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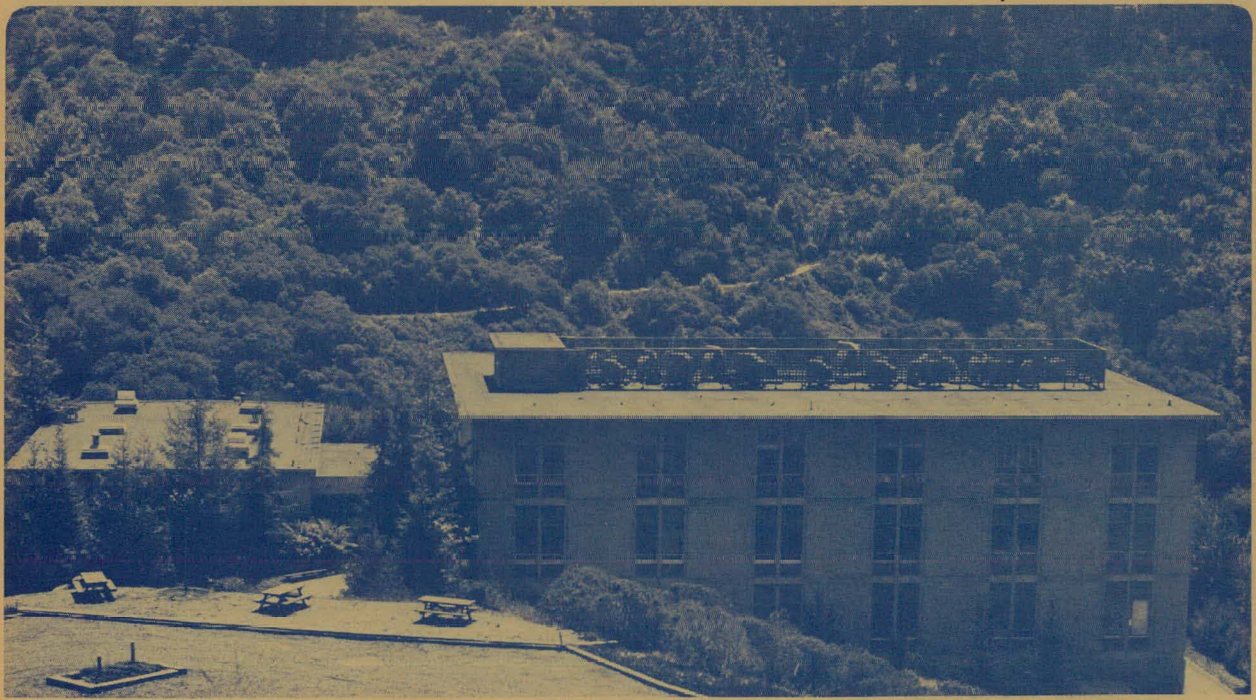

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VIBRATIONALLY HIGHLY EXCITED MOLECULES AND INTRAMOLECULAR MODE COUPLING THROUGH HIGH-OVERTONE SPECTROSCOPY

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Abstract - High overtone spectra of organic molecules can be interpreted using the local mode model for absorptions by the inequivalent C-H bonds. The spectra can be assigned using either observed C-H bond lengths or "isolated" fundamental frequencies. The spectra of trihalomethanes indicate that the dominant intramolecular mode coupling for the C-H stretching overtones is Fermi resonance with combination states with one less C-H stretching quantum plus two quanta of the C-H bending vibrations.

In recent years the intramolecular dynamics of vibrationally highly excited, polyatomic molecules have been the object of intense study. High overtone spectra ($\Delta v > 3$) yield information on the excited final state through absorption linewidths and lineshapes. For the overtone spectra of X-H containing molecules, the normal mode description of vibrational motion breaks down at high vibrational levels; instead the zeroth order basis set of individual X-H oscillators, or local modes (LM), becomes more applicable (Ref. 1). The linewidth and lineshape of the high overtone spectrum give information on the intramolecular dynamics of the vibrationally highly excited bond.

Since the absorption cross sections for these transitions are very small, typically less than one barn, laser photoacoustic spectroscopy is used to detect the overtone absorptions. The schematic of the apparatus is shown in Fig. 1. The nonresonant photoacoustic (PA) cell is placed within the cavity of a cw dye laser, either a Spectra-Physics 375 or 380C. The relative intracavity power is monitored by a Si photodiode measuring the light reflected by a cell window. This normalization signal, as well as the PA signal, are phase sensitively detected. A Commodore PET microcomputer controls the apparatus by scanning the dye laser and digitizing the PA and normalization signals from the lock-in amplifiers. The normalized spectrum is obtained by dividing these two signals and is stored on floppy disk for

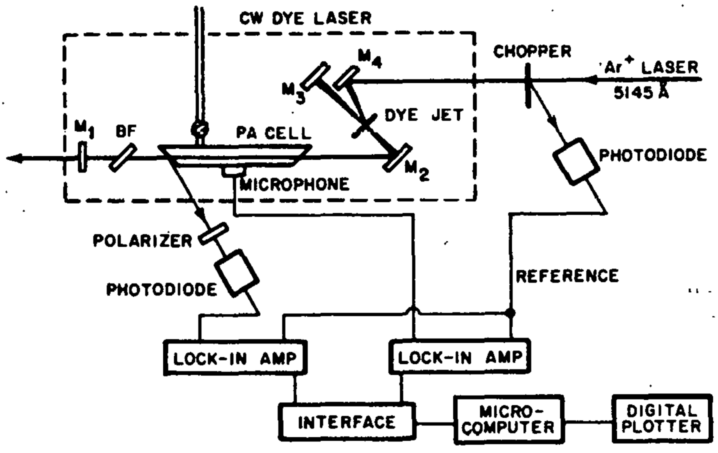

Fig. 1. Experimental apparatus for photoacoustic (PA) high overtone spectroscopy. Not shown is the stepping motor that rotates the birefringent filter (BF) of the dye laser.

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further analysis. Absorption cross sections are calibrated relative to the prominent features of the methane overtone spectrum (Ref. 2). The calibrated spectra are then plotted on a Hewlett-Packard 7225A digital plotter.

From liquid phase overtone spectra of various hydrocarbons, Albrecht and coworkers (3) found that LM absorptions by different bond types (e.g. alkyl versus aryl) were resolvable and had different spectroscopic parameters when fit to the equation for the transition energy of a one dimensional anharmonic oscillator, namely

$$\Delta E_v = (\omega_e - \omega_e x_e)\, v - \omega_e x_e\, v^2 \qquad (1)$$

where ω_e and $\omega_e x_e$ are the mechanical frequency and anharmonicity, respectively. However in the liquid phase, the intramolecular dynamics are obscured by broadening through intermolecular interactions. In gas phase spectra this source of broadening is eliminated and narrower linewidths and smaller differences within bond types are observed (Ref. 4).

The work of McKean and coworkers (5 - 7) aids in the assignment of the absorptions by the inequivalent oscillators. They showed that by replacing all the hydrogens of a molecule except one with deuteriums, the remaining C-H stretching vibration is "isolated" from the other modes of the molecule and also Fermi resonant shifts are minimized. The infrared spectrum of the C-H stretch normal mode is essentially a local mode fundamental spectrum. By varying the position of the C-H bond and analyzing the rotational band contours, they obtained "isolated" C-H stretching frequencies, ν_{CH}^{iso}, for each C-H bond of the molecule. This isolated frequency reflects the properties of that one C-H bond. McKean and coworkers (5-7) found that ν_{CH}^{iso} decreased linearly with increasing C-H bond length, and that ab initio bond length changes calculated with a 4-31G basis set (Refs. 8 & 9) were more reliable than bond lengths obtained by microwave spectroscopy.

An example of the small bond differences observable using overtone spectroscopy is shown in Fig. 2, the fifth overtone spectrum of propene. In the equilibrium configuration, the symmetry point group of the molecule is C_s.

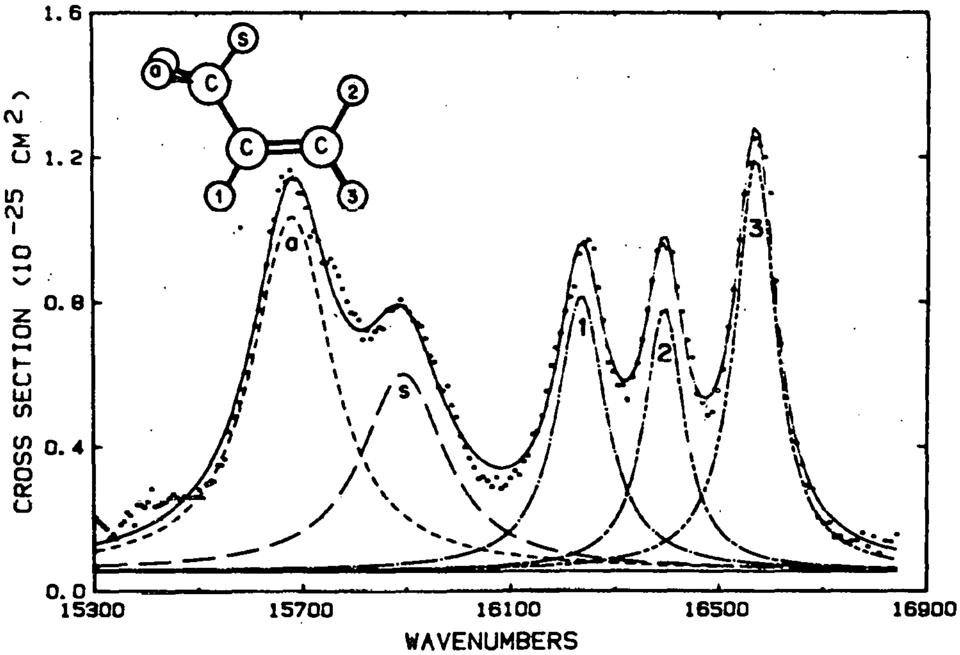

Fig. 2. Fifth overtone spectrum of gaseous propene. The dots are the experimental data and the solid line is a computer deconvolution. The letters a and s and the numbers 1, 2, and 3 give the spectral assignment.

Symmetry requires that the C-H_a out-of-plane methyl bonds be equivalent, and places no constraints on the other C-H bonds. Therefore the six C-H bonds in the molecule result in five inequivalent bond groups. The C-H stretching potential functions are sufficiently different so that five distinct spectral peaks are observed. The two peaks at 15681 and 15895 cm^{-1} are easily assigned to the out-of-plane C-H_a and in-plane C-H_s methyl bonds, while the three peaks at higher energy must arise from the three olefinic C-H bonds. The assignment of these three bands shown in Fig. 2 and tabulated in Table 1 can be obtained either from the isolated fundamentals (Ref. 7) or the ab initio bond lengths (Ref. 9); the microwave bond lengths (Ref. 10) are too uncertain to be useful.

TABLE 1. Summary of propene results. The experimental uncertainties are given in parentheses.

Bond	Energy ^{a}	r^o_{CH}(spec)^b	r^o_{CH}(calc)^b	ν^{iso}_{CH} ^{a}
H_a	15681(7)	1.101(14)	1.096	2931
H_s	15895(9)	1.088(4)	1.093	2931
H_1	16236(7)	1.093(3)	1.087	3013
H_2	16395(7)	1.094(3)	1.085	3039
H_3	16569(6)	1.084(3)	1.083	3064

Note a: units cm^{-1}.
Note b: units Å.

Using the results of propene along with other alkanes (Ref. 11), alkenes (Ref. 11) and alkyl halides (Ref. 12), one can look for correlations between the overtone transition energy and various bond parameters. The C-H bond lengths obtained by microwave or infrared spectroscopy are plotted versus

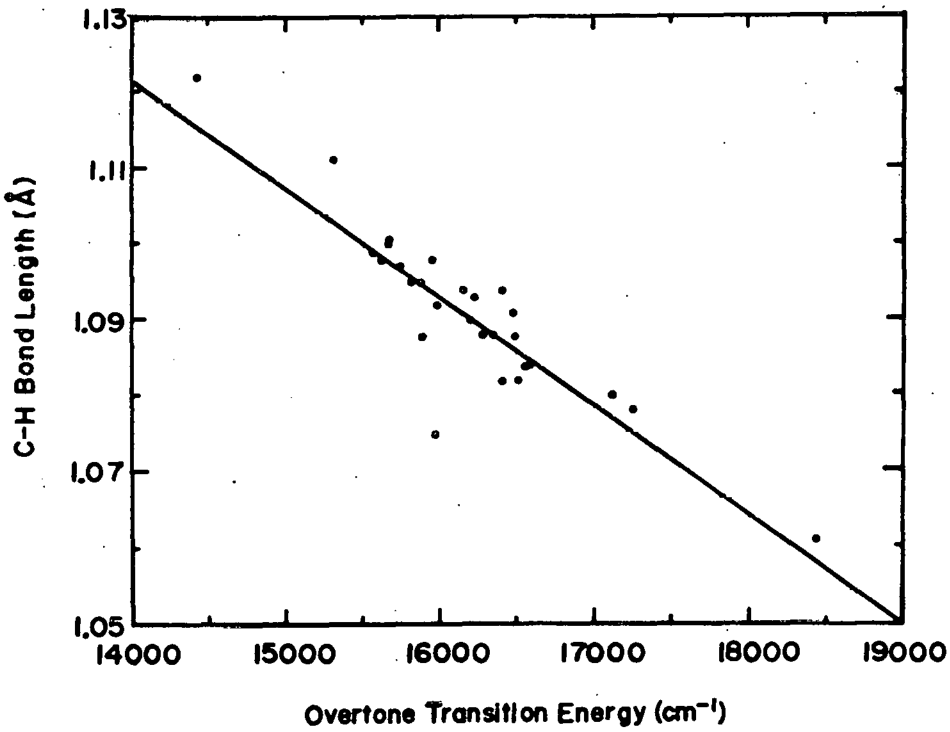

Fig. 3. Carbon - hydrogen bond lengths from infrared or microwave spectroscopy versus fifth overtone transition energy of the local mode C-H oscillator.

the overtone transition energy in Fig. 3. The data can be fit by the linear equation

$$r^{o}_{CH}(\text{spec}) = (1.328\pm0.024) - (1.466\pm0.144)\times10^{-5}\,\Delta E_6 \qquad (2)$$

where ΔE_6 is the fifth overtone transition energy from Eq. (1) in cm^{-1} and r^{o}_{CH} is in Å. The scatter in the data is mainly due to difficulties in precisely locating the hydrogen atoms using microwave spectroscopy.

The fifth overtone transition energy is plotted versus the "isolated" C-H stretching fundamental energy (Ref. 5 - 7) in Fig. 4. Here the correlation is excellent and the line represents the linear fit

$$\Delta E_6 = (-3716\pm45) + (6.62\pm0.09)\nu^{iso}_{CH}. \qquad (3)$$

Thus the isolated C-H stretching frequencies, when available, will provide an assignment more accurately than is possible using bond lengths determined by microwave spectroscopy.

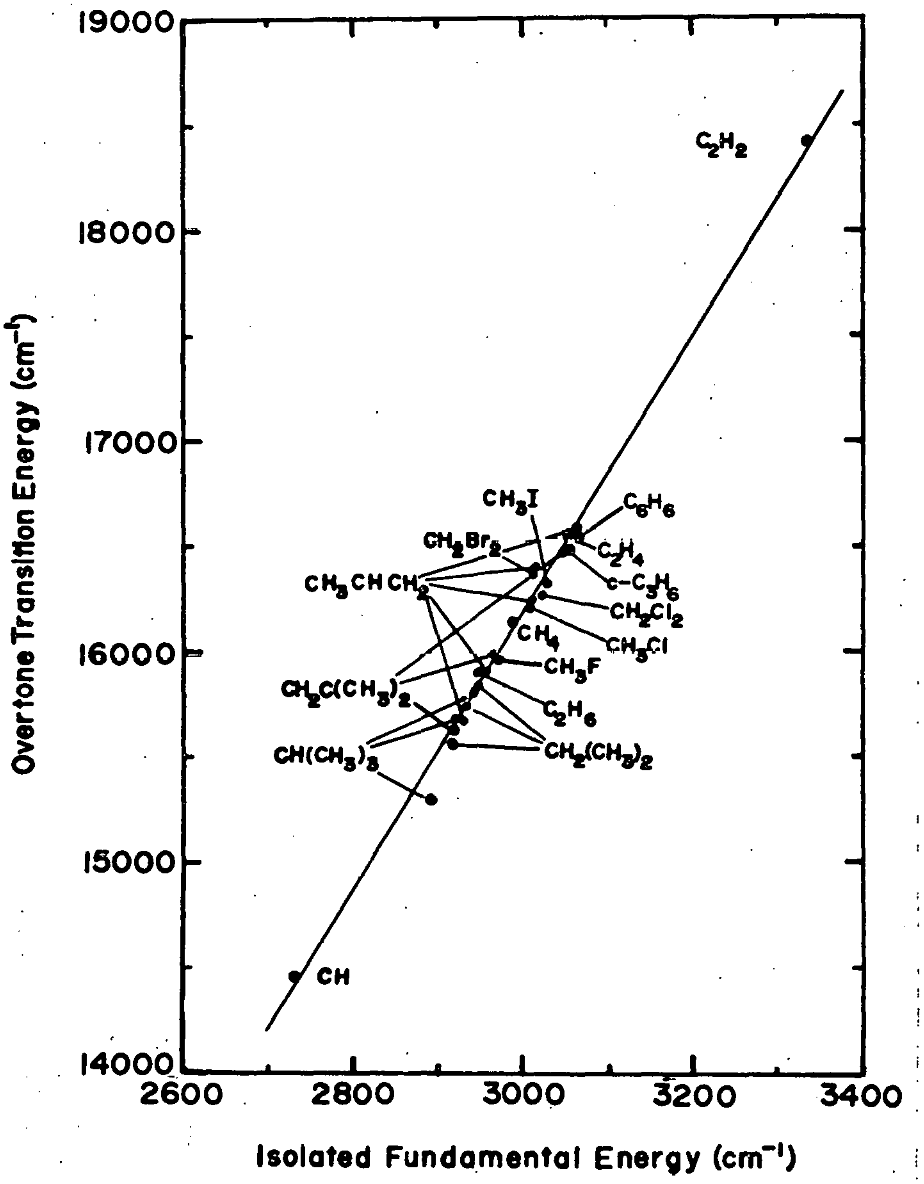

Fig. 4. Overtone transition energy versus isolated C-H stretching fundamental energy (Refs. 5 - 7).

The ability to resolve in the high overtone spectrum absorptions by single C-H bonds is tantalizing to laser photochemists interested in bond selective photochemistry. By tuning the laser to the correct wavelength, one can, in the first approximation, deposit 50 - 60 kcal/mole of vibrational energy in a single, selected C-H bond. Differences in reaction rate have been reported for excitation of C-H bonds at different distances from the site of the heavy atom rearrangement in the isomerization of allyl isocyanide (Ref. 13). Bond selectivity should be marked indeed if the reaction coordinate involves predominately C-H stretching motion and if the appropriate LM is excited. Although the oscillator strength for high overtone transitions derives from LM excitation of a single C-H bond, the observed spectral broadening indicates strong mixing with near resonant states, diluting the selectivity of excitation, as shown in Fig. 5. If coupling to these background states were uniform, then the absorption linewidths would rapidly increase with vibrational quantum number (Ref. 14). However the overtone linewidths stay approximately the same or actually decrease (Refs. 15 & 16). Some states must be more strongly coupled than others to the C-H stretching motion. To attempt to identify these strongly coupled states, the spectra of trihalomethanes were recorded (Ref. 12).

Using the LM model from the above discussion, a single peak is predicted corresponding to absorption by the lone C-H bond of the trihalomethane. However combination bands, borrowing intensity through Fermi resonances, appear in the spectrum. An example of a Fermi resonance interaction is shown in Fig. 6. The parallel band at higher energy with distinct P,Q,R structure is assigned to $6\nu_1$, while the feature at lower energy is assigned to $5\nu_1 + 2\nu_4$, where ν_1 and ν_4 are the C-H stretching and degenerate C-H bending normal modes, respectively. This type of Fermi resonance between the pure C-H stretching overtone and combination states with one less stretching quantum plus two bending quanta appear in the fundamental region and gain in importance in the overtone spectra of the trihalomethanes (Ref. 12). These resonances should dominate the energy relaxation pathway in larger molecules as seen in the right half of Fig. 5, where these combination states are represented by darker lines in the v_{CH} = 5 manifold. These combination states are more nearly resonant than the local mode combination states proposed in Refs. 14 and 15 with five stretching quanta in one

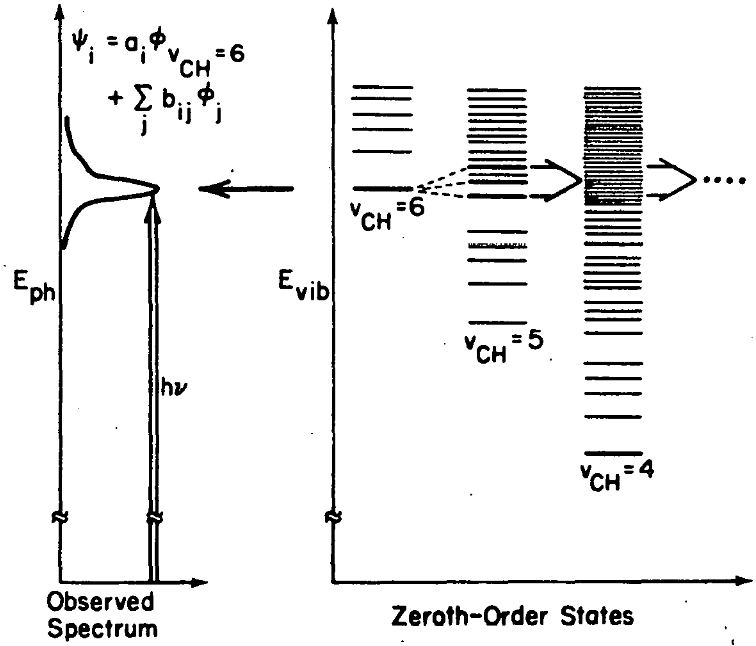

Fig. 5. Zeroth order level scheme, coupling scheme and the resulting experimental spectrum. Illustrated is a zeroth order v_{CH} = 6 state coupled strongly to nearby states built upon v_{CH} = 5 and coupled weakly to the remaining manifolds of nearly resonant states. Narrow band cw excitation produces a mixed state of the molecule, ψ_i, corresponding to an eigenstate of the molecular Hamiltonian.

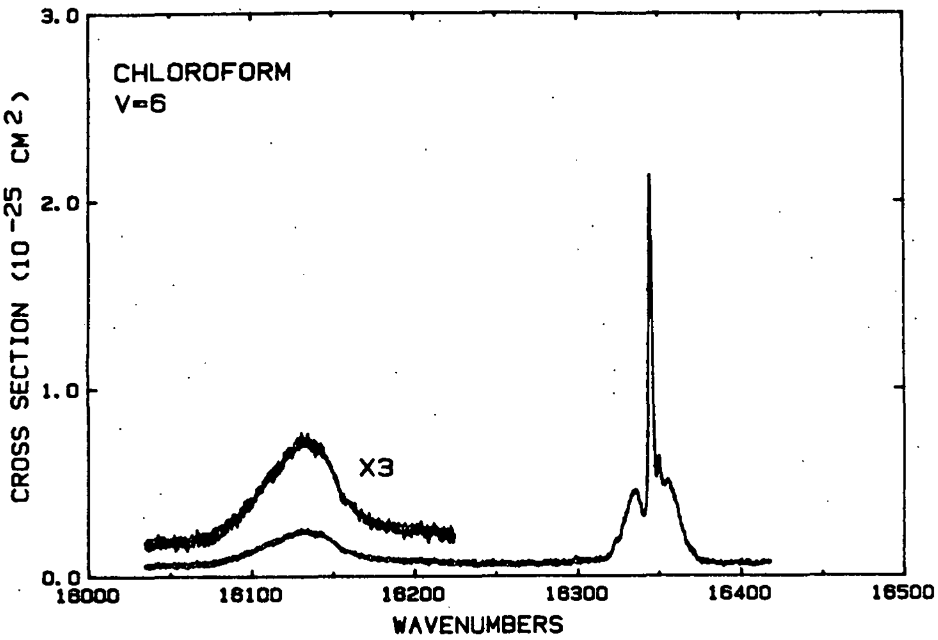

Fig. 6. Fifth overtone spectrum of gaseous chloroform. The feature at higher energy is assigned to $6\nu_1$, while the one at lower energy is assigned to $5\nu_1 + 2\nu_4$.

C-H LM plus one quantum in another, and thus are expected to play a greater role in the intramolecular vibrational energy transfer.

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