

CH-Stretching Overtone Spectra of 3-Hexyne and Butane[†]

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We have recorded vapor-phase CH-stretching overtone spectra of 3-hexyne in the $\Delta\nu_{\text{CH}} = 2-8$ regions and of 3-hexyne-*d*₁₀ in the $\Delta\nu_{\text{CD}} = 2-7$ regions. We have recorded CH-stretching overtone spectra of butane in the $\Delta\nu_{\text{CH}} = 2-7$ regions and of propane in the $\Delta\nu_{\text{CH}} = 7$ and 8 regions to facilitate comparison with the 3-hexyne spectra. The spectra were recorded at room temperature with the use of conventional and intracavity laser photoacoustic spectroscopy. The spectra can be explained in terms of a harmonically coupled local-mode model (HCAO) with one oscillator for each of the nonequivalent CH bonds. Spectral assignments are made and correlated with ab initio geometry optimized structures. The intensities of the CH stretching transitions are calculated using the HCAO local-mode model and ab initio dipole moment functions. Parameters for the calculations come from a local-mode analysis of the spectra and from ab initio calculations. Our simple calculations are in good agreement with the observed absolute and relative intensities. The ethyl group in 3-hexyne is freely rotating, but there is little difference in the CH bond length with the ethyl group position. No peaks due to internal methyl or ethyl rotation are observed in the spectra of 3-hexyne. The frequency of the in-plane methyl bond increases significantly in 3-hexyne compared to those in propane and butane.

Introduction

The overtone spectra of XH oscillators (X = C, N, O) can be explained within the local-mode model of molecular vibration.¹⁻³ The peak positions in CH-stretching overtone spectra can be calculated with a harmonically coupled anharmonic oscillator (HCAO) local-mode model with reasonable accuracy.³⁻⁵ When combined with ab initio-calculated dipole moment functions (DMF), the HCAO local-mode model has been successful in the calculation of CH-stretching overtone intensities.⁵⁻⁷

A low barrier to the internal rotation of the ethyl group ($-\text{CH}_2-\text{CH}_3$) in 3-hexyne has been suggested by Crowder and Blankenship.⁸ They found that lower-frequency peaks in the infrared (IR) spectrum could be assigned to different possible structures of 3-hexyne. The methyl group in 3-hexyne and the methyl groups in propane and butane have relatively high barriers to internal rotation (approximately 1000 cm^{-1}). In propane and butane, this has led to the observation of overtone transitions assigned to the nonequivalent in-plane (CH_{ip}) and out-of-plane (CH_{op}) methyl CH bonds.^{5,9} A low barrier to internal methyl rotation in molecules such as toluene has been found to have a significant effect on the overtone spectra, and the assignment of CH_{ip} and CH_{op} is no longer possible.¹⁰ These spectra have been successfully simulated with a model that included both CH stretching and methyl internal rotation.^{11,12} In 3-hexyne, it is unlikely that internal methyl rotation will have any influence on the CH stretching overtone spectra; however, we will investigate the effect of rotation of the ethyl group. As

the barrier to ethyl group internal rotation is low, any such influence would depend on the variation in CH bond lengths as the ethyl group rotates. Crowder and Blankenship⁸ found no influence of the ethyl group internal rotation on vibrational modes with frequencies above 600–700 cm^{-1} . This suggests that one might expect only small changes or no changes in the CH-stretching overtone spectra.

Overtone spectra of propane and butane have been published.^{5,13-17} In the present paper, we extend the previous investigations to higher-energy transitions to facilitate comparison with our spectra of 3-hexyne. We have first compared the overtone spectra of propane and butane to investigate the effect of lengthening the carbon backbone. We then compare the effect that the addition of a triple bond has on the CH stretching overtone spectra. Previously, McKean has shown that adjacent multiple bonds can have a large effect on CH stretching vibrations.⁹

We have investigated the effect of basis sets and the level of theory on calculated intensities for a series of molecules.¹⁸⁻²⁰ In general, we found that the larger the basis set the better the absolute intensities. Electron correlation mainly seemed to affect the intensity of the fundamental transition. In our previous calculations on HCN, which has a multiple bond next to the CH oscillator, we obtained quite good agreement with the calculated absolute CH stretching intensities for $\Delta\nu_{\text{CH}} = 2-7$ with an HF/6-311+G(d,p) dipole moment function.²⁰

We have calculated the CH-stretching overtone intensities for propane, butane, and 3-hexyne and compare these with the available experimental data.

Experimental Section

The compounds 3-hexyne (Aldrich, 99%), 3-hexyne-*d*₁₀ (Cambridge Isotope Laboratories, 98%), butane (Phillips 66,

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99.93%), and propane (Matheson Gas Products Canada, 99.5%) were used without any further purification. The vapor-phase spectra were recorded with a conventional spectrometer (Cary 5e) with a multipass White cell (2.25m – 21.75m) in the $\Delta\nu_{\text{CH}} = 2\text{--}5$ regions and with intracavity photoacoustic spectroscopy (ICL-PAS) in the $\Delta\nu_{\text{CH}} = 5\text{--}8$ regions. The spectra of 3-hexyne were recorded in the $\Delta\nu_{\text{CH}} = 2\text{--}8$ regions, and those of butane, in the $\Delta\nu_{\text{CH}} = 2\text{--}7$ regions, whereas propane spectra were recorded only for the $\Delta\nu_{\text{CH}} = 7$ and 8 regions. The spectra of 3-hexyne-*d*₁₀ were recorded in the $\Delta\nu_{\text{CD}} = 2\text{--}7$ regions and in the $\Delta\nu_{\text{CH}} = 2\text{--}5$ regions.

Our version of ICL-PAS has been described previously.^{21,22} Briefly, a Coherent Innova argon ion laser running at all lines was used to pump a Coherent 890 titanium/sapphire laser or a Coherent 599-01 dye laser. DCM, R6G, C6, and C102 dyes were used in the dye laser to cover the different wavelength ranges. The photoacoustic cell contained a Knowles Electronics, Inc. EK3132 electret microphone, and its signal was sent to a Stanford Research Systems SR510 lock-in amplifier. The laser was intensity modulated with a mechanical chopper, and the lock-in amplifier was referenced to the modulation frequency. The laser output power was measured and used to normalize the photoacoustic signal. The titanium/sapphire and dye lasers were tuned with a three-plate birefringent filter rotated by a stepping motor attached to a micrometer screw. The three-plate birefringent filter gives a line width of about 1 cm⁻¹.

The wavenumber axis in the $\Delta\nu_{\text{CH}} = 8$ overtone region is slightly more uncertain than in the other regions, as no absorption lines from water impurities could be used to check the wavenumber calibration.

Galactic Grams/32 (v5.03) software was utilized for spectral curve fitting of all spectra.²³ Spectral bands were curve fit with Gaussian–Lorentzian mixture functions to a linear baseline, and no other constraints were applied to the curve-fitting procedure.

Theory and Calculations

The dimensionless oscillator strength f_{eg} of a transition from the vibrational ground state *g* to a vibrational excited state *e* is given by^{5,24}

$$f_{\text{eg}} = 4.702 \times 10^{-7} (\text{cm D}^{-2}) \tilde{\nu}_{\text{eg}} |\bar{\mu}_{\text{eg}}|^2 \quad (1)$$

where $\tilde{\nu}_{\text{eg}}$ is the transition frequency in cm⁻¹ and $\bar{\mu}_{\text{eg}} = \langle e|\bar{\mu}|g\rangle$ is the transition dipole moment in debye (D).

The optimized structure of 3-hexyne that is shown in Figure 1 has *C*₂ symmetry, and thus all five CH bonds in the ethyl group are nonequivalent. In principle, we would expect five peaks in the CH-stretching overtone spectrum. However, the two methylene CH bonds and two of the methyl CH bonds have virtually identical bond lengths, and we expect to observe only three transitions. The coupling between CH-stretching oscillators is usually only significant if the oscillators share a common heavy atom.⁶ Thus, the CH-stretching overtone vibrations in 3-hexyne can, to a good approximation, be described by that of a methylene group and a methyl group.

Vibrational Model. The model Hamiltonians for two and three coupled CH-stretching oscillators have been given elsewhere, and we refer to these earlier papers for details.^{5,25,26} It suffices to outline briefly two coupled equivalent CH oscillators here.

$$(H^0 - E_{|00})/hc = (\nu_1 + \nu_2)\tilde{\omega} - (\nu_1^2 + \nu_2^2 + \nu_1 + \nu_2)\tilde{\omega}x \quad (2)$$

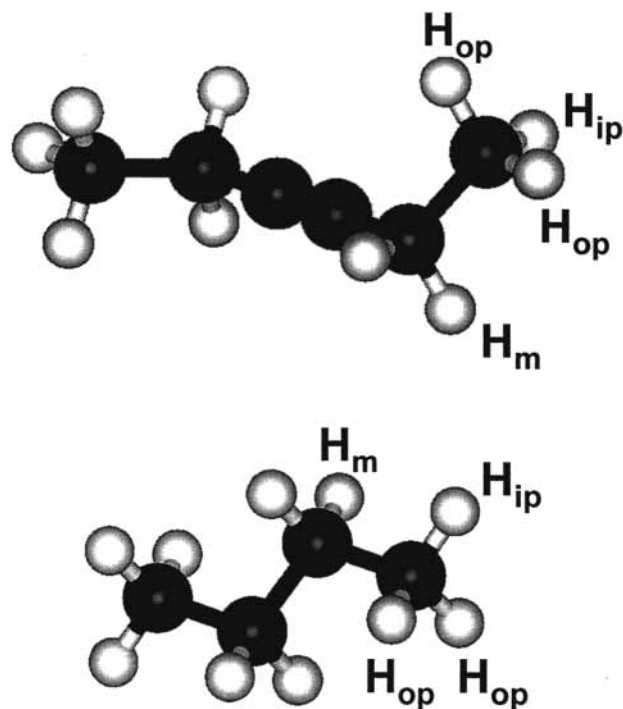


Figure 1. HF/6-311+G(d,p) optimized structures of butane (bottom) and 3-hexyne (*C*₂). Bond lengths are given in Table 1.

with the effective harmonic coupling limited to⁵

$$H'/hc = -\gamma'(a_1^+ a_2 + a_1 a_2^+) \quad (3)$$

where *a* and *a*⁺ are the usual step-up and step-down operators from harmonic oscillators. The effective coupling parameter contains both the kinetic and potential energy coupling and is given by^{4,5}

$$\gamma' = \left(-\frac{\cos \theta}{2} \left(\frac{m_{\text{H}}}{m_{\text{H}} + m_{\text{C}}} \right) - \frac{F_{12}}{2F_{11}} \right) \tilde{\omega} \quad (4)$$

where θ is the HCH angle, *m_i*, the atomic masses, and *F_{ij}*, the force constants. The angle and force constants can be calculated ab initio. The $\tilde{\omega}$ and $\tilde{\omega}x$ values are obtained from a Birge–Sponer-type fit of the observed local-mode transitions (vide infra). The model for two nonequivalent CH oscillators is similar.²⁶ The methyl group is treated similarly, with pairwise harmonic coupling between CH bonds.^{5,6,25}

Dipole Moment Function. For the methylene group, we expand the dipole moment function as

$$\bar{\mu}(q_1, q_2) = \sum_{i,j} \bar{\mu}_{ij} q_1^i q_2^j \quad (5)$$

We limit the expansion of eq 5 to sixth order for the diagonal terms and third order for the mixed terms. Diagonal expansion coefficients are calculated from 1D grids with 15 points that are generated by displacing the CH bond from -0.3 to $+0.4$ Å in 0.05-Å steps about the equilibrium geometry. The expansion coefficients are determined by fitting a sixth-order polynomial to these 1D grids. The mixed expansion coefficients are determined from a 2D grid, which is generated by displacing the CH bonds from -0.1 to $+0.1$ Å about the equilibrium. The second- and third-order mixed expansion coefficients are determined by fitting polynomials to these 2D grids. The mixed coefficients mainly affect the intensities of the less-intense

TABLE 1: Calculated CH Bond Lengths (Å)

	propane		butane ^a		3-hexyne ^b	
	HF ^c	B3LYP ^c	HF ^c	B3LYP ^c	HF ^c	B3LYP ^c
CH _m	1.0880	1.0960	1.0890	1.0970	1.0860	1.0961
CH _{op}	1.0873	1.0948	1.0872	1.0947	1.0848	1.0923
CH _{ip}	1.0863	1.0937	1.0863	1.0936	1.0860	1.0933

^a Anti conformer. ^b C₂ conformer. ^c Calculated with the 6-311+G(d,p) basis set.

transitions to local-mode combination states. The coefficients from the 5 × 5 grids are reasonably converged.

The optimized geometries and all points in the grids are calculated at a specified ab initio method with Gaussian 94.²⁷ Values of the dipole moment are calculated with the generalized density for the specified level of theory, which will provide dipole moments that are the correct analytical derivatives of the energy. The fitting of the polynomial to the grid is done with the Polyfit routine in MATLAB.²⁸

The mixed force constants F_{ij} that are used to determine the effective harmonic coupling parameter are determined from the energies associated with the 2D dipole moment grid.

We have used the HF/6-31G(d), HF/6-311+G(d,p), B3LYP/6-31G(d), and B3LYP/6-311+G(d,p) methods for geometry optimizations and for the calculation of the dipole moment derivatives. However, we experienced considerable difficulty in obtaining dipole moment derivatives that were converged beyond third order with the B3LYP methods for 3-hexyne. We calculated the derivatives using both the polynomial fit method described above and from standard numerical techniques. Neither method was successful in giving converged dipole moment derivatives. The higher-order terms in the dipole moment expansion become increasingly important for the higher overtones. Thus, we have not used the B3LYP method for the calculation of the dipole moment functions used in the intensity calculations but instead use the HF/6-311+G(d,p) method. The dipole moment expansion coefficients for butane converged up to fifth order. However, to facilitate comparison with the calculations for 3-hexyne, the HF/6-311+G(d,p) method was used in all intensity calculations. The calculated intensities with the sixth-order dipole expansion are converged to within 20% at $\Delta\nu_{\text{CH}} = 8$.

Results and Discussion

The optimized lowest-energy conformer of 3-hexyne with no imaginary frequencies has C₂ symmetry and is shown in Figure 1. Rotation around the C2–C3 bond leads to transition-state structures with C_{2v} and C_{2h} symmetry. Both have one imaginary frequency when calculated with the B3LYP/6-311+G(d,p) method. The B3LYP/6-311+G(d,p) energy of the C₂ conformer is 90 and 20 cm⁻¹ below the energies of the trans (C_{2v}) and cis (C_{2h}) transition-state structures, respectively. Thus, at room temperature, there will be free rotation of the ethyl group. At the HF/6-31G(d) level, the energies of these three structures differ by less than 10 cm⁻¹, and all three structures have no imaginary frequencies. The lowest-energy conformation of butane has the two methyl groups anti, as shown in Figure 1. A gauche conformer in which the angle between the two methyl groups is approximately 60° has a B3LYP/6-311+G(d,p) energy 288 cm⁻¹ higher than that of the anti form. Thus, the gauche conformer will be present in appreciable amounts at room temperature.

Calculated CH bond lengths of 3-hexyne, propane, and butane with the 6-311+G(d,p) basis set are reported in Table 1. We have reported these results for the C₂ conformer of 3-hexyne

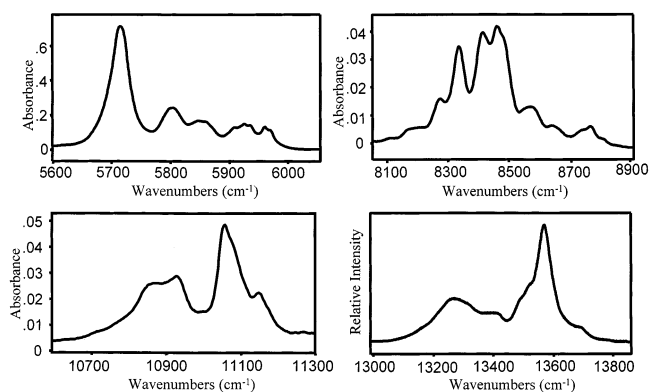


Figure 2. Room-temperature vapor-phase overtone spectra of 3-hexyne in the $\Delta\nu_{\text{CH}} = 2$ –5 regions. The spectra were recorded with a path length of 2.25 m and a pressure of 37.5 Torr for $\Delta\nu_{\text{CH}} = 2$ and 3, with a path length of 21.75 m and a pressure of 45 Torr for $\Delta\nu_{\text{CH}} = 4$, and with ICL-PAS and a pressure of 20 Torr for $\Delta\nu_{\text{CH}} = 5$.

although virtually identical values were obtained for the two transition states (C_{2v}, C_{2h}). As expected, B3LYP bond lengths are longer than HF bond lengths. In propane, the three CH bond lengths are very similar, and only at the higher overtones are three peaks associated with the three nonequivalent CH bonds clearly visible.^{5,13} Individual vibrational overtone transitions of nonequivalent bonds are consistently resolved when the bond lengths differ by as little as 1 mÅ.^{2,7} The calculated relative bond lengths are quite similar among the various methods, apart from the HF/6-311+G(d,p)-calculated CH_m bond length for 3-hexyne, which seems a little too short. An optimization of 3-hexyne with the QCISD/6-31G(d) method gave relative bond lengths almost identical to the B3LYP results in Table 1.

In the B3LYP calculation, the difference between methylene (CH_m) and methyl (CH_{ip} and CH_{op}) bond lengths increases from propane to butane to 3-hexyne. This difference is reflected in a larger observed splitting between the methylene and methyl bands. Perhaps the most interesting feature is the change in the relative bond lengths of the CH_{ip} and CH_{op} bonds. In propane and butane, the CH_{ip} bond is shorter than the CH_{op} bond, and the higher-energy peak is assigned to CH_{ip}. In 3-hexyne, the CH_{ip} bond is longer than the CH_{op} bond, and we expect a reversal in assignment.

Observed Transitions. The vapor-phase CH-stretching spectra of 3-hexyne in the $\Delta\nu_{\text{CH}} = 2$ –5 regions are shown in the four panels of Figure 2. The gas-phase CH-stretching spectra of butane in the $\Delta\nu_{\text{CH}} = 2$ –5 regions are shown in the four panels of Figure 3. In Figures 4 and 5, we show the vapor-phase spectra of propane, butane, and 3-hexyne in the regions of $\Delta\nu_{\text{CH}} = 6$ and 7. In Figure 6, we show the vapor-phase spectra of propane and 3-hexyne in the region of $\Delta\nu_{\text{CH}} = 8$. The vapor-phase CD-stretching spectra of 3-hexyne-*d*₁₀ in the regions of $\Delta\nu_{\text{CD}} = 5$ and 6 are shown in Figure 7. Characteristics of the observed CH stretching transitions in the spectra of butane and 3-hexyne-*d*₀ and the observed CD stretching transitions in 3-hexyne-*d*₁₀ are given in Tables 2–4, respectively. The frequencies, line widths, and oscillator strengths from the deconvolutions of the spectra are given in the Tables. Transitions measured with the conventional spectrometer have absolute intensities, whereas the ICL-PAS spectra provide only relative intensities within an overtone.

We fit the assigned pure local-mode peaks to a Morse oscillator (Birge–Spencer) energy expression

$$\tilde{\nu}_{v,0}/v = \tilde{\omega} - (v + 1)\tilde{\omega}x \quad (6)$$

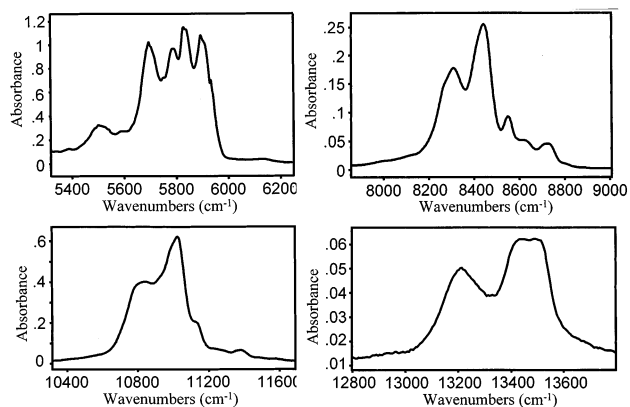


Figure 3. Room-temperature vapor-phase overtone spectra of butane in the $\Delta\nu_{\text{CH}} = 2-5$ regions. The spectra were recorded with a path length of 2.25 m and a pressure of 225 Torr for $\Delta\nu_{\text{CH}} = 2$ and 3 and with a path length of 21.75 m and a pressure of 750 Torr for $\Delta\nu_{\text{CH}} = 4$ and 5.

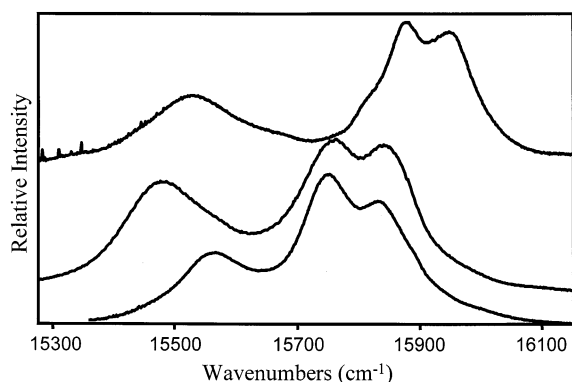


Figure 4. Room-temperature vapor-phase overtone spectra of 3-hexyne (top trace), butane (middle trace), and propane (bottom trace) in the $\Delta\nu_{\text{CH}} = 6$ region recorded with ICL-PAS.

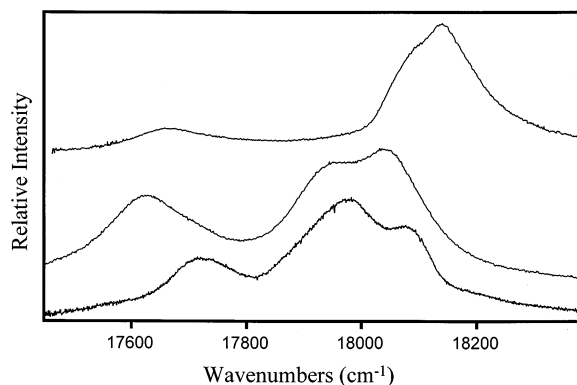


Figure 5. Room-temperature vapor-phase overtone spectra of 3-hexyne (top trace), butane (middle trace), and propane (bottom trace) in the $\Delta\nu_{\text{CH}} = 7$ region recorded with ICL-PAS.

to obtain the local-mode parameters. The local-mode parameters obtained from the butane and 3-hexyne spectra are given in Table 5. The effective coupling parameters (eq 4) for butane and 3-hexyne were calculated *ab initio*. The local-mode parameters for propane were taken from ref 5 and are given in Table 5 for comparison. The present results for propane were obtained with these parameters and an HF/6-311+G(d,p)-calculated dipole moment function. The effective coupling between the methylene CH_m oscillators in all three molecules appears to be less than the coupling between the CH bonds in the methyl group.

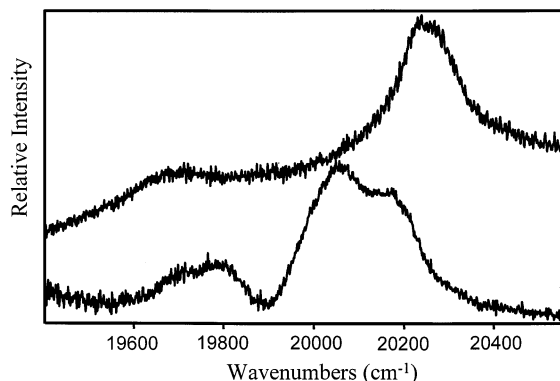


Figure 6. Room-temperature vapor-phase overtone spectra of 3-hexyne (top trace) and propane (bottom trace) in the $\Delta\nu_{\text{CH}} = 8$ region recorded with ICL-PAS.

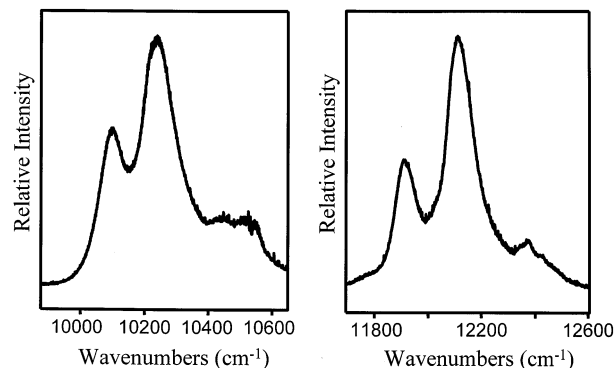


Figure 7. Room-temperature vapor-phase overtone spectra of 3-hexyne- d_{10} in the $\Delta\nu_{\text{CD}} = 5$ and 6 regions recorded with ICL-PAS.

Butane. The observed CH-stretching overtone spectra of butane are similar to the spectra of propane.⁵ This is clearly seen in Figures 4 and 5. The similarity of the CH_{ip} and CH_{op} peaks in the propane and butane spectra is in good agreement with the very similar calculated bond lengths. There is an excellent correlation between the observed local-mode frequencies in Table 5 and the B3LYP/6-311+G(d,p) bond lengths in Table 1. The CH_m oscillator in butane has a lower frequency than that in propane, as expected from the calculated bond lengths, and the observed larger splitting between methylene and methyl bands in the butane spectra reflects this. Our measured butane spectra agree well with the previously published vapor-phase spectra in the $\Delta\nu_{\text{CH}} = 3$ and 6 regions.^{13,14,17}

Two peaks that can be assigned to a Fermi resonance are observed in the methylene $\Delta\nu_{\text{CH}} = 4$ region. At the higher overtones, it appears that this resonance decreases as one of the states shifts further away in frequency and becomes more of a shoulder. In Table 2, we have combined the intensity of the resonance states to give the methylene band intensity. We deconvoluted the $\Delta\nu_{\text{CH}} = 5$ and 6 regions with the methylene band represented by both one and two peaks. The results from the two different fits are very similar in the relative methylene to methyl intensity. In the two peak fits, the frequency of the CH_m transition is taken as the weighted average of the two peaks. The local-mode parameters are found from a fit of the transitions for $\Delta\nu_{\text{CH}} = 3-7$ to eq 6. For the CH_m oscillator, we use the weighted center peak from the two-peak structure at $\Delta\nu_{\text{CH}} = 4-6$. The choice of one peak or two peaks representing the methylene band has little effect on the local-mode parameters.

There is little difference in the anharmonicities between the bonds in propane and those in butane. For both molecules, the

TABLE 2: Observed Frequencies, Line Widths, Intensities, and Peak Assignments in the CH-Stretching Overtone Spectrum of Butane

observed			calculated ^a		assignment
$\tilde{\nu}/\text{cm}^{-1}$	line width	f^b	$\tilde{\nu}/\text{cm}^{-1}$	f	
5698	76	1.35×10^{-7}	5656, 5661 5712, 5731 5747	1.4×10^{-7} 4.3×10^{-8} 4.2×10^{-8}	$ 20\rangle_{\pm}$ $ 20\rangle_{-} 0\rangle; 20\rangle_{+} 0\rangle$ $ 00\rangle 2\rangle$
5783	59	7.04×10^{-8}	5790	1.0×10^{-7}	$ 11\rangle$
5836	54	9.21×10^{-8}	5852, 5887	2.1×10^{-7}	$ 10\rangle_{\pm} 1\rangle$
5901	50	9.17×10^{-8}	5892	6.6×10^{-8}	$ 11\rangle 0\rangle$
8256	50	3.1×10^{-9}			
8305	125	4.1×10^{-8}	8302, 8303	4.0×10^{-8}	$ 30\rangle_{\pm}$
8419	77	2.5×10^{-8}	8410, 8412	2.6×10^{-8}	$ 30\rangle_{\pm} 0\rangle$
8455	55	1.8×10^{-8}	8447	1.8×10^{-8}	$ 00\rangle 3\rangle$
8552	40	5.0×10^{-9}	8530	1.4×10^{-9}	$ 21\rangle_{+}$
8625	89	6.1×10^{-9}	8581 8603, 8643, 8648	1.9×10^{-9} 6.1×10^{-9}	$ 21\rangle_{-}$ CH ₃ 21 comb
8709	52	2.9×10^{-9}	8707	1.8×10^{-9}	
8740	38	2.0×10^{-9}	8718	2.9×10^{-9}	
10 781	119	4.0×10^{-9}	10 822	4.2×10^{-9}	$ 40\rangle_{\pm}; \text{FR}$
10 862	163				
10 987	144	3.5×10^{-9}	10 977	3.3×10^{-9}	$ 40\rangle_{\pm} 0\rangle$
11 035	72	1.4×10^{-9}	11 030	2.1×10^{-9}	$ 00\rangle 4\rangle$
11 138	42	2.0×10^{-10}	11 184 11 199	2.6×10^{-11} 1.6×10^{-10}	$ 31\rangle_{+}$ $ 31\rangle_{-}$
11 366	166	3.7×10^{-10}	11 325, 11 368	4.6×10^{-10}	CH ₃ 31 comb
13 184	122	3.2×10^{-10}	13 217	5.5×10^{-10}	$ 50\rangle_{\pm}; \text{FR}$
13 247	136				
13 430	149	3.8×10^{-10}	13 421	4.9×10^{-10}	$ 50\rangle_{\pm} 0\rangle$
13 515	83	1.6×10^{-10}	13 494 13 887, 13 934	3.1×10^{-10} 4.9×10^{-11}	$ 00\rangle 5\rangle$ CH ₃ 41 comb
15 466	135	1	15 488	8.9×10^{-11}	$ 60\rangle_{\pm}; \text{FR}$
15 536	180				
15 752	130	0.87 (0.86) ^c	15 743	8.7×10^{-11}	$ 60\rangle_{\pm} 0\rangle$
15 852	107	0.64 (0.55) ^c	15 839	5.1×10^{-11}	$ 00\rangle 6\rangle$
17 637	171	0.56	17 634	1.7×10^{-11}	$ 70\rangle_{\pm}; \text{FR}$
17 729	139				
17 944	154	0.72	17 943	1.7×10^{-11}	$ 70\rangle_{\pm} 0\rangle$
18 059	158	1	18 064	9.7×10^{-12}	$ 00\rangle 7\rangle$

^a Calculated with local-mode parameters from Table 5 and an HF/6-311+G(d,p) dipole moment function. ^b Relative intensity within the overtone for $\Delta\nu_{\text{CH}} = 6$ and 7. ^c Numbers in parentheses are taken from ref 17, which gives three bands at 15 474, 15 750, and 15 833 cm^{-1} .

CH_m bond has slightly larger anharmonicity and a slightly lower frequency than the methyl CH bonds. The CH_m bond in butane is slightly longer and has a slightly lower frequency than that in propane, which leads to the CH_m band in butane at lower frequency, as seen in Figures 4 and 5.

The methylene peak in butane is broader than both the CH_{ip} and CH_{op} methyl peaks. This can be rationalized from the existence of a gauche structure in which the CH₃ groups are not 180° opposite (anti) but are at a 65° angle (gauche). The anti structure has C_{2h} symmetry whereas the gauche structure has C₂ symmetry. In the gauche structure, there are two nonequivalent CH_m bonds. One of these bonds is similar to the CH_m bonds in the anti structure whereas the other is shorter. This could lead to a broader methylene band and is another possible reason for the frequent “double-peak” structure. Recently, the abundance of the gauche structure has been calculated at the 6-31++G(d,p) level of theory (presumably HF) to be about 13%.¹⁷ Our present B3LYP/6-311++G(d,p) calculations predict a somewhat higher abundance of the gauche structure.

3-Hexyne. The methylene band is clearly observed in the $\Delta\nu_{\text{CH}} = 3, 6,$ and 7 regions. In the $\Delta\nu_{\text{CH}} = 4$ and 5 regions, the

TABLE 3: Observed Frequencies, Line Widths, Intensities, and Peak Assignments in the CH-Stretching Overtone Spectrum of 3-Hexyne

observed			calculated ^a		assignment
$\tilde{\nu}/\text{cm}^{-1}$	line width	f^b	$\tilde{\nu}/\text{cm}^{-1}$	f	
5714	37	3.1×10^{-7}	5679, 5685	4.1×10^{-7}	$ 20\rangle_{\pm}$
5802	39	1.0×10^{-7}	5740, 5770, 5777	8.8×10^{-8}	$ 20\rangle_{\pm} 0\rangle,$ $ 00\rangle 2\rangle$
5846	40	2.7×10^{-7}	5819	1.7×10^{-7}	$ 11\rangle$
5864–5964		1.3×10^{-7}	5889, 5925, 5930	1.3×10^{-7} 1.2×10^{-7}	CH ₃ 11 comb CH ₃ 11 comb
8336	45	1.8×10^{-8}	8334	5.8×10^{-8}	$ 30\rangle_{\pm}$
8413	49	2.0×10^{-8}			combination
8462	58	2.4×10^{-8}	8462	1.7×10^{-8}	$ 00\rangle 3\rangle$
8491	37	0.8×10^{-8}	8486, 8489	1.5×10^{-8}	$ 30\rangle_{\pm} 0\rangle$
8574	70	1.0×10^{-8}	8566, 8622	4.0×10^{-9}	$ 21\rangle_{\pm}$
8652	56	3.1×10^{-9}	8648, 8693, 8699	6.7×10^{-9}	CH ₃ 21 comb
8767	64	5.4×10^{-9}	8775, 8772	5.3×10^{-9}	CH ₃ 21 comb
10 863	132	2.3×10^{-9}	10 858	5.1×10^{-9}	$ 40\rangle_{\pm}$
10 930	54	0.7×10^{-9}			combination
11 051	29	0.8×10^{-9}	11 054	2.3×10^{-9}	$ 00\rangle 4\rangle$
11 080	62	1.7×10^{-9}	11 089	2.9×10^{-9}	$ 40\rangle_{\pm} 0\rangle$
11 152	56	0.8×10^{-9}			combination
			11 228, 11 245	1.8×10^{-10}	$ 31\rangle_{\pm}$
11 432	98	3.5×10^{-10}	11 401, 11 439, 11 445	5.2×10^{-10}	CH ₃ 31 comb
13 257	155	1.6×10^{-10}	13 254	6.1×10^{-10}	$ 50\rangle_{\pm}$
13 320	141	6.2×10^{-11}			
13 503	75	7.0×10^{-11}	13 525	3.3×10^{-10}	$ 00\rangle 5\rangle$
13 570	61	2.0×10^{-10}	13 573, 13 974, 14 003, 14 006	4.3×10^{-10} 5.1×10^{-11}	$ 50\rangle_{\pm} 0\rangle$ CH ₃ 41 comb
15 525	189	1	15 522	9.2×10^{-11}	$ 60\rangle_{\pm}$
15 666	109	0.07			
15 812	54	0.09			
15 873	78	0.68	15 879	5.8×10^{-11}	$ 00\rangle 6\rangle$
15 951	96	0.86	15 940	7.4×10^{-11}	$ 60\rangle_{\pm} 0\rangle$
17 668	212	0.27	17 663	1.7×10^{-11}	$ 70\rangle_{\pm}$
18 086	55	0.10			
18 153	144	1	18 114, 18 189	2.5×10^{-11}	$ 00\rangle 7\rangle,$ $ 70\rangle_{\pm} 0\rangle$
~19 700		1	19677	3.6×10^{-12}	$ 80\rangle_{\pm}$
20 249	188	~3	20 230, 20 322	5.4×10^{-12}	$ 00\rangle 8\rangle,$ $ 80\rangle_{\pm} 0\rangle$

^a Calculated with local-mode parameters from Table 5 and an HF/6-311+G(d,p) dipole moment function. ^b Relative intensity within the overtone for $\Delta\nu_{\text{CH}} = 6$ –8.

methylene band is a bit broader. There is an excellent fit of the observed transitions to eq 6, and $\tilde{\omega}_m$ and $\tilde{\omega}_{x_m}$ are well determined for the CH_m bond. The inclusion of $\Delta\nu_{\text{CH}} = 2$ in the Birge–Spencer fit increases $\tilde{\omega}_m$ and $\tilde{\omega}_{x_m}$ significantly. The fit without $\Delta\nu_{\text{CH}} = 2$ gives much better agreement with the observed peaks. Such a situation is not unusual, as coupling is much more important in the $\Delta\nu_{\text{CH}} = 2$ region. The standard deviation for the above fit is small, and the frequencies and anharmonicities are very similar to the values for propane, in good correlation with the B3LYP-calculated bond lengths in Table 1.

In 3-hexyne, the B3LYP-calculated relative CH_{ip} to CH_{op} bond lengths in Table 1 suggest a reversal of the spectral positions of the CH_{ip} and CH_{op} bands compared to those in the

TABLE 4: Observed Frequencies, Line Widths, Intensities, and Peak Assignments in the CD-Stretching Overtone Regions of 3-Hexyne- d_{10} Spectra

$\tilde{\nu}/\text{cm}^{-1}$	observed		assignment
	line width	f^a	
8206	82	1	CH ₂
8295	114	2.2	CH ₃
10 095	85	1	$ 50\rangle_{\pm}$
10 254	142	2.6	$ 50\rangle_{\pm} 0\rangle, 00\rangle 5\rangle$
11 914	89	1	$ 60\rangle_{\pm}$
12 126	136	2.6	$ 60\rangle_{\pm} 0\rangle, 00\rangle 6\rangle$
13 665	48	1	$ 70\rangle_{\pm}$
13 922	116	2.1	$ 70\rangle_{\pm} 0\rangle, 00\rangle 7\rangle$

^a Relative intensity within the overtone.

TABLE 5: Local-Mode Frequencies, Anharmonicities, and Effective Coupling Constants (cm^{-1}) of the CH Stretching Modes^a

	propane ^b	butane ^c	3-hexyne ^d
$\tilde{\omega}_m$	3036 ± 10	3017 ± 1.5	3034 ± 1
$\tilde{\omega}_{op}$	3052 ± 7	3050 ± 1.2	3068
$\tilde{\omega}_{ip}$	3060 ± 9	3057 ± 3.3	3062
$\tilde{\omega}_{xm}$	62.9 ± 1.5	62.2 ± 0.3	63.8 ± 0.1
$\tilde{\omega}_{xop}$	61.0 ± 1.1	60.7 ± 0.2	58.5
$\tilde{\omega}_{xip}$	59.9 ± 1.4	59.4 ± 0.6	59.1
γ'_m	23.4	13.0 ^e	14.3 ^e
$\gamma'_{ip,op}$	27.4	20.0 ^e	23.1 ^e
$\gamma'_{op,op}$	25.9	19.7 ^e	22.4 ^e

^a Uncertainty is 1 standard deviation. ^b Taken from ref 5. ^c From a fit of peaks $\Delta\nu_{\text{CH}} = 3-7$ with the CH_m FR in $\Delta\nu_{\text{CH}} = 4-6$. ^d From a fit to $\Delta\nu_{\text{CH}} = 3-8$ for CH_m. For the CH₃ bonds, we have estimated the values on the basis of a fit of the weighted-average CH₃ peaks in the $\Delta\nu_{\text{CH}} = 4-8$ regions, which yields 3065 ± 3 and $59.1 \pm 0.1 \text{ cm}^{-1}$. ^e Calculated from eq 4 with parameters obtained with the HF/6-311+G(d,p) method and experimental frequencies.

propane and butane spectra. For the CH_{ip} and CH_{op} peaks, the identification of individual peaks is more difficult than what we found for propane and butane. Even in the highest $\Delta\nu_{\text{CH}} = 8$ region it is difficult to deconvolute two peaks with certainty. We have used a weighted average of the peaks observed in the methyl band and have fit these to eq 6. If we exclude the $\Delta\nu_{\text{CH}} = 2$ and 3 bands, the fit is quite good and yields $\tilde{\omega} = 3065 \pm 3$ and $\tilde{\omega}_x = 59.1 \pm 0.1 \text{ cm}^{-1}$. The calculated CH_{ip} and CH_{op} bond lengths in Table 1 suggest that $\tilde{\omega}_{op}$ should be larger than $\tilde{\omega}_{ip}$. On the basis of the B3LYP-calculated bond lengths in Table 1 and a comparison with the relative bond lengths and corresponding frequencies for butane, we increased $\tilde{\omega}_{op}$ and decreased $\tilde{\omega}_{ip}$ by 3 cm^{-1} , left $\tilde{\omega}_{xop}$ unchanged, and lowered $\tilde{\omega}_{xip}$ to 58.5 cm^{-1} . These slightly modified methyl local-mode parameters lead to better agreement with the observed methyl transitions than the Birge-Sponer-fitted overall methyl-band values.

We considered the free rotation of the ethyl group in 3-hexyne as another possibility to explain the overall difficulty in resolving the presence of bands due to CH_{ip} and CH_{op} stretching transitions. We found that the bond lengths of the various CH bonds in all three structures of 3-hexyne (C_2 , C_{2v} , and C_{2h}) are virtually identical. We calculated the intensities for the various CH oscillators in the three different structures considered for 3-hexyne with the HF/6-31G(d) dipole moment function. As for the bond lengths, we found little change in the intensities for each bond upon rotation of the ethyl group. The small variations in bond lengths and presumably also frequencies with the rotation of the ethyl group will lead only to some broadening of the peaks.

TABLE 6: Relative Intensity of the CH-Stretching Pure Local Modes of the CH₃/CH₂ Groups

ν	propane		butane		3-hexyne	
	obsd	calcd ^a	obsd	calcd ^a	obsd	calcd ^a
3	2.8 ^b	1.7	1.1	1.1	0.8 ^f	0.7
4	^c	2.0	1.2	1.3	1.1	1.0
5	3.1 ^d	2.4	1.7	1.5	1.7	1.3
6	2.2 ^b (2.4) ^e	2.7	1.5 (1.4) ^e	1.6	1.6	1.5
7	5.4	2.8	3.9	1.6	3.7	1.5
8	5.6	2.8		1.5	~2 ^g	1.5

^a Calculated with the local-mode parameters in Table 5 and the HF/6-311+G(d,p) dipole moment function. ^b From ref 5. ^c Deconvolution is not meaningful. ^d Unpublished spectra. ^e From ref 17. ^f Assuming that the peak at 8413 cm^{-1} obtains its intensity from the $|30\rangle_{\pm}$ transition. ^g Deconvolution is difficult because of the sloping baseline.

The calculations correctly predict the methylene pure local-mode transition to be the dominant transition in the $\Delta\nu_{\text{CH}} = 2$ region. The methyl pure local-mode state has an intensity that is weaker than both the methyl and methylene local-mode combination transitions. We label the methyl local-mode combination states as “CH₃ 11 combinations” rather than indicate all of the states involved. The calculations overestimate the total intensity in the local-mode combination peaks.

In the $\Delta\nu_{\text{CH}} = 3$ region, the $|30\rangle_{\pm}$ transition frequency is predicted well. The observed intensity is low when compared to the calculations unless the band at 8413 cm^{-1} is assumed to steal its intensity from the $|30\rangle_{\pm}$ transition. The two peaks at 8462 and 8491 cm^{-1} are assigned to the methyl pure local-mode states $|30\rangle_{\pm}|0\rangle$ and $|00\rangle|3\rangle$. The distribution of intensity between pure local-mode peaks and local-mode combinations is predicted fairly well by the calculations.

For $\Delta\nu_{\text{CH}} \geq 4$, the pure local-mode states dominate the spectrum. The sloping baseline at $\Delta\nu_{\text{CH}} = 7$ and even more so at $\Delta\nu_{\text{CH}} = 8$ makes the deconvolution more uncertain. The frequency of the methyl band is more accurately determined because of its greater intensity.

3-Hexyne- d_{10} . The coupling between CD oscillators is significantly larger than between CH oscillators because of the increased mass of deuterium, which leads to more complicated spectra in deuterated molecules. In none of the CD-stretching spectra was it possible to observe two peaks in the methyl region. In the $\Delta\nu_{\text{CD}} = 5$ and 6 regions, which are shown in Figure 7, the methylene and methyl bands can be accurately fitted as Lorentzians. The observed CD stretching transitions in 3-hexyne- d_{10} in the $\Delta\nu_{\text{CD}} = 5-7$ regions given in Table 4 were fitted to eq 6 and yielded $\tilde{\omega}_m = 2220 \pm 0.4$ with $\tilde{\omega}_{xm} = 33.4 \pm 0.1 \text{ cm}^{-1}$ for the methylene group and $\tilde{\omega} = 2237 \pm 4.8$ with $\tilde{\omega}_x = 31.0 \pm 0.7 \text{ cm}^{-1}$ for the methyl group. These $\tilde{\omega}$ and $\tilde{\omega}_x$ values are in reasonable agreement with what one would expect from the isotopic substitution and the CH stretching parameters in Table 5.⁶

We usually use the spectra of the fully deuterated compounds to observe isolated CH stretching vibrations arising from hydrogen impurities in the deuterated sample. Some CH peaks seem to be observed, but systematic assignment is not possible. It might be possible to resolve CH peaks from the spectra of 3-hexyne- d_9 with the 3-hexyne- d_{10} spectra subtracted.

Line Widths. The line widths of the CH stretching transitions in both butane and 3-hexyne increase with increasing overtone. In 3-hexyne, the line width for the methyl band increases slowly from $\sim 40 \text{ cm}^{-1}$ at $\Delta\nu_{\text{CH}} = 2$ to $\sim 80 \text{ cm}^{-1}$ at $\Delta\nu_{\text{CH}} = 6$. The line width then increases markedly to $\sim 150 \text{ cm}^{-1}$ at $\Delta\nu_{\text{CH}} = 7$ and $\sim 190 \text{ cm}^{-1}$ at $\Delta\nu_{\text{CH}} = 8$. A significant increase in line width around $\Delta\nu_{\text{CH}} = 6$ or 7 has previously been observed in

TABLE 7: Total Absolute CH-Stretching Oscillator Strengths

ν	propane		butane		3-hexyne	
	obsd	calcd ^a	obsd	calcd ^a	obsd	calcd ^a
1		8.6×10^{-5}		1.1×10^{-4}		7.8×10^{-5}
2	4.6×10^{-7b}	5.0×10^{-7}	4.6×10^{-7}	6.1×10^{-7}	5.8×10^{-7}	9.2×10^{-7}
3	9.3×10^{-8b}	8.2×10^{-8}	1.0×10^{-7}	9.9×10^{-8}	1.0×10^{-7}	1.2×10^{-7}
4	6.1×10^{-9c}	8.9×10^{-9}	9.5×10^{-9}	1.1×10^{-8}	6.8×10^{-9}	1.1×10^{-8}
5	7.5×10^{-10c}	1.2×10^{-9}	8.6×10^{-10}	1.4×10^{-9}	5.7×10^{-10}	1.5×10^{-9}
6	8.9×10^{-11d}	2.1×10^{-10}	$1.1 \times 10^{-10,d}$	2.4×10^{-10}		2.4×10^{-10}
7		4.0×10^{-11}		4.5×10^{-11}		4.4×10^{-11}

^a Calculated with the local-mode parameters in Table 5 and the HF/6-311+G(d,p) dipole moment function. ^b Taken from ref 5. ^c Unpublished spectra. ^d Taken from ref 17 and converted to oscillator strengths.

other molecules. In neopentane, it was considered to be due to through-space interactions between the methyl groups.²⁹ In 1-propyne, the increased width of the methyl band was considered to arise from the triple bond.³⁰ The methylene bands in 3-hexyne are significantly wider than the methyl bands. The methylene group is closer to the triple bond, which could facilitate larger interaction. In the methyl group, it is possible that a more efficient pathway for energy transfer becomes available at $\Delta\nu_{\text{CH}} = 7$. This increased width at the higher overtones contributes to the difficulty in assigning the CH_{ip} and CH_{op} peaks.

Intensities. Calculated intensities of individual peaks are given in Tables 2 and 3. Agreement with experimental values relies on the deconvolution and also on mixing with other states. In Table 6, we compare the observed and calculated methyl-to-methylene intensity for the various overtones. We have not included the $\Delta\nu_{\text{CH}} = 2$ results because of significant mixing and the fact that local-mode combination bands can be more intense than the pure local-mode bands in this region.

Both the observed and calculated relative methyl-to-methylene intensity is larger for propane than for butane and 3-hexyne, as expected on the basis of the number of methyl-to-methylene CH oscillators. The methylene and methyl bands are close in energy in propane, and the observed relative intensities have more uncertainty because of the deconvolution process. The methyl-to-methylene (CH_3/CH_2) intensity ratio is predicted reasonably well at $\Delta\nu_{\text{CH}} = 6$, where the peaks are resolved. The two previous results for this overtone are in good agreement.^{5,17}

In butane and 3-hexyne, the intensities of the methyl and methylene overtone transitions are more easily determined because of the larger splitting of the bands. The calculated and observed relative intensities agree very well for $\Delta\nu_{\text{CH}} = 3-6$. For butane, our $\Delta\nu_{\text{CH}} = 6$ relative intensity is in good agreement with the previous result.¹⁷ At $\Delta\nu_{\text{CH}} = 7$, there seems to be a similar disagreement for the three molecules. It is difficult to get very good experimental values for $\Delta\nu_{\text{CH}} = 8$ mainly because of the sloping baseline and the reduced signal-to-noise ratio, which can significantly affect the deconvoluted intensities.

The observed and calculated total absolute CH-stretching overtone intensities are given in Table 7. We have included the previously reported intensities for propane and butane in the $\Delta\nu_{\text{CH}} = 6$ region and have converted them to oscillator strengths.¹⁷ The integrated cross section (ICS) can be defined as the integral of the cross section (cm^2) over the wavenumber (cm^{-1}) of the region of the band. The units of ICS thus become (cm), and conversion to oscillator strength follows from $f = 1.13 \times 10^{12} \text{ cm}^{-1} \times \text{ICS}$, where the constant is calculated from the known physical constants.²⁶ In ref 17, the integrated cross section is defined as the integral of the absorption coefficient divided by the wavenumber over the wavenumber. With this definition, conversion to oscillator strength is not strictly

possible. However, multiplication by the bond center frequency allows an approximate conversion of their intensities to the oscillator strengths given in Tables 6 and 7.

The calculated total CH stretching intensities seem to increase from propane to butane, as might be expected from the increase in the number of CH bonds. The agreement between calculated and observed total intensities is quite good for $\Delta\nu_{\text{CH}} = 2, 3$, and 4. For $\Delta\nu_{\text{CH}} = 5$ and 6, the calculations overestimate the observed intensities by about 50% at $\Delta\nu_{\text{CH}} = 5$ and by a factor of about 3 for $\Delta\nu_{\text{CH}} = 6$. Perhaps increasing the basis-set size would improve the agreement for higher $\Delta\nu_{\text{CH}}$.¹⁸⁻²⁰ The increased discrepancy with increasing ν might also indicate that a better potential than the Morse potential is required for the highest overtones.³¹ It is also possible that higher-order terms in the dipole moment expansion become more important.

Conclusions

We have used conventional and intracavity laser photoacoustic spectroscopy to measure the vapor-phase spectra of 3-hexyne ($\Delta\nu_{\text{CH}} = 2-8$) and 3-hexyne- d_{10} ($\Delta\nu_{\text{CD}} = 2-7$). We have extended previous measurements of the spectra of propane (to $\Delta\nu_{\text{CH}} = 8$) and butane (to $\Delta\nu_{\text{CH}} = 7$) to allow comparisons with the 3-hexyne spectra. Absolute oscillator strengths have been measured for $\Delta\nu_{\text{CH}} = 2-5$ for propane ($\Delta\nu_{\text{CH}} = 2, 3$ from previous work), butane, and 3-hexyne. The relative intensities of transitions involving the CH_3 and CH_2 groups have been measured for 3-hexyne and butane for $\Delta\nu_{\text{CH}} = 3-7$. Relative intensities have been obtained for propane from previous work ($\Delta\nu_{\text{CH}} = 3-6$) or from new measurements ($\Delta\nu_{\text{CH}} = 7, 8$).

We have assigned the 3-hexyne spectra successfully with a harmonically coupled local-mode model in which both the methylene oscillators and the two out-of-plane methyl oscillators are taken as equivalent. No peaks were associated with internal rotation of either the ethyl group or the methyl group. In the case of ethyl rotation, the absence of peaks arises because the CH bond lengths are essentially unchanged on rotation. For the methyl group, the barrier to internal rotation is too high to involve torsional states in the overtone spectra. We are able to account for the spectral structure despite a reversal in the ordering of in-plane and out-of-plane methyl bond lengths in 3-hexyne relative to the ordering in propane and butane.

We have calculated the intensities of the CH stretching transitions with an approach that uses the anharmonic local-mode model to obtain the wave functions and ab initio HF/6-311+G(d,p) calculations to obtain the dipole moment function. The calculations give results that are in reasonably good agreement with both absolute and relative observed intensities.

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