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Vibrational Overtone Spectroscopy of Cycloheptatriene

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The spectrum of the first through fifth vibrational overtone absorptions of cycloheptatriene is reported. The spectrum for the first and second overtones was recorded using a liquid sample, while the third, fourth, and fifth overtones were recorded for gaseous samples. A method is developed using the correlation between ab initio CH bond lengths and the local mode transition energy to predict the experimental spectra for the third, fourth, and fifth vibrational overtone spectra. These predictions were used to assign the absorption peaks for the "boat" conformer of cycloheptatriene in the gaseous spectrum. Progressions belonging to the olefinic and methylenic CH bond stretches are identified for both the gaseous and liquid data.

Introduction

The role of vibrational excitation and internal vibrational redistribution (IVR) in chemical reactions can be determined through studies of vibrational motions of molecules at energies sufficient for reaction.[1] The analysis of overtone spectra has been used to provide information about pathways of photodissociation and laser-induced reactions. Overtone spectra of large cyclic molecules, of which little is known, could be used as models for the vibrational behavior of polymers, proteins, and other macromolecules.

The overtone spectra of four-, five-, six-, seven-, and eight-member cyclic alkanes and alkenes (except for the C_8 alkene) have been recorded.[2−11a] In these spectra the progressions for the methylenic and olefinic CH stretches were identified. For the four-, five-, and six-member rings two peaks were observed at each overtone level of the methylenic progression. These peaks were assigned to the distinct axial and equatorial[3] CH bond local mode stretches. The equatorial bands were consistently more intense than the axial ones and possessed smaller anharmonicities.[8] However, for the larger seven- and eight-member cyclic alkanes only one methylenic CH stretch progression was observed in the liquid phase.[2] For the cyclic diene, cyclopentadiene, the gaseous vibrational overtone spectrum[9] clearly displayed the aliphatic (methylenic) and olefinic progressions; however, the methylenic absorptions were not well resolved and no distinction between CH_{ax} and CH_{eq} was possible. Manzanares et al.[10] recorded the second and third overtone spectra of all *cis*-1,4-polybutadiene solution in CCl_4. Although the carbon chains in polybutadiene are not cyclic, the methylenic CH oscillators are in a semirigid frame, making it possible to resolve the axial and equatorial methylenic oscillators in this polymer.

In gaseous trimethylcyclohexane, for which the axial and equatorial CH local mode oscillators were distinguished,[4] a linear relationship existed between the fourth and fifth overtone transition wavenumbers and the CH bond lengths determined from ab initio 4-31G* calculations for methane, ethane, propane, cyclohexane, *cis*-trimethylcyclohexane, and acetone. This correlation between bond length and transition wavenumber is expected to work best when only molecules of similar type are included.[4] In addition to the typical pattern in bond length ordering in saturated hydrocarbons (r_{CH}(methyl) < r_{CH}(methylene) < r_{CH}(methyne)), the pattern for axial and equatorial bond lengths (r_{CH}(eq) < r_{CH}(ax)) was reported.[4,5]

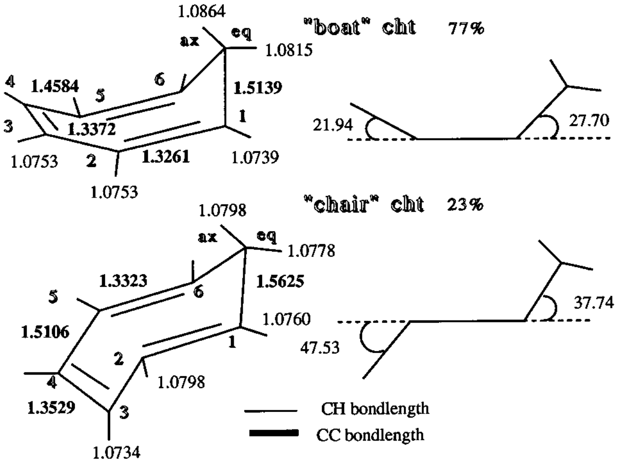

Figure 1. "Boat" and "chair" conformers of cycloheptatriene and their optimized bond lengths and geometry calculated using the HF level of theory (3-21G(*) basis set).

To investigate the relative importance of ring inversion and Fermi resonance in cyclic molecules, the overtone spectra of cyclohexene-3,3,6,6-d_4[6] and cyclopentene-3-h_1 were studied.[7] Two coupling modes were considered: Fermi resonance coupling with combination states involving CH_2 and CCH deformations and coupling with the large amplitude motions. Only Fermi resonance coupling was observed[6a] in cyclohexene because the characteristic time for ring inversion is too slow to couple with the high-energy states. The energy barrier between two equivalent "half-chair"conformations of cyclohexene was calculated to be 4700 cm^{-1}.[6b] However, both types of coupling occurred for cyclopentene. Selective deuteration created monohydrogenated −3-h_1 and −4-h_1 cyclopentenes, thus, eliminating the Fermi resonance coupling. The remaining transitions in the experimental spectra were assigned to the CH stretch overtones and combinations of CH stretching vibrations and puckering motions of the cyclopentene ring.

For benzene the local mode picture[11a] is simple because all CH oscillators are equivalent and only one peak appears at each overtone in the high overtone spectrum. The lower overtone spectrum of benzene, being more complicated, has been analyzed by the algebraic method, where the Hamiltonian is expressed in terms of elements of Lie algebra and where coupling of oscillators is described by operators.[11b,c]

Cycloheptatriene is a special molecule among cyclic hydrocarbons, since, in addition to its three conjugated double bonds, it also possesses a methylenic group. Electron diffraction[12] and

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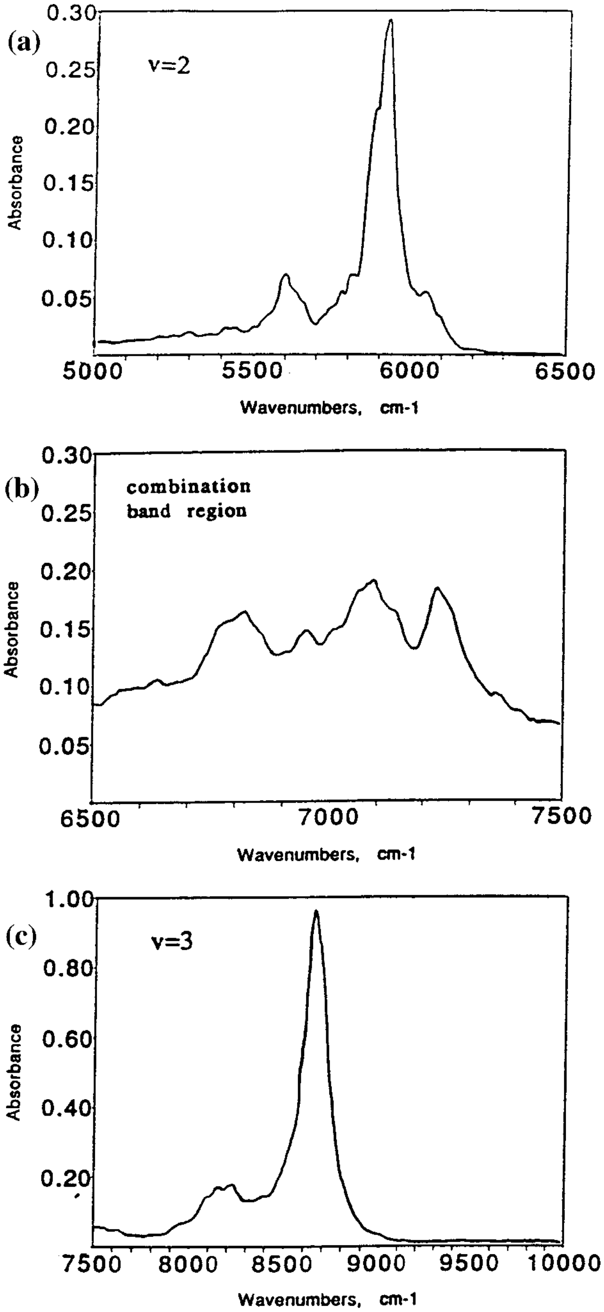

Figure 2. Vibrational overtone spectra of liquid cycloheptatriene at the first overtone (a), second overtone (c), and combination band (b) regions between these two overtones recorded at room temperature.

microwave data[13] suggest that cycloheptatriene in the gas phase possesses the "boat" conformation, although the microwave spectrum[13] indicates the possibility that puckering of the ring may be important. The most stable calculated conformation[14] of cycloheptatriene is a "perturbed boat" conformation, which is a linear combination of 77% "boat" and 23% "chair" (Figure 1). The barrier for the ring inversion was calculated to be about 6 kcal/mol,[14] but no energies were determined for the puckering of cycloheptatriene from "boat" to "chair". The degree of interaction of the methylenic hydrogens with the conjugated π-system is different in both conformers, and therefore, these hydrogens can be referred to as pseudoaxial and pseudoequatorial CH oscillators. In addition, different olefinic CH oscillators may exist in these conformations. Owing to steric factors, the olefinic CH oscillators nearest the methylenic CH bonds ($CH_{1,6}$ in Figure 1) should have different bond lengths compared to the other olefinic CH bonds.

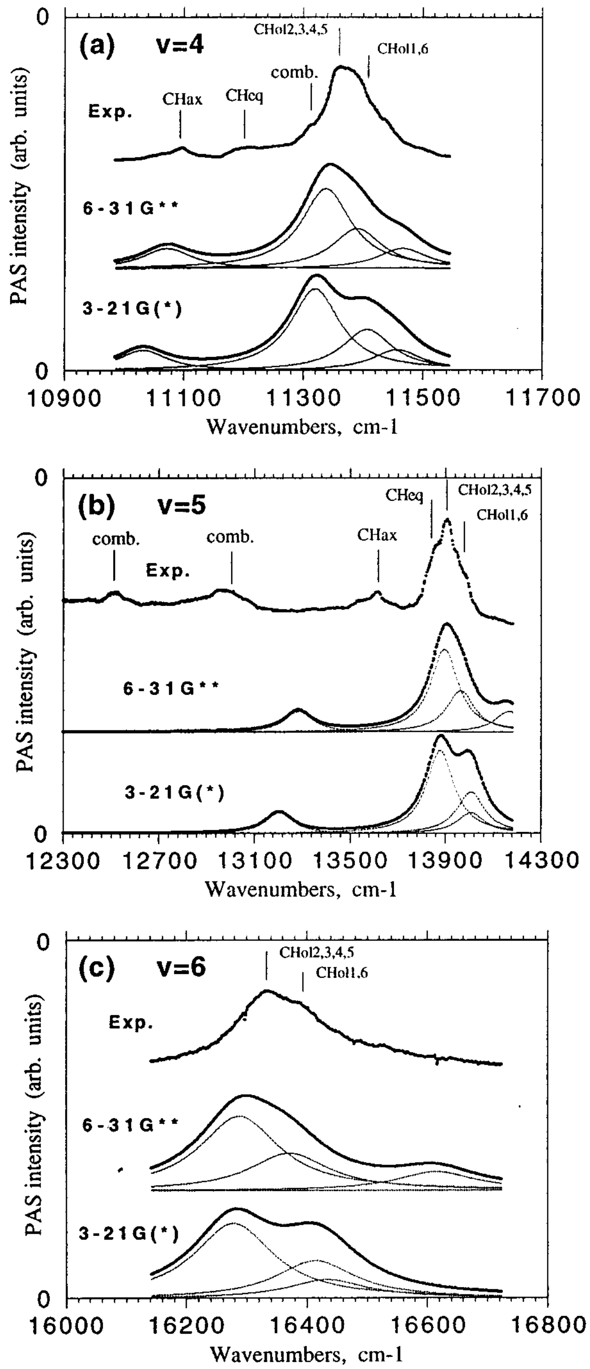

Figure 3. Comparison of the experimental (upper line) and estimated from the correlation (6-31G** (middle line), 3-21G(*) (lower line)) spectra of cycloheptatriene (HF level of theory) at the third (a), fourth (b), and fifth (c) overtones. The smaller peaks under the estimated spectra are the contributions from the different CH oscillators of cycloheptatriene. The experimental spectra were recorded for gaseous cycloheptatriene at room temperature.

The IR and Raman spectra of cycloheptatriene were recorded by Paulick and colleagues.[15] Three transitions (3060, 3027, and 3015 cm^{-1}) were reported in the CH stretch fundamental region. A normal coordinate analysis has allowed the transitions from 200 to 3060 cm^{-1} to be assigned to the various normal modes.[15]

The correlation between CH bond length and transition wavenumber in vibrational spectroscopy has been well documented.[4,5,16] An excellent correlation exists between CH bond lengths of isolated oscillators in partially deuterated samples and the fundamental CH stretching wavenumbers.[5] This relationship also pertains to vibrational overtone transition

TABLE 1: Experimental and Predicted Peak Positions and Assignments for Cycloheptatriene

	transition wavenumbers				
	estimated				
quantum number (v)	3-21G(*)	6-31G**	observed	intensity	assignment
2			5588	m[a]	$1v\mathrm{CH}_{2\mathrm{str}}(2838^{b}) + 2v\mathrm{CH}_{2\mathrm{bend}}(1393) = 5624$
					$1v\mathrm{CH}_{2\mathrm{str}}(2966) + 2v\mathrm{CH}_{2\mathrm{bend}}(1393) = 5752$
			5783	w	$2v\mathrm{CH}^{\mathrm{ax}}$
			5800	w	$2v\mathrm{CH}^{\mathrm{eq}}$
			5867	l.en.sh.	$2v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5}$
			5905	s	$2v\mathrm{CH}^{\mathrm{ol}}_{1,6}$
			6029	w	$1v\mathrm{CH}_{\mathrm{str}}(3027) + 2v\mathrm{CC}_{\mathrm{str}}(1534) = 6095$
combination band region between $\Delta v = 2$ and $\Delta v = 3$			6820	w	$2v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + v\mathrm{CH}_{\mathrm{bend}}(973) = 6878$
			6927	w	$2v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + v\mathrm{CH}_{\mathrm{bend}}(1192) = 7097$
			7090	w	$2v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + v\mathrm{CH}_{\mathrm{bend}}(1218) = 7123$
			7227	w	$2v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + v\mathrm{CH}_{\mathrm{bend}}(1393) = 7260$
3			7948	vw	$2v\mathrm{CH}^{\mathrm{ol}}_{1,6} + 2v\mathrm{CH}_{\mathrm{bend}}(1049) = 8003$
			8227	w	$2v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + 2v\mathrm{CH}_{\mathrm{bend}}(1192) = 8251$
					$2v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + 2v\mathrm{CH}_{\mathrm{bend}}(1218) = 8303$
					$2v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + 2v\mathrm{CH}_{\mathrm{bend}}(1235) = 8337$
					$2v\mathrm{CH}^{\mathrm{eq}} + 2v\mathrm{CH}_{2\mathrm{wag}}(1298) = 8396$
			8652	s	$3v\mathrm{CH}^{\mathrm{ax}}$
					$3v\mathrm{CH}^{\mathrm{eq}}$
					$3v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5}$
					$3v\mathrm{CH}^{\mathrm{ol}}_{1,6}$
4	11 032	11 072	11 094	w	$4v\mathrm{CH}^{\mathrm{ax}}$
	11 457	11 466	11 216	w	$4v\mathrm{CH}^{\mathrm{eq}}$
			11 313	l.en.sh.	$3v\mathrm{CH}^{\mathrm{eq}} + 2v\mathrm{CH}_{2\mathrm{bend}}(1393) = 11\,366$
	11 320	11338	11 366	s	$4v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5}$
	11 407	11 390	11 437	h.en.sh.	$4v\mathrm{CH}^{\mathrm{ol}}_{1,6}$
5			12 520	w	$4v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + v\mathrm{CH}_{\mathrm{bend}}(1192) = 12\,558$
			13 080	m	$4v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5} + v\mathrm{CC}_{\mathrm{str}}(1662) = 13\,099$
	13 205	13 285	13 622	m	$5v\mathrm{CH}^{\mathrm{ax}}$
	14 006	14 165	13 864	l.en.sh.	$5v\mathrm{CH}^{\mathrm{eq}}$
	13 877	13 894	13 915	s	$5v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5}$
	14 005	13 962	13 981	h.en.sh.	$5v\mathrm{CH}^{\mathrm{ol}}_{1,6}$
6	16 278	16 288	16 331	s	$6v\mathrm{CH}^{\mathrm{ol}}_{2,3,4,5}$
	16 414	16 371	16 375	h.en.sh.	$6v\mathrm{CH}^{\mathrm{ol}}_{1,6}$

[a] vw, very weak; w, weak; m, medium; s, strong; l.en.sh., low-energy shoulder; h.en.sh., high-energy shoulder. [b] Normal mode frequencies are taken from ref 15.

wavenumbers and calculated ab initio bond lengths.[4,16a,c] However, when a wide variety of CH bond types (such as olefinic, methylenic, etc.) are included, the correlation fit is not as satisfactory.[4] The correlation can be improved if CH bonds of only one particular type are considered, especially in the case when individual CH oscillators are isolated from the other oscillators and/or little coupling occurs between those oscillators.

With the large experimental database of vibrational overtone transition wavenumbers of different types of CH oscillators, a correlation between calculated CH bond length and overtone transition wavenumber for specific types of CH oscillators (olefinic, methylenic, methyl, aromatic, etc.) can be generated. These data can be used to predict an unknown overtone spectrum or to assign experimental spectra of molecules with CH oscillators of known type and length. To use this method, only geometry optimization calculations and conformational analysis for a given molecule are required. This direct correlation method was used in our previous work[17] to generate the spectrum of *cis*-1,3-butadiene, a molecule that is difficult to study experimentally. The predicted spectrum was used to assign the third overtone transitions for butadiene iron tricarbonyl. In this report, the overtone spectrum of gaseous cycloheptatriene at the third, fourth, and fifth overtone regions will be interpreted. These assignments will be used to guide the assignments of the liquid cycloheptatriene spectrum.

Experiment

The first and second overtone spectrum of cycloheptatriene was recorded at 4 cm^{-1} resolution on a Mattson FT near-IR spectrometer with a tungsten lamp and quartz beam splitter. A PdSe detector was used to record the spectra in the 4000−9000 cm^{-1} region. The first overtone spectrum was recorded for a solution of cycloheptatriene in CCl_4 (1:5 C_7H_8:CCl_4 ratio). The second overtone spectrum was recorded for neat liquid cycloheptatriene.

The third, fourth, and fifth overtone spectra of gaseous cycloheptatriene were obtained using an intracavity laser photoacoustic spectrometer that has been previously described.[17] The sample was vacuum-transferred into the photoacoustic cell with argon added to obtain a total pressure of approximately 500 Torr.

The excitation source was an argon ion laser, which pumped a Spectra-Physics Model 3900S CW Ti:sapphire laser or dye laser with a three-plate birefringent filter (2 cm^{-1} bandwidth). Two regions of the Ti:sapphire laser (10 000−11 765 cm^{-1} and 11 765−14 286 cm^{-1}) were used to record the third and fourth overtone spectra. A rhodamine 6G dye (16 000−17 500 cm^{-1}) was used to record the fifth overtone spectrum of cycloheptatriene.

Ab initio geometry optimization and single-point energy calculations were performed by SPARTAN, Version 4.0, purchased from Waveform Inc. at the HF level of theory using 3-21G(*) and 6-31G** basis sets.

Results and Discussion

The experimental vibrational overtone spectrum of cycloheptatriene is presented in Figures 2 (liquid sample) and 3 (gaseous sample). The absorption wavenumbers are tabulated

TABLE 2: Parameters Used for Correlations at Different Overtones[b]

molecule	bond length, Å		transition wavenumbers, cm^{-1}			ref
	3-21G(*)	6-31G**	$\Delta v = 4$	$\Delta v = 5$	$\Delta v = 6$	
(a) Olefinic Correlation Paramters						
cyclopentadiene	1.0690	1.0740	11 652	14 264	16 780	9
2-methylcyclopentadiene	1.0691	1.0739	11 564		16 659	our work
	1.0696	1.0745	11 590	14 200	16 617	
	1.0702	1.0754	11 623		16 767	
cyclooctatetraene	1.0767	1.0795	11 284	13 762	16 176	our work
1,3-butadiene	1.0757	1.0787	11 342	13 875	16 288	18
	1.0744	1.0769	11 448	14 034	16 465	
	1.0724	1.0750	11 558	14 166	16 645	
2-methyl-1,3-butadiene	1.0755	1.0783	11 343	13 895	16 270	18
	1.0727	1.0753	11 520	14 145	16 540	
2,3-dimethyl-1,3-butadiene	1.0741	1.0767	11 490	14 110	16 525	18
	1.0701	1.0726	11 600	14 250	16 700	
propylene	1.0752	1.0786	11 290	13 820	16 240	18
	1.0752	1.0780	11 415	13 980	16 440	
	1.0733	1.0757	11 485	14 093	16 570	
1,5-hexadiene	1.0765	1.0798	11 237	13 820	16 130	18
	1.0752	1.0780	11 392	14 085	16 360	
	1.0733	1.0757	11 480	14 145	16 530	
1,7-octadiene	1.0768		11 211	13 720	16 120	18
	1.0755					
	1.0734		11 428	14 005	16 475	
1,9-decadiene	1.0765		11 205	13 710	16 080	18
	1.0752					
	1.0733		11 429	14 005	16 475	
1-hexene	1.0766	1.0800	11 204	13 710	16 080	18
	1.0752	1.0781				
	1.0734	1.0757	11 422	14 020	16 470	
1-octene	1.0766		11 190	13 690	16 070	18
	1.0753					
	1.0734		11 425	14 015	16 470	
2-methyl-2-butene	1.0776		11 143	13 642	16 030	18
ethylene	1.0737			14 077	16 550	18
(b) Methylenic Correlation Parameters						
cyclopentadiene	1.0866	1.0893	11 100[a]	13 252	15 505	9
cyclohexane	1.0853	1.0871	11 175[a]	13 315	15 605	8
	1.0868	1.0896	11 038[a]	13 127	15 376	
3-methylcyclohexane	1.0873	1.0910	10 930[a]	13 010	15 247	4
	1.0882	1.0912	10 817[a]	12 916	15 134	
	1.0867	1.0883	11 066[a]	13 197	15 485	
cyclopentane	1.0825	1.0855	11 256[a]	13 770[a]	16 163[a]	8
	1.0847	1.0886	11 124[a]	13 583[a]	15 912[a]	

[a] Transition wavenumbers are estimated from the Birge−Sponer plot parameters. [b] Bond lengths were calculated using the HF level of theory.

in Table 1. Cycloheptatriene can be considered as an almost "pure" local mode molecule, since only coupling between the two methylenic oscillators should occur. This idea is supported by recent work modeling *trans*-1,3-butadiene[19] with the harmonically coupled anharmonic oscillators (HCAO) model. Almost no coupling was found between terminal and nonterminal CH oscillators of *trans*-1,3-butadiene in the HCAO model. In cycloheptatriene, the correlation between CH bond lengths and peak wavenumbers should be helpful in assigning the overtone spectrum.

We have used a direct correlation method to assign the major peaks in the spectrum. This method involves combining the results of ab initio CH bond length calculations and transition wavenumbers for the specific CH oscillators (olefinic and methylenic). The transition energies and ab initio CH bond lengths for the molecules used in the correlations are presented in Table 2. All available experimental overtone data were used to generate the CH olefinic correlations including cyclic olefins and dienes as well as open-chain olefins and dienes. For the methylenic CH oscillators only data for axial and equatorial CH bonds were included in the correlation. This was done to improve the correlation by including CH oscillators of one particular type. The inclusion of the methylenic data for open-chain hydrocarbons significantly degrades the fit to a straight line. The correlations for third, fourth, and fifth overtones for both used basis sets are presented in Figures 4 (olefinic) and 5 (methylenic).

The geometry of both "boat" and "chair" cycloheptatriene was optimized using the same basis sets that were used to derive the correlations. The results are given in Table 3. Next, the relative stability of these two conformers must be considered. The electron diffraction[12] and microwave spectroscopic results[13] indicate that cycloheptatriene exists in a "boat" conformation in the vapor phase. No experimental evidence for the existence of the "chair" conformer has been found. However, calculations[14] suggest that cycloheptatriene possesses a "boat" conformation with a constant admixture of 23% "chair" character to the "boat" form. In cycloheptatriene the C_3C_4 and the methylenic group are forced above the plane formed by $C_1C_2C_5C_6$, producing a "boat" conformer (Figure 1). Puckering of the olefinic part of the molecule can force the methylenic end to move in a ring inversion motion through a planar intermediate.[20] The barrier for the ring inversion was estimated to be about 6 kcal/mol.[14] To assume the "chair" conformation for cycloheptatriene, the double bonds opposite one another (C_1C_2 and C_5C_6) must twist, becoming almost trans in their

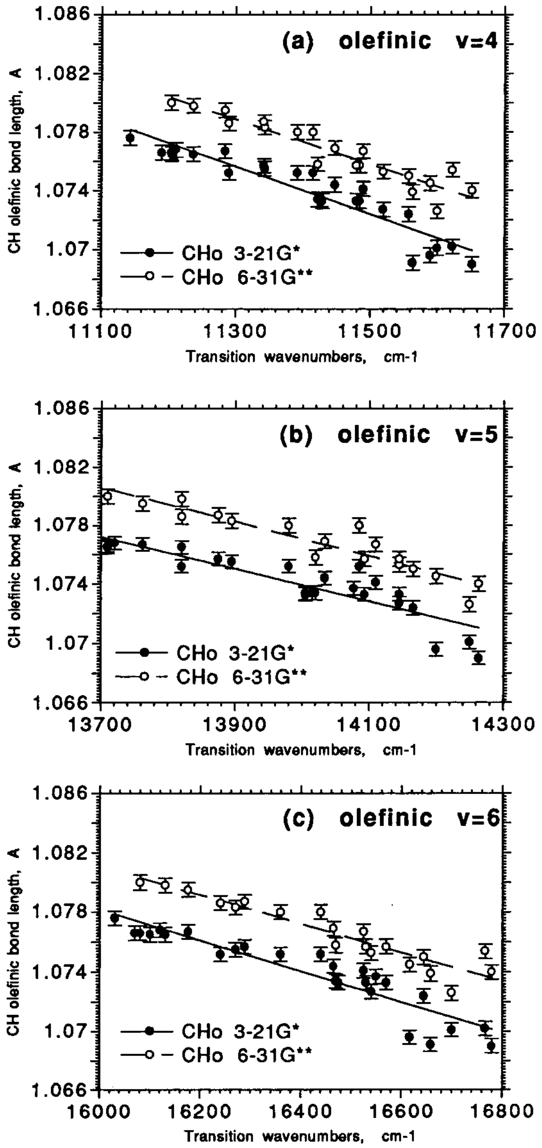

Figure 4. Correlation between CH bond length (HF level of theory) and overtone peak position for olefinic oscillators at third, fourth, and fifth overtones (3-21G(*) (●), 6-31G** (○)). The standard least-squares deviations are shown for each point. Correlation parameters from 3-21G(*) are the following: for $v = 4$, $r_{\mathrm{CH}} = 1.2584 - (1.6175 \times 10^{-5})\nu_{\mathrm{CH}}$; for $v = 5$, $r_{\mathrm{CH}} = 1.2276 - (1.0975 \times 10^{-5})\nu_{\mathrm{CH}}$; for $v = 6$, $r_{\mathrm{CH}} = 1.2427 - (1.0284 \times 10^{-5})\nu_{\mathrm{CH}}$. Correlation parameters from 6-31G** are the following: for $v = 4$, $r_{\mathrm{CH}} = 1.2513 - (1.5259 \times 10^{-5})\nu_{\mathrm{CH}}$; for $v = 5$, $r_{\mathrm{CH}} = 1.2413 - (1.1732 \times 10^{-5})\nu_{\mathrm{CH}}$; for $v = 6$, $r_{\mathrm{CH}} = 1.2347 - (9.6023 \times 10^{-6})\nu_{\mathrm{CH}}$.

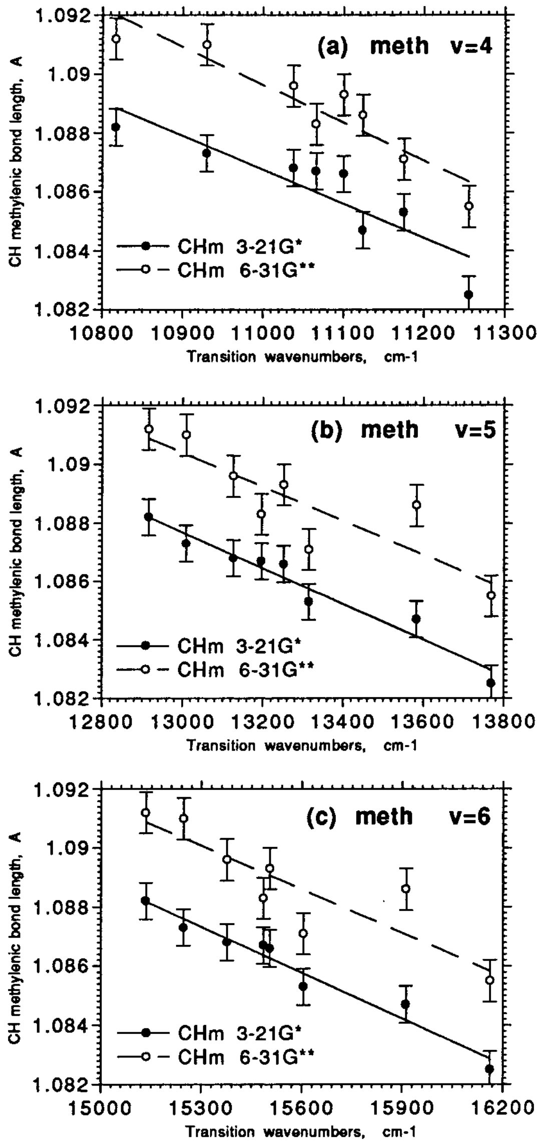

Figure 5. Correlation between CH bond length (HF level of theory) and overtone peak position for methylenic oscillators at third, fourth, and fifth overtones (3-21G(*) (●), 6-31G** (○)). The standard least-squares deviations are shown for each point. Correlation parameters from 3-21G(*) are the following: for $v = 4$, $r_{\mathrm{CH}} = 1.2137 - (1.1539 \times 10^{-5})\nu_{\mathrm{CH}}$; for $v = 5$, $r_{\mathrm{CH}} = 1.1672 - (6.1188 \times 10^{-6})\nu_{\mathrm{CH}}$; for $v = 6$, $r_{\mathrm{CH}} = 1.1661 - (5.1480 \times 10^{-6})\nu_{\mathrm{CH}}$. Correlation paramters from 6-31G** are the following: for $v = 4$, $r_{\mathrm{CH}} = 1.2319 - (1.2934 \times 10^{-5})\nu_{\mathrm{CH}}$; for $v = 5$, $r_{\mathrm{CH}} = 1.1657 - (5.7958 \times 10^{-6})\nu_{\mathrm{CH}}$; for $v = 6$, $r_{\mathrm{CH}} = 1.1652 - (4.9112 \times 10^{-6})\nu_{\mathrm{CH}}$.

geometry. This situation introduces a steric strain in the ring of more than 40 kcal/mol, since the positioning of one trans double bond in a seven-member ring requires about 20.3 kcal/mol.[21] Our ab initio single-point energy calculations (Table 3) indicated that the "chair" conformer of cycloheptatriene is about 101.3 kcal/mol (3-21G(*) basis set) or 104.8 kcal/mol (6-31G**) higher in energy than the "boat". These arguments lead to our interpretation of the experimental overtone data where only the "boat" conformer was considered to estimate peak positions from the derived correlations. These peak positions were used to generate the overtone spectra for $\Delta v = 4$, 5, and 6 transitions.

Peak intensities were estimated according to the number of equivalent CH oscillators and their ratios to the other types of CH oscillators in the molecule. According to the results of ab initio geometry optimization, the "boat" cycloheptatriene has two different CH olefinic oscillators and two distinct methylenic CH bonds (Table 3), which brings the total to four local modes contributing to the overall absorption at each overtone. For "boat" cycloheptatriene the ratio of $\mathrm{CH}_{2,3,4,5}$ to $\mathrm{CH}_{1,6}$ to $\mathrm{CH}_{\mathrm{ax}}$ to $\mathrm{CH}_{\mathrm{eq}}$ was 4:2:1:1. Therefore, the peak due to $\mathrm{CH}_{2,3,4,5}$ should be 2 times more intense than the $\mathrm{CH}_{1,6}$ peak and so on. These are approximate relative intensities only, and the predicted spectrum would benefit from more reliable relative intensity calculations that take into account the change in the dipole moment with changes in the local mode vibrational coordinate. This type of calculation exists for 1,3-butadiene.[19] To illustrate the improvements possible, the direct correlation method was applied to the prediction of the 1,3-butadiene $\Delta v = 4$ CH overtone spectrum, which was previously assigned by several research groups.[18,19] The predicted (6-31G** basis set) and experimental third overtone spectra of *trans*-1,3-butadiene are compared in Figure 7 where the lower predicted spectrum used a proportion of 1:1:1 of CH oscillators and the middle spectrum used a proportion of 1:1.3:1.8 obtained from the oscillator

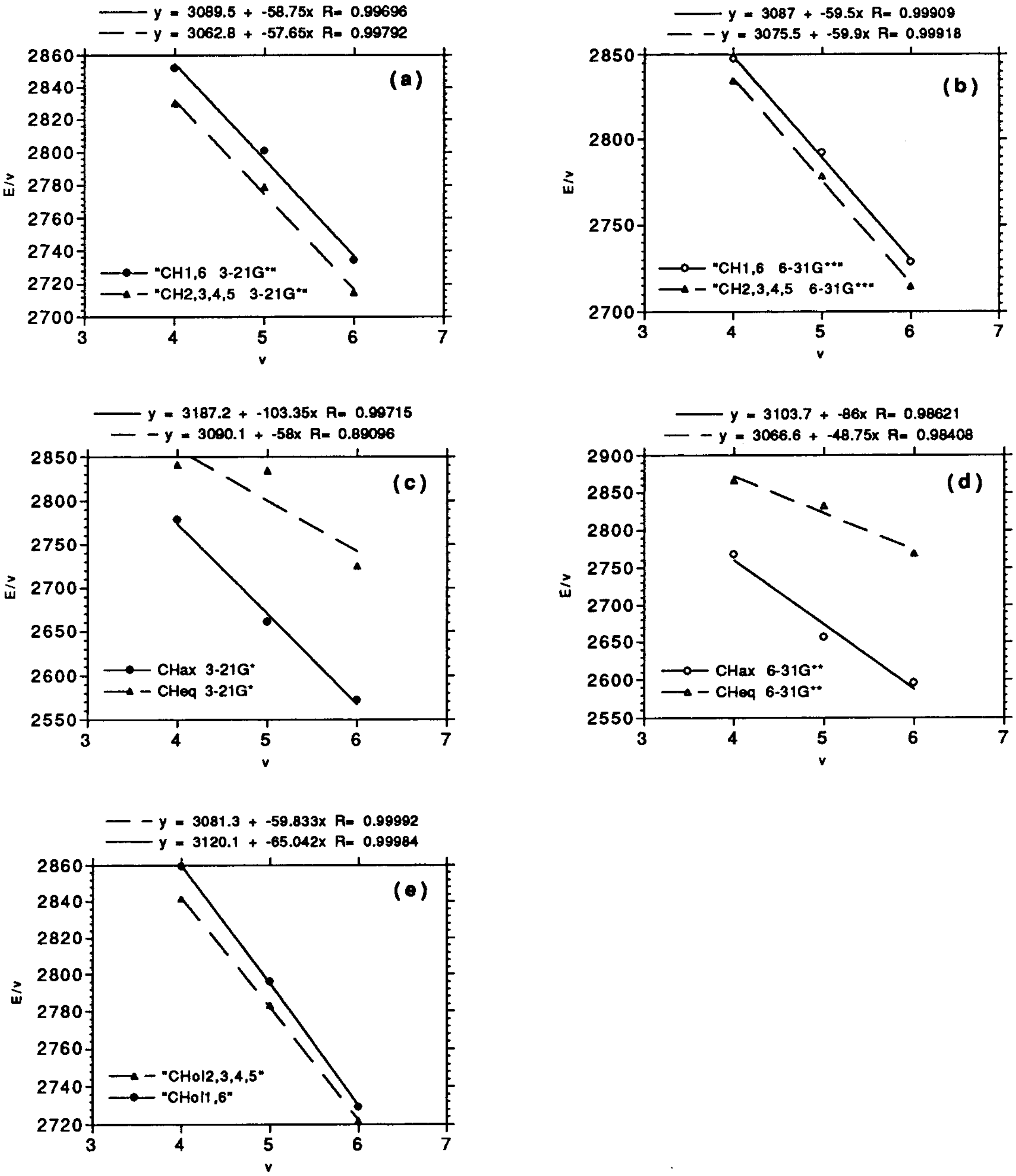

Figure 6. Birge−Sponer plots for olefinic ((a) 3-21G(*), (b) 6-31G**) and methylenic ((c) 3-21G(*), (d) 6-31G**) transitions predicted by the correlations (HF level of theory) and for olefinic transitions (e) observed experimentally.

strength calculations.[19] The middle spectrum reproduces the experimental spectrum more successfully; however, the same assignments would result from both predicted spectra. The lowest energy transition belongs to the longest CH bond (nonterminal), and the two high-energy transitions belong to the terminal-cis and the shortest terminal-trans CH oscillators for butadiene.

Peak widths were estimated using the experimental spectra. The width of the predicted peak was estimated to be about half the width of the most broad and intense transition in the experimental spectrum. This estimation is based on the assumption that two different CH olefinic oscillators of the "boat" cycloheptatriene contribute to the main absorption. In this case the full width at the half-maximum should be approximately twice the width of each contributing peak. The widths of all predicted peaks were assumed to be the same within the particular overtone. The peak widths used for $\Delta v = 4$, 5 and 6 were 50, 70, and 80 cm^{-1}, respectively.

The predicted and experimental spectra are in satisfactory agreement for all three gas-phase overtones (Figure 3). Although the peak positions determined from the method are approximate and the peak widths and relative intensities are estimated, the pattern in the spectrum is well reproduced. Based on this agreement, assignments for the experimental absorptions were made. The assignments are summarized in Table 1.

The most intense band centered at 11 366 cm^{-1} in the third overtone region is due to the olefinic CH bonds (CH$_{1,6}$ and CH$_{2,3,4,5}$). The weak peak at 11 216 cm^{-1} is assigned to the CH$_{eq}$ of cycloheptatriene. The lowest energy transition at 11 094 cm^{-1} belongs to the CH$_{ax}$ oscillator.

At the fourth overtone region the situation is almost the same. The most intense transition consists of transitions of the CH$_{1,6}$ and CH$_{2,3,4,5}$ bond stretches. In addition, the CH$_{eq}$ of the "boat" conformer also contributes to the peak. The separation between the CH$_{ax}$ and CH$_{eq}$ peaks has increased relative to that observed at the third overtone. The peak to the red from the most intense peak is assigned to the CH$_{ax}$ bond stretch transition (13 622 cm^{-1}).

At the fifth overtone region only one broad intense transition occurs. This peak belongs to the olefinic CH$_{1,6}$, CH$_{2,3,4,5}$, and

TABLE 3: Optimized Ab Initio Bond Lengths, Angles, and Energies for Different Conformers of Cycloheptatriene Calculated Using the HF Level of Theory

	cht "boat"		cht "chair"	
	3-21G(*)	6-31G**	3-21G(*)	6-31G**
Olefinic CH Bond Lengths (Å)				
CH 1,6	1.0739	1.0775	1.0760	1.0783
CH 2,5	1.0753	1.0783	1.0798	1.0825
CH 3,4	1.0753	1.0783	1.0734	1.0782
Methylenic CH Bond Lengths (Å)				
CH "axial"	1.0864	1.0887	1.0798	1.0824
CH "equatorial"	1.0815	1.0836	1.0778	1.0820
CC Bond Lengths (Å)				
CC 1−2, 5−6	1.3261	1.3280	1.3323	1.3358
CC 2−3, 4−5	1.4584	1.4614	1.5106	1.4991
CC 3−4	1.3372	1.3378	1.3529	1.3563
CC 6−7, 7−1	1.5139	1.5091	1.5625	1.5426
Angles with C1C2C5C6 Plane (deg)				
methylenic part	27.7	25.9	37.7	37.6
olefinic part	21.9	21.0	47.5	46.3
Ab Initio Energy (hartree)				
	−268.1798	−269.6961	−268.0184	−269.5291

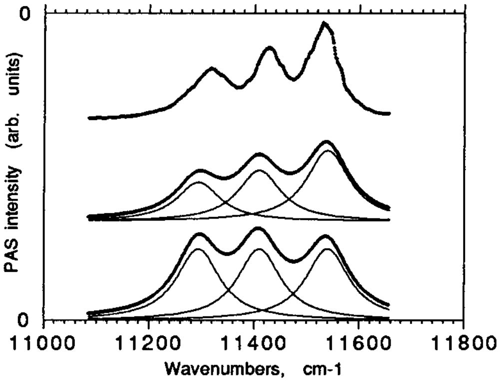

Figure 7. Comparison of the experimental (upper line) and estimated from the correlation (middle and lower lines) spectra of *trans*-1,3-butadiene (HF level of theory, 6-31G** basis set) at the third overtone region. For the middle predicted spectrum the relative intensity of CH oscillators of 1:1.3:1.8 was used. For the lower predicted spectrum the relative intensity of 1:1:1 was used. The smaller peaks under the estimated spectra are the contributions from the different CH oscillators of *trans*-1,3-butadiene.

CH_{eq} of the "boat" cycloheptatriene. No absorptions to the red of the observed transition were detected.

The experimental peak wavenumbers for the olefinic transitions were also fitted to Birge−Sponer plots (Figure 6e). The resulting mechanical frequencies and anharmonicities are, respectively, 3141 and 59.8 cm^{-1} for $\mathrm{CH}_{2,3,4,5}$ and 3185 and 65.0 cm^{-1} for $\mathrm{CH}_{1,6}$. As a further check of the validity of the direct correlation method, the predicted peak positions for each type of CH oscillator in cycloheptatriene were plotted in Birge−Sponer plots (parts a−d of Figure 6). For all olefinic CH bonds it is possible to obtain reasonable vibrational frequencies and anharmonicities from these plots. However, the transition energies estimated for the methylenic CH stretches do not fit the expected Birge−Sponer straight lines. This may indicate that the method, as we have implemented it, does not take into account the unique bonding situations of the two methylenic hydrogens in cycloheptatriene. The methylenic group is just above the $C_1C_2C_5C_6$ plane of the molecule, resulting in different interactions of the two methylenic hydrogens with the olefinic π-system. In the ab initio calculations for cycloheptatriene (Table 3) the CH "axial" is significantly longer than the CH "equatorial" ($r_{\mathrm{CHax}} - r_{\mathrm{CHeq}}$ is 0.0049 Å for 3-21G(*) basis set and 0.0051 Å for 6-31G** basis set). In cyclohexane, for example, the difference between CH_{ax} and CH_{eq} is only 0.0015 Å (3-21G(*)) and 0.0025 Å (6-31G**). For most of the molecules included in the methylenic correlations the axial and equatorial CH bonds are of a different type than the CH_2 group in the cycloheptatriene. This can be responsible for the unsatisfactory fit to the Birge−Sponer plots. Another possible reason for the poor fit for the methylenic CH bond absorptions could be interactions within the methylenic group itself. Two CH oscillators inside the CH_2 group can couple to one another.[22] This coupling may increase the scatter in the correlation and be responsible for the poor fit to the Birge−Sponer plots.

For all three gaseous overtone regions the agreement between the experimental and predicted spectra is better for the 6-31G** basis set as opposed to the 3-21G(*). This is not surprising, since the 6-31G** is more sophisticated and better describes the bond length differences in cycloheptatriene, which directly influences the predicted spectrum. The calculation using the 6-31G** basis set, however, required about 12 times more computer time than the 3-21G(*) basis set, for which the agreement between the experiment and predictions is still acceptable.

In addition to the pure CH overtone transitions, other peaks were observed at the third and fourth overtone regions. Suggested assignments can be made (Table 1) for these peaks using "local mode−normal mode" combinations. The low-energy shoulder of the olefinic peak at 11 313 cm^{-1} was assigned to the combination of $3v\mathrm{CH}_{eq}$ with two quanta of CH_2 bend. The peaks at 12 520 and13 080 cm^{-1} are most likely combination bands of overtone transitions and CH bend or CC stretch. These bands are suggested to belong to the combinations of $3v\mathrm{CH}_{2,3,4,5}$ with one quanta of CH bend and CC stretch.

The first and second overtone spectra of cycloheptatriene recorded in liquid phase (Figure 2) are consistent with the local mode sequence observed at the higher overtones in the gas phase. The intense transition attributed to the olefinic CH's was observed in both overtone regions. In both low overtones several close-lying transitions to the red of the main peak were observed. However, it was difficult to identify the transitions due to the methylenic CH oscillators. The presence of many combination bands of the same or greater intensity than CH_{ax} or CH_{eq} peaks hindered our assignments in this region. Therefore, our designations for CH_{ax}, CH_{eq}, and the combination bands can only be suggested assignments. For the first overtone partially resolved weak peaks to the red of the intense olefinic peak were assigned to the axial and equatorial CH. For the second overtone, based on the extrapolation from the Birge−Sponer plots of gaseous data, we believe that the methylenic CH oscillators are hidden underneath the intense olefinic peak. Both CH overtones and combinations are assigned in Table 1.

All our suggested assignments for the combination bands in the lower overtone regions involved interaction of $(v - 1)$ CH stretch overtones with one or two quanta of CC stretch, CH olefinic bend and bend twist or wag of the CH_2 group. However, the coupling between $\mathrm{CH}_{2,3,4,5}$ olefinic overtone and CH_2 motions, which are separated from each other by several bonds, is unlikely. Therefore, only interaction within one particular type of oscillator (olefinic or methylenic) and interactions of CH olefinic overtones with CC_{str} were considered for the combinations. For example, only coupling between CH_{ax} or CH_{eq} and CH_2 bend, twist, or wag was taken into account. In the first overtone region all combination bands were assigned to the "normal mode−normal mode" combinations. Combinations bands lying above the first overtone region were attributed to the "local mode−normal mode" type. The energy mismatch between experimental transitions and transition wavenumbers obtained from the assignment (last column of the Table 1) can be accounted for by the anharmonicity of CC stretching and CH bending motions.

Conclusions

The overtone spectrum of cycloheptatriene was recorded for the third, fourth, and fifth ($\Delta v = 4$, 5, and 6) vibrational overtone regions. The peaks were assigned to vibrational transitions of the different CH oscillators of the "boat" conformer of cycloheptatriene using a direct correlation method. This method assigns the peaks by comparing the experimental spectrum to a spectrum generated from ab initio bond lengths for the target molecule and a correlation of the CH bond lengths and overtone peak transitions from other previously assigned overtone spectra. It was possible to achieve a satisfactory agreement between experimental and predicted spectra for all overtones in the gaseous spectrum. The agreement was better for the higher level calculations (6-31G**). The proposed direct correlation method can be useful in the assignment of the overtone spectra of other molecules. The assignments from the gaseous spectrum guided our assignments for the liquid-phase spectrum of the $\Delta v = 2$ and 3 regions.

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