascribed to a slight reduction of the FWHM of each component, which will appear most clearly in the dip between the peaks. The fact that the positions appear to be more widely split upon cooling to 189 K is consistent with the fit by Wong[51] of each peak to a Lorentzian function to obtain a separation between the two components of 99 cm^{-1}.

Cyclopropane (C_3H_6)

The 5–0 C–H stretch overtone spectrum of cyclopropane (Fig. 9), while not nearly so well defined in appearance as the fundamentals, does have recognizable structure. The main Q branch peaks at $\approx 14\,059$ cm^{-1} and the R branch at $\approx 14\,085$ cm^{-1}. The shoulder to the red is reduced significantly by cooling to 178 K. This is somewhat surprising

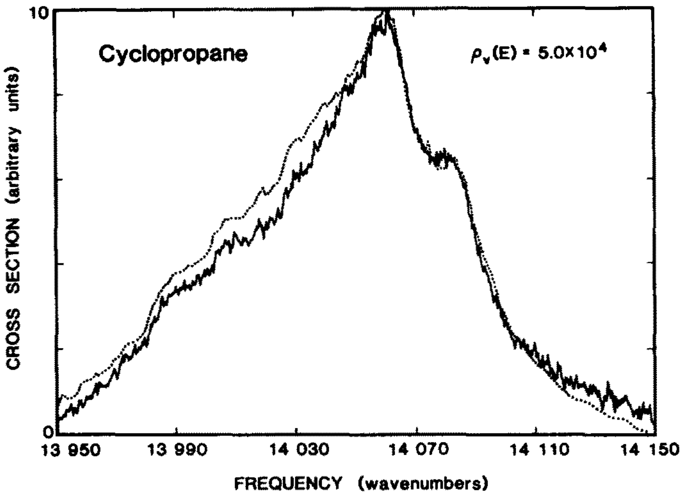

FIG. 9. 5←0 cyclopropane photoacoustic spectra. Dotted line taken at room temperature, solid line at 178 K.

since hot bands should only constitute some 10% of the band intensity at room temperature. The shoulder containing the R branch contour is affected only slightly, if at all, by the temperature. If the data are correct, this band is extensively mixed, i.e., it shows significant homogeneous broadening in the sense that a significant part of the bandwidth would remain at absolute zero. Because of the nonconvergence of room and low temperature scans at the edges, the data should be treated with caution. Cyclopropane is probably an intermediate case, showing only small temperature effects. The band is slightly broader than perpendicular fundamental bands. Since the bond dipole approximation does predict a hybrid band, the homogeneous contribution is still rather small compared to the overall width. The homogeneous contribution to the width seems to be significantly higher in the 6–0 band of cyclopropane than the 5–0. The room temperature spectrum of 6–0[51] is much less structured and considerably broader, with a FWHM of 95 ± 5 cm^{-1}. We obtained the spectrum at 178 K and observed no reduction in width. Because of a low signal to noise ratio, however, we can only say that the width could not have decreased by more than 5%.

Dimethyl ether (C_2H_6O)

Like propane, dimethyl ether exists in conformations with inequivalent methyl C–H bonds. The spectra of the 4–0, 5–0, and 6–0 overtones have been studied by Fang, Meister, and Swofford[52] in connection with this.

We have studied only the 5–0 stretching overtone peak at 13 660 cm^{-1} which is shown in Fig. 10. This peak, which was assigned by Fang *et al.* to the in-plane C–H oscillator, has a FWHM of ≈ 170 cm^{-1}. Obviously, this is far greater than one expects for a single vibrational band. It is slightly asymmetric, having a longer tail on the low frequency side. There may be a slight reduction in the relative intensity of this tail at low temperature; however, the rest of the band shows no temperature dependence to within experimental error. Because a large etaloning effect was present in the spectrum, it has been smoothed slightly. The etalon effect

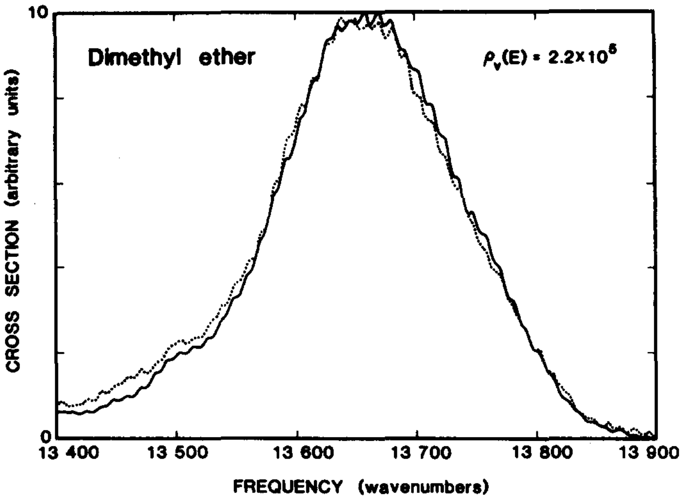

FIG. 10. 5←0 dimethyl ether photoacoustic spectra. Dotted line taken at room temperature, solid line at 189 K.

was reduced by this but can still be seen in Fig. 10. These "wiggles" are not real.

Isobutane (C_4H_{10})

This is the largest (heaviest) hydrocarbon which we have studied. Again, conformational inequivalence of C–H bonds can exist. The 5–0 stretching overtone is shown in Fig. 11. Presumably, the two more intense peaks are due to methyl C–H oscillators while the weak feature at 13 240 cm^{-1} may be due to the remaining C–H oscillator (it could also be buried under the two intense peaks). As in the case of dimethyl ether, the spectrum was noisy and has been smoothed slightly. The residual wiggles are not real features of the isobutane spectrum. The FWHM of the strongest band in Fig. 11 is found to be 107 ± 6 cm^{-1} at room temperature. The profiles can be fit rather well using Lorentzian line shapes. There appears to be a reduction of $\approx 4\%$ in the FWHM of the 13 460 cm^{-1} peak at 189 K, and a slight reduction in the blue shoulder. These conclusions are not entirely certain. However, it is quite possible that the methyl groups in isobutane are more isolated than those in propane as far as intermode coupling to the other C–H oscillators is concerned. It is known[51] that the 5–0 2,2-dimethyl propane band has a FWHM of 64 cm^{-1}. Here the methyl groups do not have a C–H oscillator on an adjacent carbon atom to couple to.

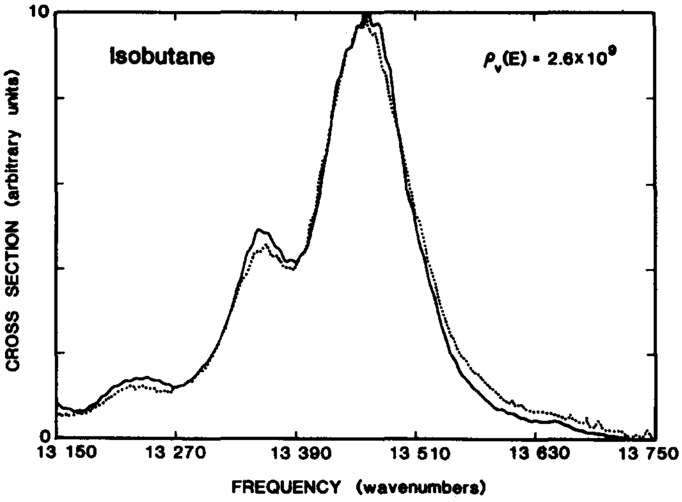

FIG. 11. 5←0 isobutane photoacoustic spectra. Dotted line taken at room temperature, solid line at 189 K.

CONCLUDING REMARKS

In this study we have achieved only moderate temperature changes and the experimental accuracy is not sufficiently high to detect changes in bandwidth smaller than a few percent. Nevertheless, it is clear from the results (summarized in Table I) and discussion that the vast majority of hydrocarbon 5–0 and 6–0 C–H stretching overtone bands have upper states which are highly mixed with other states. Such a conclusion is consistent with other work which we have mentioned. The distribution of oscillator strength to the other states leads to a complicated band structure which normally decreases the temperature dependence of the band from the expected $T^{1/2}$ dependence of a simple band. The temperature dependent interactions produce what can be called "homogeneous" structure or gray state congestion. Presumably, a band which shows no temperature dependence must have a very extensively mixed upper state indeed.

The temperature independence of the overtone bands of molecules investigated here correlates roughly with the density of states and with the degree of saturation. Other factors are important determinants of spectral widths and temperature independence as well, such as conformational inequivalence of the C–H oscillators and the number and positions of the oscillators. Hot bands can contribute significantly also, as the spectrum of propyne has demonstrated. Still, they are clearly not so important in the larger molecules as the state mixing. Rigid ring structures tend to be associated with overtone spectra having relative narrow spectral features as compared to alkanes with the same number of carbon atoms. The greater FWHM for alkanes can probably be attributed, in part, to splittings caused by conformational inequivalence and interactions between C–H oscillators on adjacent carbon atoms. The latter interaction applies also to a rigid ring; however, the number of C–H oscillators per carbon atom is higher for the alkanes and may lead to greater congestion. The orientations of the various bonds with respect to each other in the two types of molecules may be highly influential as far as intermode coupling is concerned. According to Hutchinson, Hynes, and Reinhardt,[22] the magnitude of intermode interactions which can lead to IVR are very much dependent on geometry. In the alkanes, they propose that a 2:1 nonlinear Fermi resonance between the C–H stretch and a local HCC bending mode is largely responsible for the energy flow. In the substituted acetylenes 1:1 CH stretch: CC stretch resonances are thought to be of primary importance.[22] It is interesting to note that the Hutchinson, Hynes, and Reinhardt model for alkanes does not predict relaxation in ethane, in spite of the experimental observation of broad ethane overtone bands. They suggest that, in ethane, CH stretching and rocking motions on the secondary carbon may be significant to the relaxation. If the observed ethane bands are indeed broadened because of such an intermode mixing process which leads to IVR, the bands of CH_3CD_3 and C_2D_5H should be relatively narrow. Of course, a broadened overtone band does not in itself indicate that an IVR process is taking place (for example, the broadening caused by conformational inequivalence has nothing to do with IVR) and one cannot infer an IVR lifetime without further information. Nevertheless, we do believe that a significant portion of the broad width of the overtone bands for many molecules is associated with interactions that lead to IVR.

As a general rule, any band which is much broader than its expected rotational width and shows relatively little structure can be expected to have a large temperature independent component. The greater the bandwidth of these molecules, the smaller the percentage reduction in FWHM is likely to be upon cooling. There is no doubt that the details of the individual molecules determine the bandwidths. This includes the set of vibrational frequencies for the molecule and its molecular structure and symmetry. These factors influence the extent of state mixing, since they determine the positions of the energy levels and the magnitudes of the coupling matrix elements between them. It is possible to have a fairly high density of states with relatively little state mixing, as the spectrum of methyl acetylene proves. When a molecule is partially deuterated, the structure of the C–H overtone bands appears to simplify, yet the density of states has been increased. We intend to explore the temperature dependence of the overtone bands of partially deuterated hydrocarbons in the future.

We have not discussed so far the importance of Coriolis coupling in these congested overtone bands. There is no reason to doubt that these couplings are important and must be considered in any detailed analysis. However, since Coriolis coupling strength increases with J, the temperature dependence of a band is unlikely to be diminished by these interactions (in fact, it could be increased). Because of this, we believe that the Fermi resonance type of interaction is, at least in the majority of cases, more important in determining the appearance of overtone bands.

The work of Quack and co-workers[17–21] has led to significant understanding of the overtone spectra of molecules containing single C–H oscillators. When there are multiple C–H oscillators, the C–H bending mode is usually much less prominent in the spectrum. The reason for this may be that the excited state levels are more extensively mixed with background states, with the result that no single eigenstate has a large interaction with the bending state (which itself may be extensively mixed with background levels). The result seems to be a smearing out of the band structure. The fact that this smearing effect consistently applies when there are multiple C–H oscillators is badly in need of a quantitative theoretical explanation. In addition, there is a need for high quality theoretical treatments to elucidate the other observations which have been made here and elsewhere. In particular, if the detailed experimental results for propyne and methane could be reproduced theoretically, this would represent a major step forward in our understanding of overtone spectra.

On the basis of this study, it is easy to predict that the high C–H stretch overtone bands ($v \geqslant 5$) of larger hydrocarbons like benzene will show a temperature dependence which is far less than that expected for simple bands. While a jet-cooled spectrum of such an overtone band may show some vibrational structure and some reduction in the FWHM, it seems unlikely that the overall appearance would be strikingly different.

ACKNOWLEDGMENTS

We would like to thank Knowles Electronics for the donation of the BL-1785 microphones, Pat Vaccaro for helpful discussions and the National Science Foundation for funding this study under Grant CHE 85-05926.

[1] B. R. Henry, Acc. Chem. Res. **10**, 207 (1977).

[2] M. S. Child and L. Halonen, Adv. Chem. Phys. **57**, 1 (1984); M. S. Child, *ibid.* **45**, 45 (1985).

[3] E. L. Sibert III, W. P. Reinhardt, and J. T. Hynes, Chem. Phys. Lett. **92**, 455 (1982); J. Chem. Phys. **81**, 1115 (1984).

[4] R. G. Bray and M. J. Berry, J. Chem. Phys. **71**, 4909 (1979).

[5] P. J. Nagy and W. L. Hase, Chem. Phys. Lett. **54**, 73 (1978); **58**, 482 (1978).

[6] D. F. Heller and S. Mukamel, J. Chem. Phys. **70**, 463 (1979); S. Mukamel, J. Phys. Chem. **88**, 832 (1984).

[7] M. Sage and J. Jortner, Chem. Phys. Lett. **62**, 451 (1979); Adv. Chem. Phys. **47**, 293 (1981).

[8] P. R. Stannard and W. Gelbart, J. Phys. Chem. **85**, 3592 (1981).

[9] C. J. Cerjan, S.-H. Shi, and W. H. Miller, J. Phys. Chem. **86**, 2244 (1982).

[10] K. Von Puttkamer, H.-R. Dübal, and M. Quack, Faraday Discuss. Chem. Soc. **75**, 197 (1983).

[11] D. Douketis, D. Anex, G. Ewing, and J. P. Reilly, J. Phys. Chem. **89**, 4173 (1985).

[12] L. J. Butler, T. M. Ticich, M. D. Likar, and F. F. Crim, J. Chem. Phys. **85**, 2331 (1986).

[13] G. A. West, R. P. Mariella, J. A. Pete, W. B. Hammond, and D. F. Heller, J. Chem. Phys. **75**, 2006 (1981).

[14] E. S. McGinley, and F. F. Crim, J. Chem. Phys. **85**, 5741 (1986).

[15] R. H. Page, Y. R. Shen, and Y. T. Lee, Phys. Rev. Lett. **59**, 1293 (1987).

[16] G. J. Scherer, K. K. Lehmann, and W. Klemperer, J. Chem. Phys. **81**, 5319 (1984).

[17] A. Amrein, H.-R. Dübal, and M. Quack, Mol. Phys. **56**, 727 (1985).

[18] H.-R. Dübal and M. Quack, J. Chem. Phys. **81**, 3779 (1984).

[19] H.-R. Dübal and M. Quack, Mol. Phys. **53**, 257 (1984); J. E. Baggott, M.-C. Chuang, R. N. Zare, H.-R. Dübal, and M. Quack, J. Chem. Phys. **82**, 1186 (1985).

[20] M. Lewerenz and M. Quack, Chem. Phys. Lett. **123**, 197 (1986).

[21] J. Segall, R. N. Zare, H.-R. Dübal, M. Lewerenz, and M. Quack, J. Chem. Phys. **86**, 634 (1987).

[22] J. S. Hutchinson, J. T. Hynes, and W. P. Reinhardt, J. Phys. Chem. **90**, 3528 (1986).

[23] J. S. Hutchinson, W. P. Reinhardt, and J. T. Hynes, J. Chem. Phys. **79**, 4247 (1983).

[24] J. S. Hutchinson, E. L. Sibert III, and J. T. Hynes, J. Chem. Phys. **81**, 1314 (1984).

[25] S. L. Coy and K. K. Lehmann, J. Chem. Phys. **84**, 5239 (1986).

[26] G. M. Stewart and J. D. McDonald, J. Chem. Phys. **78**, 3907 (1983).

[27] G. M. Stewart, M. D. Ensminger, T. J. Kulp, R. S. Ruoff, and J. D. McDonald, J. Chem. Phys. **79**, 3190 (1983).

[28] H. L. Kim, T. J. Kulp, and J. D. McDonald, J. Chem. Phys. **87**, 4376 (1987).

[29] D. J. Nesbitt and S. R. Leone, Chem. Phys. Lett. **87**, 123 (1982).

[30] D. W. Chandler, W. E. Farneth, and R. N. Zare, J. Chem. Phys. **77**, 4447 (1982).

[31] J. K. Messer and F. C. De Lucia, Phys. Rev. Lett. **53**, 2555 (1984).

[32] A. M. Smith, U. G. Jørgensen, and K. K. Lehmann, J. Chem. Phys. **87**, 5649 (1987).

[33] D. C. Tardy and B. S. Rabinovitch, J. Chem. Phys. **48**, 1427 (1968); G. Z. Whitten and B. S. Rabinovitch, *ibid.* **41**, 1883 (1964); **38**, 2466 (1963).

[34] H. Vedder and R. Mecke, Z. Phys. **86**, 137 (1933).

[35] L. P. Giver, J. Quant. Spectrosc. Radiat. Transfer **19**, 311 (1978).

[36] L. Halonen and M. S. Child, Mol. Phys. **46**, 239 (1982); J. Chem. Phys. **79**, 4355 (1983).

[37] I. Abram, A. de Martino, and R. Frey, J. Chem. Phys. **76**, 5727 (1982).

[38] J. W. Perry, D. J. Moll, A. Kuppermann, and A. H. Zewail, J. Chem. Phys. **82**, 1195 (1985).

[39] L. Halonen and A. G. Robiette, J. Chem. Phys. **84**, 6861 (1986).

[40] W. H. J. Childs, Proc. R. Soc. Londen Ser. A **153**, 555 (1936).

[41] J. S. Margolis and K. Fox, Astrophys. J. **158**, 1183 (1969).

[42] G. Herzberg, *Infared and Raman Spectra* (Van Nostrand, Princeton, 1945).

[43] M. W. Crofton, J. H. Gutow, C. G. Stevens, and R. N. Zare (unpublished results).

[44] J. M. Jasinski, Chem. Phys. Lett. **123**, 121 (1986).

[45] M. J. Berry, Proceedings of Robert A. Welch Foundation XXVIII, 133, November 1984.

[46] T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, United States Dept. of Commerce, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. 39 (U.S. GPO, Washington, D.C., 1972).

[47] J. L. Duncan, D. C. McKean, P. D. Maalinson, and R. D. McCulloch, J. Mol. Spectrosc. **46**, 232 (1973).

[48] M. W. Crofton, J. H. Gutow, C. G. Stevens, and R. N. Zare (manuscript in preparation).

[49] J. S. Hutchinson, J. Chem. Phys. **82**, 22 (1985).

[50] K. V. Reddy, D. F. Heller, and M. S. Berry, J. Chem. Phys. **76**, 2814 (1982).

[51] J. S. Wong, Doctoral Dissertation, University of California, Berkeley, 1981, University Microfilms Int.

[52] H. L. Fang, D. M. Meister, and R. L. Swofford, J. Phys. Chem. **88**, 410 (1984).