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July 1981

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LOCAL MODE SPECTRA OF INEQUIVALENT C-H OSCILLATORS IN
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CYCLOALKANES AND CYCLOALKENES
~~~~~

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Abstract

Local mode spectra of cycloalkanes and cycloalkenes are observed using both gas phase high overtone and isotopically isolated fundamental spectroscopy. The shapes of the bands reflect the changes in the C-H bonds during the conformational motion. Absorptions by axial and equatorial type C-H bonds are resolved in cyclobutane, cyclopentane, cyclopentene and cyclohexane and the isotopically isolated fundamentals are close to the frequencies extrapolated from the overtones except for liquid cyclohexane. The equatorial bands are consistently more intense than the axial ones.

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I. INTRODUCTION

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The cycloalkanes and cycloalkenes exhibit considerable conformational diversity and thus a variety of C-H bonds in different environments. The conformations interconvert - some very rapidly - and thus this series of molecules provides a unique opportunity to examine the effect of well defined motion on C-H overtone spectra. Of particular interest is the question of the effect of motion on the local mode (LM) picture¹ of the overtones. Previous work^{2,3} has shown that in the liquid phase, multiple peaks appear in the overtone spectra. These peaks were interpreted as a "map" of the distribution of C-H bonds in their various conformational environments. In this paper the previous work is extended by studying the overtone spectra of the gas phase species and the "local mode C-H fundamental" spectra of the monohydro impurities inevitably present in a perdeutero sample.

II. EXPERIMENTAL

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Laser photoacoustic (LPA) spectra of the overtones were obtained using the apparatus described previously,⁴ with a PA cell length of 12.5 cm. Some of the absorption cross sections were calibrated relative to a methane standard,⁵ and a CDC 7600 computer or the on-line Commodore PET microcomputer deconvolved the overtone spectra into a sum of Lorentzians plus a linear background. Spectroquality samples of cyclohexane, cyclopentane and cyclopentene from Matheson,

Coleman and Bell were thoroughly degassed by several freeze-pump-thaw cycles. Cyclobutane from Columbia Organic Chemicals was transferred in vacuo from its original vial to a liquid nitrogen cooled finger leaving behind a nonvolatile yellow syrup. Cyclopropane (Matheson, 99% min. purity) was used without further purification.

Infrared spectra in the fundamental C-H stretching region were taken on a Nicolet 8000HV Fourier Transform Infrared Spectrometer with an evacuated optical path, using a liquid nitrogen cooled InSb detector. Resolution was nominally 0.5 cm^{-1} for both gas and liquid phase spectra. Gas phase spectra were taken in a 16 cm cell with pressures of 40 and 60 torr of cyclohexane- d_{12} and cyclopentane- d_{10} , respectively. Liquid phase spectra of the same samples were taken in sealed cells with 100 μ spacers. Samples of cyclohexane- d_{12} and cyclopentane- d_{10} were obtained from Merck, Sharp and Dohme of Canada at a stated isotopic purity of 99 atom % D. They were degassed by the freeze-pump-thaw method and used without further purification. A curve fitting program supplied with the Nicolet system was used to deconvolute the liquid phase infrared spectra in the fundamental region into a sum of two Lorentzians and an adjustable baseline.

I. RESULTS

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The observed spectra are displayed in Figs. 1 - 7. Attempts to find the C-H overtones of cyclohexane- d_{11} and cy-

clopentane-d₉ were unsuccessful. The much higher concentration of C-D bonds than C-H bonds means that even weak C-D overtones can swamp C-H overtones. For example the second overtone of the C-D stretches made it impossible to clearly identify the first overtone of the C-H stretch.

In Table I the peak positions, linewidths, and integrated cross sections are summarized for all resolvable hydrogens. Harmonic frequencies, anharmonicities and calculated C-H bond dissociation energies are summarized in Table II for cyclohexane, cyclopentane and cyclopropane. Table III gives the observed gas-liquid shifts for cyclohexane and cyclopentane.

IV. DISCUSSION

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A. Spectral Assignments

Cyclohexane:

The infrared spectrum in the C-H stretching region of cyclohexane-d₁₁ is shown in Fig. 1. The shapes of the observed rotational envelopes assign conclusively the higher frequency mode to the equatorial bond, and the lower to the axial bond,⁸ in agreement with recent ab initio calculations which predict a shorter equatorial bond.⁹ The liquid phase spectrum of this region exhibits much broader bands (compared to the gaseous Q branches) shifted down in frequency from the gas phase values by 10 and 7 cm⁻¹ for the equatorial and axial bonds, respectively.

The least squares deconvolutions of the cyclohexane

overtone spectra in Fig. 2 fit the experimental spectra quite well to a sum of two Lorentzians. These two bands again correspond to LM absorptions of the axial and equatorial bonds in the stable chair conformation. The interconversion of the two bond types through inversion of the chair form (about 10^3 sec^{-1} at room temperature¹⁰) is much too slow to motionally average the inequivalent bands.²

Cyclopentane:

Cyclopentane pseudorotates rapidly, interchanging its C-H bonds among axial-like, equatorial-like and eclipsed positions on a time scale of about $4 \times 10^{-13} \text{ sec}$.² However, the overtone spectrum of liquid cyclopentane shows bands that are distinctly doubled.^{2,3} The major components appear about 100 cm^{-1} apart and are approximately attributable to the C-H bonds at the axial and equatorial positions. Even the fast pseudorotation is too slow to motionally average these peaks and the overtones are thought to represent an inhomogeneous superposition of components distributed according to the probability of finding a given C-H bond in a conformation with a certain axial-equatorial character and a given overtone frequency. The overtone band has an intensity given approximately by²

$$I(\Delta\nu) = [1 - (\Delta\nu/\Delta\nu_{\text{max}})^2]^{-1/2} \quad (1)$$

where $\Delta\nu$ is the displacement from the center of the bands and $\Delta\nu_{\text{max}}$ is the maximum displacement. The liquid phase bands do not have quite this shape because the intensities vary

with conformation (see below) and so Eq. (1) would have to be convoluted with another (unknown) function as well as with a broadening function to reproduce the observed spectra.

The gas phase overtone spectra (Fig. 4) look like the liquid phase spectra but are better resolved. Attempts were made to fit the experimental sixth overtone to a sum of Lorentzians and possible fits were found using either two or three Lorentzians. The three Lorentzian fit is shown in Fig. 4 and listed in Table I. The two Lorentzian fit was not as satisfactory. It gave much wider bands and a weighted chi-square eight times larger than the three Lorentzian fit. The center band of the three shows that there is indeed intensity from the methylene bands in the eclipsed conformation, but of course this division into exactly three bands is only an approximation to the expected complex band shape. The fifth overtone band was also fit (Table I) but a badly sloping baseline makes this fit less reliable.

The infrared spectra of the fundamental C-H stretching bands of cyclopentane-d₉ look similar to those for cyclohexane-d₁₁, but the component bands are broader and less well resolved. In the gas phase spectrum (Fig. 3), Q branches can be seen, although the rotational structure is ill-defined and broad. The liquid phase spectrum also shows two bands, which are reasonably well fit by two Lorentzians. However the widths are much greater than in cyclohexane-d₁₁, and the splitting is somewhat less. Similar splittings have been seen¹¹ in the

infrared and Raman spectra of the C-D stretching modes of cyclopentane-d₁. The doubled bands appear both in the gas and solid phases with a splitting of about 40 cm⁻¹. The liquid phase band looks similar to that of Fig. 3, except that the lower frequency band is the more intense.

The fundamental spectra of gaseous cyclopentane-d₉ should show both rotational and pseudorotational structure, with a spacing of the pseudorotational structure of about 4 cm⁻¹. The overall shape of the band is expected to be complex, particularly since the isotopic substitution breaks the fivefold symmetry. Two maxima can be seen in both gas and liquid phase spectra, and are interpreted in the same way as for the overtones, namely as an average over the pseudorotation motion. In other words, the complex pseudorotation structure of the gas phase band is washed out at 0.5 cm⁻¹ resolution into a band contour approaching a simple classical average.

For this average to involve no motional averaging, $2\pi\Delta\nu\tau$ must be greater than one, with $\Delta\nu$ the spectral splitting and τ the characteristic exchange time for pseudorotational motion. For the fundamental transition $\Delta\nu$ is only about 25 cm⁻¹ for both the gas and the liquid. The reduced mass of cyclopentane-d₉ is higher than that of cyclopentane-h₁₀ however,¹² so that τ becomes approximately 6×10^{-13} sec, and $2\pi\Delta\nu\tau \approx 3$ so that no significant narrowing is expected. Indeed the splitting of ~ 25 cm⁻¹ agrees with the extrapolation of the splitting of the high overtone levels for the liquid. (The two gas phase overtone transitions ob-

served are too few to permit accurate extrapolation. See Sec. IV.B.)

Cyclobutane:

The equilibrium configuration of cyclobutane is known to be puckered, with a barrier to interconversion of only one to two kcal mol⁻¹.^{13,14} As a result, the C-H bonds can be considered axial and equatorial on a sufficiently short timescale. Indeed, ab initio calculations with 4-31G or 6-31G* basis sets predict equatorial bond lengths to be larger than axial by 0.002 and 0.001 Å, respectively.¹⁴ The fifth overtone spectrum in Fig. 5 shows a multiple peaked structure with four bands, as summarized in Table I. The strong peaks at 15732 and 15847 cm⁻¹ are assigned to absorptions by the "axial" and "equatorial" C-H bonds and the weaker bands as unspecified combinations. However since the puckering frequency¹³ is only about 200 cm⁻¹, the observed spectrum must again be an average² over the thermally populated, puckering vibrational states. Using the results from the previous study of gaseous alkanes and alkenes,⁴ equilibrium bond lengths of 1.097 and 1.096 Å are predicted for the axial and equatorial C-H bonds, respectively.

Cyclopropane:

Cyclopropane exists in a planar, rigid configuration with D_{3h} symmetry. All bonds are equivalent by symmetry, and only one peak is observed in the overtone spectra in Fig. 6 as expected.

Cyclopentene:

Cyclopentene is similar to cyclobutane in that the equilibrium geometry is puckered, with a barrier¹⁵ of about 0.66 kcal mol⁻¹ between the two conformations. Liquid phase overtone spectra² suggested the presence of four methylenic bands, one pair from the apex methylene group and a second, more intense pair from the two methylene groups adjacent to the carbon-carbon double bond. In the spectra, the more intense inner features were assigned to the two methylene groups adjacent to the double bond while the weaker, outer shoulders were assigned to the apex methylene absorptions. However the broad linewidths in the liquid phase made the assignment tentative.

Results of computer deconvolutions of the gas phase cyclopentene spectra are illustrated in Fig. 7. Four Lorentzians were used to fit the methylene bands. The fifth overtone spectrum on the bottom of Fig. 7 shows two intense bands labelled "1" and "3" at 15270 and 15655 cm⁻¹, respectively. These bands are assigned to the pseudoaxial and pseudoequatorial LM's, respectively, of the methylene groups adjacent to the double bond. The weaker features at 15449 and 15861 cm⁻¹ are assigned to the axial ("2") and equatorial ("4") C-H bonds of the apex methylene group. The σ - π interaction¹⁶ between the π electrons of the C-C double bond and the σ electrons of the adjacent C-H bonds is expected to weaken the latter, shifting their absorptions to lower energy.⁴ The sixth overtone spectrum in Fig. 7 shows

more clearly the same, four peaked structure in the methylene band.

B. Anharmonicity Parameters

The LM absorptions approximately follow the transition energy equation of a one-dimensional anharmonic oscillator¹:

$$\Delta E_v = (\omega_e - \omega_e x_e)v - \omega_e x_e v^2 \quad (2)$$

where ω_e is the harmonic frequency and $\omega_e x_e$ is the anharmonicity. In Fig. 8, a Birge-Sponer plot of $\Delta E_v/v$ vs v , is given for the axial and equatorial C-H LM absorptions of gaseous and liquid² cyclohexane. The filled (open) symbols represent the gaseous (liquid) results. The gas phase results are fit well by the straight line illustrated using the parameters from Eq. (2) summarized in Table II. However the liquid phase fundamental results from cyclohexane-d₁₁ do not fall on the same line as those of the liquid phase overtones of cyclohexane-h₁₂. The liquid overtone data from Ref. 3 give essentially the same results. Conversely, the Birge-Sponer plots for cyclopentane in Fig. 9 show good linear fits for the axial and equatorial absorptions in both gas and liquid phase spectra, as does the plot for gaseous cyclopropane (not shown).

The anharmonicity parameters from Eq. (2) and the implied C-H bond dissociation energies shown in Table II show clearly several trends in both the gas and liquid phase results. The harmonic frequencies and C-H bond dissociation

energies increase while the anharmonicities decrease with decreasing ring size. The effect on the energies can be understood in terms of changes in the hybridization of the C-H bonds.^{17,18} As the degree of ring strain increases from cyclohexane through cyclopropane, the degree of p character increases in the endocyclic C-C bonds to maximize the orbital overlap. As a result the exocyclic C-H bonds gain in s character, becoming shorter and stronger and increasing in vibrational frequency.

C. Linewidths and Intensities

Linewidths and intensities of the gas phase spectra are also summarized in Table I. The values of these parameters unfortunately are more sensitive than the peak positions to the choice of lineshape in the computer deconvolution, and thus are less well determined. Lorentzians were chosen under the assumption of homogeneous broadening by intramolecular energy transfer and dephasing. Inspection of the computer deconvolutions in the figures shows that the Lorentzian lineshapes accurately fit the upper portions of the bands. However the Lorentzian tails contribute too much intensity on the wings, pushing the computed backgrounds too low and overestimating the peak areas. Deviations from Lorentzian lineshapes give rise to actual uncertainties in the peak areas of 10 - 20 %, which are greater than the computed standard errors quoted in Table I. The choice of lineshape also affects the computed widths since the areas and widths are strongly correlated. Only cyclohexane and cyclopropane

have sufficiently well resolved spectra for accurate linewidth determinations and comparisons.

In these two molecules, we see contrasting linewidth trends. For cyclohexane the linewidths for both axial and equatorial absorptions are seen to increase from $\Delta v=5$ through $\Delta v=7$. The width of the one cyclopropane absorption increases from $\Delta v=5$ to $\Delta v=6$, then decreases monotonically from $\Delta v=6$ through $\Delta v=8$. This latter behavior is similar to that of benzene^{19,20} in which the linewidths of the near-Lorentzian absorptions are seen to increase, reach a maximum value and then decrease with vibrational quantum number. However the cyclopropane lineshapes are non-Lorentzian with distinct shoulders and asymmetries, and the observed narrowing with quantum number is probably due to the gradual loss of this structure with increasing vibrational quantum number.

The integrated cross sections for the higher energy equatorial absorptions are consistently more intense in both gas and liquid phase^{2,3} spectra. One might expect that the more anharmonic LM's would have more intense absorptions. In the cyclic hydrocarbons, the less anharmonic equatorial LM's have more intense absorptions, the dipole moment function instead of the mechanical anharmonicity must determine the intensities of the LM absorptions. Indeed, it has been demonstrated that the mechanical anharmonicity has little effect on the integrated cross sections of the LM bands of gaseous alkanes and alkenes.⁴

D. Gas-liquid frequency shifts

The observed gas-liquid frequency shifts, $\Delta\nu_{gl}$, for the methylenic absorptions in cyclohexane and cyclopentane are given in Table III. The liquid phase overtone transition frequencies reported in Refs. 2 and 3 differ by as much as 60 cm^{-1} , reflecting the difficulties in locating the peak positions in poorly resolved spectra. Thus, the gas-liquid shifts are given using both sets of liquid phase frequencies.

Although the shifts for a given bond in a given molecule vary considerably and almost randomly over the range of overtones, the gas-liquid shifts for the equatorial C-H bonds are uniformly larger than those for the axial bonds. It is also interesting to note that for the fundamental absorptions of cyclohexane- d_{11} and cyclopentane- d_9 , the average gas-liquid shifts are significantly different, 8.5 and -1.5 cm^{-1} , respectively.

V. SUMMARY

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The spectra of C-H overtones of a series of cyclic alkanes and alkenes and the fundamental isolated local mode spectra of cyclohexane and cyclopentane have been presented. In all cases the gas phase spectra show bands that are narrower than the liquid phase spectra. All the spectral bands have a shape that is approximately given by the distribution of C-H frequencies over the conformational motion of the molecule. There is no evidence for motional narrowing. The C-H fundamentals for cyclopentane- d_9 , cyclohexane- d_{11} and

cyclopropane-d₅ are at frequencies given by extrapolation from the overtone frequencies and thus conform to the local mode model. An exception is the liquid phase results for cyclohexane for which the extrapolation does not work. This implies different liquid phase shifts for the fundamental and overtones. The axial bands are systematically stronger than the equatorial bands. Both this and the gas-liquid frequency shifts are not understood. The gas phase spectra of cyclopentene are better resolved than the liquid phase spectra and have allowed a more precise assignment of the various methylenic bands.

VI. ACKNOWLEDGEMENTS

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J.S.W. and C.B.M. were supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48 and by the U.S. Army Research Office, Triangle Park, NC. R.A.M. and H.L.S. were supported in part by the National Science Foundation. The krypton ion laser used to take the fifth overtone spectra was provided by the San Francisco Laser Center which is supported by the National Science Foundation under Grant No. CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University. The authors thank L. Schäfer and R.G. Bray for communicating their results prior to publication.

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Table I. Peak positions,^a linewidths^a and integrated cross sections (area)^b for the spectra of cycloalkanes and cycloalkenes.^c

Molecule	Assign	ν	FWHM	Area
c-C ₆ D ₁₁ H(g)	ax	2891 ^d	... ^d	... ^d
v=1	eq	2923	...	...
c-C ₆ D ₁₁ H(l)	ax	2884(0.3) ^e	16(1) ^e	1.00(0.06) ^{e,f}
v=1	eq	2913(0.3)	19(1)	1.32(0.08)
c-C ₆ H ₁₂ (g)	ax	13127(6)	123(5)	20.8 (0.7)
v=5	eq	13315(5)	139(2)	47.4 (0.8)
v=6	ax	15376(6)	195(4)	7.64(0.15)
	eq	15605(5)	147(2)	8.71(0.12)
v=7	ax	17496(6)	200(5)	1.00(0.02) ^e
	eq	17764(6)	168(3)	1.27(0.02)
c-C ₅ D ₉ H(g)	ax	2910 ^d	... ^d	... ^d
v=1	eq	2934	...	...
c-C ₅ D ₉ H(l)	ax	2910(0.3) ^e	44(1) ^e	1.00(0.05) ^{e,f}
v=1	eq	2937(0.3)	33(1)	1.09(0.05)

Table I. Peak positions,^a linewidths^a and integrated cross sections (area)^b for the spectra of cycloalkanes and cycloalkenes(continued).^c

Molecule	Assign	ν	FWHM	Area
c-C ₅ H ₁₀ (g)	...g	15538 (7)	257 (9)	4.5 (0.3)
v=6	...	15777(13)	208 (7)	5.4 (0.9)
	...	15833 (8)	113(18)	1.7 (0.7)
v=7	...g	17650 (9)	225 (14)	1.0 (0.1) ^f
	...	17860(22)	395 (73)	1.7 (0.5)
	...	18024 (6)	176 (8)	1.8 (0.2)
c-C ₄ H ₈ (g)	comb.	15510(39)	214 (46)	0.4 (0.3)
v=6	ax	15732 (8)	122 (14)	1.7 (0.3)
	eq	15847 (7)	149 (6)	5.5 (0.3)
	comb.	16455(36)	204(120)	0.8 (0.6)
c-C ₃ H ₆ (g)				
v=1		3056 ^h		
v=3		8800 ⁱ		
v=5		14059 (5) ^j	86 (4) ^j	40.4 (4) ^j
v=6		16506 (9) ^j	95 (5) ^j	6.1 (0.6) ^j
v=7		18816 ⁱ	75 ⁱ	
v=8		21095 ⁱ	70 ⁱ	

Table I. Peak positions,^a linewidths^a and integrated cross sections (area)^b for the spectra of cycloalkanes and cycloalkenes (continued).^c

Molecule	Assign	ν	FWHM	Area
c-C ₅ H ₈ (g)	1 ^k	15269(11)	235 (20)	2.1 (0.2)
	v=6			
	2	15449(28)	165(123)	0.3 (0.3)
	3	15656 (9)	241 (20)	3.3 (0.4)
	4	15861 (9)	149 (17)	1.0 (0.2)
	5	16607 (5)	80 (1)	3.47(0.05)
	v=7			
	1 ^k	17350(10)	302(15)	1.00(0.07) ^f
	2	17540(12)	198(34)	0.27(0.07)
	3	17814 (7)	266(10)	1.25(0.05)
	4	18102 (7)	236(11)	0.71(0.04)

^aUnits: cm⁻¹.

^bUnits: 10⁻²³ cm² cm⁻¹ molec⁻¹.

^cUncertainties in parentheses are the standard errors of the non-linear least squares fit. Frequency uncertainties are standard errors plus 5 cm⁻¹.

^dSpectra showed overlapped rotational structure. Only Q branch frequencies were determined (to better than 1 cm⁻¹).

^eErrors were determined by adjusting the parameters until the fit became visibly worse.

^fIntensities are relative.

^gThree Lorentzians were used to approximate the distribution of axial-equatorial bond character. See Sec.IV.A.

^hCyclopropane-d₅ data from Ref. 6.

ⁱRef. 7.

^jEstimated peak positions, widths and uncertainties. Areas measured with planimeter.

^kSee Fig. 7 for peak assignments.

Table II. Harmonic frequencies ω_e ,^a anharmonicities $\omega_e x_e$,^a and C-H bond dissociation energies^b of the cycloalkanes.

Molecule	Assign	ω_e	$\omega_e x_e$	$D_e(\text{C-H})^c$
c-C₆H₁₂				
gas	ax	3021 ± 4 ^d	65.4 ± 0.6 ^d	99.7 ± 1.2 ^d
	eq	3051 ± 2	64.3 ± 0.4	103.4 ± 0.8
liquid	ax	3006 ± 9	65.0 ± 1.5	99.4 ± 2.9
	eq	3032 ± 7	63.9 ± 1.5	102.7 ± 3.0
c-C₅H₁₀				
gas	"ax"	3039 ± 5	64.5 ± 0.8	102.3 ± 1.6
	"eq"	3053.9 ± 0.3	60.0 ± 0.1	111.0 ± 0.2
liquid	"ax"	3043 ± 2	66.4 ± 0.3	99.7 ± 0.6
	"eq"	3063 ± 1	63.5 ± 0.3	105.6 ± 0.6
c-C₃H₆				
gas		3175 ± 4	60.4 ± 0.6	119.2 ± 1.5

^aUnits: cm⁻¹.

^bUnits: kcal mol⁻¹.

^cCalculated from $D_e = \omega_e^2 / 4\omega_e x_e$.

^dThe quoted uncertainties are the standard errors of the linear regression.

Table III. Gas-liquid frequency shifts^a for the methylene bands of cycloalkanes.

Molecule	Δv	$\Delta v_{gl}(ax)^b$	$\Delta v_{gl}(eq)^b$
c-C ₆ D ₁₁ H	1	7	10
c-C ₆ H ₁₂	5	21 (47)	87 (85)
	6	62 (81)	65 (125)
	7	74 (72)	96 (100)
c-C ₅ D ₉ H	1	0	-3
c-C ₅ H ₁₀	6	67 (74)	82 (90)
	7	75 (50)	131 (95)

^aUnits: cm⁻¹.

^b $\Delta v_{gl} \equiv v_g - v_l$. Values of v_l from Ref. 2 (Ref. 3).

Figure Captions

Fig. 1. Liquid (top) and gas (bottom) phase FTIR spectra of the C-H stretching fundamental region of cyclohexane-d₁₁.

Fig. 2. Fourth (bottom, pressure: 63 torr), fifth (67 torr), and sixth (top, 67 torr) overtone spectra of gaseous cyclohexane taken with the LPA spectrometer. The dots are the experimental data and the solid line represents the results of the computer deconvolutions.

Fig. 3. Liquid (top) and gas (bottom) phase FTIR spectra of the C-H stretching fundamental region of cyclopentane-d₉.

Fig. 4. Fifth (bottom, pressure: 107 torr) and sixth (top, 110 torr) overtone spectra of gaseous cyclopentane. The dots (top) represent the experimental data and the solid line represents the results of the "three Lorentzian" deconvolution.

Fig. 5. Fifth overtone spectrum of gaseous cyclobutane (pressure: 106 torr). The dots are the experimental data and the solid line represents the results of the computer deconvolution.

Fig. 6. Fourth (bottom, pressure: 168 torr) and fifth (top, 151 torr) overtone spectra of gaseous cyclopropane.

Fig. 7. Fifth (bottom, pressure: 143 torr) and sixth (top, 111 torr) overtone gaseous cyclopentene. The dots are the experimental data and the solid lines represent the computer deconvolutions. The numbers 1 through 5 give the spectral assignment. In the molecular diagram the apex carbon atom lies below the plane of the four other carbon atoms, giving axial character to hydrogen atoms "1" and "2" and equatorial character to "3" and "4".

Fig. 8. A plot of $\Delta E_v/v$ vs v for the axial and equatorial absorptions of cyclohexane. The slope gives $-\omega_e x_e$ and the y-intercept gives $(\omega_e - \omega_e x_e)$ for each bond type.

Fig. 9. A plot of $\Delta E_v/v$ vs v for the axial and equatorial absorptions of cyclopentane.

XBL 818-11199

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XBL 818-11203

XBL 818-11272

XBL 818-11202

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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