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A Local Mode Description of the CH-Stretching Overtone Spectra of the Cycloalkanes and Cycloalkenes

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Abstract: The overtone spectra of the cycloalkanes, cyclopentane to cyclooctane, and three cycloalkenes (cyclopentene, cyclohexene, and cycloheptene) are measured in the liquid phase up to $\Delta v_{\mathrm{CH}} = 7$ for the cycloalkanes and up to $\Delta v_{\mathrm{CH}} = 6$ for the cycloalkenes. The principal bands in the cyclopentane and cyclohexane spectra correspond to axial and equatorial CH bonds. We demonstrate that these bands correspond to the properties of the CH bonds in the static limit, and for cyclopentane introduce a possible definition for axial and equatorial bonds. Single bands are observed in cycloheptane and cyclooctane and their structures explained. The overtone bands of the cycloalkenes are principally composed of two peaks, one corresponding to the olefin hydrogens and one corresponding to the methylene hydrogens. The methylene peak shows some doublet structure in cyclopentene and cyclohexene which can be understood on the same basis as in the corresponding saturated molecules. The local mode frequencies and diagonal local mode anharmonicity constants are obtained from an analysis of the spectral data.

I. Introduction

The local mode model has been successfully applied to explain the CH-stretching vibrational overtone spectra of many molecules.[2-5] In this model, the principal features of the spectrum are associated with modes of vibration with all the quanta for the transition localized in a single CH oscillator. These local modes are sensitive to differences among the nonequivalent CH bonds in the molecules. For example, transitions involving aryl and alkyl hydrogens in toluene and the xylenes have been resolved,[2b] as have transitions for the CH_3, CH_2, and CH hydrogens in the alkanes.[5] In fact, characteristic local mode frequencies and local mode anharmonicities have been found for CH_3 and CH_2 oscillators for a whole series of alkane molecules.[5]

For a pure local mode overtone where all v_i quanta are absorbed in a single chemical bond, the transition energy, ΔE, has been found to be given by[3,6,7]

$$\Delta E = v_i \omega_i + v_i^2 X_{ii} \tag{1}$$

A plot of $\Delta E/v_i$ vs. v_i will yield ω_i, the local mode frequency, as the intercept and X_{ii}, the local mode diagonal anharmonicity constant, as the slope. This simple two-parameter model fits the observed overtones with $\Delta v_{\mathrm{CH}} \geq 3$.[3-7]

The cycloalkanes and cycloalkenes have CH bonds which interchange among chemically inequivalent sites. The various interchanges occur with a wide range of different rates. We expect that the overtone spectra may vary—some of the spectra may show the static splittings of the inequivalent sites and some may be motionally averaged. The degree of motionally averaging is characterized by the quantity $2\pi\tau\Delta\nu$, where τ is the interchange limited lifetime of the molecule at one site and $\Delta\nu$ is the static splitting of the spectral feature. If this quantity is much greater than 1, the spectral feature displays the static splitting $\Delta\nu$.[8]

We report on the splittings of the CH overtone bands. The splittings provide a measure of the changing properties of CH bonds as a function of conformation.

II. Experimental Section

The spectra corresponding to $\Delta v_{\mathrm{CH}} = 3$ and 4 were measured on a Cary 14 spectrophotometer operated in the infrared mode. The 0-1 absorbance scale slidewire was used and the spectra were measured in 1- ($\Delta v_{\mathrm{CH}} = 3$) and 10-cm ($\Delta v_{\mathrm{CH}} = 4$) cells. The spectra for $\Delta v_{\mathrm{CH}} = 5$, 6, and 7 were determined either with the Cary 14 and a 0.1 absorbance scale slidewire or with the Cary 118, Cary 218, or Perkin-Elmer 555 using 0.1, 0.02, and 0.01 absorbance scales. For $\Delta v_{\mathrm{CH}} = 5$, 6, and 7 the spectra were measured in 10-cm cells. All samples were run vs. air as a reference. Frequencies for $\Delta v_{\mathrm{CH}} = 5$, 6, and 7 were measured to ±0.5 nm, which results in errors of $\sim\pm 8$ cm^{-1} for $\Delta v_{\mathrm{CH}} = 5$ and of $\sim\pm 15$ cm^{-1} for $\Delta v_{\mathrm{CH}} = 7$.

The samples used were all of commercial spectral grade or comparable quality. The spectra show sloping base lines which are intrinsic features of the overtone spectra. The spectra of contaminated samples show much more strongly sloping base lines. Furthermore, we found that the various spectrometers had a variety of not quite straight instrumental (i.e., no sample) base lines which could lead to bizarre

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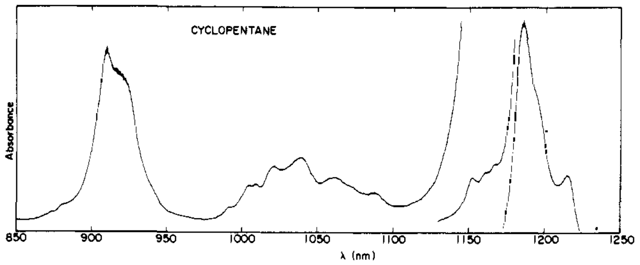

Figure 1. The overtone spectrum of liquid cyclopentane at room temperature in the region from $\Delta\nu_{CH} = 3$ to $\Delta\nu_{CH} = 4$ in a 1-cm cell for $\Delta\nu_{CH} = 3$ and 10-cm cell for $\Delta\nu_{CH} = 4$, 0–1 absorbance slidewire.

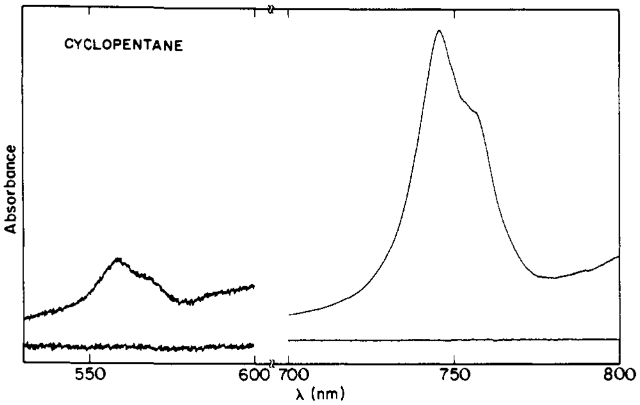

Figure 2. The overtone spectrum of liquid cyclopentane at room temperature in a 10-cm cell in the region of $\Delta\nu_{CH} = 5$ and $\Delta\nu_{CH} = 7$. The base line shows the noise level. The scale offset was changed when the sample was introduced in order to put both the base line and the spectrum on the same scale. Absorbance scale was 0.1 for $\Delta\nu_{CH} = 5$ and 0.01 for $\Delta\nu_{CH} = 7$. The filter change on the Cary 219 in the $\Delta\nu_{CH} = 7$ region was frozen out to maintain a straight base line.

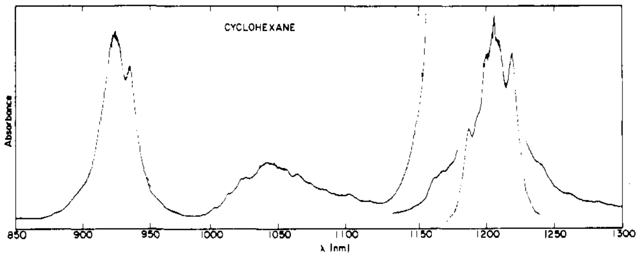

Figure 3. The overtone spectrum of liquid cyclohexane at room temperature in the region of $\Delta\nu_{CH} = 3$ and $\Delta\nu_{CH} = 4$. Taken under the same conditions as Figure 1.

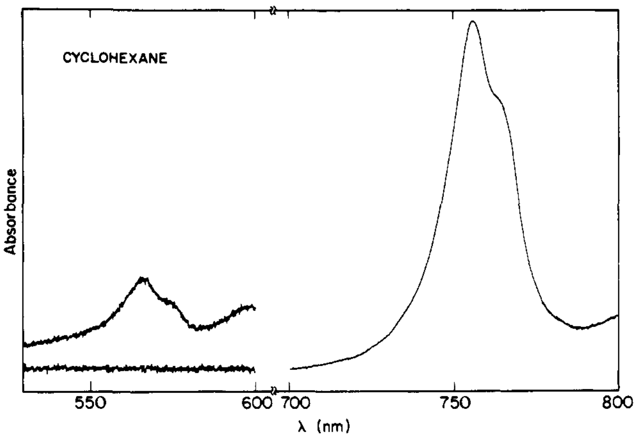

Figure 4. The overtone spectrum of liquid cyclohexane at room temperature in the region of $\Delta\nu_{CH} = 5$ and $\Delta\nu_{CH} = 7$. Taken under the same conditions as Figure 2.

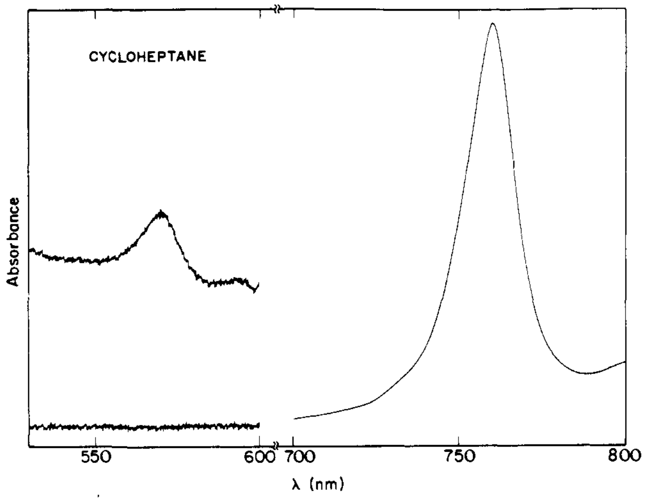

Figure 5. The overtone spectrum of liquid cycloheptane at room temperature in the region of $\Delta\nu_{CH} = 5$ and $\Delta\nu_{CH} = 7$. Taken under the same conditions as Figure 2.

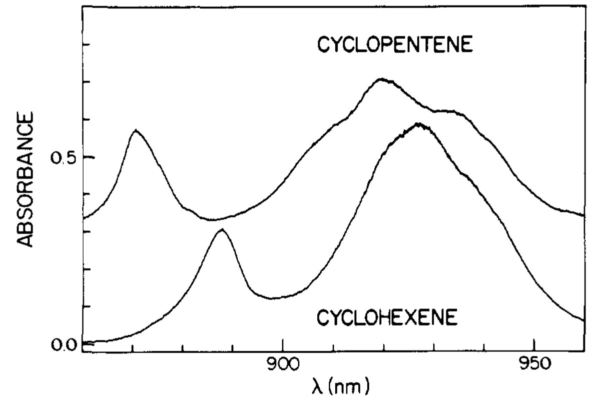

Figure 6. The overtone spectrum of liquid cyclopentene and cyclohexene at room temperature in the region of $\Delta\nu_{CH} = 4$, 10-cm cell. The cyclopentene absorbance has been offset by 0.2 absorbance units.

results. All of these problems become more serious for the higher order and weaker transitions and contribute to the error of locating the true maximum of the band. However, the changes in base lines due to either impurities or spectrometer idiosyncrasies were easily identifiable upon running multiple samples and using a variety of spectrometers. We believe the results to be reliable to within the precision we report.

III. Results

The overtone spectra of cyclopentane and cyclohexane in the spectral region from $\Delta\nu_{CH} = 3$ to $\Delta\nu_{CH} = 7$ are given in Figures 1–4. Figure 5 gives the spectrum for $\Delta\nu_{CH} = 5$ and $\Delta\nu_{CH} = 7$ for cycloheptane. Figure 6 shows the $\Delta\nu_{CH} = 4$ overtone transitions of both cyclopentene and cyclohexene. Figure 7 gives the spectrum for cycloheptene in the region from $\Delta\nu_{CH} = 3$ to $\Delta\nu_{CH} = 6$. The relative absorbances of the various bands have been altered through changes in cell path length and amplification, as noted in the figure captions.

The maxima for all reasonably resolved overtone peaks in the spectral regions studied are given in Table I. Cyclopentane and cyclohexane show split overtone bands, while cycloheptane and cyclooctane show single peaks. For $\Delta\nu_{CH} = 3$ in cyclopentane, the band shape is significantly different than for the higher overtones owing to residual normal mode structure (vide infra), and only the most intense peak position is given. For the three cycloalkenes studied (cyclopentene, cyclohexene, and cycloheptene), two maxima are listed, with the olefinic CH bands lying on the high-energy side of the ring methylene CH bands. In cyclopentene and cyclohexene, in particular, the methylene bands are very broad and only the maxima of the dominant components are listed.

Table I. Observed Band Maxima for the CH-Stretching Overtone Spectra of Several Cycloalkanes and Cycloalkenes (cm^{-1})

molecule	assignment	$\Delta v_{CH} = 3$	$\Delta v_{CH} = 4$	$\Delta v_{CH} = 5$	$\Delta v_{CH} = 6$	$\Delta v_{CH} = 7$
cyclopentane		8431	10 977	13 405 ± 8	15 723	17 889 ± 15
			10 850	13 228	15 480	17 575
cyclohexane		8302	10 834	13 228	15 540	17 668
		8210	10 706	13 106	15 314	17 422
cycloheptane				13 149	15 432	17 544
cyclooctane				13 149	15 408	17 483
cyclopentene	methylene[a]	8372	10 876	13 271	15 528	
	olefin	8776	11 475	14 035	16 488	
cyclohexene	methylene[a]	8268	10 782	13 175	15 456	
	olefin	8624	11 261	13 784	16 181	
cycloheptene	methylene	8292	10 773	13 158	15 429	
	olefin	8607	11 236	13 717		

[a] The main peak of a complex band; see text.

Table II. Diagonal Local Mode CH-Stretching Anharmonicity Constants and Local Mode CH-Stretching Frequencies Calculated from the Observed Maxima of Table I

molecule	assignment	X_{11}, cm^{-1}	σ_X[b]	ω_1, cm^{-1}	σ_ω[b]	D(C-H),[c] kcal
cyclopentane[a]		−63.1	1.3	2998	7	102
		−67.2	0.9	2982	5	94
cyclohexane[a]		−60.4	1.9	2949	10	103
		−62.0	2.2	2925	12	99
cycloheptane		−62.0	4.1	2941	25	100
cyclooctane		−66.0	4.1	2961	25	95
cyclopentene	methylene	−67.3	2	2990	9	95
	olefin	−59.4	1.6	3104	7	116
cyclohexene	methylene	−60.1	0.9	2936	4	102
	olefin	−59.2	0.9	3052	4	112
cycloheptene	methylene	−63.9	3.5	2952	16	97
	olefin	−62.8	3.0	3058	12	106

[a] The higher energy component is listed first. [b] The standard deviation. [c] Calculated from $D = -\omega^2/4X$.

The local mode frequencies, ω_1, and the diagonal local mode anharmonicity constants, X_{11}, have been calculated by a least-squares analysis of eq 1 using the experimentally observed local mode maxima of Table I. The results are given in Table II along with standard deviations for ω_1 and X_{11}. Our previous experience with straight-chain alkanes, which contain both CH_3 and CH_2 contributions to the overtone bands, shows that deconvolution of the bands results in very little change in the local mode parameters. For CH_3, the average of X_{11} changed only from −61.0 to −61.2 cm^{-1} and ω_1 changed from 2984 to 2985 cm^{-1}, upon deconvolution of the bands.

IV. Discussion

A. Spectral Structure in the Cycloalkanes. The principal bands in the overtone spectra of cyclopentane and cyclohexane in Figures 1-4 are centered around approximately 1200, 900, 750, 640, and 570 nm. They correspond to $\Delta v_{CH} = 3, 4, 5, 6$, and 7, respectively, with all of the quanta localized in a single CH oscillator. The much lower intensity peaks or shoulders to the high-energy side of the pure local mode overtones for $\Delta v_{CH} = 3$, and just barely perceptible at the base of the $\Delta v_{CH} = 4$ peaks, correspond to local mode combinations where the vibrational quanta are distributed over two local CH oscillators. The increased local mode character with increasing energy is apparent in the decrease of these combination bands from $\Delta v_{CH} = 3$ to $\Delta v_{CH} = 4$, until they are no longer detectable at $\Delta v_{CH} = 5$. In past studies of the dihalomethanes[4] and the alkanes,[5] the bands between $\Delta v_{CH} = 3$ and $\Delta v_{CH} = 4$, and between $\Delta v_{CH} = 4$ and $\Delta v_{CH} = 5$, have been assigned to combinations of the pure local mode overtones with one quantum of a lower frequency normal mode. Similar bands are present in the cycloalkane spectra in these regions, and they too decrease in intensity with increasing transition frequency at a faster rate than the pure CH local mode overtones.

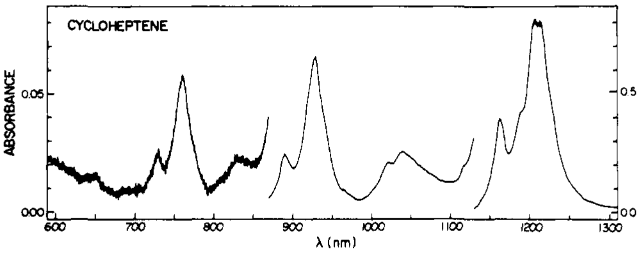

Figure 7. The overtone spectrum of liquid cycloheptene at room temperature in the region from 1300 to 600 nm: 1300–1130 nm, 1-cm cell, 0–1 slidewire; 1130–870 nm, 10-cm cell, 0–1 slidewire; 870—600 nm, 10-cm cell, 0–0.1 slidewire.

As we noted in the last section, both cyclohexane and cyclopentane exhibit doublet structure in their overtone bands. These doublet structures persist up to the highest overtones we have observed and both halves of the doublets maintain about the same relative intensities with increasing Δv. We therefore assign the splitting to a splitting of the local mode band rather than to combination bands. The splitting in the cyclohexane spectrum can be understood on the basis of two distinct types of CH bonds in the most stable conformation of the molecule.[9] The axial and equatorial CH bonds of this chair conformation are interconverted by the "inversion" of the chair, a process which occurs at about 10^3/s at room temperature.[10] The interchange limited lifetime due to this process times the splitting of 100-200 cm^{-1} observed in the overtone spectrum is much greater than one, and therefore the splitting represents the static differences between the two types of CH bonds.

The splitting seen for cyclopentane seems, at first sight, to be anomalous, since the CH bonds interconvert rapidly by pseudorotation[11] and no clear distinction among the different

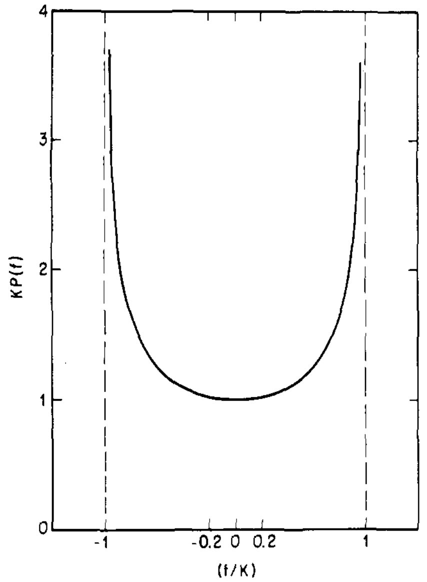

Figure 8. A plot of the idealized shape of the overtone bands $P(f)$ observed in cyclopentane vs. the degree of axial or equatorial character $f(\phi)$. $P(f) = 1/K[(1 - f^2/K^2)^{1/2}]$ and f will be proportional to the degree of displacement of the CH overtone from the band center.

types of CH bonds is usually made.[9] The pseudorotation motion may be described in terms of the out-of-plane displacements, Z_j, of the carbon atom from the average plane of the molecule:

$$Z_j = \left(\frac{2}{5}\right)^{1/2} q \cos\left(\frac{2\pi}{5} j + \phi\right) \qquad (2)$$

$$j = 1, 2, 3, 4, 5$$

where q is the pseudorotation amplitude and ϕ is the pseudorotation angle. There is no significant potential-energy barrier to motion in ϕ.[12] Therefore, the rate of motion is determined by the kinetic energy and we may set

$$\frac{1}{2} m_r \dot{\phi}_{av}^2 = \frac{1}{2} kT \qquad (3)$$

where kT is the thermal energy, m_r is the reduced mass for the motion, and $\dot{\phi}_{av}$ is the root-mean-square angular velocity. The reduced mass is approximately 8×10^{-40} g cm^2,[13] and this gives $\dot{\phi}_{av} \simeq 7 \times 10^{12}$ rad/s at 300 K. A change of $\Delta\phi = \pi$ is required to interchange the relative positions of the two CH bonds on a methylene group and such a change will take place in about 4×10^{-13} s. The observed splittings of 100-200 cm^{-1} correspond to times of 3×10^{-14} to 5×10^{-14} s. Thus even the very fast pseudorotation is too slow to average the splitting observed, and the splitting must approximately reflect the static distribution of CH bonds.

To obtain a qualitative picture of the distribution of the CH bond positions, we consider the axial-equatorial nature of the CH bonds on the nth carbon atom to depend on the difference, $\omega_{n-1,n} - \omega_{n,n+1}$, of the torsional angles about the adjacent CC bonds. If the torsional angles are zero, the methylene groups are eclipsed and the CH bonds have no axial or equatorial character. If the torsional angles are alternately +60 and −60°, then the local geometry is much like that in cyclohexane and one of the CH bonds is "axial" and the other is "equatorial". It has been shown that the torsional angles depend on ϕ as do the Z_j of eq 2:[14]

$$\omega_{ij} = C \cos\left[\frac{4\pi}{5}(i + j)/2 + \phi + \frac{\pi}{2}\right] \qquad (4)$$

where C is a constant.

Consider methylene group 1; for it

$$f(\phi) = (\omega_{51} - \omega_{12}) = K \cos\left(\phi + \frac{9\pi}{5}\right) \qquad (5)$$

where K is another constant and $f(\phi)$ characterizes the axialness or equatorialness of the CH bonds. Thus $f(\phi)$ is expected to be approximately proportional to the displacement of the CH overtone from the band center.[15] The intensity of the band at a given frequency will be proportional to the probability of finding the CH at a given $f(\phi)$, and this is $1/|\partial f/\partial \phi|$. Thus the line shape is characterized by the function $1/(K^2 - f^2)^{1/2}$, shown in Figure 8. This has a form which correlates with the double peak structure of the observed spectra.[15]

The actual band is, of course, broadened by a variety of perturbations. The widths of the overtone band components in cyclohexane and cyclopentane are approximately the same, and therefore the perturbations, such as intermolecular interactions, which contribute to the width are also the same. The intensity of the band components varies with a number of factors, one of which is anharmonicity. Thus, it is not surprising that the two components of the cyclopentane and cyclohexane bands are not of equal intensity.

Alternate definitions of axial-equatorial character could have been used, for example, definitions based on the distances between hydrogen atoms 1,3 to each other in the ring. Such definitions would lead to the same qualitative result, since the distances are also given approximately by formulae similar to eq 2, 4, and 5.

Cycloheptane and cyclooctane just show a series of single overtone bands. The width of these bands is somewhat greater than the width of the individual cyclohexane band components. For these larger rings, axial and equatorial are usually not defined, the geometrical relationships involving the pseudorotation coordinate are much more complicated,[16] and so the individual contributions to the overall bands are not resolved.

B. Spectral Structure in the Cycloalkenes. In the three cycloalkenes there are two sets of principal bands. One set is centered around approximately 1210, 930, 760, and 650 nm (Figure 6), and the other at 1140, 870, 710, and 610 nm for cyclopentene and 10-20 nm higher for both cyclohexene and cycloheptene. These bands correspond to the $\Delta v_{CH} = 3, 4, 5,$ and 6 local mode overtones for the methylene and olefin hydrogens, respectively. The olefin bands are considerably narrower than the corresponding methylene bands.

Local mode combination bands are just discernible on the high-energy side of the $\Delta v_{CH} = 3$ alkyl peaks. These bands are less well resolved than for the cycloalkanes owing to both an increased bandwidth for the methylene overtone and the presence of the higher energy olefin overtone. Combination bands with lower frequency normal modes are also present as in the cycloalkane spectra.

Conformational structure is again observed in the methylene overtone bands of both cyclopentene and cyclohexene, although individual components are less well resolved than in cyclopentane and cyclohexane. The widths of the full methylene band contours are also broader in cyclopentene and cyclohexene than in the corresponding cycloalkanes. Cycloheptene shows a series of single methylene components with widths comparable to the full width of the cyclopentane and cyclohexane bands.

The situation for cyclopentene is, in some ways, similar to that for cyclopentane. The methylene hydrogens are interchanged from "axial" to "equatorial" through an out-of-plane motion, the ring bend. This motion is governed by a double minimum potential with a barrier of approximately 230 cm^{-1}, which is slightly above kT at room temperature.[17] Both the quantum states below the barrier and those above the barrier lead to an average conformation which is out of plane.[17] For the states above the barrier, both the quantum-mechanical and the classical probabilities peak near the classical turning points—and this yields a situation much like that of Figure 8. The spectrum results from a thermal distribution over all the states. In the out-of-plane conformation, the methylene hydrogens opposite the double bond will exhibit the most "axial-equatorial" character, while the four hydrogens on the two equivalent methylene groups adjacent to the double bond will have some axial-equatorial character, but less so. Thus, for a particular out-of-plane conformation, we expect a superposition of two pairs of split bands: one pair due to the apex methylene group, and one pair with greater intensity but less splitting due to the other two methylene groups.

The spectrum we observed shows what appear to be four components in the $\Delta v_{\mathrm{CH}} = 4$ spectrum (Figure 6) of the methylene region, with maxima at approximately 910, 920, 935, and 940 nm. Higher overtones show only two resolved peaks, similar in shape to the $\Delta v = 4$ band of cyclohexene in Figure 6; the splitting of the $\Delta v = 5$ band is about 220 cm^{-1} and that of the $\Delta v = 6$ band is about 380 cm^{-1}. The width and asymmetry of the peaks suggest that they may each consist of two components. Thus we can interpret the more intense inner pair of components (920 and 935 nm for $\Delta v_{\mathrm{CH}} = 4$) as arising from the methylene groups adjacent to the double bond, and the outer pair of components (910 and 940 nm) as arising from the apex methylene group. The splitting at $\Delta v_{\mathrm{CH}} = 4$ for the inner pair of peaks is approximately 170 cm^{-1}, and for the outer pair approximately 350 cm^{-1}. Both of these are larger than the splitting in cyclopentane for $\Delta v_{\mathrm{CH}} = 4$ of $\sim$125 cm^{-1}.

In cyclohexene, the hydrogen atoms can be characterized as one of four types in the lowest energy, relatively rigid "half-chair" configuration. Axial and equatorial bonds are found at C_4 and C_5, while the bonds at C_3 and C_6 are usually referred to as "pseudoaxial" or "pseudoequatorial".[9] This description is confirmed by microwave studies.[18] Thus, we might expect the spectrum to be a superposition of two split bands, one due to the axial and equatorial bonds and one, with less splitting, resulting from the pseudoaxial and pseudoequatorial bonds. The spectrum shows a clear doublet structure similar to that in cyclohexane but with components broader than in cyclohexane. This is consistent with our interpretation of one component as resulting from the superposition of axial and pseudoaxial bands and the other from equatorial and pseudoequatorial bands.

Cycloheptene is thought to exist in a single rigid conformation.[9] No clear distinction exists between the different alkyl hydrogens, and thus a single methylene overtone band is observed, analogous to cycloheptane and cyclooctane. It is slightly narrower than the band in cycloheptane, possibly owing to the reduction in the number of methylene hydrogens from 14 to 10.

In each of the three alkene molecules, the two olefin CH bonds exist in nearly identical molecular environments, and this accounts for the narrowness of the olefin overtone bands relative to the methylene overtone bands.

C. Local Mode Parameters. For the straight-chain alkanes, we were able to assign a characteristic set of local mode parameters to primary, secondary, and tertiary CH bonds. For the cycloalkanes and cycloalkenes we would hope also to be able to characterize the differences among the local mode parameters for the various CH bonds. One useful relationship is that which relates the dissociation energy, D, of a CH bond to the parameters of eq 1:

$$D = -\omega^2/4X \tag{6}$$

This relationship follows from assuming eq 1 holds to the dissociation limit or from the assumption of a Morse potential function.[2a,7] The values of the dissociation energies calculated from eq 6 are listed in Table II. The expected standard deviation of D is appreciable—a few percent or larger.

The local mode frequencies and the calculated dissociation energies of the olefin hydrogens (Table II) are higher than those of the methylene hydrogens. Both of these differences are in accord with the change from the sp^2 character of the olefinic bond to the sp^3 character of the methylene bond.[19]

The changes in the parameters of the CH bonds in the different conformations of the cycloalkanes are intriguing. However, the dissociation energies of Table II do not correspond in any simple fashion to the thermodynamic dissociation energies. These thermodynamic dissociation energies are about 94–95 kcal/mol for the cycloalkanes,[20] not quite the same as the numbers of Table II.

Better resolved spectra, such as those that might be obtained from gas-phase spectra, would make it possible to obtain more quantitative relations between the local mode properties and conformation, especially for the cycloalkenes which contain a number of inequivalent groups.

This study also suggests the possibility of simply distinguishing conformations in noncyclic molecules, provided that the different conformations have CH bonds of different enough properties. Although the information to be obtained will be limited by the large line widths, the extraordinary simplicity of this technique makes it promising.

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