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Relative Intensities of Nonequivalent CH Bonds in the Local Mode Overtone Spectra of 1,3- and 1,4-Cyclohexadiene

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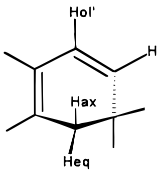
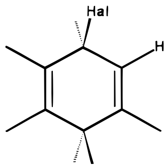
The CH stretching overtone spectra of 1,3- and 1,4-cyclohexadiene have been recorded in the regions corresponding to $\Delta v = 2-6$. Bands are assigned as overtones of the various nonequivalent CH bonds. Oscillator strengths have been calculated according to the harmonically coupled anharmonic oscillator (HCAO) local mode (LM) model, with *ab initio* dipole moment functions. The theoretical values have been compared to experimental values, and good agreement is found between predicted intensities and measured relative intensities within an overtone band. For 1,4-cyclohexadiene, shoulders were observed approximately 100 cm^{-1} above and below the pure LM transition for $\Delta v \geq 4$. These are assigned as (±) combinations with a low-frequency ring-puckering mode.

Introduction

The molecular structures of 1,3-cyclohexadiene (**I**) and 1,4-cyclohexadiene (**II**) have been subjects of continuing interest, particularly with regard to their planarity. There has been little controversy concerning **I**, for which the microwave spectrum[1] shows a twisted C_2 geometry. The aliphatic CH bonds occupy axial and equatorial positions relative to the ring; the nearly degenerate olefinic CH are denoted ol and ol′. In contrast, early analyses[2,3] of the IR and Raman spectra of **II** could not rule out the possibility of a nonplanar minimum, and various electron diffraction,[4,5] rotational Raman,[6] and NMR[7] measurements were similarly inconclusive. Subsequent analyses of the far-IR[8] and Raman[9] spectra of the ring-puckering and twisting modes in both molecules were successfully used to establish a barrier to planarity of 1099 cm^{-1} in **I** and the planar minimum in **II**. At room temperature, a significant fraction of **II** molecules will be in one of the first few vibrational levels of the low-frequency puckering mode.[8]



I



II

The gas-phase spectra of CH stretching overtones can provide remarkably accurate information on small differences in the bond lengths of nonequivalent CH bonds. The positions of band maxima and anharmonicities are well described by the LM model[10−13] and can be related to bond lengths calculated in *ab initio* geometry optimizations, provided that reasonably large split-valence basis sets are employed.[14,15] Because of this sensitivity, the overtone spectra can be used as a probe of molecular structure and conformation. More recently, calculation of overtone intensities has become more reliable; functions based on *ab initio* dipole moments have been used successfully to fit the relative intensities of bands due to the nonequivalent CH bonds in, for example, propane,[10] dimethyl ether and acetone,[11] 1,3-butadiene,[12] and the axial and equatorial CH bonds in cyclohexane.[13]

The variations among the CH bonds that would be expected to arise from the differences in planarity and bond strength in **I** and **II** are small, yet they are sufficient to lead to a separation of several hundred wavenumbers between the bands in the higher overtones. In addition, there may be differences in the relative intensities of these bands. A preliminary study of some of the overtones of these molecule has been reported.[16] We have now recorded the CH stretching vibrations for $\Delta v = 2-6$ and analyzed them within the harmonically coupled anharmonic oscillator (HCAO) LM model. Fully optimized geometries and dipole moment functions have been calculated at the HF level of theory. Dipole moment functions have been generated as a series expansion in the two CH stretching coordinates for the aliphatic CH$_2$ and a single CH coordinate for the olefinic CH. We consider the effect of the different anharmonicities on relative intensities and discuss the probable nature of the additional features observed in the spectra, apart from the pure LM bands.

Experimental Section

The samples were obtained from Lancaster Synthesis Inc, 98% purity, and used without further purification. Near-IR spectra were obtained on a Digilab FT-IR at 1 cm^{-1} resolution in the region from 3800 to 10 000 cm^{-1}. This region includes both the first and second CH stretching overtones. A long-path "White" cell (Wilmad Glass, Buena, NJ) was employed to increase signal. Spectra in the regions of the second, third, and fourth overtones have been previously recorded[16] with a Beckman 5270 spectrometer. A variable path-length gas cell

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(Wilkes Scientific Corp., South Northwalk, CT, model 5720) with NaCl windows was used to increase signal. A heating jacket was constructed for the cell, and an operating temperature of 85 °C was maintained by circulating water from a constant temperature heating bath (Haake, Berlin). The evacuated cell was loaded with vapor above a liquid sample kept in a sidearm and maintained at a lower temperature to avoid condensation within the cell. Spectra were recorded at a nominal resolution of 2 cm^{-1}.

Spectra in the regions of the fourth and fifth CH stretching overtones were recorded with an intracavity laser photoacoustic spectrometer (ICL-PAS), pumped with a Coherent Innova 200 argon ion laser. The details of the ICL-PAS have been described elsewhere.[17] The sample was attached to a vacuum line and degassed. Approximately 30 Torr of sample was introduced into a 1 L spherical mixing chamber equipped with a pressure gauge. Xenon was added as a buffer gas to a total pressure of about 300 Torr and allowed to mix overnight. An aliquot of the prepared sample mixture was introduced into an evacuated PA resonance cell,[18] 15 cm long, with an EK3132 microphone at one end.

The dye laser frequency was tuned with a three-plate birefringent filter; resolution in the overtone region varies from 0.6 to 2 cm^{-1}. For each dye region, initial calibration was achieved by passing a fraction of the extracavity beam into a Spex 14018 double monochromator (spectral band-pass 0.3 cm^{-1}) and by determining the frequency for different settings of the micrometer that rotates the birefringent filter. A small amount of water was introduced as internal standard when final calibration of frequencies was required.[19] The fourth overtone region was recorded with pyridine 2; two dyes, DCM and R6G, were required to encompass the fifth overtone region.

Spectra were imported into SpectraCalc or Bomem Grams/386 (both from Galactic Corp.)[20] for analysis. The spectra were normalized to the intracavity laser power in the usual manner[21]

$$P_{\mathrm{i}} = P_{\mathrm{e}}\left[\frac{2 - T(\lambda)}{T(\lambda)}\right] \tag{1}$$

where P_{i} = intracavity power, P_{e} = extracavity power, and $T(\lambda)$ represents the wavelength dependence of the output coupler transmission. Where possible, band maxima and intensities were determined by curve-fitting with the spectral deconvolution options in this software. Where an entire region was assumed to owe its intensity to a particular overtone transition, the area was determined by integration across the region.

Calculation of Overtone Intensities

The oscillator strength of a vibrational transition from the vibrational ground state, g, to the vibrationally excited state, e, is given by[10,22]

$$f_{\mathrm{eg}} = 4.702[cmD^{-2}]\tilde{\nu}_{\mathrm{eg}}|\vec{\mu}_{\mathrm{eg}}|^2 \tag{2}$$

where $\tilde{\nu}_{\mathrm{eg}}$ is the vibrational wavenumber of the transition and $\vec{\mu}_{\mathrm{eg}} = \langle \mathrm{e}|\vec{\mu}|\mathrm{g}\rangle$ is the transition dipole moment matrix element in debye (D). Thus, we need both the dipole moment function and the vibrational wave functions in order to calculate vibrational oscillator strengths.

We use the harmonically coupled anharmonic oscillator (HCAO) LM model to describe the CH stretching vibrational modes of the molecules. The coupling between CH bonds is significant only when they are attached to the same carbon atom;[11,12] therefore, we have neglected coupling between CH bonds attached to different centers. Within this approximation, **I** is described by a single CH oscillator for each of the two nonequivalent olefinic bonds (CH_{ol}, $CH_{ol'}$) and an asymmetric CH_2 group for the aliphatic bonds (CH_{ax}, CH_{eq}). Similarly, **II** is described by a single CH oscillator for CH_{ol} and a symmetric CH_2 group for CH_{al}. The HCAO LM models for a symmetric CH_2 group, an asymmetric CH_2 group, and a single CH bond have been described in detail elsewhere,[10,12,13] and we only give a brief outline here. The eigenstates are labeled $|v_1\rangle_{ol}$, $|v_2\rangle_{ol'}$, and $|v_1\rangle_{ax}|v_2\rangle_{eq}$ in **I** and $|v\rangle_{ol}$ and $|v_1v_2\rangle_{\pm}$ in **II**. The number of quanta in any oscillator is given by v_i and the ± symbol indicates that the appropriately symmetrized combinations must be used for equivalent bonds in the CH_2 group of **II**. The olefinic CH in **I** are technically distinct, but both experiment and calculations indicate that they are too similar to be distinguished in practice.

For a single CH bond, the Hamiltonian is simply that of a Morse oscillator:[12]

$$\frac{\hat{H} - E_{|0\rangle}}{hc} = v_{\mathrm{i}}\tilde{\omega}_i - (v_i^{\,2} + v_i)\tilde{\omega}_i x_i \tag{3}$$

where $\tilde{\omega}_i$ and $\tilde{\omega}_i x_i$ are the LM frequency and anharmonicity, respectively, and $E_{|0\rangle}$ is the energy of the vibrational ground state. The CH_2 groups are treated in a similar manner, with Morse oscillators describing the diagonal Hamiltonian and the off-diagonal terms given by harmonic terms.[10,13] The equations for the symmetric CH_2 group are identical to the equations used for the methylene group in propane[10] and, for the asymmetric CH_2, to the equations used for cyclohexane.[13] The one additional parameter needed to describe a CH_2 group is the effective coupling parameter, γ', which contains both kinetic and potential energy coupling. The fundamental spectra are too complicated to be assigned in LM terms. Thus γ' is estimated from ab initio calculations of the force constants and the optimized geometry.[10] For a symmetric CH_2 group, as in **II**, $\gamma' = (\gamma - \phi)\tilde{\omega}$ where the kinetic coupling $\gamma = -{}^1/_2(G_{12}/G_{11})$ and the potential coupling $\phi = {}^1/_2(F_{12}/F_{11})$.[10] G_{ij} is the Wilson **G** matrix and F_{ij} are the usual force constants, where i and j refer to the two CH stretching coordinates. The effective coupling between CH stretching oscillators and the mixed dipole moment function terms mainly affects the transitions to LM combination states, which typically appear only in the lower overtones.

The dipole moment function is expressed as a series expansion in the internal CH stretching coordinates. For an isolated CH stretching oscillator we have[12]

$$\vec{\mu} = \sum_i \vec{\mu}_i q^i \tag{4}$$

where $\vec{\mu}_i$ is 1/i! times the ith order derivative of the dipole moment function with respect to the internal coordinate q. To determine the expansion coefficients, $\vec{\mu}_i$, we use *ab initio* molecular orbital theory to calculate the dipole moment as a function of a single internal coordinate, the CH bond length. A one-dimensional grid consisting of seven points around the equilibrium geometry, with a step size of 0.1 Å, i.e., a maximum displacement of ±0.3 Å, is calculated. This ensures a reasonable mapping of the dipole moment function and limits round-off errors.[13] We limit the expansion in eq 4 to fourth order.

For the CH_2 group, a two-dimensional grid in the two internal displacement coordinates is calculated. This provides both the diagonal and mixed terms, i.e., those that depend on two internal coordinates, in the dipole moment expansion. Only second- and third-order mixed terms are included.[13]

TABLE 1: Observed and Calculated Frequencies and Intensities, and Assignments for CH Stretching Vibrational Spectra of Vapor-Phase 1,3-Cyclohexadiene (I)

state	observed		calculated			
	$\tilde{\nu}$ (obsd)[a]	rel intens	$\tilde{\nu}$ (LM)[a,b]	f[b] (LM)	$\tilde{\nu}$ (ai)[a,c]	f[c] (ai)
$\|1\rangle_{\mathrm{ax}}\|0\rangle_{\mathrm{eq}}$	2800−2975 (FR)[d]	1.19	2854	2.19×10^{-5}	2870	2.19×10^{-5}
$\|0\rangle_{\mathrm{ax}}\|1\rangle_{\mathrm{eq}}$		1.00	2946	1.91×10^{-5}	2931	1.88×10^{-5}
$\|1\rangle_{\mathrm{ol}}$	3000−3100	5.33	3037	1.18×10^{-5}	3035	1.18×10^{-5}
$\|1\rangle_{\mathrm{ol'}}$			3037	1.23×10^{-5}	3031	1.23×10^{-5}
$\|2\rangle_{\mathrm{ax}}\|0\rangle_{\mathrm{eq}}$	5596		5571	1.40×10^{-7}	5614	1.84×10^{-7}
$\|0\rangle_{\mathrm{ax}}\|2\rangle_{\mathrm{eq}}$	5746	1.00	5751	1.01×10^{-7}	57309	1.10×10^{-7}
$\|1\rangle_{\mathrm{ax}}\|1\rangle_{\mathrm{eq}}$	5795		5809	1.47×10^{-7}	5806	1.49×10^{-7}
$\|2\rangle_{\mathrm{ol}}$	5949	1.07	5956	1.78×10^{-7}	5953	1.78×10^{-7}
$\|2\rangle_{\mathrm{ol'}}$	5949		5956	2.50×10^{-7}	5943	2.49×10^{-7}
$\|3\rangle_{\mathrm{ax}}\|0\rangle_{\mathrm{eq}}$	8173	1.58	8146	4.18×10^{-8}	8228	4.13×10^{-8}
$\|0\rangle_{\mathrm{ax}}\|3\rangle_{\mathrm{eq}}$	8431	1.00	8439	3.63×10^{-8}	8410	3.66×10^{-8}
$\|2\rangle_{\mathrm{ax}}\|1\rangle_{\mathrm{eq}}$	8518	0.28	8511	0.37×10^{-8}	8538	0.37×10^{-8}
$\|1\rangle_{\mathrm{ax}}\|2\rangle_{\mathrm{eq}}$	8625	0.33	8623	0.22×10^{-8}	8614	0.20×10^{-8}
$\|3\rangle_{\mathrm{ol}}$	8765	2.81	8757	3.62×10^{-8}	8752	3.63×10^{-8}
$\|3\rangle_{\mathrm{ol'}}$	8765		8757	4.66×10^{-8}	8738	4.68×10^{-8}
$\|4\rangle_{\mathrm{ax}}\|0\rangle_{\mathrm{eq}}$	10583	1.0	10581	5.68×10^{-9}	10715	4.97×10^{-9}
$\|0\rangle_{\mathrm{ax}}\|4\rangle_{\mathrm{eq}}$	10989		10995	4.69×10^{-9}	10963	4.57×10^{-9}
$\|3\rangle_{\mathrm{ax}}\|1\rangle_{\mathrm{eq}}$			11088	0.17×10^{-9}	11155	0.16×10^{-9}
$\|1\rangle_{\mathrm{ax}}\|3\rangle_{\mathrm{eq}}$			11281	0.17×10^{-9}	11273	0.16×10^{-9}
$\|4\rangle_{\mathrm{ol}}$	11441	1.2	11440	4.43×10^{-9}	11434	4.44×10^{-9}
$\|4\rangle_{\mathrm{ol'}}$	11441		11440	5.56×10^{-9}	11414	5.62×10^{-9}
$\|5\rangle_{\mathrm{ax}}\|0\rangle_{\mathrm{eq}}$	12874	*e*	12875	8.03×10^{-10}	13073	6.31×10^{-10}
$\|0\rangle_{\mathrm{ax}}\|5\rangle_{\mathrm{eq}}$	13440	*e*	13420	6.11×10^{-10}	13390	5.77×10^{-10}
$\|5\rangle_{\mathrm{ol}}$	14006	*e*	14007	5.57×10^{-10}	13998	5.59×10^{-10}
$\|5\rangle_{\mathrm{ol'}}$	14006		14007	6.91×10^{-10}	13972	7.02×10^{-10}
$\|6\rangle_{\mathrm{ax}}\|0\rangle_{\mathrm{eq}}$	15031	*f*	15003	1.52×10^{-10}	15303	9.21×10^{-11}
$\|0\rangle_{\mathrm{ax}}\|6\rangle_{\mathrm{eq}}$	15705	*f*	15721	8.49×10^{-11}	15691	8.16×10^{-11}
$\|6\rangle_{\mathrm{ol}}$	16455	*g*	16472	7.82×10^{-11}	16444	7.85×10^{-11}
$\|6\rangle_{\mathrm{ol'}}$	16455		16472	9.63×10^{-11}	16412	9.84×10^{-11}

[a] $\tilde{\nu}$ in units of cm^{-1}. [b] Calculated with the experimentally determined LM parameters given in Table 3 and the HF/6-31G(d) dipole moment function. [c] Calculated with the HF/6-31G(d) *ab initio* determined LM parameters and dipole moment function. [d] Fermi resonance interactions with first overtone of CH_2 deformation modes. [e] Relative intensities too uncertain because of low laser power at extreme ends of spectrum. [f] Recorded with DCM. [g] Recorded with R6G dye.

The optimized geometry and the dipole moment at displaced geometries are all calculated with Gaussian 94.[23] We have used the Hartree−Fock level of theory with the 6-31G(d) and 6-311+G(d,p) basis sets as defined within Gaussian 94. Previous calculations have shown that the HF/6-31G(d) method gives good relative intensities within a given overtone,[10−13] whereas larger basis sets are required to improve on the absolute overtone intensities.[24,25] Electron correlation seems to have little effect on overtone intensities and was not used here.[24,26]

The intensities calculated with the HF/6-311+G(d,p) dipole moment function had not converged with a fourth-order dipole expansion for the highest overtones, $\Delta v_{\mathrm{CH}} = 5$ and 6. This convergence problem was alleviated by increasing the order of the dipole moment function expansion to sixth order for the diagonal terms. To obtain converged sixth-order derivatives, we increased the grid size to nine points and used a smaller step size of 0.05 Å, i.e., maximum displacement of ±0.2 Å. This nine-point grid allowed us to obtain intensities that showed good convergence up to $\Delta v = 6$.

The LM parameters for an isolated CH stretching mode can be calculated from *ab initio* values of the force constant and the derivative of the force constant along the internal CH stretching coordinate associated with the CH stretching mode.[27,28] Fundamental IR frequencies of the normal modes have long been calculated with *ab initio* methods. At the Hartree−Fock level, these calculated normal mode harmonic frequencies are of the order of 10 percent too high; thus, it is common to apply scaling factors to the calculated frequencies. We have taken a similar approach here to obtain a theoretical estimate of the LM parameters.[28] To determine the scaling factors for the different nonequivalent CH bonds, we calculated the *ab initio* LM parameters, $\tilde{\omega}$ and $\tilde{\omega}x$ for each of the nonequivalent CH bonds in naphthalene,[29] cyclohexane,[13] and *trans*-2-butene,[30] molecules for which experimental LM parameters had been measured. We then determined scaling factors for an olefinic and an aliphatic CH bond as the average of the ratios of calculated to experimental frequencies and anharmonicities for the appropriate CH bonds. Scaling factors were calculated with both the HF/6-31G(d) and HF/6-311+G(d,p) methods. For an olefinic CH bond, we obtained average scaling factors of 0.949 for $\tilde{\omega}$ and 0.942 for $\tilde{\omega}x$ with the HF/6-311+G(d,p) method, and for an aliphatic CH bond, we obtained 0.954 and 0.970, respectively. We estimate the error in the *ab initio* $\tilde{\omega}$ and $\tilde{\omega}x$ to be of the order of 10 and 1 cm^{-1}, respectively. Overall the scaled *ab initio* LM parameters should provide a good estimate of $\tilde{\omega}$ and $\tilde{\omega}x$.

Results and Discussion

The CH stretching spectra for $\Delta v = 2−6$ of **I** are presented in Figures 1−5, and those for **II** in Figures 6−10. The observed peak positions, relative intensities, and assignments are given in Tables 1 and 2. In the lower overtone spectra, $\Delta v = 2$ and 3, there is some localization within a region, but transitions to the LM−LM combination states are predicted to have significant intensity and are indeed observed. There are also numerous LM normal mode combination bands, indicating that coupling to other modes is still very important. The major bands have been tentatively assigned on the basis of both frequency and relative intensity. In the spectra of both molecules, the overtones with $\Delta v \geq 4$ exhibit essentially pure LM behavior. The fairly narrow, simple bands, separated by several hundred wavenum-

TABLE 2: Observed and Calculated Frequencies and Intensities, and Assignments for CH Stretching Vibrational Spectra of Vapor-Phase 1,4-Cyclohexadiene (II)

	observed		calculated			
state	$\tilde{\nu}$ (obsd)[a]	rel intens	$\tilde{\nu}$ (LM)[a,b]	f[b] (LM)	$\tilde{\nu}$ (ai)[a,c]	f[c] (ai)
$\|1,0\rangle_-$	2750−2940 (FR)[d]	1.17	2896	1.65×10^{-5}	2880	1.63×10^{-5}
$\|1,0\rangle_+$	2750−2940 (FR)[d]		2886	2.92×10^{-5}	2870	2.89×10^{-5}
$\|1\rangle_{ol}$	2940−3170	1.00	3019	3.01×10^{-5}	3017	3.01×10^{-5}
$\|2,0\rangle_+$	5640	1.52	5632	1.31×10^{-7}	5621	1.77×10^{-7}
$\|2,0\rangle_-$	5640		5633	2.65×10^{-7}	5622	3.37×10^{-7}
$\|1,1\rangle$	5739	0.22	5783	2.29×10^{-7}	5751	2.43×10^{-7}
$\|2\rangle_{ol}$	5916	1.00	5921	3.83×10^{-7}	5916	3.81×10^{-7}
$\|3,0\rangle_+$	8223	1.21	8225	6.68×10^{-8}	8241	6.55×10^{-8}
$\|3,0\rangle_-$	8223		8225	4.03×10^{-8}	8241	4.04×10^{-8}
$\|2,1\rangle_-$	∼8530	0.03	8535	0.69×10^{-8}	8507	0.06×10^{-8}
$\|2,1\rangle_+$	∼8530		8515	0.05×10^{-8}	8487	0.60×10^{-8}
$\|3\rangle_{ol}$	8700	1.00	8704	8.22×10^{-8}	8696	8.23×10^{-8}
$\|4,0\rangle_+$	10668	1.00	10669	6.40×10^{-9}	17032	6.37×10^{-9}
$\|4,0\rangle_-$	10668		10669	8.00×10^{-9}	10732	5.41×10^{-9}
$\|3,1\rangle_-$			11117	0.05×10^{-9}	11116	0.05×10^{-9}
$\|3,1\rangle_+$			11115	0.31×10^{-9}	11114	0.24×10^{-9}
$\|4\rangle_{ol}$	11371	1.15	11368	10.0×10^{-9}	11358	10.1×10^{-9}
$\|5,0\rangle_+$	12980		12962	0.99×10^{-9}	13095	6.41×10^{-10}
$\|5,0\rangle_-$	12980	1.2	12962	1.04×10^{-9}	13095	7.54×10^{-10}
$\|5\rangle_{ol}$	13930	1.0	13915	1.25×10^{-9}	13901	12.6×10^{-10}
$\|6,0\rangle_+$	15095	*f*	15107	1.91×10^{-10}	15330	0.73×10^{-10}
$\|6,0\rangle_-$	15095	*f*	15107	1.40×10^{-10}	15330	1.18×10^{-10}
$\|6\rangle_{ol}$	16332	*g*	16343	1.74×10^{-10}	16325	1.77×10^{-10}

[a] $\tilde{\nu}$ in units of cm^{-1}. [b] Calculated with the experimentally determined LM parameters given in Table 3 and the HF/6-31G(d) dipole moment function. [c] Calculated with the HF/6-31G(d) *ab initio* determined LM parameters and dipole moment function. [d] Fermi resonance interactions with first overtone of CH_2 deformation modes. [e] Relative intensities too uncertain because of low laser output power at extreme ends of spectrum. [f] Recorded with DCM. [g] Recorded with R6G dye.

TABLE 3: Local Mode Parameters for the CH Bonds in 1,3- and 1,4-Cyclohexadiene

bond	$\tilde{\omega}_{expt}$[a]	$\tilde{\omega}x_{expt}$[a]	$\tilde{\omega}_{calc}$[b]	$\tilde{\omega}x_{calc}$[b]	$\tilde{\omega}_{calc}$[c]	$\tilde{\omega}x_{calc}$[c]
		1,3-Cyclohexadiene				
CH_{ax}[d]	2997 ± 2	70.2 ± 0.4	3000	64.2	2999	64.1
CH_{eq}[d]	3074 ± 17	64.9 ± 3.2	3055	62.8	3060	62.9
CH_{ol}[d]	3155 ± 1	58.9 ± 0.1	3153	58.9	3152	59.0
$CH_{ol'}$[d]	3155 ± 1	58.9 ± 0.1	3149	59.1	3145	59.2
		1,4-Cyclohexadiene				
CH_{al}[e]	3041 ± 6	74.7 ± 1.3	3003	64.0	3013	63.9
CH_{ol}[e]	3138 ± 6	59.1 ± 1.2	3136	59.3	3131	59.4

[a] Uncertainties are 1 standard deviation. [b] Calculated at HF/6-31G(d) level of theory. [c] Calculated at HF/6-311+G(d,p) level of theory. [d] 1,3-Cyclohexadiene. Fit of $\Delta v = 4$, 5, 6. See text. [e] 1,4-Cyclohexadiene. Fit of $\Delta v = 3$, 4, 5, 6.

bers, may be assigned to each of the unique CH oscillators: $CH_{ol,\,ol'}$, CH_{ax}, and CH_{eq} for **I** and CH_{ol} and CH_{al} for **II**.

***Ab Initio* and Experimental LM Parameters.** Observed maxima ($\tilde{\nu}$) that have been assigned as pure LM peaks have been fitted to the Morse oscillator equation:

$$\tilde{\nu}/v = \tilde{\omega} - (v + 1)\tilde{\omega}x \tag{5}$$

The values of the experimental LM parameters $\tilde{\omega}$ and $\tilde{\omega}x$, obtained from this Birge−Spöner fit, are given in Table 3, along with the calculated and scaled *ab initio* values. The agreement between the HF/6-31G(d) and HF/6-311+G(d,p) calculated values is very good and suggests that the procedure used to obtain these parameters is reasonable. Comparison to the experimental LM parameters is very good for the olefinic CH stretching modes in **I** and **II**, with discrepancies less than 10 cm^{-1} for $\tilde{\omega}$ and less than 0.3 cm^{-1} for $\tilde{\omega}x$. The agreement is reasonable for the CH_{eq} bond in **I**, whereas it is rather poorer for the weakest aliphatic CH bonds: CH_{ax} in **I** and CH_{al} in **II**. For these two bond types, the calculated values of $\tilde{\omega}x$ are about 10 cm^{-1} smaller than the experimental values. The *ab initio* calculations indicate that their anharmonicities should be the largest in the cyclohexadienes; however, the differences are still significantly beyond the expected uncertainties in the *ab initio* LM parameters.

We have investigated the possibility that the experimental $\tilde{\omega}x$ values are in error for CH_{al} and CH_{ax}. The $\Delta v = 3$ aliphatic spectral region exhibits several bands for both molecules rather than a simple LM profile. This indicates that there are still strong couplings to other modes, often CH bend vibrations that appear as combinations of $(v - 1)$ quanta of CH stretch plus 2 quanta of a bending mode. Fermi resonant interactions affect both position and intensity, making it difficult to assign the bands easily. We determined the experimental LM parameters using only $\Delta v = 4$, 5 and 6 for the Birge−Spöner fits. Better correlation is necessary when fewer points are used; however, the values may better reflect LM behavior. The regression yields a lower value for the anharmonicity of CH_{ax} in **I** (70.2 ± 0.4 instead of 73.8 ± 1.1 cm^{-1}). The uncertainty is much lower, and we believe the accuracy of the result is better. This anharmonicity is still higher than either theoretical value (Table 3).

The anharmonicity for CH_{al} in **II** is hardly changed (74.7 ± 1.4 instead of 75.6 ± 2.7 cm^{-1}), leading us to believe that it may indeed be unusually high. If this is true, it may also be manifested in the relative intensities of the aliphatic and olefinic bands. To test this possibility, we have calculated the intensity using first the experimental and then *ab initio* values for the LM parameters, along with the ab initio value for γ' [vide infra]. The results are given in Tables 1 and 2. For $\Delta v \geq 4$, the LM−LM combinations are calculated to contribute less than 1% of the total intensity and no bands are observed. The calculated data for these transitions have been omitted.

The effective coupling parameter, γ', contains both kinetic and potential energy couplings and is calculated from the **F** and **G** matrix elements,[10,13] determined from *ab initio* optimization and frequency calculations. We have calculated *ab initio* values

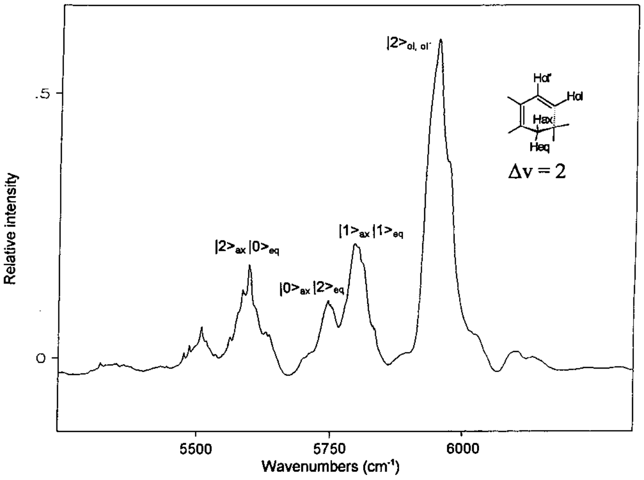

Figure 1. Room-temperature spectrum of 1,3-cyclohexadiene in the region of Δv (CH) = 2, recorded in the gas phase on a Digilab FTS-40 FT-IR. Path length is 2 m, and pressure is 60 Torr.

for γ' with the HF/6-31G(d), HF/6-311+G(d,p), and HF/6-311++G (2d,2p) basis sets. For **I**, we get 13.0 cm^{-1} (13.0, 11.2 cm^{-1}) and for **II**, 5.6 cm^{-1} (5.1, 3.5 cm^{-1}), with the larger basis set results given in brackets. The small variation in the calculated values for g′ suggests that it is reasonable to use γ' = 13 and 5 cm^{-1} in the calculations for **I** and **II**, respectively. The value of the effective coupling constant for **I** is similar to the value for cyclohexane[13] (15 cm^{-1}), whereas **II** is quite small compared to values obtained for the CH$_2$ group in molecules such as propane[10] (20 cm^{-1}). However, it has been found that the calculated overtone intensities of the dominant transitions do not depend significantly on the values of the effective coupling parameter.[10] Furthermore, the effect of g′ on the transition energies is minimal for the pure LM states, $|v0\rangle_\pm$. The splitting of the $|v0\rangle_+$ and $|v0\rangle_-$ states is seen mainly in the fundamental region, where it is $2\gamma'$, and decreases with increasing overtone. LM combination bands are evident mainly in the $\Delta v = 2$ overtone region, where the states $|1\rangle_{ax}|1\rangle_{eq}$ in **I** and $|1,1\rangle$ in **II** obtain intensity from both the effective coupling term and the mixed terms in the dipole moment function.

1,3-Cyclohexadiene: Band Assignments and Intensities. Molecule **I** is stable in the twisted conformer and has four nonequivalent CH bonds.[1] There is a well-established empirical relationship between the optimized CH bond length from an *ab initio* calculation and the location of the overtone band maximum.[14,15] The *ab initio* calculations show the olefinic CH to have nearly identical bond lengths (1.0762 and 1.0765 Å, from HF/6-31G(d) optimization), so separation of their overtone maxima is not expected to appear at the lower overtones. The CH$_{ax}$ and CH$_{eq}$ bond lengths are calculated to be 1.0905 and 1.0854 Å and will be well separated in all cases. In the Δv = 2 region (Figure 1), we assign the band at 5596 cm^{-1} to $|2\rangle_{ax}|0\rangle_{eq}$ and a second band of similar intensity at 5795 cm^{-1} to $|1\rangle_{ax}|1\rangle_{eq}$. The weaker band at 5746 cm^{-1} is probably due to the transition to the $|0\rangle_{ax}|2\rangle_{eq}$ state. The relative intensities of these three bands, from a curve-fitting procedure, is found to be (2.1):(1.0):(2.3), in general agreement with the calculations, LM (1.4):(1.0):(1.5) and ab initio (1.67):(1.0):(1.35). The intense band at 5949 cm^{-1} arises from transitions to the $|2\rangle_{ol}$ and $|2\rangle_{ol'}$ states. The aliphatic intensity is taken as the sum of all the bands in the aliphatic region. At the Δv = 2 level, the total aliphatic to olefinic intensity is calculated to be (1.15):(1.00), with the experimental LM parameters, and (1.33):(1.00) with the *ab initio* parameters. This is in moderate agreement with the observed relative intensity of (1.0):(1.1).

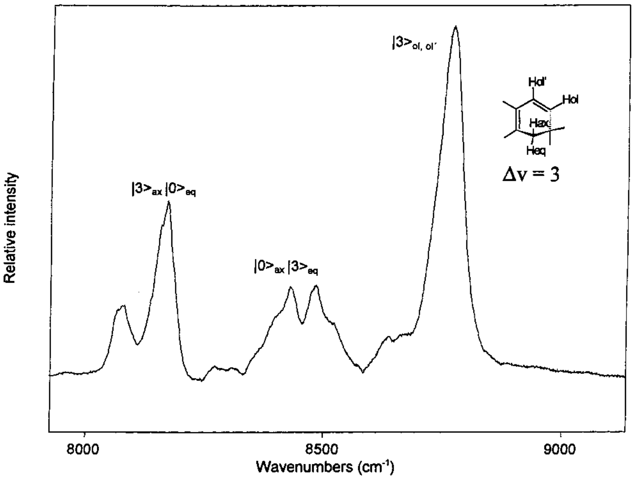

Figure 2. Room-temperature spectrum of 1,3-cyclohexadiene in the region of Δv (CH) = 3, recorded in the gas phase on a Digilab FTS-40 FT-IR. Path length is 2 m, and pressure is 60 Torr.

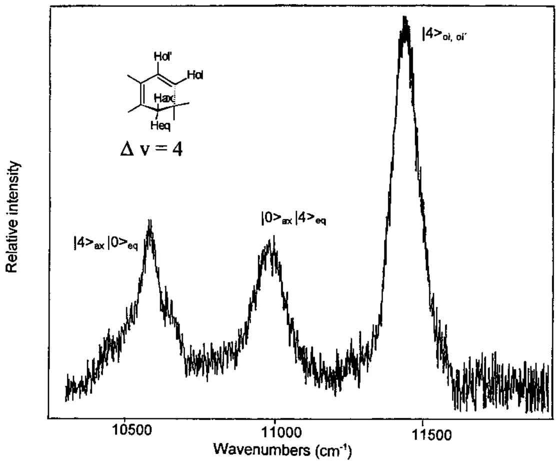

Figure 3. Room-temperature spectrum of 1,3-cyclohexadiene in the region of Δv (CH) = 4, recorded in the gas phase on a Beckman 5270. Path length is ~10 m.

For Δv = 3 (Figure 2), the aliphatic to olefinic intensity ratio is calculated to be (1.0):(1.0) with either parameter set, again in good agreement with the observed relative intensity of (1.0):(1.1). As noted in the discussion of the LM parameters for the CH$_{ax}$ and CH$_{eq}$, there was some uncertainty about the assignment of the pure LM transitions, since there are multiple plausible assignments for the bands in this region. A shoulder at 8518 cm^{-1} is tentatively assigned as $|2\rangle_{ax}$ $|1\rangle_{eq}$, and another, centered around 8625 cm^{-1}, as $|1\rangle_{ax}$ $|2\rangle_{eq}$. The relative intensities of the bands in the regions assigned as axial and equatorial are found by direct integration of the entire area in the region. The CH$_{ax}$ and CH$_{eq}$ ratio is found to be (1.4):(1.0), in good agreement with the calculated ratios of (1.2):(1.0) (LM) and (1.1):(1.0) (ab initio); see Table 1.

For the higher overtones, $\Delta v \geq 4$ (Figures 3−5), we see three broad bands corresponding to the aliphatic CH$_{ax}$ and CH$_{eq}$ bonds and the four nearly equivalent CH$_{ol,ol'}$. Again, the CH$_{ax}$ overtone is assigned to the lowest frequency band, in agreement with positions calculated with the *ab initio* estimated $\tilde{\omega}$ and $\tilde{\omega}x$ values. In the Δv = 4 region, we see good agreement between calculated and observed relative intensities for the aliphatic and olefinic regions; however, differences between the calculations with the experimental and ab initio estimated LM parameters are starting to show. The ratio between the axial and equatorial CH bands is calculated to be (1.3):(1.0) with experimental $\tilde{\omega}$ and $\tilde{\omega}x$,

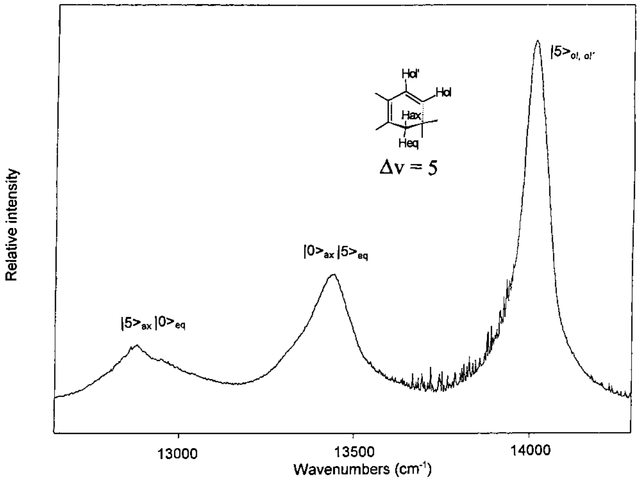

Figure 4. Room-temperature spectrum of 1,3-cyclohexadiene in the region of Δv (CH) = 5, recorded in the gas phase with ICL-PAS, pyridine 2 dye, unnormalized.

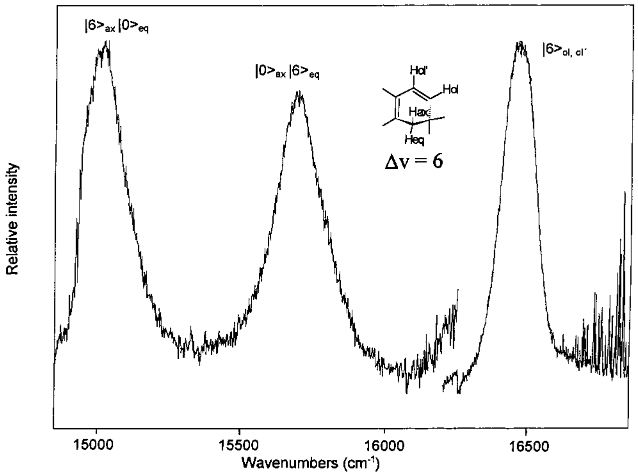

Figure 5. Room-temperature spectrum of 1,3-cyclohexadiene in the region of Δv (CH) = 6, recorded in the gas phase with ICL-PAS, DCM (14850−16250 cm^{-1}), R6G (16200−16850 cm^{-1}).

whereas use of the *ab initio* parameters gives only (1.1):(1.0). This difference between the intensity calculations with the two LM parameter sets increases with increasing overtone number. The experimental values are estimated to be about (1.0):(1.0); however, these early spectra[16] are rather noisy (Figure 3) and there is a larger experimental error here. As predicted from the calculations, the intensities of the other bands in the manifold are quite insignificant, and no bands are observed.

At $\Delta v = 5$ (Figure 4), we calculated CH_{ax} to CH_{eq} intensity ratios of (1.3):(1.0) and (1.1):(1.0) with the LM and *ab initio* estimated $\tilde{\omega}$ and $\tilde{\omega}x$ values, respectively (Table 1). The ratio for the calculated total aliphatic to olefinic intensity is (1.1):(1.0) from the experimental LM parameters and (1.0):(1.0) from the *ab initio* LM parameters. Unfortunately, it was not possible to test these predictions through comparison with experimental intensities. The entire $\Delta v = 5$ spectral region was recorded with the ICL-PAS system, using the dye pyridine 2. The unnormalized spectrum (Figure 4) cannot be used for intensity. The recorded intensity must be corrected for both the transmittance of the output coupler and for the laser power (eq 1). The tunable range of this dye does go just beyond the low end of the CH_{ax} band; however, the output laser power was only about 3 mW at this point, compared to 60 mW near the dye laser maximum. As the end of the tunable range is approached, there is greater instability in the power. The uncertainty in the latter was too great to allow for a reliable intensity correction.

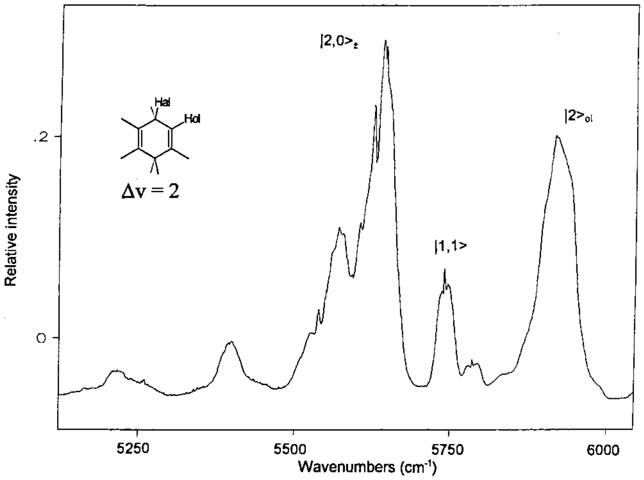

Figure 6. Room-temperature spectrum of 1,4-cyclohexadiene in the region of Δv (CH) = 2, recorded in the gas phase on a Digilab FTS-40 FT-IR. Path length is 2 m, and pressure is 60 Torr.

The CH_{ax} and CH_{eq} bands show slight shoulders that might be due to hot bands associated with the very low-energy (97 cm^{-1}) ring twist mode.[9,30] Similar behavior was observed in the 1,4-cyclohexadiene CH_2 bands (vide infra).

At the highest recorded overtone, $\Delta v = 6$ (Figure 5), we expected that the CH_{ol} and $CH_{ol'}$ overtones might appear as two overlapping bands of similar intensity. Some indication of this is found in the full width at half-maximum, which, at $\Delta v = 5$, is 87 cm^{-1} for the olefinic band in **I**, compared to 75 cm^{-1} in **II**; at $v = 6$, the corresponding values are 142 and 109 cm^{-1}, respectively. However, it was not possible to satisfactorily deconvolute the $\Delta v = 6$ overtone into two bands. This is not unusual, since some actual separation, and the appearance of a small valley between the band maxima, is generally required for a deconvolution program to produce a successful fit.

The separation between the aliphatic and olefinic CH at this overtone is so large ($CH_{ax} = 150\ 34$ cm^{-1}; $CH_{ol} = 163\ 32$ cm^{-1}) that they could not be recorded with a single dye. The aliphatic region was recorded with DCM, the olefinic with R6G; thus, it was not possible to compare the intensities of the aliphatic to olefinic CH. Even within the DCM dye region, it was not possible to obtain relative intensities for axial to equatorial, since the laser power again became very weak at the low end of the CH_{ax} band.

1,4-Cyclohexadiene: Band Assignment and Intensities. The HF/6-31G(d) optimized bond length of the CH_{al} is 1.0900 Å while that of the CH_{ol} is 1.0776 Å. Excluding differences in anharmonicities, the overtones should appear at energies similar to those of the CH_{ax} and $CH_{ol,ol'}$ in **I**. The spectrum of the $\Delta v = 2$ region (Figure 6) shows transitions to the pure LM aliphatic $|2,0\rangle_{\pm}$ and olefinic $|2\rangle_{ol}$ states as broad bands with maxima at 5640 and 5916 cm^{-1}, respectively. The calculated band maxima and relative intensities agree well with the observations. The assignment of the transition to the LM combination state $|1,1\rangle$ is more problematic. Since the coupling in the CH_2 group is weak, the transition to $|1,1\rangle$ mainly gains intensity from the mixed term in the dipole expansion. We calculate the position of this peak to be 5784 cm^{-1} with the experimental LM parameters and 5751 cm^{-1} with the *ab initio* LM parameters. Either the medium band at 5739 cm^{-1} or the weaker band at 5782 cm^{-1} might be assigned as this transition. An alternative explanation is that the band at 5739 cm^{-1} and the smaller band

TABLE 4: Observed and Calculated Intensity of Aliphatic Relative to Olefinic Band in 1,4-Cyclohexadiene

		6-31G(d)		6-311+G (d,p)[a]	
Δv	observed	LM[b]	ai[c]	LM[b]	ai[c]
1	1.2	1.52	1.50	1.45	1.44
2	1.5	1.65	2.02	2.53	2.97
3	1.2	1.36	1.34	2.13	1.99
4	0.9	1.53	1.26	2.21	1.63
5	1.2	1.82	1.26	2.04	1.32
6		2.23	1.31	2.24	1.36

[a] Series function for dipole moment expansion extended to sixth order. [b] LM parameters from experiment. [c] LM parameters from *ab initio* calculations.

at 5782 cm^{-1} are some Fermi resonant coupled mixture of the $|1,1\rangle$ transition and a combination involving one quantum of CH stretch and two quanta of another mode (e.g., 3032 cm^{-1} + (2 × 1358 cm^{-1})). Such a combination could easily shift the relative frequencies of both bands, as well as mix the intensities. The transition to the $|1,1\rangle$ peak is calculated to have an intensity that is higher than the sum of the intensities of the 5739 and 5782 peaks. Not much difference is seen between the two different calculations. A complete assignment of the various bands in the $\Delta v = 2$ region was attempted; however, there are so many possibilities that no unequivocal assignments could be made. Thus, the $\Delta v = 2$ region cannot yet be used to distinguish between the possible anharmonicities for the aliphatic CH.

The spectra and assignments for **II** are much simpler than for **I**, since each overtone is dominated by only two strong bands, one for CH_{al} and one for CH_{ol}. The observed and calculated intensity ratios for the aliphatic and olefinic bands have been collected in Table 4. The experimental intensity ratio in the $\Delta v = 2$ region is (1.7):(1.0) and agrees quite well with the calculated intensity ratio of (1.6):(1.0) from the experimental LM parameters and less well with the value of (2.0):(1.0) from the *ab initio* LM parameters, both calculated with the HF/6-31G(d) dipole moment function. The difference in the choice of parameters for the calculated ratios becomes more pronounced at the higher overtones. Regardless of basis set, for $\Delta v \geq 3$ the intensity ratio calculated with the *ab initio* LM parameters is always lower than that obtained with experimental LM parameters. The difference becomes more pronounced with increasing overtone level. The $\Delta v = 5$ region was recorded with the ICL-PAS and the pyridine 2 dye. The relative intensities are found to be about (1.15 ± 0.2):(1.0) from experiment, (1.8):(1.0) for the experimental LM parameters, and (1.3):(1.0) for the *ab initio* LM parameters. The uncertainty in the experimental measurement makes it difficult to distinguish between the two calculations; however the *ab initio* LM parameters seem to be preferable. The relative intensities at $\Delta v = 6$ are predicted to be (2.2):(1.0) from the experimental LM parameters and only (1.3):(1.0) from the *ab initio* LM parameters. Since it was not possible to record the entire region with a single dye, we were unable to determine which set of parameters might be preferred.

It is apparent from the spectra of all the overtones of **II** (Figures 6−10) that the CH_{al} regions do not give a pure single band structure as would be expected, at least for $\Delta v \geq 4$, from the equivalence of the four aliphatic CH bonds. However, the fundamental ring-puckering mode in **II** has a vibrational frequency[8,9] of about 108 cm^{-1}. Thus, the first few vibrational levels of this mode are significantly populated at room temperature. Evidence for this is found in the far-IR spectrum.[8] In a classical sense, this means that the molecule will spend an appreciable amount of time in a molecular structure that is not planar. This will clearly affect the aliphatic CH bonds. We have estimated the variation in the CH_{al} bond length of about 1 mÅ for nonplanar conformers up to an energy of 400 cm^{-1}. Even such a small variation will cause a significant broadening

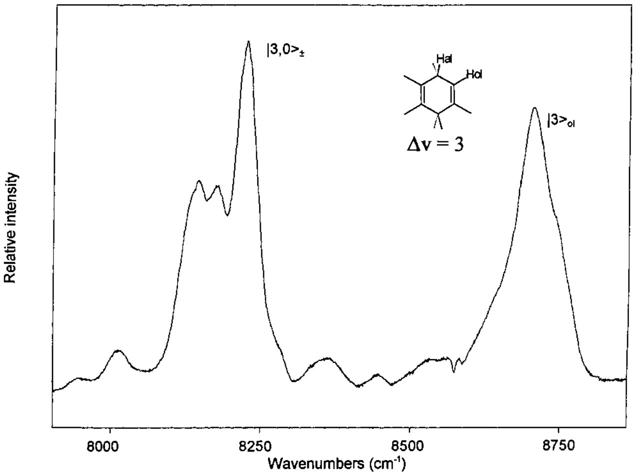

Figure 7. Room-temperature spectrum of 1,4-cyclohexadiene in the region of Δv (CH) = 3, recorded in the gas phase on a Digilab FTS-40 FT-IR. Path length is 2 m, and pressure is 60 Torr.

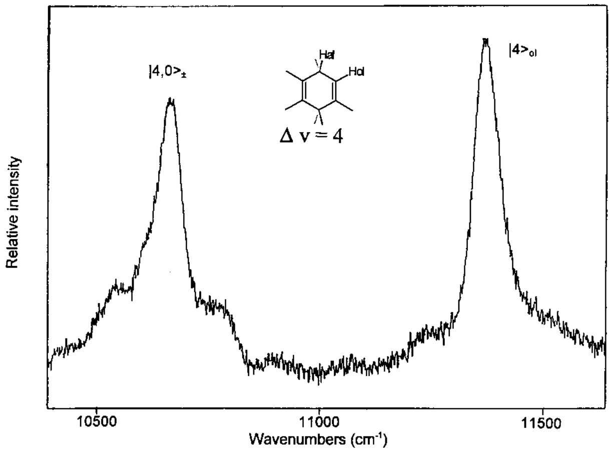

Figure 8. Room-temperature spectrum of 1,4-cyclohexadiene in the region of Δv (CH) = 4, recorded in the gas phase on a Beckman 5270. Path length is ~10 m.

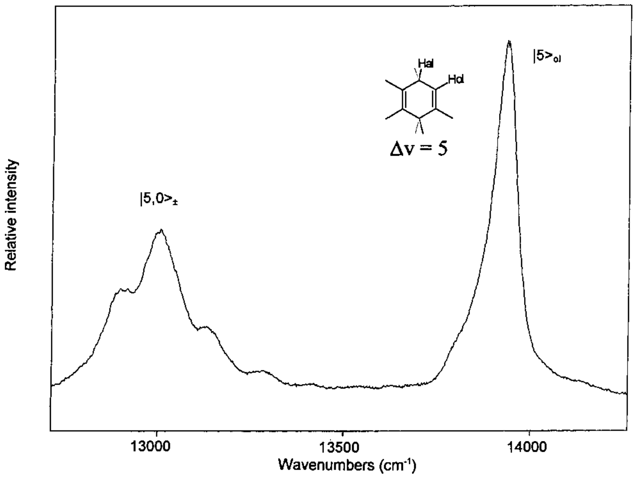

Figure 9. Room-temperature spectrum of 1,4-cyclohexadiene in the region of Δv (CH) = 5, recorded in the gas phase with ICL-PAS, pyridine 2 dye, unnormalized.

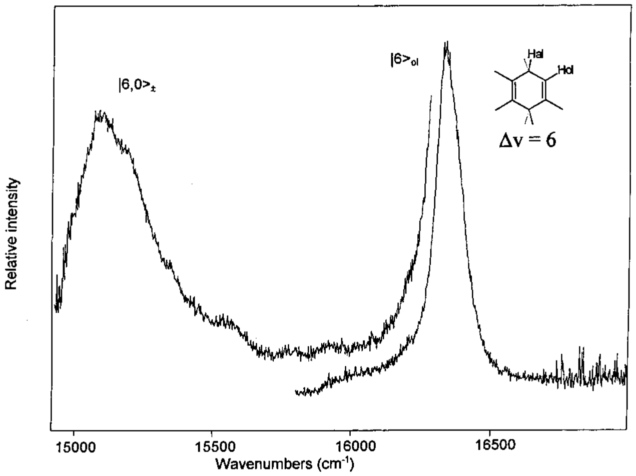

Figure 10. Room-temperature spectrum of 1,4-cyclohexadiene in the region of Δv (CH) = 6, recorded in the gas phase with ICL-PAS, DCM (14850−16250 cm^{-1}), R6G (16200−16850 cm^{-1}).

of the involved overtone bands. Furthermore, owing to the low vibrational frequency of the ring-puckering mode, hot bands and combinations of LM and ring-puckering mode bands can occur. The spectra at $\Delta v = 2$ and 3 include too many combination bands to be easily interpreted. However, the CH_{al} regions of $\Delta v = 4$ and 5 clearly exhibit a single strong band flanked by two shoulders at approximately ±110 cm^{-1}, which are probably attributable to the puckering mode. In intensity comparisons for v ≥ 3, we have taken the area of the entire band for the aliphatic intensity, since we assume that all bands in this region obtain their intensity from the dominant pure LM transition. The observation of these shoulders is of some interest in relation to recent papers on the elimination of H_2 from **I** and **II**.[31,32] It has been suggested that in the photodissociation of the latter molecule the reaction pathway would involve a transition state in which the aliphatic CH bonds were stretched by about 35% from their equilibrium values and that the molecule would be in a boat conformation, that is, at the extreme of a pucker vibration. Our spectra indicate that, in the ground-state molecule at least, transitions involving the two vibrations necessary to follow the reaction path can be observed.

Conclusion

The CH stretching overtones in 1,3- and 1,4-cyclohexadiene are readily interpreted within the HCAO LM model. Nonequivalent CH bonds give rise to well-resolved bands in the higher overtones ($\Delta v \geq 4$). In both molecules, the olefinic CH bonds are much shorter and the overtones are observed as single, well-resolved bands at the high-frequency end of each overtone region. In the twisted equilibrium conformation of the 1,3-cyclohexadiene, the olefinic bonds are of two types, but these are sufficiently similar that they are not resolved in the spectra, though there is some indication of separation in the band at $\Delta v = 6$. The aliphatic CH bonds may be described as axial and equatorial. The latter are shorter, with overtones that are several hundred wavenumbers higher than the axial. In the planar 1,4-cyclohexadiene, only two types of CH bond are found: aliphatic and olefinic. Where comparison is experimentally feasible, relative intensities of the CH overtone bands calculated from *ab initio* dipole moment functions are in good agreement with the observed relative intensities within each overtone. Shoulders on the aliphatic CH overtone bands for $\Delta v \geq 4$ are attributed to the population of very low-frequency ring modes, a ring twist in the 1,3-cyclohexadiene and a pucker in 1,4-cyclohexadiene.

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(20) Spectra Calc and Bomem Grams are both products from Galactic Industries Corp.

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