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CH-Stretching Overtone Spectra of *cis*- and *trans*-1,3-Pentadiene

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The room-temperature vapor-phase overtone spectra of *cis*- and *trans*-1,3-pentadiene (piperylene) have been recorded in the 5000−17500 cm^{-1} region with the use of conventional and intracavity laser photoacoustic spectroscopy. The presence of five nonequivalent olefinic CH bonds and one methyl group in each molecule complicates assignment of the spectra. We have used a harmonically coupled anharmonic oscillator local mode model with one oscillator for each of the nonequivalent CH bonds to calculate the CH-stretching overtone spectra and thus facilitate assignment of the spectra. Our calculated spectra are in good agreement with the observed spectra. The observed high overtone spectra are distinctively different despite the similarity of the two molecules and the numerous and broad transitions.

Introduction

The 1,3-pentadienes are commonly combined with butadiene to form butadiene-1,3-pentadiene copolymers which are used to make rubber with a variety of uses. The resultant products include tires with strength, abrasion resistance, and a good compromise between tensile strength and heat build-up. The rubber is also used for flooring in gyms and for roofing material with good adhesion to concrete and iron.[1] In the processing lines, near-infrared (NIR) spectroscopy can be used as a guide to follow the progress of the reaction, however no information is available on assignment of the various transitions.

Previously, the vapor-phase infrared (IR) spectra of *cis*- and *trans*-1,3-pentadiene have been recorded by Rasmussen and Brattain in the 700−5000 cm^{-1} region.[2] The following characteristic features were identified: a strong peak at 773 cm^{-1} in the *cis*-1,3-pentadiene spectrum and a strong peak at 820 cm^{-1} in the *trans*-1,3-pentadiene spectrum. In addition, bands in the 1390 and 1470 cm^{-1} regions were assigned to HCH-bending vibrations, and bands in the 1600 and 1660 cm^{-1} regions were assigned to C═C-stretching vibrations for the cis and trans compounds, respectively. These bands were confirmed in later work by Compton et al. who recorded vapor-, liquid-, and solid-phase IR spectra as well as argon matrix isolation IR spectra and liquid- and solid-phase Raman spectra.[3] Several bands were observed in the CH-stretching region from 2860 to 3090 cm^{-1} and correspond to both the olefinic and methyl CH-stretching modes. Vibrational overtone spectra of butadiene polymers have also been recorded.[4,5]

Previously, CH-stretching overtone spectra have been recorded of related smaller, simpler molecules. These are 1,3-butadiene, which contains the same olefinic backbone as the 1,3-pentadienes, and *cis*- and *trans*-2-butene, which contain the methyl group attached to a C═C backbone.[6,7] The CH-stretching overtone spectra of 1,3-butadiene (up to $\Delta v_{\mathrm{CH}} = 7$) and of the two 2-butenes (up to $\Delta v_{\mathrm{CH}} = 9$) were explained in terms of a harmonically coupled anharmonic oscillator (HCAO) local mode model.[6,7] The HCAO local mode model, combined with ab initio calculated dipole moment functions, has been used successfully to model these and other CH-stretching overtone spectra.[8]

We have recorded CH-stretching overtone spectra of *cis*- and *trans*-1,3-pentadiene, in the regions corresponding to $\Delta v_{\mathrm{CH}} = 2-6$. The structures of the 1,3-pentadienes are shown in Figure 1. In 1,3-butadiene, there are only three nonequivalent CH bonds and the CH-stretching overtone spectra are relatively simple with three isolated peaks at each overtone.[6] The replacement of a terminal hydrogen atom in 1,3-butadiene with a methyl group to form the 1,3-pentadienes leads to five nonequivalent olefinic CH bonds and a methyl group, which significantly complicates the spectra. The peak positions and intensities of the CH-stretching overtone transitions have been calculated with the HCAO local mode model combined with ab initio dipole moment functions calculated at the Hartree−Fock level of theory with the 6-311++G(2d,2p) basis set. We use these calculations to facilitate assignment of the recorded spectra and to investigate the contribution of the methyl group relative to the olefinic CH-stretching transitions.

Experimental Section

The samples, *cis*-1,3-pentadiene (Aldrich, 98%) and *trans*-1,3-pentadiene (Aldrich, 96%), were dried over molecular sieve pellets to remove trace amounts of water and degassed by several freeze−pump−thaw cycles on a vacuum line.

Room-temperature vapor-phase spectra in the $\Delta v_{\mathrm{CH}} = 2-3$ regions were recorded with a conventional spectrometer (Cary 500) with a 4.8 m path length cell fitted with Infrasil windows.

The room-temperature vapor-phase spectra in the $\Delta v_{\mathrm{CH}} = 4-6$ regions were recorded with intracavity laser photoacoustic spectroscopy (ICLPAS). The details of our ICLPAS setup have been described elsewhere.[9] Spectra in the $\Delta v_{\mathrm{CH}} = 4-5$ regions were recorded with a tunable titanium:sapphire laser (Coherent 890) with two different output couplers which covered the region from 10 500 to 15000 cm^{-1}. Spectra in the $\Delta v_{\mathrm{CH}} = 6$ region

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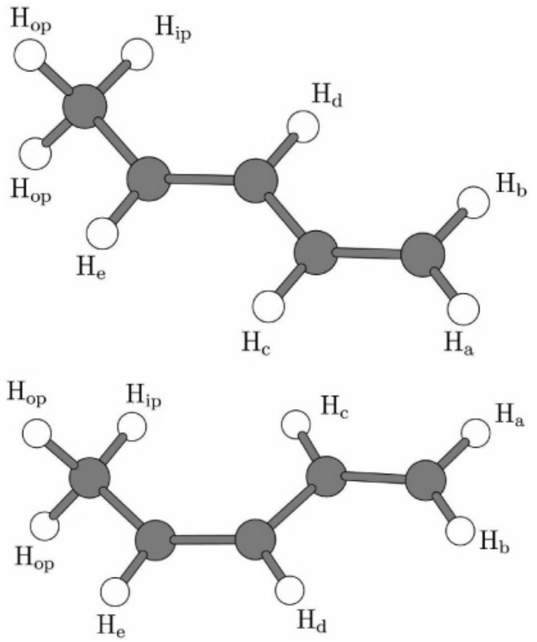

Figure 1. HF/6-311++G(2d,2p) optimized structure of *trans*-1,3-pentadiene (top) and *cis*-1,3-pentadiene (bottom) and the labeling of the nonequivalent CH bonds.

were recorded with a tunable dye laser (Coherent 599) and the dye rhodamine 6G which covered the region from 16 000 to 17 500 cm^{-1}. The photoacoustic cell is approximately 10 cm long and was fitted with a Knowles Electronics EK3133 microphone.

The experimental oscillator strength *f* of an absorption band can be determined from the conventional spectra and the following equation[10]

$$f = 2.6935 \times 10^{-9}\ (\mathrm{K}^{-1}\ \mathrm{Torr\ m\ cm})\ \frac{T}{pl}\int A(\tilde{\nu})\ \mathrm{d}\tilde{\nu} \quad (1)$$

where p is the sample pressure in the cell, l is the path length, and A is the absorbance. Since the photoacoustic signal is proportional to absorbance with an unknown proportionality constant, we can only obtain relative oscillator strengths in the ICLPAS spectra. Each overtone region has been deconvoluted into a number of Lorentzian bands with a straight baseline with the Grams program.[11] The wavenumber accuracy of the spectra is approximately ±1 cm^{-1}.

Theory and Calculations. The dimensionless oscillator strength f_{eg} of a vibrational transition from the ground state g to a vibrational excited state e is given by[10,12]

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

where $\tilde{\nu}_{eg}$ is the transition frequency in cm^{-1} and $\vec{\mu}_{eg} = \langle e|\vec{\mu}|g\rangle$ is the transition dipole moment in Debye (D). Oscillator strengths from eq 2 can be directly compared to experimental oscillator strengths from eq 1.

The optimized structures of *cis*- and *trans*-1,3-pentadiene have C_s symmetry, and all five olefinic CH bonds are nonequivalent. The methyl group in each of the 1,3-pentadienes has one in-plane CH (CH$_{ip}$) bond and two out-of-plane CH (CH$_{op}$) bonds. These methyl groups will act like hindered methyl rotors.[13] The coupling between CH-stretching oscillators is usually only significant if the oscillators share a common heavy atom, and we have limited the coupling to this case.[6] To a good approximation, the CH bonds in *cis*- and *trans*-1,3-pentadiene can be divided into three groups, olefinic CH bonds where the carbon is bonded to only one hydrogen (CH$_{c,d,e}$), terminal CH$_2$ olefinic (methylene) bonds (CH$_{a,b}$), and CH$_3$ (methyl) bonds.

Vibrational Model. The model Hamiltonians for an isolated CH-stretching oscillator as well as for two and three coupled CH-stretching oscillators have been given elsewhere, and we refer to these earlier papers for details.[6,12,14] Briefly, for two coupled nonequivalent CH oscillators such as the methylene groups, the Hamiltonian is[14]

$$(H^0 - E^0_{|00>})/hc = v_1\tilde{\omega}_1 - (v_1^{\,2} + v_1)\tilde{\omega}_1 x_1 + v_2\tilde{\omega}_2 - (v_2^{\,2} + v_2)\tilde{\omega}_2 x_2 \quad (3)$$

with the perturbation

$$H^1/hc = -\gamma'_{12}(a_1 a_2^+ + a_1^+ a_2) \quad (4)$$

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

$$\gamma'_{12} = \left(-\frac{\cos\theta}{2}\left(1 + \frac{m_\mathrm{C}}{m_\mathrm{H}}\right)^{-1} - \frac{F_{12}}{2\sqrt{F_{11}F_{22}}}\right)\sqrt{\tilde{\omega}_1\tilde{\omega}_2} \quad (5)$$

where θ is the H$_1$CH$_2$ angle, m_C and m_H are the atomic masses, and the F_{ij} are the force constants. The angle and force constants can be calculated ab initio. The $\tilde{\omega}$ and $\tilde{\omega}x$ values can be obtained from a Birge−Sponer fit of observed pure local mode transitions or can be obtained from ab initio calculated potential curves.[15,16] We use a combination of both methods. The methyl group is treated similarly as two nonequivalent CH$_2$ groups CH$_{ip}$H$_{op}$ and CH$_{op}$H$_{op}$, with pairwise harmonic coupling between CH bonds.[12]

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

$$\vec{\mu}(q_1,q_2) = \sum_{i,j}\vec{\mu}_{ij}q_1^i q_2^j \quad (6)$$

where the coefficients $\vec{\mu}_{ij}$ are given by

$$\vec{\mu}_{ij} = \frac{1}{i!j!}\frac{\partial^{i+j}\vec{\mu}}{\partial q_1^i \partial q_2^j}\Big|_e \quad (7)$$

The expansion of eq 6 has been limited to fifth order for the diagonal terms and third order for the mixed terms. The diagonal expansion coefficients are obtained from ab initio calculated one-dimensional (1D) grids with nine points that are generated by displacing the CH bond from −0.2 to +0.2 Å in 0.05 Å steps about the equilibrium geometry. The mixed expansion coefficients are determined from an ab initio 2D 9 × 9 grid, which is generated by displacing the CH bonds from −0.2 to +0.2 Å about the equilibrium. The expansion coefficients $\vec{\mu}_{ij}$ are determined by standard numerical techniques and are reasonably converged.[14] The mixed coefficients mainly affect the intensities of the less intense transitions to local mode combination states (states where the vibrational energy is distributed over more than one CH oscillator). The optimized geometries and all points in the grids are calculated at a specified ab initio method with Gaussian94.[17] The dipole moment functions of the methyl groups can be expanded in a similar manner as two methylene groups, CH$_{ip}$H$_{op}$ and CH$_{op}$H$_{op}$.

We have used the HF/6-311++G(2d,2p) and B3LYP/6-311++G(2d,2p) ab initio methods. However, we experienced

TABLE 1: Calculated CH Bond Lengths (in Å) for 1,3-Pentadiene[a]

	trans HF	*cis* HF	*trans* B3LYP	*cis* B3LYP
CH_{ip}	1.0817	1.0790	1.0896	1.0874
CH_{op}	1.0846	1.0846	1.0932	1.0930
CH_{op}	1.0846	1.0846	1.0932	1.0930
CH_e	1.0773	1.0760	1.0864	1.0848
CH_d	1.0764	1.0753	1.0864	1.0850
CH_c	1.0758	1.0730	1.0856	1.0833
CH_b	1.0743	1.0743	1.0828	1.0829
CH_a	1.0724	1.0725	1.0804	1.0806

[a] With the 6-311++G(2d,2p) basis set.

considerable difficulty in obtaining dipole moment derivatives that were converged beyond third order with the B3LYP method similar to what was found for 3-hexyne.[18] As higher order terms in the dipole moment expansion become increasingly important for the higher overtones, we have used the HF method to calculate overtone intensities.

Results and Discussion

The cis and trans isomers of 1,3-pentadiene are both stable isomers. For both isomers, the optimized structure has C_s symmetry and all fundamental harmonic frequencies are calculated to be positive, indicating that the structures are indeed minima. B3LYP/6-311++G(2d,2p) ab initio calculations show that the *trans*-1,3-pentadiene is about 1.5 kcal mol^{-1} lower in energy. The barrier to cis−trans conversion is likely to be high, and we see no evidence of conversion between *cis*- and *trans*-1,3-pentadiene in our spectra.

The labeling of the nonequivalent CH bonds is shown in Figure 1 with their ab initio calculated bond lengths given in Table 1. As expected, the B3LYP bond lengths are longer than the HF bond lengths, but the relative bond lengths are similar, although there are small differences in order between the two methods. Individual vibrational overtone transitions of nonequivalent bonds are consistently resolved in room-temperature spectra when the bond lengths differ by as little as 1 mÅ.[19,20] In jet expanded, rotationally cold spectra, the peaks narrow to about 5 cm^{-1} and it is possible to resolve peaks where bond length differences are less than 0.1 mÅ.[21] In both *cis*- and *trans*-1,3-pentadiene, some of the olefinic CH bonds have bond lengths which differ by about 0.5−0.7 mÅ and we only expect to be able to resolve the corresponding peaks at higher overtones.

The vapor-phase CH-stretching spectra of *cis*- and *trans*-1,3-pentadiene in the regions corresponding to $\Delta v_{CH} = 2-6$ are shown in Figures 2−6. The trans spectra are shown in the top panels and the cis in the bottom panels. The frequencies, line widths, and oscillator strengths obtained from the deconvolutions of the spectra are given in Tables 2 and 3.

We have fitted the assigned pure local mode peaks in the $\Delta v_{CH} = 3-6$ regions to a two-parameter Morse oscillator (Birge−Sponer) energy expression

$$\tilde{\nu}_{v0}/v = \tilde{\omega} - (v + 1)\tilde{\omega}x \tag{8}$$

to obtain the experimental local mode parameters, frequency $\tilde{\omega}$, and anharmonicity $\tilde{\omega}x$. The local mode parameters obtained from the *trans*-1,3-pentadiene and *cis*-1,3-pentadiene spectra are given in Tables 4 and 5, respectively. The generally small size of the uncertainties in Tables 4 and 5 indicates that the two-parameter fit of eq 8 is reasonable and corroborates our assignment of the pure local mode peaks. The $\Delta v_{CH} = 2$ transitions were not included due to the large amount of coupling between the bonds which results in peaks that do not correspond to pure local mode transitions in this region. The ordering of the local mode frequencies $\tilde{\omega}$ is in accordance with the ab initio CH bond lengths given in Table 1. The shorter the bond, the higher is the local mode frequency.[19] Some of the local mode parameters could not be determined from experiment due to overlapping bands. In Tables 4 and 5, we also list the ab initio calculated parameters. As expected, the HF/6-311++G(2d,2p) calculated local mode frequencies are somewhat higher than the experimental values, and we have scaled these calculated frequencies and anharmonicities to compensate for inaccuracies in the ab initio method.[15,16] We have used scaling factors obtained from comparing calculated and observed parameters for the cis terminal CH bond in 1,3-butadiene to scale the olefinic parameters and for the CH_{ip} bond in *trans*-2-butene to scale the methyl parameters.[6,7] The same scaling factors were used for both *cis*- and *trans*-1,3-pentadiene. The scaling brings the parameters into quite good agreement with those bonds for which it was possible to find experimental values and supports our assignment. To obtain better scaling factors, we used a few of the well-assigned peaks in the *cis*- and *trans*-1,3-pentadiene spectra. To determine the olefinic scaling factors for *trans*-1,3-pentadiene, we use the CH_a transitions as they are strong, isolated, clearly defined peaks. The CH_{op} peak was used to determine the methyl group scaling factors. For *cis*-1,3-pentadiene, we used the CH_b and CH_{op} peaks, respectively. We find that the scaling factors obtained this way are similar to those determined from the 1,3-butadiene and *trans*-2-butene spectra.[22]

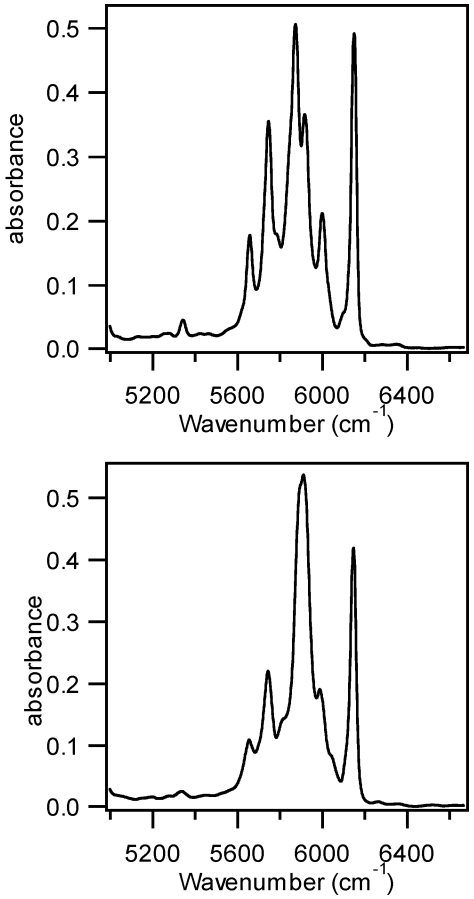

Figure 2. Room-temperature vapor-phase overtone spectra of *trans*-1,3-pentadiene (top) and *cis*-1,3-pentadiene (bottom) in the $\Delta v_{CH} = 2$ region. The spectra were measured with conventional spectroscopy with a cell path length of 4.8 m and a pressure of 22 Torr for *trans*-1,3-pentadiene and 25 Torr for *cis*-1,3-pentadiene.

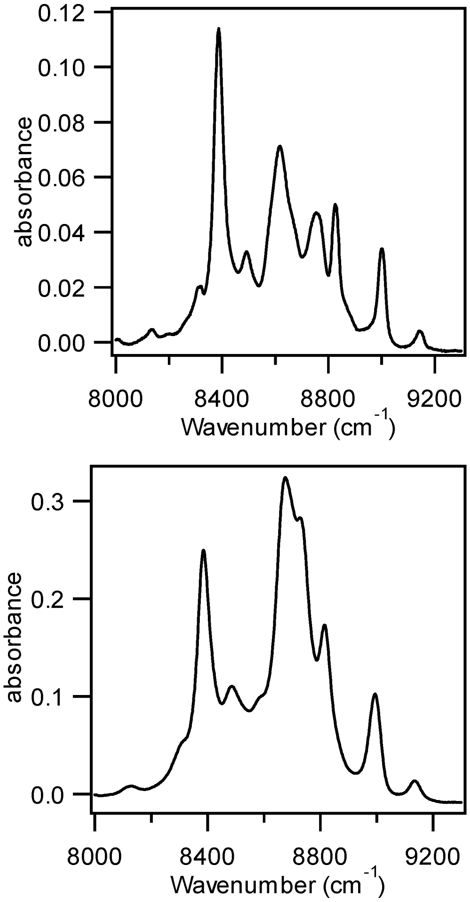

Figure 3. Room-temperature vapor-phase overtone spectra of *trans*-1,3-pentadiene (top) and *cis*-1,3-pentadiene (bottom) in the $\Delta v_{CH} = 3$ region. The spectra were measured with conventional spectroscopy with a cell path length of 4.8 m and a pressure of 50 Torr for *trans*-1,3-pentadiene and 180 Torr for cis-1,3-pentadiene, respectively.

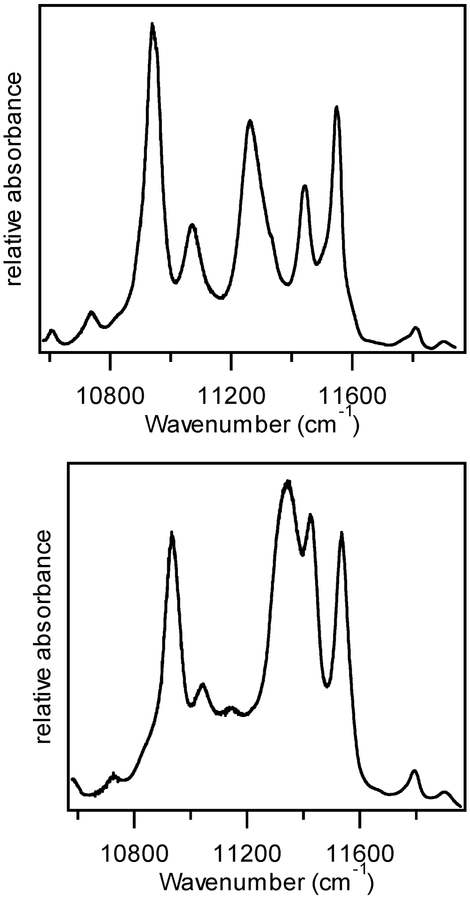

Figure 4. Room-temperature vapor-phase overtone spectra of *trans*-1,3-pentadiene (top) and *cis*-1,3-pentadiene (bottom) in the $\Delta v_{CH} = 4$ region. The spectra were measured by Ti:Sapph ICL-PAS with a sample pressure of 50 Torr.

We compare the experimental local mode parameters for *cis*- and *trans*-1,3-pentadiene with experimental parameters of 1,3-butadiene for the olefinic bonds and *trans*-2-butene for the methyl bonds. The measured local mode frequencies of the olefinic CH$_a$ are 3172 cm^{-1} (trans) and 3163 cm^{-1} (cis) which compare well with an $\tilde{\omega}$ value of 3171 cm^{-1} for the corresponding methylene CH bond of 1,3-butadiene.[6] Similarly, the frequencies of the olefinic CH$_b$ are 3154 cm^{-1} (trans) and 3147 cm^{-1} (cis) which compare well with an $\tilde{\omega}$ value of 3150 cm^{-1} for the corresponding methylene CH bond of 1,3-butadiene.[6] The nonterminal CH bond in 1,3-butadiene has a local mode frequency of 3122 cm^{-1}, which is in the range of the nonterminal CH frequencies of the pentadienes, apart from the CH$_c$ frequency in cis.[6] A similar agreement is found for the anharmonicities with the higher frequency modes having smaller anharmonicities.

For the methyl group in *trans*-1,3-pentadiene, the experimental frequencies are 3045 cm^{-1} for CH$_{op}$ and 3065 cm^{-1} for CH$_{ip}$, which are similar to the values found for the methyl groups in *cis*- and *trans*-2-butene and propane.[7,12] The frequency of the CH$_{ip}$ oscillator is consistently higher than that in the CH$_{op}$. In molecules such as acetone and dimethyl ether, the difference between the local mode parameters of the two bonds is significantly higher due to the nearby oxygen atom.[23] In *cis*-1,3-pentadiene, the spectrum is complicated by internal rotation of the methyl group. As expected, the olefinic frequencies are significantly higher than those of the methyl CH bonds, and the higher overtone spectra show separated methyl and olefinic regions. If the barrier to internal methyl rotation is low, then this rotation can couple to the CH-stretching modes and can have a significant effect on CH-stretching overtone spectra.[13]

The effective coupling parameters (eq 5) are similar for both *trans*- and *cis*-1,3-pentadiene and were calculated ab initio. The values (after scaling of local mode frequencies) are 44 cm^{-1} for the methylene group, 14 cm^{-1} for the CH$_{op}$H$_{op}$ group, and 22 cm^{-1} for the CH$_{op}$H$_{ip}$ group. These values are very similar to the ab initio calculated γ' values between the two terminal CH bonds in 1,3-butadiene (42−50 cm^{-1}) and for the methyl group in the 2-butenes (15 and 22 cm^{-1}).[6,7]

The calculated frequencies and oscillator strengths for the CH-stretching transitions in *trans*- and *cis*-1,3-pentadiene, shown in Tables 2 and 3, were obtained with the molecule specific scaled local mode parameters in Tables 4 and 5 (last two lines) and the HF/6-311++G(2d,2p) ab initio calculated coupling parameters and dipole moment functions.

Local mode combination states have quanta in a number of different local modes. The intensity of transitions to the combination states decreases rapidly with increasing overtone (thus the success of the local mode model).[8,19] However, at lower overtones, they can carry significant intensity. For example, a local mode combination state gives rise to the strongest transition in the $\Delta v_{CH} = 2$ region of the cyclohexane spectrum.[14] As the olefinic region is close to the methyl region, this becomes an issue in assigning the olefinic transitions of the lower overtones, as methyl local mode combination states can lie in this region.

There is little difference in the frequencies, anharmonicities, and coupling parameters between the bonds in *cis*- and *trans*-

1,3-pentadiene. For both molecules, the CH methyl bonds have a slightly larger anharmonicity and slightly lower frequency than the olefinic CH bonds.

TABLE 2: Observed Line Widths, Observed and Calculated Frequencies and Oscillator Strengths, and Peak Assignments for the CH-Stretching Overtone Spectra of *trans*-1,3-Pentadiene

observed			calculated[a]		
$\tilde{\nu}$ (cm^{-1})	line width (cm^{-1})	f[b]	$\tilde{\nu}$ (cm^{-1})	f	assignment
5658	33	4.46×10^{-8}			
5746	45	1.38×10^{-7}	5702	1.59×10^{-7}	$\|2\rangle_{op}$
			5712	7.26×10^{-8}	$\|2\rangle_{op}$
5792	26	1.24×10^{-8}	5773	5.33×10^{-8}	$\|2\rangle_{ip}$
5843	53	7.31×10^{-8}	5840	8.53×10^{-8}	$\|1\rangle_{op}\|1\rangle_{op}$
5875	43	1.71×10^{-7}	5890	9.45×10^{-8}	$\|2\rangle_{e}$
			5897	5.69×10^{-8}	$\|1\rangle_{ip}\|1\rangle_{op}$
			5899	2.04×10^{-7}	$\|1\rangle_{ip}\|1\rangle_{op}$
5913	16	8.40×10^{-9}	5912	5.67×10^{-8}	$\|2\rangle_{d}$
5925	39	9.41×10^{-8}	5926	6.48×10^{-8}	$\|2\rangle_{c}$
			5930	5.90×10^{-8}	$\|2\rangle_{b}$
6003	50	9.01×10^{-8}	5988	4.52×10^{-8}	$\|2\rangle_{a}$
6150	28	1.43×10^{-7}	6145	1.74×10^{-7}	$\|1\rangle_{a}\|1\rangle_{b}$
8388	43	2.26×10^{-8}	8382	2.29×10^{-8}	$\|3\rangle_{op}$
8488	63	6.08×10^{-9}	8487	5.69×10^{-9}	$\|3\rangle_{ip}$
8613	78	2.30×10^{-8}	8593	4.71×10^{-9}	$\|1\rangle_{op}\|2\rangle_{op}$
			8651	7.39×10^{-9}	$\|1\rangle_{ip}\|2\rangle_{op}$
8663	78	6.66×10^{-9}	8661	1.01×10^{-8}	$\|3\rangle_{e}$
			8678	4.01×10^{-9}	$\|2\rangle_{op}\|1\rangle_{op}$
			8694	5.58×10^{-9}	$\|3\rangle_{d}$
			8716	6.57×10^{-9}	$\|3\rangle_{c}$
8748	65	1.11×10^{-8}	8749	8.44×10^{-9}	$\|3\rangle_{b}$
8772	26	1.71×10^{-9}			
8828	35	7.61×10^{-9}	8805	7.89×10^{-9}	$\|3\rangle_{a}$
9001	31	5.63×10^{-9}	8977	5.91×10^{-9}	$\|1\rangle_{a}\|2\rangle_{b}$
9145	27	9.78×10^{-10}	9137	1.38×10^{-9}	$\|2\rangle_{a}\|1\rangle_{b}$
10942	60	1.0	10931	1.78×10^{-9}	$\|4\rangle_{op}$
11076	62	0.33	11079	4.98×10^{-10}	$\|4\rangle_{ip}$
11259	67	0.62	11277	2.87×10^{-10}	$\|1\rangle_{op}\|3\rangle_{op}$
			11296	3.09×10^{-10}	$\|1\rangle_{op}\|3\rangle_{op}$
11305	113	0.51	11317	7.67×10^{-10}	$\|4\rangle_{e}$
			11335	3.39×10^{-10}	$\|1\rangle_{ip}\|3\rangle_{op}$
			11361	4.61×10^{-10}	$\|4\rangle_{d}$
			11390	5.44×10^{-10}	$\|4\rangle_{c}$
11443	47	0.35	11447	6.18×10^{-10}	$\|4\rangle_{b}$
11509	66	0.15			
11550	38	0.46	11522	8.10×10^{-10}	$\|4\rangle_{a}$
13236	77	0.46			
13334	73	1.0	13356	1.66×10^{-10}	$\|5\rangle_{op}$
13376	65	1.46			
13555	81	1.17	13546	5.45×10^{-11}	$\|5\rangle_{ip}$
			13840	3.07×10^{-11}	$\|1\rangle_{ip}\|4\rangle_{op}$
13766	66	1.86	13856	7.62×10^{-11}	$\|5\rangle_{e}$
13819	114	1.53	13948	5.98×10^{-11}	$\|5\rangle_{d}$
			13952	5.77×10^{-11}	$\|5\rangle_{c}$
13968	64	0.50	13976	1.91×10^{-11}	$\|4\rangle_{ip}\|1\rangle_{op}$
14017	81	0.96	14029	6.18×10^{-11}	$\|5\rangle_{b}$
14082	59	0.25			
14144	41	1.77	14124	8.94×10^{-11}	$\|5\rangle_{a}$
			15656	2.06×10^{-11}	$\|6\rangle_{op}$
			15890	7.85×10^{-12}	$\|6\rangle_{ip}$
			16264	3.36×10^{-12}	$\|5\rangle_{op}\|1\rangle_{op}$
16172	118	1.0	16279	1.01×10^{-11}	$\|6\rangle_{e}$
16251	72	0.34	16391	8.17×10^{-12}	$\|6\rangle_{d}$
			16398	7.95×10^{-12}	$\|6\rangle_{c}$
16443	88	0.56	16495	8.44×10^{-12}	$\|6\rangle_{b}$
16611[c]	51	0.40	16611	1.28×10^{-11}	$\|6\rangle_{a}$
16648[c]	74	0.51			

[a] Calculated with the local mode parameters given in the last two lines of Table 4. [b] For the regions $\Delta v_{CH} \geq 4$, relative intensities within each overtone are given. [c] Likely Fermi resonance.

TABLE 3: Observed Line Widths, Observed and Calculated Frequencies and Oscillator Strengths, and Peak Assignments for the CH-Stretching Overtone Spectra of *cis*-1,3-Pentadiene

observed			calculated[a]		
$\tilde{\nu}$ (cm^{-1})	line width (cm^{-1})	f[b]	$\tilde{\nu}$ (cm^{-1})	f	assignment
5655	67	5.33×10^{-8}			
5744	54	1.10×10^{-7}	5696	1.24×10^{-7}	$\|2\rangle_{op}$
			5706	7.66×10^{-8}	$\|2\rangle_{op}$
5815	47	3.14×10^{-8}	5815	1.09×10^{-7}	$\|2\rangle_{ip}$
5888	51	1.84×10^{-7}	5889	1.37×10^{-7}	$\|2\rangle_{e}$
			5906	7.56×10^{-8}	$\|2\rangle_{d}$
			5911	5.95×10^{-8}	$\|2\rangle_{b}$
			5915	5.02×10^{-8}	$\|1\rangle_{ip}\|1\rangle_{op}$
5921	55	2.36×10^{-7}	5918	2.10×10^{-7}	$\|1\rangle_{ip}\|1\rangle_{op}$
5996	49	6.73×10^{-8}	5967	4.38×10^{-8}	$\|2\rangle_{a}$
			5970	6.18×10^{-8}	$\|2\rangle_{c}$
6147	30	1.49×10^{-7}	6126	1.72×10^{-7}	$\|1\rangle_{a}\|1\rangle_{b}$
8387	55	1.68×10^{-8}	8379	2.02×10^{-8}	$\|3\rangle_{op}$
8491	114	1.23×10^{-8}			
8579	68	3.06×10^{-9}	8574	4.82×10^{-9}	$\|3\rangle_{ip}$
			8648	4.36×10^{-9}	$\|1\rangle_{op}\|2\rangle_{op}$
8664	53	9.29×10^{-9}	8656	1.46×10^{-8}	$\|3\rangle_{e}$
			8675	7.59×10^{-9}	$\|1\rangle_{ip}\|2\rangle_{op}$
8689	88	2.34×10^{-8}	8681	7.92×10^{-9}	$\|3\rangle_{d}$
8738	61	1.38×10^{-8}	8718	9.09×10^{-9}	$\|3\rangle_{b}$
8818	59	1.09×10^{-8}	8771	7.73×10^{-9}	$\|3\rangle_{a}$
			8780	6.31×10^{-9}	$\|3\rangle_{c}$
8993	47	7.14×10^{-9}	8947	5.96×10^{-9}	$\|1\rangle_{a}\|2\rangle_{b}$
9139	55	1.68×10^{-9}	9107	1.33×10^{-9}	$\|2\rangle_{a}\|1\rangle_{b}$
10935	65	1.00	10934	1.55×10^{-9}	$\|4\rangle_{op}$
11045	64	0.26			
11140	145	0.51	11212	4.16×10^{-10}	$\|4\rangle_{ip}$
11215	48	0.03			
11310	77	0.66	11305	1.11×10^{-9}	$\|4\rangle_{e}$
11355	106	1.67	11340	6.55×10^{-10}	$\|4\rangle_{d}$
11430	55	0.73	11402	6.52×10^{-10}	$\|4\rangle_{b}$
11538	56	0.94	11472	8.27×10^{-10}	$\|4\rangle_{a}$
			11474	5.94×10^{-10}	$\|4\rangle_{c}$
13379	66	1.00	13370	1.00×10^{-10}	$\|5\rangle_{op}$
13489	42	0.14			
13579	69	0.16			
13686	67	0.26	13727	4.72×10^{-11}	$\|5\rangle_{ip}$
13842	64	1.09	13835	1.11×10^{-10}	$\|5\rangle_{e}$
13881	86	2.38	13880	7.47×10^{-11}	$\|5\rangle_{d}$
13953[c]	97	1.92	13968	6.51×10^{-11}	$\|5\rangle_{b}$
14010[c]	68	1.30			
14137	54	2.13	14051	6.97×10^{-11}	$\|5\rangle_{c}$
			14057	8.99×10^{-11}	$\|5\rangle_{a}$
14178	42	0.39			
			15686	1.80×10^{-11}	$\|6\rangle_{op}$
			16126	6.93×10^{-12}	$\|6\rangle_{ip}$
16268	84	1.0	16248	1.46×10^{-11}	$\|6\rangle_{e}$
16294	135	1.34	16302	1.12×10^{-11}	$\|6\rangle_{d}$
16377	92	0.34			
16433	93	1.29	16417	9.08×10^{-12}	$\|6\rangle_{b}$
16583	64	0.21			
16648	74	1.12	16512	9.89×10^{-12}	$\|6\rangle_{c}$
			16523	1.24×10^{-11}	$\|6\rangle_{a}$

[a] Calculated with the local mode parameters given in the last two lines of Table 5. [b] For the regions $\Delta v_{CH} \geq 4$, relative intensities within each overtone are given. [c] Likely Fermi resonance.

***trans*-1,3-Pentadiene.** The calculated and observed frequencies and oscillator strengths of the local mode CH-stretching transitions in *trans*-1,3-pentadiene are given in Table 2 and the corresponding spectra in Figures 2−6.

The CH bonds in the methyl group are the longest CH bond lengths in *trans*-1,3-pentadiene, hence these CH transitions will occur at the lowest frequency. The methyl group in *trans*-1,3-pentadiene has a relatively high barrier to internal methyl rotation (1.80 kcal mol^{-1} equivalent to 629 cm^{-1}),[24] which

TABLE 4: Experimental and Calculated Local Mode Parameters for *trans*-1,3-Pentadiene

	CH_a	CH_b	CH_c	CH_d	CH_e	CH_{ip}	CH_{op}
$\tilde{\omega}^a$	3172 ± 3	3154 ± 3			3107 ± 4	3065 ± 3	3045 ± 5
$\tilde{\omega}x^a$	57.1 ± 0.5	59.0 ± 0.6			58.9 ± 0.7	59.1 ± 0.6	62.0 ± 1.0
$\tilde{\omega}^b$	3344	3324	3305	3298	3287	3201	3237
$\tilde{\omega}x^b$	62.6	62.7	63.1	63.2	63.4	64.5	63.7
$\tilde{\omega}^c$	3157	3138	3120	3113	3103	3081	3048
$\tilde{\omega}x^d$	57.9	58.0	58.4	58.4	58.6	60.7	61.5
$\tilde{\omega}^e$	3172	3154	3136	3129	3119	3079	3045
$\tilde{\omega}x^f$	57.1	57.4	57.7	57.8	58.0	61.3	62.1

[a] Experimental parameters, uncertainties are one standard deviation. [b] Unscaled HF/6-311++G(2d,2p) calculated parameters. [c] The calculated frequencies were scaled using a 1,3-butadiene scaling factor of 0.944 for the olefinic bonds and a *trans*-2-butene(ip) scaling factor of 0.952 for the methyl bonds.[6,7] [d] The calculated anharmonicities were scaled using a 1,3-butadiene scaling factor of 0.925 for the olefinic bonds and a *trans*-2-butene(ip) scaling factor of 0.954 for the methyl bonds.[6,7] [e] The calculated frequencies were scaled using a *trans*-1,3-pentadiene scaling factor of 0.9489 for the olefinic bonds and 0.9513 for the methyl bonds (see text). [f] The calculated anharmonicities were scaled using a *trans*-1,3-pentadiene scaling factor of 0.915 for the olefinic bonds and 0.963 for the methyl bonds (see text).

TABLE 5: Experimental and Calculated Local Mode Parameters for *cis*-1,3-Pentadiene

	CH_a	CH_b	CH_c	CH_d	CH_e	CH_{ip}	CH_{op}
$\tilde{\omega}^a$	3163 ± 2	3147 ± 5	3163 ± 2	3135 ± 2	3135 ± 2		3035 ± 5
$\tilde{\omega}x^a$	55.8 ± 0.3	58.2 ± 1.0	55.8 ± 0.3	60.2 ± 0.4	60.2 ± 0.4		59.9 ± 1.0
$\tilde{\omega}^b$	3343	3324	3337	3306	3298	3269	3202
$\tilde{\omega}x^b$	62.6	62.6	62.6	63.4	63.6	62.9	64.5
$\tilde{\omega}^c$	3156	3138	3150	3121	3113	3112	3049
$\tilde{\omega}x^d$	57.9	57.9	57.9	58.6	58.8	60.0	61.5
$\tilde{\omega}^e$	3165	3147	3159	3130	3122	3098	3035
$\tilde{\omega}x^f$	58.2	58.2	58.2	59.0	59.1	58.4	59.9

[a] Experimental parameters, uncertainties are one standard deviation. [b] Unscaled HF/6-311++G(2d,2p) calculated parameters. [c] The calculated frequencies were scaled using a 1,3-butadiene scaling factor of 0.944 for the olefinic bonds and a *trans*-2-butene(ip) scaling factor of 0.952 for the methyl bonds.[6,7] [d] The calculated anharmonicities were scaled using a 1,3-butadiene scaling factor of 0.925 for the olefinic bonds and a *trans*-2-butene(ip) scaling factor of 0.954 for the methyl bonds.[6,7] [e] The calculated frequencies were scaled using a *cis*-1,3-pentadiene scaling factor of 0.9467 for the olefinic bonds and 0.9478 for the methyl bonds (see text). [f] The calculated anharmonicities were scaled using a *cis*-1,3-pentadiene scaling factor of 0.930 for the olefinic bonds and 0.929 for the methyl bonds (see text).

results in the methyl group being effectively locked into position. As a result, we expect to observe two peaks for the methyl group, one for the CH_{op} bonds and one for the CH_{ip} bond, as is often seen in the CH-stretching overtone spectra of methyl groups.[12] The CH_{ip} bond is shorter than the CH_{op} bond, and hence, the higher frequency peak is assigned to CH_{ip}. These two transitions are seen among the intense peaks as the two lower frequency transitions in Figures 4 and 5, with an approximate 2:1 intensity ratio.

The calculated frequencies of the transitions in *trans*-1,3-pentadiene (Table 2) show that the methyl group local mode combination transitions extend from the CH_{ip} pure local mode peak right through to where the CH_e and CH_d pure local mode olefinic transitions occur and close to the CH_c and CH_b peaks. The methyl local mode combination bands have oscillator strengths that are calculated to be similar or stronger than those of the olefinic transition in the $\Delta v_{CH} = 2$ region, similar in the $\Delta v_{CH} = 3$ region, and clearly weaker in the $\Delta v_{CH} = 4$ region. Consequently, it is difficult to assign these peaks in the $\Delta v_{CH} = 2$ and 3 regions.

The bond lengths of CH_c and CH_d are similar (1.0758 and 1.0764 Å, respectively), which results in the two bonds having frequencies $\tilde{\omega}$ that are very similar and so the peaks are difficult to resolve. The situation is further complicated by the longest olefinic bond, CH_e, which is very close to the CH_d bond length. The CH_e peak is predicted to be strong at each overtone and overlaps with the $CH_{c,d}$ peaks.

The CH_a and CH_b bonds are significantly shorter than the other olefinic CH bonds. The associated pure local mode overtone transitions are therefore located beyond the regions of the local mode methyl combination peaks and the other olefinic bonds. The CH_a and CH_b transition are both calculated to have high intensities and are assigned as the two strong, high-energy peaks in the $\Delta v_{CH} = 4-6$ regions (Figures 4−6).

In the $\Delta v_{CH} = 2$ overtone, the olefinic local mode combination state $|1\rangle_a|1\rangle_b$ is observed as the highest frequency transition. This transition is calculated to be among the strongest transitions in the $\Delta v_{CH} = 2$ region.

There are possible Fermi resonances in the higher overtone regions. One example is in the $\Delta v_{CH} = 6$ region where the high-energy CH_a transition is better deconvoluted into two peaks. In the case of Fermi resonance, the frequency of the CH transition used to determine the local mode parameters is taken as the intensity weighted average of the two peaks.

The relative intensities within each overtone are predicted reasonably well for all overtones, as are the absolute intensities in the lower overtones, $\Delta v_{CH} = 2-3$. In Figure 7, we show the observed and calculated relative intensities of the olefinic transitions in the $\Delta v_{CH} = 6$ region.

***cis*-1,3-Pentadiene.** The calculated and observed frequencies and oscillator strengths of the CH-stretching transitions in *cis*-1,3-pentadiene are given in Table 3 and the corresponding spectra in Figures 2−6.

The methyl group in *cis*-1,3-pentadiene has a significantly lower barrier to internal rotation than *trans*-1,3-pentadiene. Microwave studies have found the barrier to methyl rotation to be 0.74 kcal mol^{-1} (258 cm^{-1}) for *cis*-1,3-pentadiene.[24] Rong and Kjaergaard have found that at barrier heights above 450 cm^{-1} the methyl group is effectively locked in position and the coupling between rotation and CH-stretching is effectively decoupled.[13] At lower barrier heights, the methyl band profile becomes more complex and the spectra of the methyl group can no longer simply be assigned only to CH_{ip} and CH_{op} peaks. As the barrier height decreases, weak bands arise between the CH_{op} and CH_{ip} transitions. As mentioned, the barrier in *trans*-

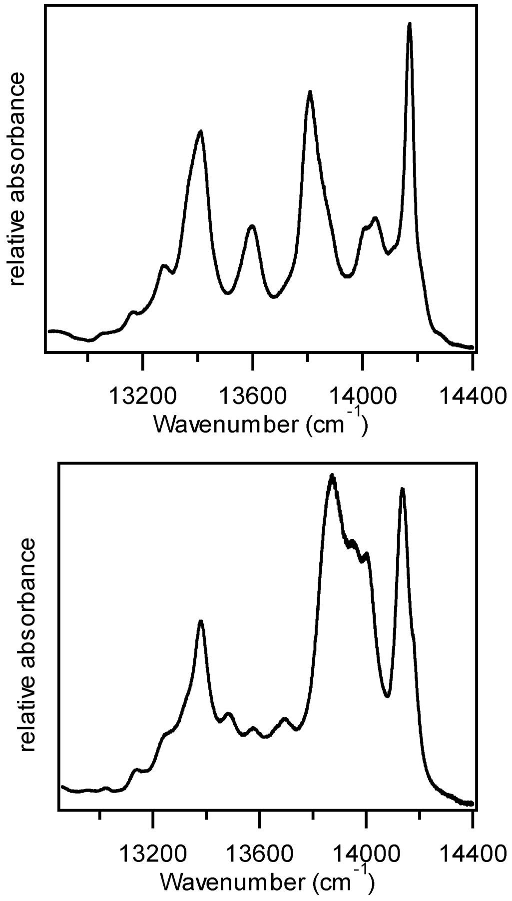

Figure 5. Room-temperature vapor-phase overtone spectra of *trans*-1,3-pentadiene (top) and *cis*-1,3-pentadiene (bottom) in the $\Delta v_{CH} = 5$ region. The spectra were measured by Ti:Sapph ICLPAS with a sample pressure of 50 Torr.

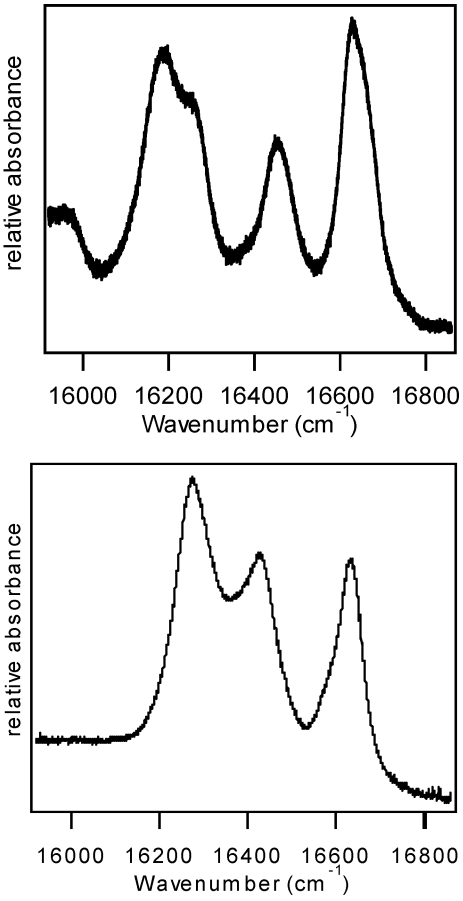

Figure 6. Room-temperature vapor-phase overtone spectra of *trans*-1,3-pentadiene (top) and *cis*-1,3-pentadiene (bottom) in the olefinic $\Delta v_{CH} = 6$ region. The spectra were measured by dye ICLPAS with a sample pressure of 50 Torr.

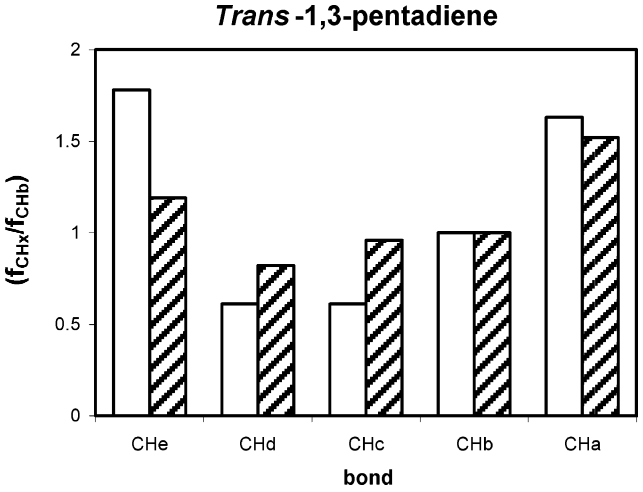

Figure 7. Observed (open) and calculated (hatched) relative total intensities (CH_x/CH_b) of *trans*-1,3-pentadiene in the $\Delta v_{CH} = 6$ overtone.

1,3-pentadiene is relatively high and the methyl region is simply two peaks. In *cis*-1,3-pentadiene, the barrier is around 258 cm^{-1} and the methyl band is expected to be more complex. This is seen in Figure 5, where the band profile of the methyl region (~13200−13700 cm^{-1}) looks remarkably similar to the corresponding region in the CH-stretching overtone spectrum of acetone, a molecule with only methyl groups and for which the barrier to internal rotation is about 250 cm^{-1}.[23] Thus the observed profile in the methyl region of *cis*-1,3-pentadiene is consistent with a barrier around 200−300 cm^{-1}.[13] The calculated barriers with the HF/6-311++G(2d,2p) method are 751 and 356 cm^{-1} for *trans*- and *cis*-1,3-pentadiene, respectively, in reasonable agreement with the microwave barriers.

The splitting between the methyl in-plane and out-of-plane peaks is expected to be greater in the *cis*-1,3-pentadiene spectrum compared to the trans spectrum, since the predicted bond length difference is almost twice as large. This expectation is born out in the spectrum and is particularly evident at $\Delta v_{CH} = 4$ and 5 (see Figures 4 and 5 and Tables 2 and 3).

The calculated local mode frequencies and oscillator strengths of the transitions of *cis*-1,3-pentadiene show that the methyl local mode combination transitions do not have significant intensity within the olefinic region for $\Delta v_{CH} \geq 3$. Hence, they will have little contribution to the olefinic regions compared to what we found for the high-barrier *trans*-1,3-pentadiene. It is thus not necessary to carry out the laborious calculation of the internal methyl rotation spectrum, and we have not included internal methyl rotation in the present paper. As a result, we do not expect the calculated methyl peak positions to agree well with the complex and overlapped experimental peak positions.

The olefinic CH_d and CH_e bonds have similar bond lengths of 1.0760 and 1.0753 Å, respectively. The olefinic CH_b bond is shorter at 1.0743 Å, which is sufficiently shorter than the CH_d and CH_e bonds to give a separate peak in the spectrum. The CH_a and CH_c bond lengths are very similar at 1.0730 and 1.0725 Å, respectively. These bond lengths explain the $\Delta v_{CH} = 6$ spectrum of the olefinic region shown in Figure 6, which has three bands corresponding to the $CH_{d,e}$ bonds, the CH_b bond,

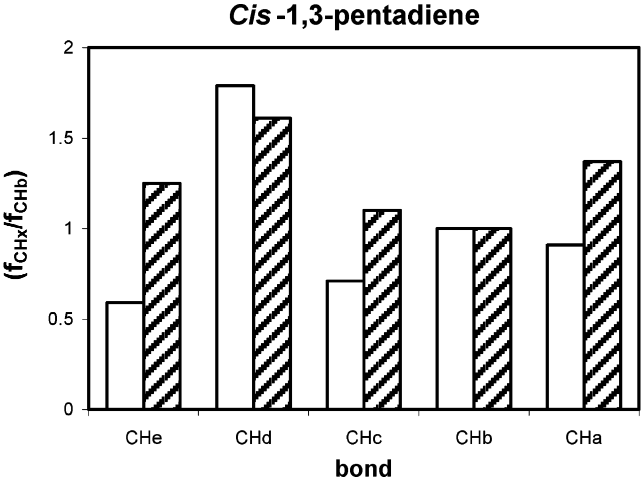

Figure 8. Observed (open) and calculated (hatched) relative total intensities (CH_x/CH_b) of *cis*-1,3-pentadiene in the $\Delta v_{CH} = 6$ overtone.

and the $CH_{a,c}$ bonds. Similar to what we saw for *trans*-1,3-piperylene in the $\Delta v_{CH} = 2$ region, the olefinic local mode combination transition $|1\rangle_a|1\rangle_b$ shows up as the strongest peak at high energy.

In the $\Delta v_{CH} = 4$ and 5 region, the total methyl to olefinic intensity is calculated to be approximate 1:2 which is in good agreement with the observed spectra in Figures 4 and 5. In Figure 8, we show the relative total intensities of both the observed and calculated olefinic transition in the $\Delta v_{CH} = 6$ region of *cis*-1,3-pentadiene. From Figure 8, it is clear that the calculation has approximated the relative intensities well.

Conclusion

We have measured the vapor-phase overtone spectra of *cis*- and *trans*-1,3-pentadiene in the regions corresponding to $\Delta v_{CH} = 2-6$ and have determined the experimental frequencies and oscillator strengths of the CH-stretching transitions. The molecules contain five nonequivalent CH bonds and one methyl group, which make the CH-stretching overtone spectra complex. The methyl regions of the observed CH-stretching overtone spectra of *cis*- and *trans*-1,3-pentadiene are very different due to the changes in barrier height to internal methyl rotation. In *trans*-1,3-pentadiene, the barrier is high and the methyl region is simple, however the methyl local mode transitions extend into the olefinic region. In *cis*-1,3-pentadiene, the methyl local mode combinations bands are separated from the olefinic region but the barrier is low, complicating the methyl region. The measured profiles of the methyl regions of *cis*- and *trans*-1,3-pentadiene are in agreement with their respective methyl barrier heights.

We have used vibrational wave functions from the harmonically coupled anharmonic oscillator local mode model combined with ab initio HF/6-311++G(2d,2p) dipole moment functions to calculate frequencies and oscillator strengths of the CH-stretching transitions. The assignment of our spectra was assisted by these calculations. The calculated local mode frequencies and oscillator strengths with this simple local mode model capture most of the measured features and are necessary tools in spectral assignment. The local mode calculation has reproduced both the pure local mode transitions, which dominate higher overtone regions, and the dominant local mode combination transitions, which are significant in the lower overtone regions.

The olefinic regions of the *cis*- and *trans*-1,3-pentadiene are similar and consist of three well-defined peaks due to similarities of some of the CH bonds and the resulting overlap. There are clear differences in the spectra, and these are in agreement with our calculations.

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