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Publication Date

1981-12-01



Lawrence Berkeley Laboratory

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Materials & Molecular Research Division

Submitted to The Journal of Chemical Physics

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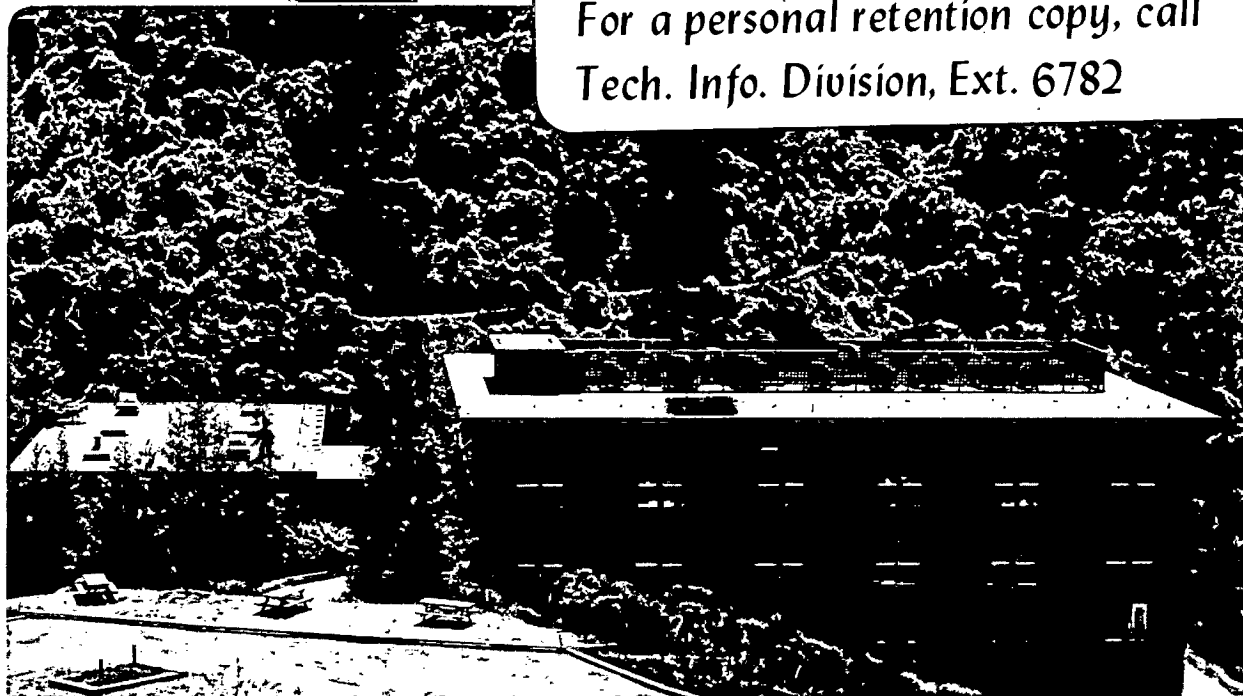
James S. Wong and C. Bradley Moore

December 1981

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Inequivalent C-H Oscillators Of Gaseous Alkanes And Alkenes
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In Laser Photoacoustic Overtone Spectroscopy  
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ABSTRACT

The overtone spectra of the C-H stretching vibrations of several gaseous alkanes and alkenes were observed using laser photoacoustic spectroscopy. Resolvable peaks are seen for each chemically or sterically equivalent C-H bond and are assigned using the local mode model. The fifth overtone transition energies decrease linearly with increasing C-H bond lengths. Spectral shifts corresponding to 0.001 Å bond length differences are observed. Linear correlations of bond length and anharmonicity with fundamental C-H stretching frequency allow a Morse potential for CH bonds to be defined in terms of a single parameter. The integrated cross section per C-H oscillator for the fifth overtone spectra varied mostly within a factor of two about the average value of $(1.08 \pm 0.28) \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1}$.

I. INTRODUCTION

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In the last few years high overtone spectra have been recorded for a considerable number of organic molecules.<sup>1-15</sup> Local modes (LM) are used to interpret these spectra<sup>15-23</sup> in much the way that normal modes have been used to systematize fundamental vibrational spectra. A local mode, the stretching of a single chemical bond, is the most anharmonic vibration of a molecule and therefore the one with the largest oscillator strength in high overtone transitions. Absorption peak energies are fit by the one dimensional anharmonic oscillator equation<sup>6</sup>

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

where  $\omega_e$  and  $\omega_e x_e$  are the mechanical frequency and anharmonicity, respectively. The transition energies,  $\Delta E_v$ , have been found<sup>2,4,6</sup> from liquid phase spectra to occur in the order methylene < methyl < aryl  $\approx$  olefin < acetylenic, the same order as the bond dissociation energies<sup>24</sup> and the  $\omega_e$ 's of single C-H fundamentals. Unfortunately, intermolecular interactions in the liquid phase broaden the individual peaks and obscure small spectral shifts or splittings due to slight differences in the chemical bonding. Even so, absorptions assignable to axial and equatorial C-H bonds are reported for cycloalkanes and cycloalkenes.<sup>4,14</sup>

Gas phase spectra exhibit much narrower lines, and allow smaller shifts to be observed.<sup>9,15</sup> Three peaks were observed in the high overtone spectra of propane, corresponding to

absorptions by the methylene, out-of-plane methyl and in-plane methyl LM's, the latter two split by only  $100 \text{ cm}^{-1}$ .<sup>15</sup> In the present work, it is shown that the C-H bond lengths from infrared and microwave spectra or from ab initio calculations can be used to interpret the spectra of several alkanes and alkenes. The correlations of vibrational frequency with structure in the fifth overtone spectra of alkanes and alkenes reported in this work will aid in assigning the spectra and structure of more complicated molecules of photochemical interest.

Absolute absorption cross sections are measured. The integrated absorptions are given for resolvable hydrogens and are found to vary mostly within a two-fold range.

## II. EXPERIMENTAL

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The high overtone spectra of these very weak transitions were obtained using intracavity dye laser photoacoustic (PA) spectroscopy.^{8,15} A nonresonant spectrophone cell²⁵ was used so that the same modulation frequency could be used for all samples, so that the sensitivity was higher at lower pressures and so that variations in photoacoustic signal with changes in beam location within the cell were minimized. The middle section of the cell is composed of 6 mm i.d. pyrex tubing to which a greaseless, 4 mm stopcock was attached. A rectangular hole was cut in the glass tubing for the microphone. The Knowles BT-1759 subminiature microphone is mounted inside a stainless steel holder which was epoxied to

the cell with Torr-Seal. The two ends of the cell are 6 mm i.d. quartz tubing to which quartz windows (Lambda/Airtron BW-10) are mounted at Brewster's angle with glass transfer tape (Vitta Corporation G1015). These sections are attached to the middle section through graded quartz-to-pyrex seals. Thus the quartz windows can be flamed thoroughly in an oxygen-rich atmosphere to burn off any deposits or dust that contribute to the background PA signal.

The PA cell is mounted inside the cavity of either a Spectra-Physics model 375 or 380C cw dye laser (Rhodamine B). Tuning was performed by a three plate birefringent filter that yielded a laser linewidth of approximately 1 cm^{-1} . The insertion loss of the cell is less than 3%. A low transmittance ($1 \pm_{-0.5}^{+1.0}$ %) output coupler was used to maximize the intracavity power circulating through the cell (approximately 20 W when pumped with 6 W all lines from an argon ion laser (Spectra Physics 171-17)). Two fourth overtone spectra were taken with Oxazine 1 in the 380C ring dye laser pumped by the red lines of a Spectra-Physics 171-01 krypton ion laser. The laser wavelength is calibrated as a function of the birefringent filter micrometer drive setting by a monochromator. Slight changes in wavelength with dye laser cavity alignment from day to day limit the accuracy of the calibration to about $\pm 5 \text{ cm}^{-1}$.

The relative intracavity power is monitored by a Si photodiode and polarizer which measure the light reflected by a cell window. This normalization signal, $R(\nu)$, as well

as the photoacoustic signal, $P(\nu)$, are phase sensitively detected. The experimental apparatus is controlled by a Commodore PET microcomputer which scans the birefringent filter and digitizes (12 bit resolution) the photoacoustic and normalization signals from the lock-in amplifiers. Variations in the laser power are compensated for by dividing these two signals. The resultant normalized spectrum, $N(\nu) = P(\nu)/R(\nu)$, is stored on cassette tape or floppy disk for further analysis.

To test the contribution of torsional vibrations to the overtone spectrum, a simple, heatable PA cell was constructed out of 1/4" copper tubing soft soldered to a copper "tee". The cell was heated with nichrome wire and the temperature monitored with a copper-constantan thermocouple. The cell was not heated above 100 °C to avoid damaging the Torr-Seal that secured the Brewster's angle windows to the cell.

The performance of this crude cell was relatively poor with respect to PA signal, optical insertion loss in the laser cavity, and PA background. Overall performance was generally a factor of 2 to 3 poorer than the room temperature cell.

The absorption cross sections of many spectra were calibrated relative to the absorbance of the overtone spectra of methane^{26,27}. It is easily shown^{27,28} that the photoacoustic signal, $P(\nu, \omega)$, as a function of radiation frequency, ν , and chopping frequency, ω , in a cylindrical nonresonant spectrophone is given by

$$P(\nu, \omega) \propto \frac{W_0 \sigma(\nu) n \ell}{T_0 C_V \omega V} S(P, \gamma, T). \quad (2)$$

Here W_0 is the extracavity power of the laser and T_0 is the transmittance of the output coupler so that W_0/T_0 is proportional to the intracavity power. The absorption cross section at frequency ν is $\sigma(\nu)$, n is the number density of absorbing molecules, C_V is the heat capacity at constant volume and ℓ and V are the cell length and volume, respectively. $S(P, \gamma, T)$, the microphone sensitivity, is a function of pressure, heat capacity ratio, γ , and temperature, as shown by the following equation²⁹

$$S(P, \gamma, T) = S_{\text{rated}} (1+B) \left\{ 1 + B \frac{P \gamma T_{\text{STP}}}{P_{\text{atm}} \gamma_{\text{air}} T} \right\}^{-1} \quad (3)$$

where $B \approx 1$. To minimize the sensitivity variations, the methane reference spectrum was taken at the same pressure as the sample spectrum. These spectra were not corrected for variations in γ . This causes an underestimation of the cross sections by less than 3%.

Absolute absorption cross sections as a function of frequency, $\sigma_s(\nu)$, were obtained from the normalized photoacoustic spectrum, $N_s(\nu)$, using the equation

$$\sigma(\nu) = \sigma_{m, \text{peak}} \frac{W_{0,m}(\nu_0) R_s(\nu_0) C_{V,s} N_s(\nu)}{W_{0,s}(\nu_0) R_m(\nu_0) C_{V,m} N_m(\nu_{\text{peak}})} \quad (4)$$

The subscripts "s" and "m" refer to the sample and to methane, respectively. $\sigma_{m, \text{peak}}$ is the maximum value (2.23×10^{-25} cm² molec⁻¹) of the methane absorption cross section at frequency $\nu_{\text{peak}} \approx 16150$ cm⁻¹.²⁶ The term containing $W_0(\nu_0)$ and

$R(\nu_0)$ in Eq. (4) compensates for changes in the intracavity power and in the alignment of the reference photodiode between the sample and methane spectra. The compensation is usually about 10% and always less than 40%.

Methane was chosen as the reference molecule because of its large absorption cross section and small heat capacity, leading to a large photoacoustic signal, and because it is easily pumped out of the spectrophone cell and vacuum line. The methane absorption bands show sharp structure and under high resolution show individual vibration-rotation lines³⁰ whose widths are determined by Doppler and pressure broadening. Thus the use of methane as a calibration standard must be carefully considered since the laser linewidth is larger than the width of these individual lines. However, the density of vibration-rotation lines within the bands has been estimated³¹ to be greater than 100 per cm^{-1} . Since the Doppler width for the 6190 Å band is 0.05 cm^{-1} and the self-broadened width³¹ at 100 torr is 0.01 cm^{-1} , the lines are severely overlapped, and the structure observed is due to absorption of the stronger lines on top of a "continuum" absorption. The laser mode spacing is 0.016 cm^{-1} and 0.007 cm^{-1} for the linear and ring cavity dye lasers, respectively. There should be no deviation from Beer's law with the laser running at 1 cm^{-1} linewidth since the absorption cross sections of the individual lines are small ($< 1.5 \times 10^{-25} \text{ cm}^2$), the laser is run well above threshold, and the photoacoustic signal derives from the actual power absorbed. The laser PA

spectrum will accurately follow the absorption spectrum as long as the laser tunes smoothly. Unfortunately, the output frequency spectrum sometimes consists of two or more peaks separated by about 1 cm^{-1} and the tuning is not perfectly continuous. As a result, the observed methane peak absorption varies between the three strongest lines in Fig. 1. These problems arise from imperfect design of the commercial, three-plate birefringent tuning element.³² Because of these limitations and difficulties in keeping the laser beam passing through the same region³³ of the PA cell during the sample and methane spectra, the observed cross sections of the same molecule varied by 10% from day to day. The peak absorption of the methane spectrum of Giver²⁶ has uncertainties of $\pm 3\%$, and is an average of five spectra every several \AA , smoothing out the fine structure that would be measured at higher resolution. Thus the overall uncertainty of the cross sections reported in this work is less than $\pm 15\%$.

All gas handling was done in a greaseless vacuum line. Spectral quality liquid samples from Matheson, Coleman and Bell were thoroughly degassed by several freeze-pump-thaw cycles. Gaseous samples from Matheson were used without further purification. Spectra were obtained at the following pressures: ethane (c.p.), 104 torr; propane (research), purity, 117 torr; n-butane (instrument), 110 torr; n-pentane, 113 torr; n-hexane, 90 torr; methylpropane (c.p.), 151 torr; ethene (c.p.), 153 torr; propene (c.p.), 151 torr; methylpropene (c.p.), 127 torr; and cis-2-butene (research), 147 torr.

III. RESULTS

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Figure 1 shows the fifth overtone spectra of the n-alkanes from methane to n-hexane. Figures 2 through 8 show the spectra of methylpropane, ethene, propene, methylpropene and cis-2-butene. Peak positions and assignments, and other data are summarized for a number of molecules in Table I.8,34-58

The spectra of propane, propene, methylpropane, methylpropene and cis-2-butene were fit by a nonlinear least squares computer program to a sum of Lorentzians plus a constant background. For each spectral peak, a peak position, linewidth and integrated cross section, as well as the standard errors of the nonlinear least squares fit for each parameter, were determined. The spectral fits are seen to be reasonably accurate, at least as far as determining the peak positions is concerned. However they are not perfect, especially in the wings. See, for example, in the spectrum of methylpropane the asymmetric lineshape of the C-H<sub>t</sub> absorption peak and the high energy wing of the C-H<sub>a</sub> peak. The Lorentzian lineshapes assumed in the deconvolutions have considerable intensity far from band center, and the presence of the slight shoulders on the wings lowers the baseline and causes over-estimation of the peak areas. The area of the C-H<sub>t</sub> peak of methylpropane is underestimated due to the computed tails of the methyl peaks.

For the spectra of the other molecules, the peak areas were integrated using a planimeter and linewidths exclusive of shoulders were estimated directly. The baseline used

intersected the observed spectra on both sides of the peak(s). Thus this method underestimates the peak area for those molecules with near-Lorentzian lineshapes, while it is more accurate for molecules whose width is dominated by the rotational structure. The error limits quoted allow generously for these difficulties. The data on linewidths<sup>59-67</sup> and integrated cross sections are collected in Tables II and III, respectively.

Spectra of methylpropene were taken at temperatures up to 100 °C in order to check the contribution of hot bands to line broadening. Unfortunately the poor signal-to-noise ratio and sloping baselines prevented accurate deconvolution to determine linewidths. To look for increases in linewidths, the ratio of the valley height between the methyl absorptions to the C-H<sub>a</sub> peak height was compared. A modest 7 % increase in the average value of this ratio was observed upon raising the temperature from 25 to 100 °C; however difficulties in assigning the baselines caused uncertainties in this ratio of ± 5 %. Spectra over a much broader temperature range are needed.

#### IV. DISCUSSION

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A. Assignment criteria

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The gas phase high overtone spectra exhibit peaks corresponding to each distinguishable H atom. Unambiguous assignments of spectra may sometimes be made from spectra of

selectively deuterated molecules.<sup>9</sup> Equally definitive assignments are possible when local mode fundamental frequencies,  $\nu_{\text{CH}}^{\text{iso}}$ , are available. McKean and coworkers<sup>24,56-58</sup> have studied the C-H fundamental spectra of hydrocarbons in which all but one H has been substituted by D. The lone C-H stretch is decoupled from the C-D stretching vibrations as well as from the first overtones of the bends. Thus  $\nu_{\text{CH}}^{\text{iso}}$  is observed. Since anharmonicities,  $\omega_e x_e$  from Eq. (1), decrease systematically as  $\omega_e$  increases,<sup>6,14</sup> the high overtone peaks occur in the same sequence as the  $\nu_{\text{CH}}^{\text{iso}}$ . These frequencies correlate well with C-H bond lengths in the  $v = 0$  ground state:<sup>24</sup>

$$r_{\text{CH}}^{\text{O}}(\text{\AA}) = 1.402 - (1.035 \times 10^{-4}) \nu_{\text{CH}}^{\text{iso}} (\text{cm}^{-1}). \quad (5)$$

Thus either the sequence of  $\nu_{\text{CH}}^{\text{iso}}$  or of  $r_{\text{CH}}^{\text{O}}$  for a molecule, as shown in Table I, gives a reliable assignment of the high overtone spectrum. Previously established correlations of vibrational frequency or bond strength with chemical structure may allow assignments to be made in the absence of  $r_{\text{CH}}^{\text{O}}$  or  $\nu_{\text{CH}}^{\text{iso}}$  data. Since the integrated absorption cross section per C-H does not vary greatly,<sup>6</sup> relative intensities may also be helpful in making assignments. The spectra presented here are assigned in Sec. IV.B. and structure-frequency correlations as strengthened by these results are examined in IV.C. The shapes and widths of spectral features are discussed in IV.D. and the integrated intensities in IV.E.

B. Assignments  
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The n-alkane spectra in Fig. 1 show the smooth progression $\nu_{\text{CH}_4} > \nu_{-\text{CH}_3} > \nu_{-\text{CH}_2-}$. There are single absorption bands for CH_4 and C_2H_6 as appropriate for a local mode overtone when all H's are symmetrically equivalent. For the higher alkanes a separate peak corresponds to $-\text{CH}_2-$ group absorptions and shifts to low frequency as the chain grows longer. The assignments for propane¹⁵ follow unambiguously from both $\nu_{\text{CH}}^{\text{iso}}$ ⁵⁷ and $r_{\text{CH}}^{\text{O}}(\text{calc})$.⁵⁴ The inequivalence of methyl H's in the plane of the C atoms, one H_s , and the out of the plane, two H_a 's, clearly splits the $-\text{CH}_3$ group absorption in gas phase spectra. The $r_{\text{CH}}^{\text{O}}(\text{calc})$ and intensity ratios support this assignment. This datum supports McKean's generalization⁵⁷ that a C-H trans to a C-C will have a higher frequency than one one trans to a C-H. The broadening of bands as the alkane chain lengthens is presumably due to thermal population of rotamers⁶⁸ with gauche rather than all trans C-C bond configurations.

The three peaks for $(\text{CH}_3)_3\text{CH}$, Fig. 2, are readily assigned from the $\nu_{\text{CH}}^{\text{iso}}$. The relative intensities and reported bond lengths support this assignment. The H_t frequency fits at the low end of the series CH_4 , $-\text{CH}_3$, $-\text{CH}_2-$, $-\overset{|}{\text{C}}\text{H}-$. The reversal of the H_a and H_s $-\text{CH}_3$ peaks compared to the n-alkanes follows the rule that C-H's trans to C-C are higher in frequency than those trans to C-H (structure in Fig. 2).

The greater s orbital contribution to olefinic C-H bonds causes them to absorb at higher frequencies than do alkanes.

The single peak for ethene, Fig. 3, arises from its four symmetrically equivalent H's.

The five peaks of the fifth overtone, propene spectrum, Fig. 5, are assigned using the $\nu_{\text{CH}}^{\text{iso}}$ or equivalently the r_{CH}^{O} (calc). McKean²⁴ ascribes the weakening of the methyl out-of-plane C-H_a bonds to their interaction with π electrons. The higher frequency C-H_s bond lies in the π nodal plane. The β substitution of a methyl group slightly strengthens the trans olefinic bond (C-H₃) and significantly weakens the cis (C-H₂) compared to C₂H₄. The C-H₁ bond α to the methyl group is weakened even further.

Methylpropene, Fig. 7, is assigned from the $\nu_{\text{CH}}^{\text{iso}}$ values.⁵⁷ The olefinic C-H frequency is roughly the average of those for C-H₂ and C-H₃ of propene and the methyl splitting is analogous to that of propene, though larger.

For cis-2-butene, Fig. 8, there are no data or bond lengths or $\nu_{\text{CH}}^{\text{iso}}$ to aid in the assignment of the spectrum. The microwave spectra⁵⁹ do give the equilibrium geometry of Fig. 8. The single peak at 16256 cm⁻¹ is at the expected frequency and of an appropriate intensity for the two identical olefinic C-H's. The remaining absorption shows three peaks rather than the two expected for the a and s hydrogens of the two methyl groups. The four H_a's in the structure absorb at the lowest frequency due to the σ - π interaction. The two H_s's would be at higher frequency and less intense. The peaks labelled a and s at 15595 and 15725 cm⁻¹ fit these expectations and are at frequencies in accord with expectations

from methylpropene and propene. Based on the total intensity and on the clear assignment of the olefinic H's, the peak labelled ? at 15952 cm^{-1} is almost surely a methyl absorption. This feature could be due to molecules in excited states of methyl hindered rotation. Low barrier heights,⁵⁹⁻⁶³ 0.45 to 0.74 kcal/mole, have been reported; thus such states should be thermally populated. Furthermore, calculations^{69,70} on ethane indicate that the C-H bonds are about 0.002 Å shorter at the top of the torsional barrier than at the equilibrium position. This may provide a rationale for the blue shift. The existence of another configuration might account for the absorption; a Fermi resonance involving five quanta of C-H stretch and 2 of H bending is also conceivable. Since the manufacturer's sample purity of 99.9% was verified by gas chromatography, an impurity is not responsible for the ? peak. Thermally populated excited states of methyl rotation seem to provide the most attractive explanation for the ? feature. In an attempt to test this explanation, spectra were taken at temperatures ranging from 23 °C to 90 °C and normalized to the peak absorbance of the olefinic band. The background absorptions increase about 20 % over this range and the signal-to-noise ratio of these spectra are poor, so computer deconvolutions were not attempted. The absorption maxima in the region of the C-H_A, C-H_S and "?" all decreased by about 5 % relative to the olefinic peak absorption, so the hot cell experiments were inconclusive.

Gas phase high overtone spectroscopy should become a useful

tool for determining molecular configurations. Each inequivalent C-H bond usually gives a resolvable peak. The absolute frequencies and shifts of peaks are correlated, often in a known way, to structure and conformation. As more spectra of known conformations become available these correlations will allow unknown structures to be determined and will permit excitation of bonds in specific steric positions.

C. C-H bond lengths, isolated fundamentals and overtone
~~~~~  
transition energies  
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The r_{CH}^O bond lengths determined spectroscopically are plotted against the fifth overtone transition energies in Fig. 9.8, 34-38. The data are fit by the linear equation

$$r_{CH}^O(\text{spec}) = (1.328 \pm 0.024) - \nu_{v=6} / (69\ 160 \pm 690) \quad (6)$$

with a correlation coefficient of -0.846. There is considerable scatter in the data, mainly because the spectroscopically determined rotational constants are not sensitive to the precise location of the hydrogen atoms.

Mizugai and Katayama⁷¹ have studied the overtone spectra of various liquid phase heterocyclic compounds and found that the r_{CH}^S bond lengths of the local mode oscillator, determined from microwave spectra of isotopically substituted molecules, decreased linearly with its local mode frequency shift from the benzene absorption maximum and is approximately given by

$$r_{CH}^S = 1.084 \text{ \AA} - 8 \times 10^{-5} \Delta \nu_V (\text{cm}^{-1}) / \nu \quad (7)$$

where v is the upper state vibrational quantum number. Using 16467 cm^{-1} as the peak frequency of the liquid phase, fifth overtone, benzene absorption,⁷² one obtains

$$r_{\text{CH}}^{\text{O}} = 1.304 - 1.333 \times 10^{-5} \nu_{v=6}. \quad (8)$$

The ab initio r_{CH}^{O} bond lengths calculated using a 4-31G basis set^{54,55} are plotted vs fifth overtone transition frequency in Fig. 10. In this case the scatter is much smaller, though partly because there are fewer data points. These data can be fit by the linear equation

$$r_{\text{CH}}^{\text{O}}(\text{calc}) = (1.319 \pm 0.022) - (1.426 \pm 0.134) \times 10^{-5} \nu_{v=6} \quad (9)$$

with a correlation coefficient of -0.966 . For the relatively complex molecules summarized here, the ab initio changes of bond length correlate more reliably with the fifth overtone frequencies than do the microwave results.

Small differences in C-H bond lengths may be reliably determined from high overtone spectra. McKean has already shown the utility of CH bond lengths determined from $\nu_{\text{CH}}^{\text{iso}}$.^{56,57} In the fifth overtone spectra, a bond length change of only 0.001 \AA corresponds to a shift of 69 cm^{-1} , just resolvable. Since peaks may be located with 7 cm^{-1} accuracy, bond length changes are given to 10^{-4} \AA . It is not clear whether the frequency-bond length correlation is valid on such a fine scale and we certainly do not suggest that absolute bond lengths may be determined to such an accuracy. However, bond length differences derived from high overtone data should be quite useful in refining structures based on rotational spectra.

Fifth overtone transition energies are plotted vs

"isolated" C-H stretching fundamental frequencies in Fig. 11. The line illustrates the linear fit

$$\nu_{v=6}(\text{cm}^{-1}) = (-3716 \pm 45) + (6.62 \pm 0.09) \nu_{\text{CH}}^{\text{iso}}. \quad (10)$$

The degree of correlation is remarkable considering the large differences in the anharmonicities. The linear relationship implied between $\nu_{\text{CH}}^{\text{iso}}$ and $\omega_e x_e$ of Eq. (1) is

$$\omega_e x_e = 123.9 \pm 1.5 - (2.07 \pm 0.03) \times 10^{-2} \nu_{\text{CH}}^{\text{iso}}, \quad (11)$$

or between $\omega_e x_e$ and ω_e is

$$\omega_e x_e = 119.0 \pm 1.5 - (1.99 \pm 0.03) \times 10^{-2} \omega_e \quad (12)$$

This same correlation of overtone frequency with $\nu_{\text{CH}}^{\text{iso}}$ was found by Hayward and Henry⁷³ in the case of the fourth overtone spectral frequencies albeit with a smaller number of molecules and a smaller range of frequencies.

Since $\omega_e x_e$ and r_e are linearly related to ω_e , then a Morse potential function for CH bonds may be given to within a few percent accuracy up to about one half of the dissociation limit in terms of a single parameter, ω_e .

The wide range over which this correlation in Fig. 11 is valid and the universality of the C-H stretching potential function implied thereby underscores the utility of high overtone spectroscopy.

D. Spectral linewidths and lineshapes

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The linewidths of resolvable peaks are summarized in Table II. Also included is a rough estimate of the contribution of the rotational structure to the linewidth from the bandwidths of the P,R structure of the infrared fundamental

transitions. Many molecules show line broadening beyond the rotational structure, attributable to coupling of the LM oscillator to other vibrations.<sup>8,19</sup>

Among the bands showing definite broadening, the methyl group absorptions show the widest variation in widths, ranging from  $64 \text{ cm}^{-1}$  for the fourth overtone of dimethylpropane<sup>70</sup> to almost  $200 \text{ cm}^{-1}$  for the fifth overtones of propene and methylpropene. The widths of the olefinic absorptions range from  $60 - 120 \text{ cm}^{-1}$  and are always narrower than the methyl group absorptions of the same molecule. The fifth overtone methyl band widths show a modest decrease with increase in barrier height (Table II), suggesting that torsional hot bands might be responsible for the broadening. However, this mechanism would also broaden the fourth overtones, whose methyl bands are quite narrow, and thus can be ruled out. It is interesting that the methyl bands of propene and methylpropene, Figs. 4 through 7, show much larger changes in widths with vibrational quantum number than do propane<sup>15</sup> and cyclohexane<sup>34</sup> and also show large deviations from Lorentzian lineshapes. The distinct shoulders to the low energy side of the fourth overtone methyl bands in Figs. 4 and 6, may be Fermi resonant combination bands<sup>74</sup> with four C-H stretching quanta plus two quanta of the  $-\text{CH}_3$  bending vibrations.<sup>15</sup> Such combination bands with carbon-hydrogen bends have been positively identified in the overtone spectra of various halomethanes.<sup>13,35,75,76</sup> For the infrared fundamentals and the lower overtones, these combination states start out lower than the overtones since

$2 \times \nu_{\text{CH}} \text{ bend} < \nu_{\text{CH}} \text{ stretch}$ . However, the anharmonicity of the C-H stretches pulls the overtones into resonance with these combination states for larger  $\Delta\nu_{\text{CH}}$  transitions. Thus, a "clump" of combination states, lying just below the methyl overtones for  $\Delta\nu_{\text{CH}}=5$ , would move into resonance for  $\Delta\nu_{\text{CH}}=6$ , Figs. 5 and 7, borrowing intensity from the overtones and broadening the bands. Since the C-H stretch anharmonicity would eventually pull the overtones out of resonance with these combination states, higher overtone transitions should narrow.

#### E. Integrated cross sections

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For the wide variety of molecules shown in Table III the integrated cross sections per C-H oscillator are mostly concentrated within a two-fold range. The average value weighted by the number of C-H bonds per spectral peak is $(1.08 \pm 0.28) \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1}$. This value is to be compared to the integrated absorbance per C-H oscillator from the fifth overtone, liquid phase spectra obtained by Burberry et al⁶ of $(3.4 \pm 0.6) \times 10^{-3} \text{ l mole}^{-1} \text{ cm}^2$, which corresponds to an integrated cross section of $(1.30 \pm 0.23) \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1}$. This value must be corrected for the bulk dielectric properties of the liquids²³ before comparison with the gas phase values. The indices of refraction at the sodium D line range from 1.372 for n-hexane to 1.498 for benzene, resulting in multiplicative correction factors of 0.819 to 0.749, respectively. Taking the appropriate factor for each molecule, the average integrated cross section

per C-H from the liquid phase spectra corrected to gas phase is $(0.95 \pm 0.20) \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1}$, in excellent agreement with the value determined in this work.

In Table III there are obviously no systematic variations in cross section with bond type. The integrated cross sections of the trichloromethane C-H and methylpropane C-H_t are seen to be unusually small, while that of the fluoromethane band is unusually large. Some of the peaks in the propene spectrum, namely C-H_s and C-H₃ are also larger than the norm. Although integrated cross sections clearly do not permit H atoms to be counted as in NMR, peak intensities can still be of value in making assignments.

The assignment of the cis-2-butene spectrum discussed in Sec. IV.B. hypothesized that the peak labelled "?" in Fig. 8 arose from absorptions by methyl group C-H bonds. The integrated cross sections (units $10^{-23} \text{ cm}^2 \text{ cm}^{-1}$) for the assigned C-H_a and C-H_s oscillators are only 0.52 and 0.53, respectively, while that of the olefinic C-H₁ bond is 1.20. If the peak labelled "?" arises from methyl absorptions, then the integrated cross section per methyl C-H becomes $1.03 \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1}$ which is very close to the above average value.

Figure 12 shows the integrated cross section per C-H vs the anharmonicity, $w_e x_e$, of the oscillator. The lack of dependence on mechanical anharmonicity implies that higher order terms in the dipole moment expansion determine the intensities. Burberry and Albrecht²³ have shown that a two parameter empirical fit of the dipole moment function for a

C-H bond reproduced the experimental C-H and C-D overtone intensities in various deuterated benzenes. However, the significant variations in intensities found here seem to preclude any universal dipole moment function for C-H bonds.

V. SUMMARY

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High overtone spectroscopy in the gas phase is a sensitive probe of CH bonding. Relatively subtle steric differences give split absorption bands and chemically distinct CH bonds give widely spaced absorption peaks. Different molecular conformations may be distinguished and identified. Under low resolution or with liquid phase broadening, steric effects are manifested by an apparent spectral broadening.

The growing number of available spectra and the strong correlations of overtone frequencies with bond lengths and isolated fundamental frequencies make spectral assignments relatively clear cut. By determining C-H bond length changes from high overtone spectra, more accurate molecular geometries may be deduced from rotational spectra.

The linear decrease of anharmonicity with increase in fundamental CH stretching frequency allows CH stretching potential functions to be expressed in terms of a single parameter for energies up to at least half the dissociation limit and for a wide chemical range of CH's.

Many of the spectra presented are analyzed as simple sums of nearly Lorentzian peaks, one for each distinguishable C-H. Others are more complex and exhibit evidence of Fermi



resonances or multiple conformers. These effects must be clearly understood before spectra may be used to derive conformations, bond lengths, intermode couplings or energy transfer broadening linewidths. The integrated cross sections per CH bond lie mostly within the range  $(0.85 - 1.7) \times 10^{-23} \text{ cm}^2 \cdot \text{cm}^{-1}/\text{molecule}$ . The values do not correlate with  $\omega_e x_e$ ; thus intensities must be caused by electrical rather than mechanical anharmonicity.

#### VI. ACKNOWLEDGEMENTS

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This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48 and by the U.S. Army Research Office, Triangle Park, NC. The krypton ion laser was provided by the San Francisco Laser Center which is supported by the National Science Foundation under Grant No. CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University. The authors thank J.K. Frisoli for assistance in the construction of the elevated temperature cell and K.V. Reddy and M.J. Berry for sharing their knowledge of cell design and of many yet to be published spectra. The authors also thank B.R. Henry for preprints of his work and H.L. Strauss and Y.-S. Yen for several enlightening discussions on methyl groups.

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TABLE I. Peak assignments, transition energies of fifth overtone spectra, C-H bond lengths and isolated C-H stretching frequencies.
   
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| Molecule      | Assignment         | $\nu$<br>( $\text{cm}^{-1}$ ) | $r_{\text{CH}}^{\text{O}}(\text{spec})^{\text{a}}$<br>( $\text{\AA}$ ) | $r_{\text{CH}}^{\text{O}}(\text{calc})^{\text{b}}$<br>( $\text{\AA}$ ) | $\nu_{\text{CH}}^{\text{iso}}$<br>( $\text{cm}^{-1}$ ) |
|---------------|--------------------|-------------------------------|------------------------------------------------------------------------|------------------------------------------------------------------------|--------------------------------------------------------|
| Methane       |                    | 16150                         | 1.094 [39]                                                             | 1.093[54]                                                              | 2992[56]                                               |
| Ethane        |                    | 15824                         | $1.095 \pm 0.002$ [40]                                                 | 1.094[54]                                                              | 2950[56]                                               |
| Propane       | H <sub>m</sub>     | 15562                         | $1.099 \pm 0.002$ [41]                                                 | 1.096[54]                                                              | 2920[57]                                               |
|               | H <sub>a</sub>     | 15746                         | 1.097                                                                  | 1.095                                                                  | 2936                                                   |
|               | H <sub>s</sub>     | 15845                         | $1.092 \pm 0.009$                                                      | 1.094                                                                  | 2950                                                   |
| Butane        | -CH <sub>2</sub> - | 15473                         |                                                                        |                                                                        |                                                        |
|               |                    | 15751                         |                                                                        |                                                                        |                                                        |
|               | -CH <sub>3</sub>   | 15829                         |                                                                        |                                                                        |                                                        |
| Pentane       | -CH <sub>2</sub> - | 15472                         |                                                                        |                                                                        |                                                        |
|               | -CH <sub>3</sub>   | 15793 <sup>c</sup>            |                                                                        |                                                                        |                                                        |
| Hexane        | -CH <sub>2</sub> - | 15478                         |                                                                        |                                                                        |                                                        |
|               | -CH <sub>3</sub>   | 15795 <sup>c</sup>            |                                                                        |                                                                        |                                                        |
| Methylpropane | H <sub>t</sub>     | 15305                         | $1.111 \pm 0.001$ [42]                                                 |                                                                        | 2894[57]                                               |
|               | H <sub>s</sub>     | 15683                         | $1.103 \pm 0.003$                                                      |                                                                        | 2924                                                   |
|               | H <sub>a</sub>     | 15804                         | 1.095                                                                  |                                                                        | 2943                                                   |
| Ethene        |                    | 16550                         | $1.088 \pm 0.002$ [43]                                                 | 1.084[54]                                                              | 3060[56]                                               |
| Propene       | H <sub>a</sub>     | 15681                         | $1.101 \pm 0.014$ [44]                                                 | 1.096[55]                                                              | 2931[58]                                               |
|               | H <sub>s</sub>     | 15895                         | $1.088 \pm 0.004$                                                      | 1.093                                                                  | 2959                                                   |
|               | H <sub>1</sub>     | 16236                         | $1.093 \pm 0.003$                                                      | 1.087                                                                  | 3013                                                   |
|               | H <sub>2</sub>     | 16395                         | $1.094 \pm 0.003$                                                      | 1.085                                                                  | 3039                                                   |
|               | H <sub>3</sub>     | 16569                         | $1.084 \pm 0.003$                                                      | 1.083                                                                  | 3064                                                   |
| Methylpropene | H <sub>a</sub>     | 15628                         | $1.098 \pm 0.003$ [45]                                                 |                                                                        | 2924[58]                                               |
|               | H <sub>s</sub>     | 15978                         | $1.075 \pm 0.010$                                                      |                                                                        | 2965                                                   |
|               | H <sub>1</sub>     | 16474                         | $1.091 \pm 0.002$                                                      |                                                                        | 3050                                                   |



TABLE I. Peak assignments, transition energies of fifth overtone spectra, C-H bond lengths and isolated C-H stretching frequencies (continued).

| Molecule            | Assignment     | $\nu$<br>( $\text{cm}^{-1}$ ) | $r_{\text{CH}}^{\text{o}}$ (spec)<br>( $\text{\AA}$ ) | $r_{\text{CH}}^{\text{o}}$ (calc)<br>( $\text{\AA}$ ) | $\nu_{\text{CH}}^{\text{iso}}$<br>( $\text{cm}^{-1}$ ) |
|---------------------|----------------|-------------------------------|-------------------------------------------------------|-------------------------------------------------------|--------------------------------------------------------|
| <u>Cis-2-butene</u> | H <sub>a</sub> | 15595                         |                                                       |                                                       |                                                        |
|                     | H <sub>s</sub> | 15725                         |                                                       |                                                       |                                                        |
|                     | H <sub>?</sub> | 15952                         |                                                       |                                                       |                                                        |
|                     | H <sub>1</sub> | 16256                         |                                                       |                                                       |                                                        |
| Cyclopropane        |                | 16504[34]                     | 1.082 ± 0.003[46]                                     | 1.083[55]                                             | 3056[56]                                               |
| Benzene             |                | 16550[8]                      | 1.084 ± 0.005[47]                                     |                                                       | 3065[56]                                               |
| Furan               | H <sub>2</sub> | 17121[35]                     | 1.080 ± 0.002[48]                                     |                                                       |                                                        |
|                     | H <sub>1</sub> | 17223                         | 1.078 ± 0.002                                         |                                                       |                                                        |
| Chloromethane       |                | 16216[36]                     | 1.090 ± 0.002[49]                                     |                                                       | 3012[56]                                               |
| Dichloromethane     |                | 16265[36] <sup>c</sup>        | 1.088 ± 0.005[50]                                     |                                                       | 3025[56]                                               |
| Fluoromethane       |                | 15972[36]                     | 1.098 [51]                                            |                                                       | 2976[56]                                               |
| Iodomethane         |                | 16325[36]                     | 1.088 ± 0.002[52]                                     |                                                       | 3029[56]                                               |
| Dibromomethane      |                | 16387[36]                     | 1.082 ± 0.010[50]                                     |                                                       | 3040[56]                                               |
| Ethyne              |                | 18430[37]                     | 1.061 [53]                                            |                                                       | 3336[56]                                               |
| C-H                 |                | 14469[38]                     | 1.122 [38]                                            |                                                       | 2733[38]                                               |

a.  $r^{\text{s}} + 0.003 \text{ \AA}$ . C-H bond lengths for microwave spectra of isotopically substituted molecules underestimate the  $r^{\text{o}}$  bond lengths. See Ref. 24.

b.  $r^{\text{e}}(\text{calc}) + 0.011 \text{ \AA}$ . Calculated equilibrium bond lengths underestimate the  $r^{\text{o}}$  bond lengths.

c. Split band.

Table II. Linewidths ( $\text{cm}^{-1}$ ) of overtone spectra and barrier height (kcal/mole) for methyl group rotation

| Molecule        |       | FWHM         | Barrier Height  |           |
|-----------------|-------|--------------|-----------------|-----------|
| Methane         |       | $196 \pm 5$  |                 |           |
| Ethane          |       | $139 \pm 3$  | 2.74 [65]       |           |
| Propane         | v=6   | $H_m$        | $147 \pm 15$    | 2.95 [66] |
|                 |       | $H_a$        | $101 \pm 7$     |           |
|                 |       | $H_s$        | $123 \pm 11$    |           |
|                 | v=7   | $H_m$        | $118 \pm 3$     |           |
|                 |       | $H_a$        | $193 \pm 2$     |           |
|                 |       | $H_s$        | $71 \pm 3$      |           |
| Methylpropane   | $H_t$ | $46 \pm 17$  | 3.90 [65,67]    |           |
|                 | $H_s$ | $102 \pm 5$  |                 |           |
|                 | $H_a$ | $75 \pm 2$   |                 |           |
| Dimethylpropane |       | $64^a$       | 4.29 [66]       |           |
| Ethene          |       | $145 \pm 5$  |                 |           |
| Propene         | $H_a$ | $186 \pm 8$  | 1.994 [61]      |           |
|                 | $H_s$ | $197 \pm 16$ |                 |           |
|                 | $H_1$ | $113 \pm 7$  |                 |           |
|                 | $H_2$ | $91 \pm 7$   |                 |           |
|                 | $H_3$ | $95 \pm 4$   |                 |           |
| Methylpropene   | $H_a$ | $198 \pm 5$  | 2.30 [61]       |           |
|                 | $H_s$ | $179 \pm 9$  |                 |           |
|                 | $H_1$ | $61 \pm 2$   |                 |           |
| Cis-2-butene    | $H_a$ | $172 \pm 6$  | 0.486[61]       |           |
|                 | $H_s$ | $175 \pm 22$ | 0.450[62]       |           |
|                 | $H_?$ | $343 \pm 18$ | 0.748[59]       |           |
|                 | $H_1$ | $121 \pm 2$  | 0.731[63]       |           |
|                 |       |              | 0.319,0.450[60] |           |

a. Fourth overtone data from Ref. 64.

Table III. Integrated cross sections for fifth overtone transitions.

| Molecule         | Assignment     | Integrated Cross Section <sup>a</sup> | Number of C-H's | Cross Section per C-H <sup>a</sup> |
|------------------|----------------|---------------------------------------|-----------------|------------------------------------|
| Methane          |                | 5.55                                  | 4               | 1.39 ± 0.14                        |
| Ethene           |                | 4.23                                  | 4               | 1.06 ± 0.11                        |
| Propene          | H <sub>a</sub> | 2.86                                  | 2               | 1.43 ± 0.21                        |
|                  | H <sub>s</sub> | 1.69                                  | 1               | 1.69 ± 0.31                        |
|                  | H <sub>1</sub> | 1.35                                  | 1               | 1.35 ± 0.21                        |
|                  | H <sub>2</sub> | 1.05                                  | 1               | 1.05 ± 0.17                        |
|                  | H <sub>3</sub> | 1.71                                  | 1               | 1.71 ± 0.24                        |
|                  | Total          | 8.65                                  | 6               | 1.44 ± 0.23                        |
| Methylpropane    | H <sub>t</sub> | 0.24 <sup>b</sup>                     | 1               | 0.24 ± 0.24                        |
|                  | H <sub>s</sub> | 2.66                                  | 3               | 0.89 ± 0.13                        |
|                  | H <sub>a</sub> | 5.02                                  | 6               | 0.85 ± 0.11                        |
|                  | Total          | 7.91                                  | 10              | 0.79 ± 0.13                        |
| Methylpropene    | H <sub>a</sub> | 5.22                                  | 4               | 1.31 ± 0.16                        |
|                  | H <sub>s</sub> | 2.50                                  | 2               | 1.25 ± 0.19                        |
|                  | H <sub>1</sub> | 2.19                                  | 2               | 1.09 ± 0.14                        |
|                  | Total          | 9.91                                  | 8               | 1.24 ± 0.16                        |
| Cis-2-butene     |                | 6.81                                  | 8               | 0.85 ± 0.06                        |
| Cyclopropane     |                | 6.06                                  | 6               | 1.01 ± 0.15                        |
| Fluoromethane    |                | 5.26                                  | 3               | 1.75 ± 0.26                        |
| Trifluoromethane |                | 1.20                                  | 1               | 1.20 ± 0.18                        |
| Dichloromethane  |                | 2.04                                  | 2               | 1.02 ± 0.15                        |
| Iodomethane      |                | 2.67                                  | 3               | 0.89 ± 0.13                        |
| Chloromethane    |                | 2.96                                  | 3               | 0.99 ± 0.15                        |
| Trichloromethane |                | 0.51                                  | 1               | 0.51 ± 0.08                        |
|                  |                |                                       | average         | 1.08 ± 0.28                        |

a. Units:  $10^{-23}$  cm<sup>2</sup> cm<sup>-1</sup> molec<sup>-1</sup>.

b. See text.

FIGURE CAPTIONS

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Figure 1. Fifth overtone photoacoustic spectrum of the gaseous n-alkanes (Absorbance is in arbitrary units).

Figure 2. Fifth overtone photoacoustic spectrum of gaseous methylpropane. The dots are the experimental data and the solid line is the computer deconvolution. The letters t, s, and a represent the spectral assignment.

Figure 3. Fifth overtone photoacoustic spectrum of ethene.

Figure 4. Fourth overtone photoacoustic spectrum of gaseous propene.

Figure 5. Fifth overtone photoacoustic spectrum of gaseous propene. The dots are the experimental data and the solid line is the computer deconvolution. The letters a and s and the numbers 1, 2, and 3 represent the spectral assignment.

Figure 6. Fourth overtone photoacoustic spectrum of gaseous methylpropene.

Figure 7. Fifth overtone photoacoustic spectrum of gaseous methylpropene. The dots are the experimental data and the solid line is the computer deconvolution. The a, s

and 1 represent the spectral assignment.

Figure 8. Fifth overtone photoacoustic spectrum of gaseous cis-2-butene. The dots are the experimental data and the solid line is the computer deconvolution. The a, s and 1 represent the tentative spectral assignment.

Figure 9. Carbon-hydrogen bond lengths from infrared or microwave spectroscopy vs fifth overtone transition energy of the local mode oscillator.

Figure 10. Ab initio carbon-hydrogen bond lengths⁵³⁻⁵⁴ using a 4-31G basis set vs fifth overtone transition energy of the local mode oscillator.

Figure 11. Overtone LM transition energy vs isolated C-H stretching energy.⁵⁵⁻⁵⁷

Figure 12. Integrated cross section per C-H oscillator as a function of its mechanical anharmonicity.

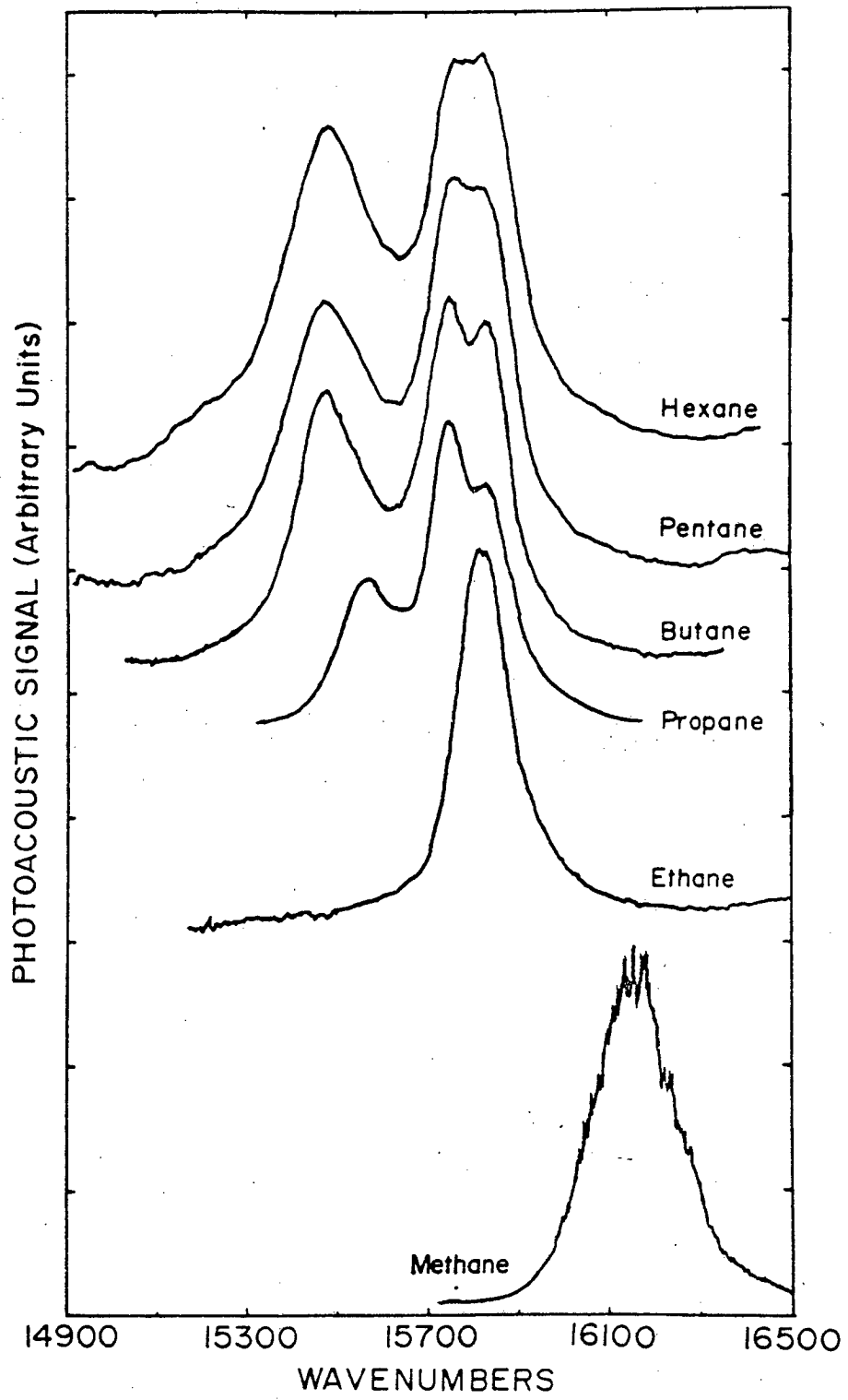


Fig. 1

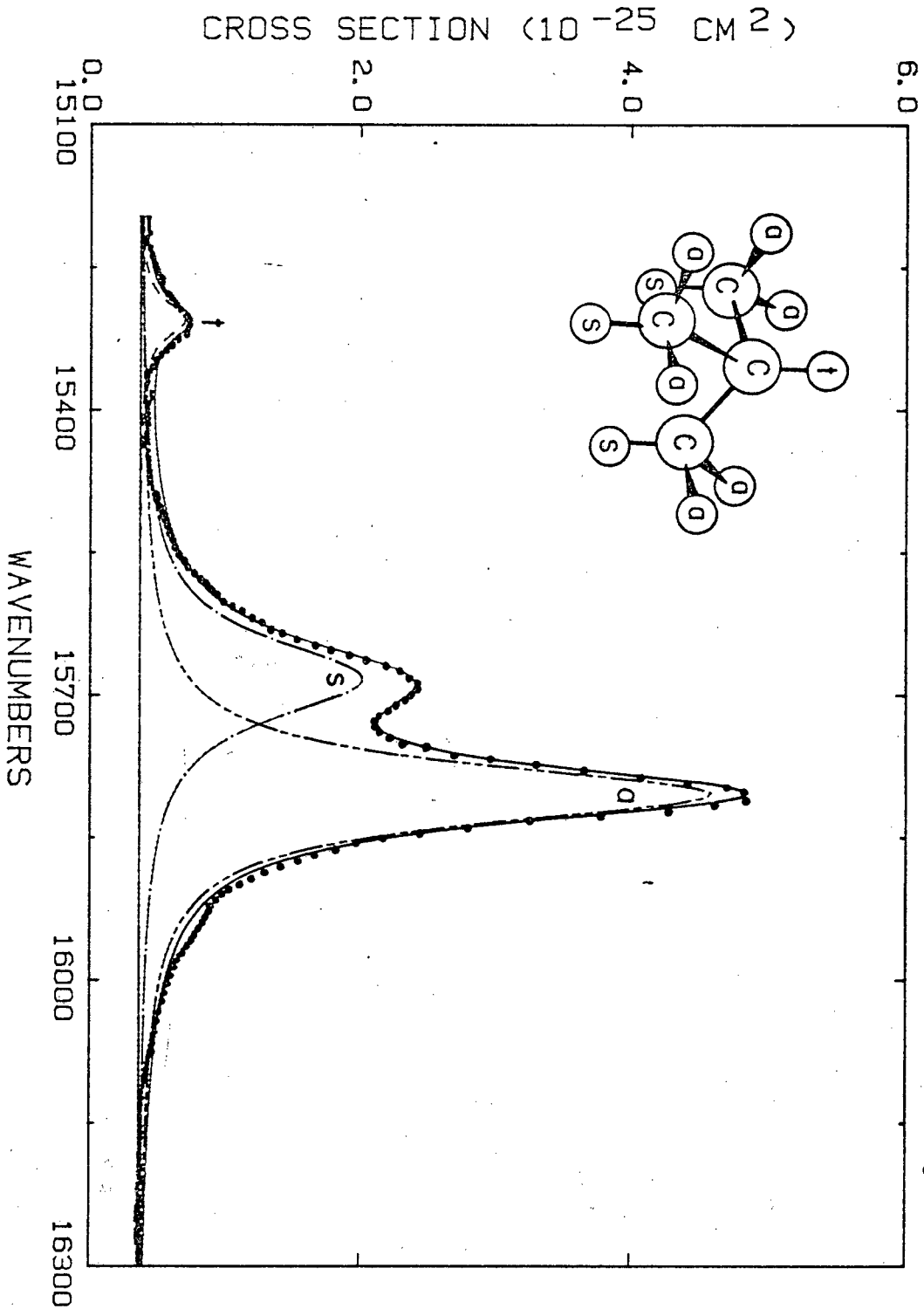


Fig. 2

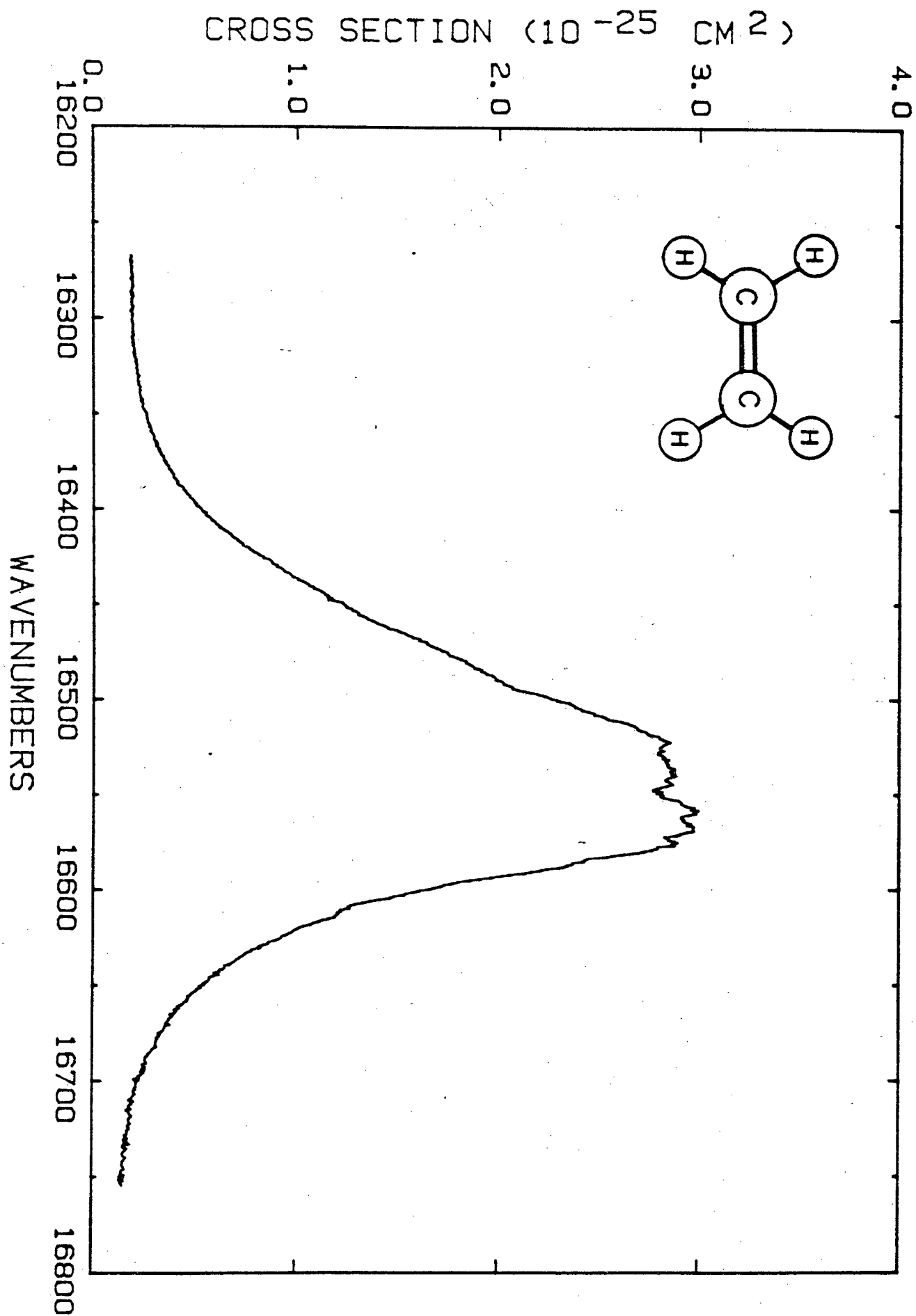


Fig. 3

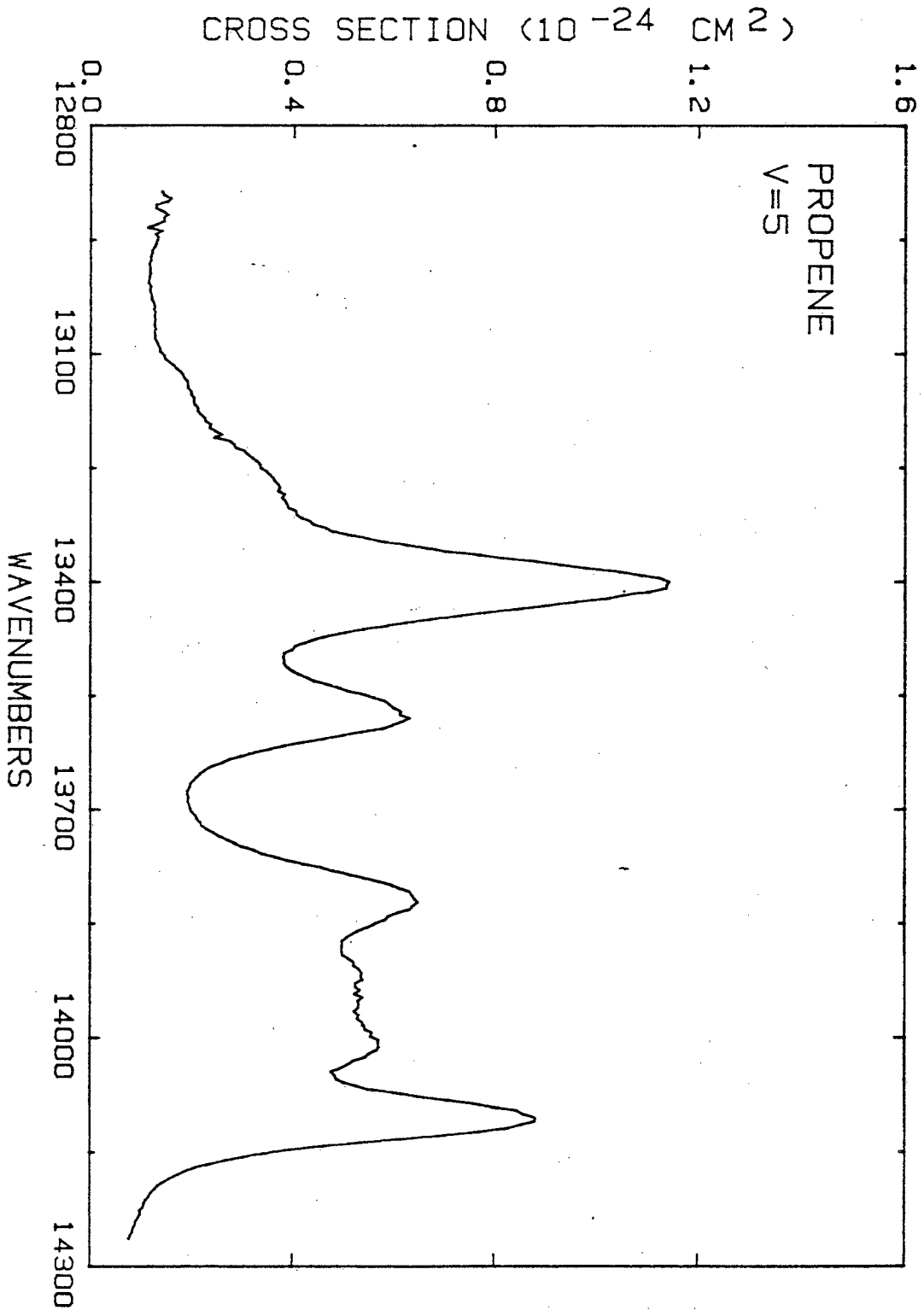


Fig. 4

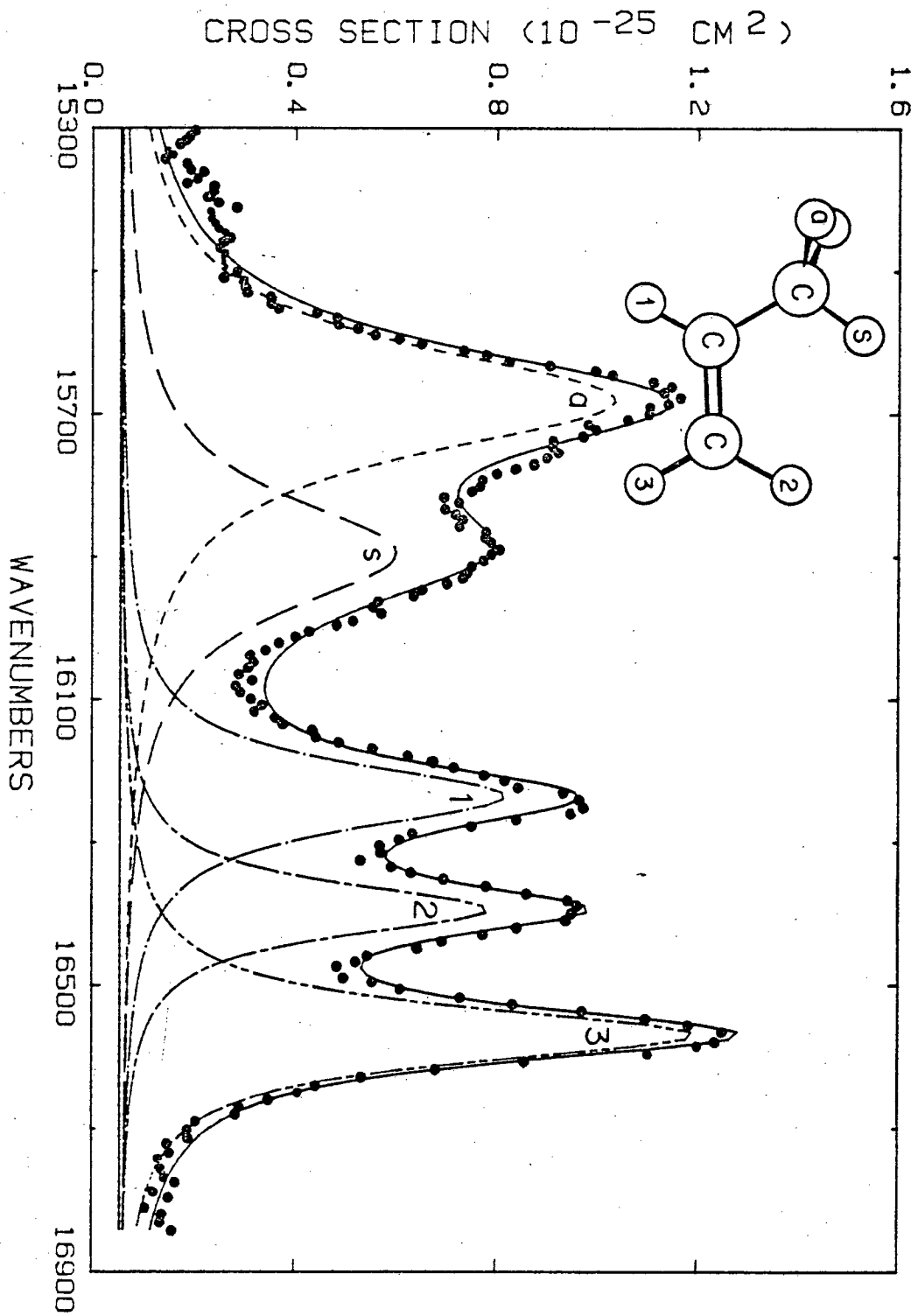


Fig. 5

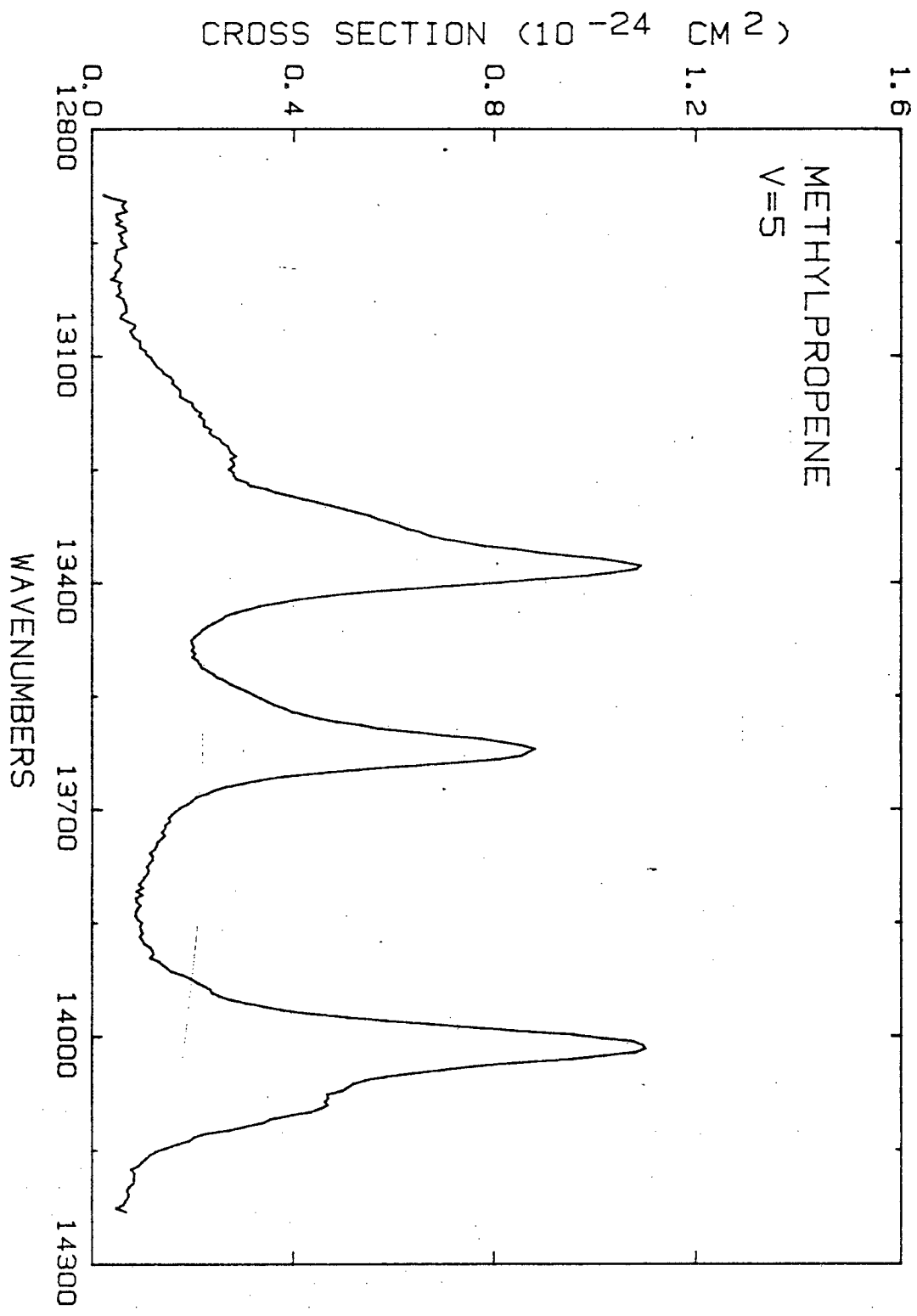


Fig. 6

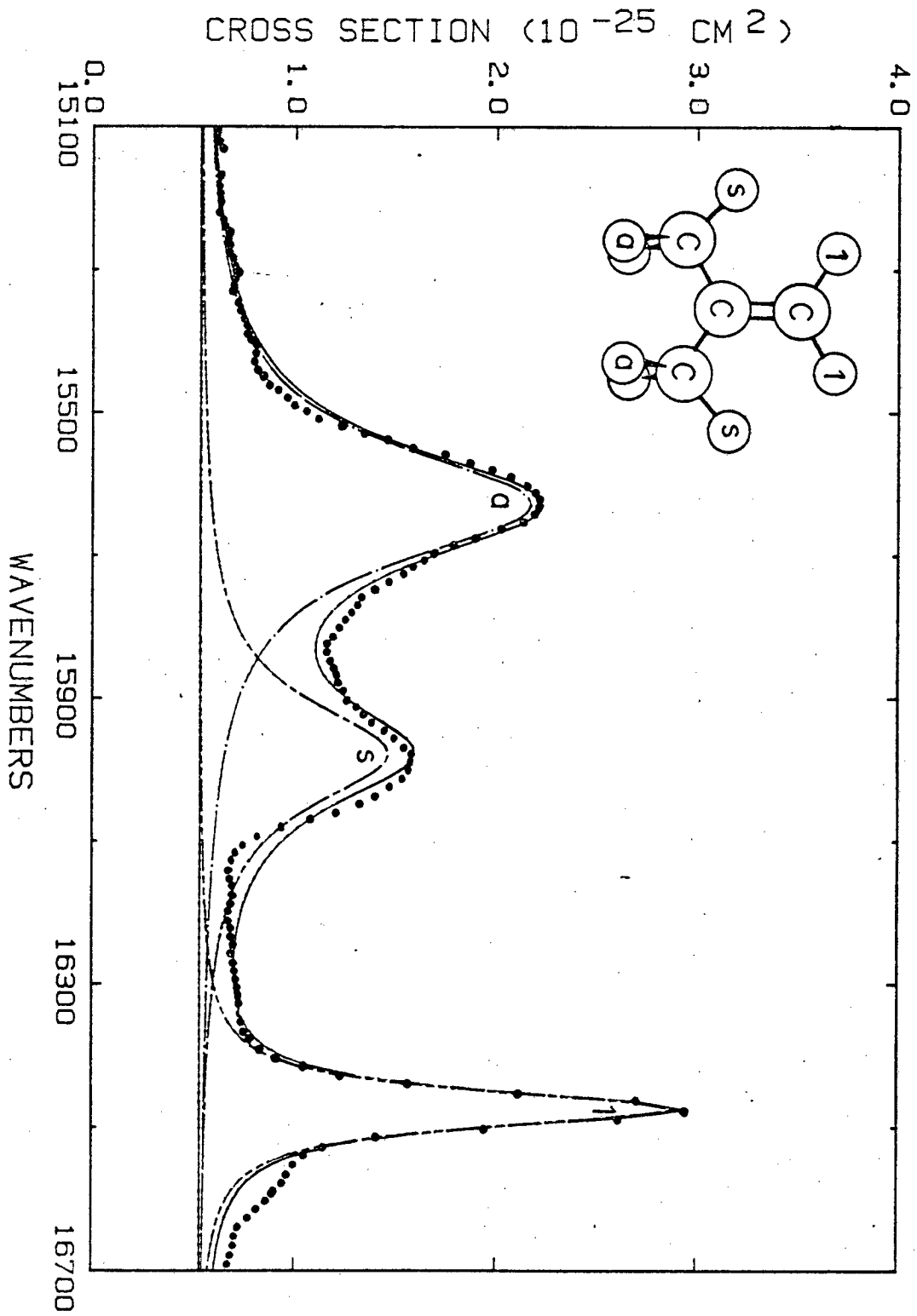


Fig. 7

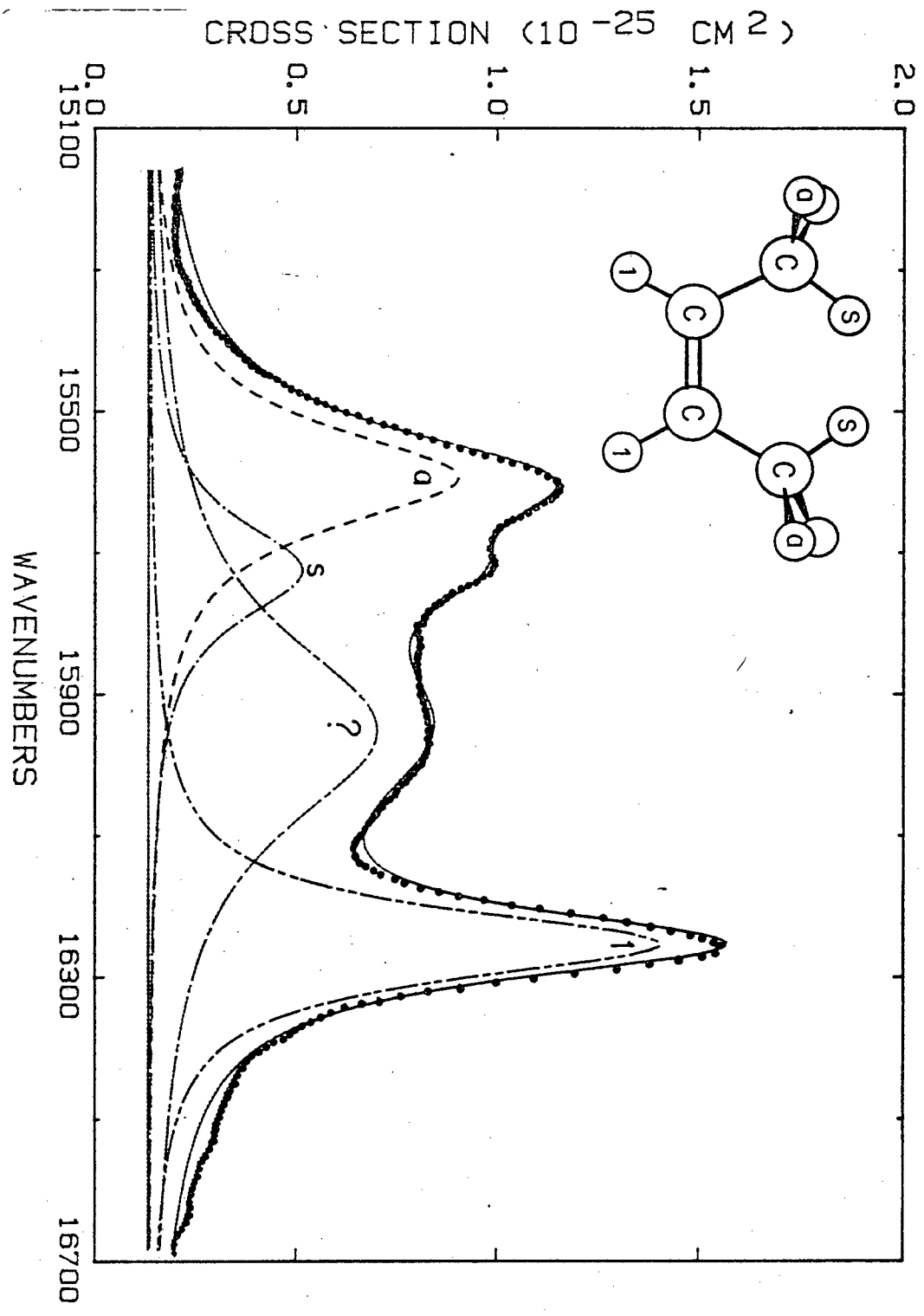


Fig. 8

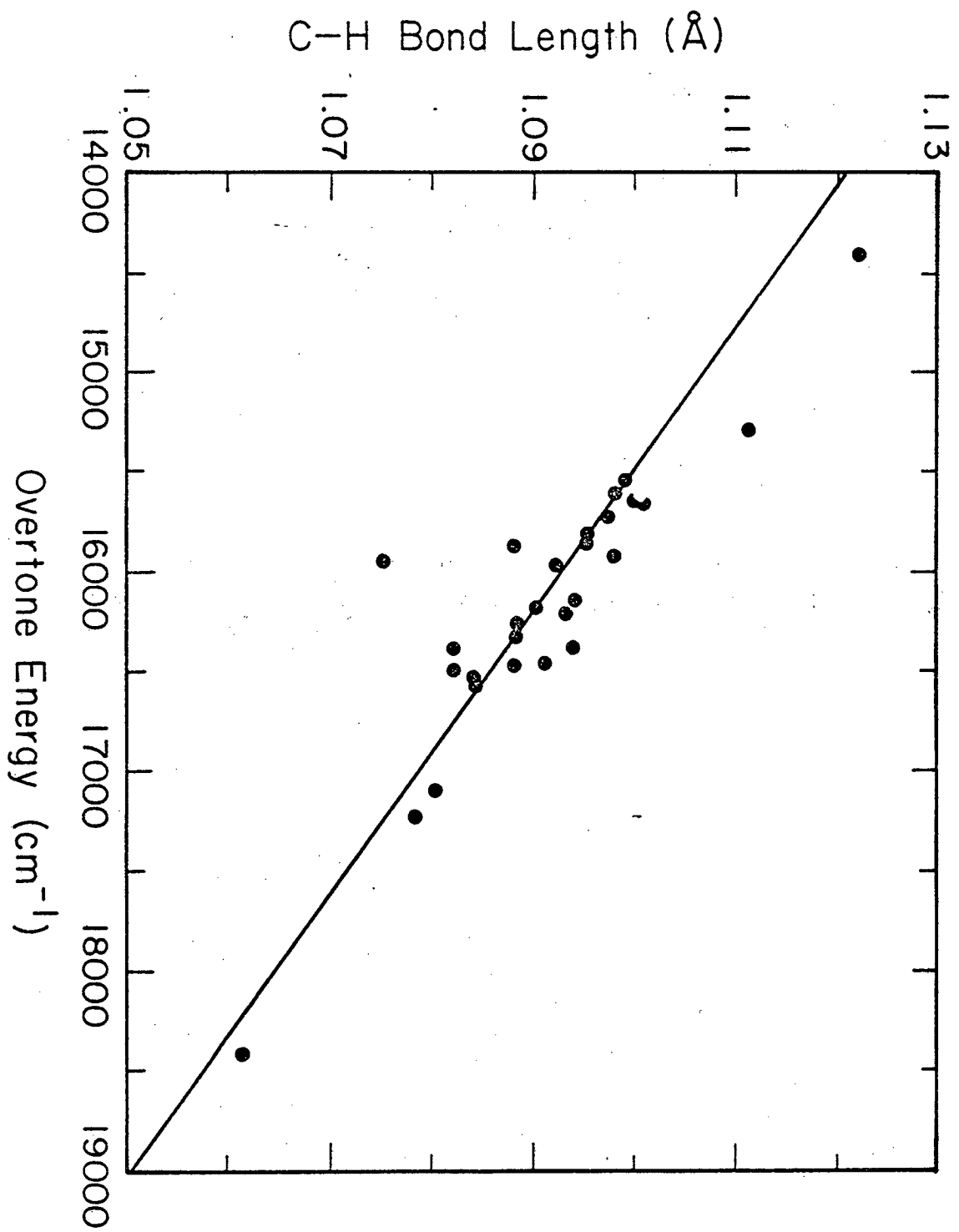


Fig. 9

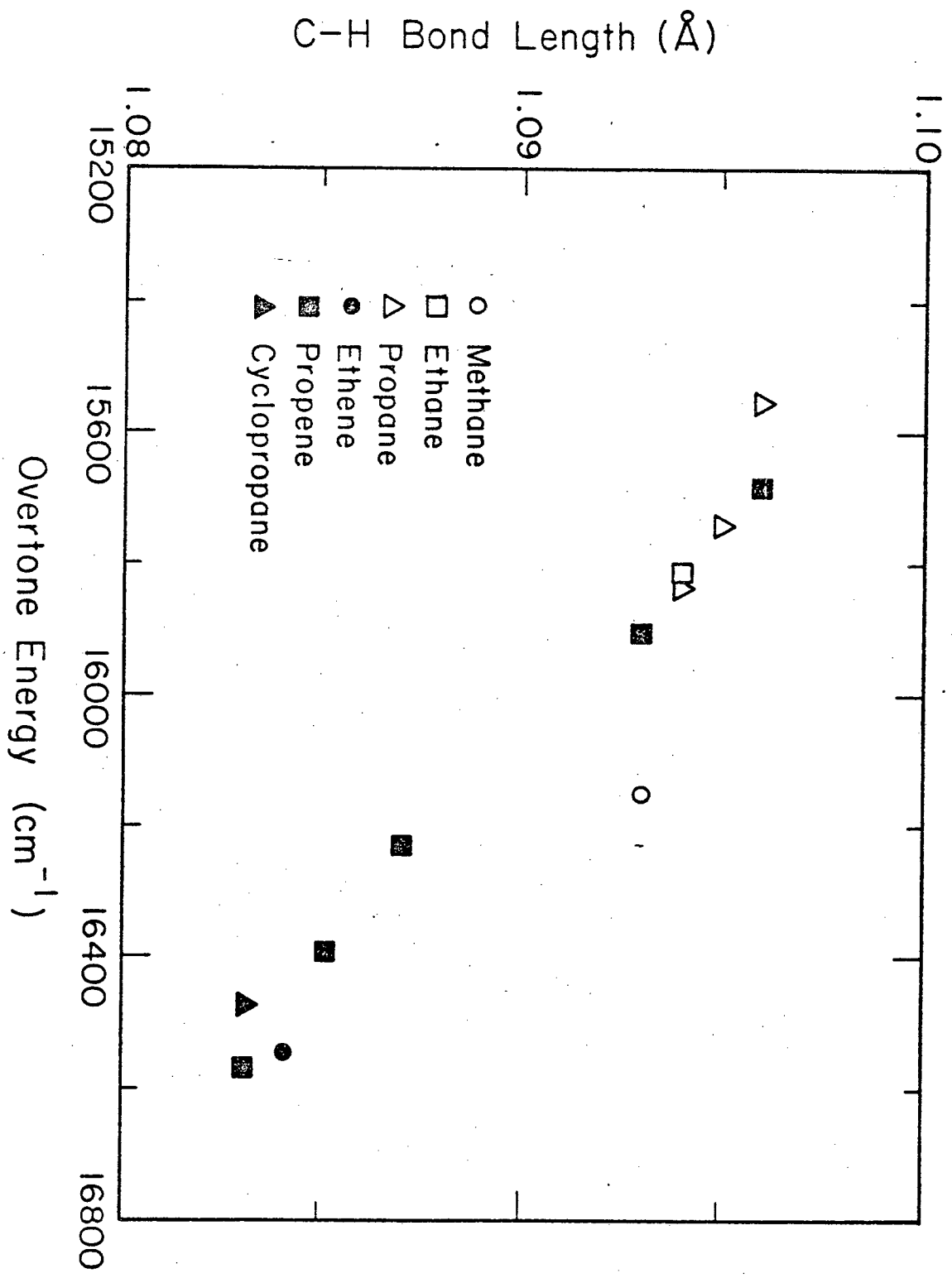


Fig. 10

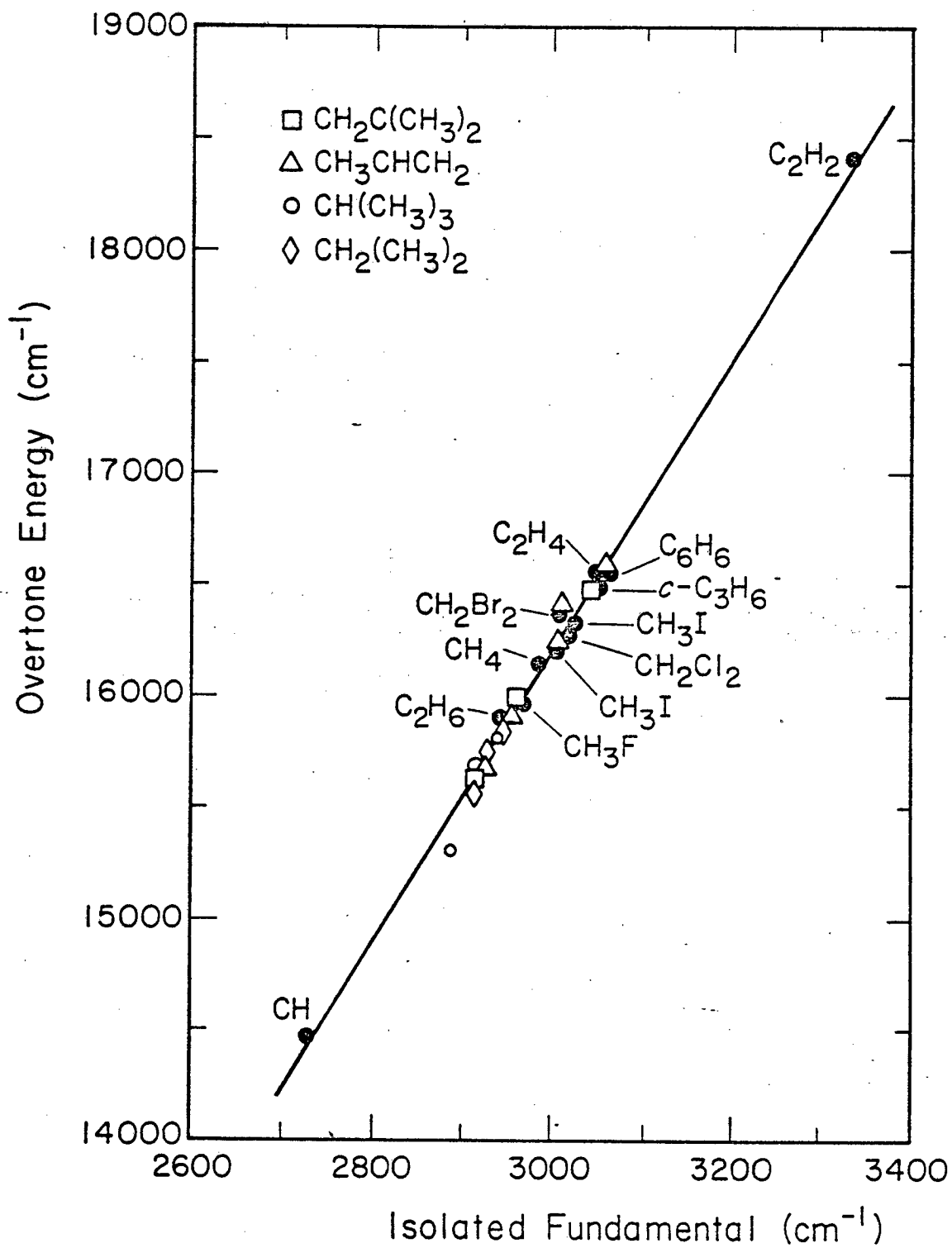


Fig. 11

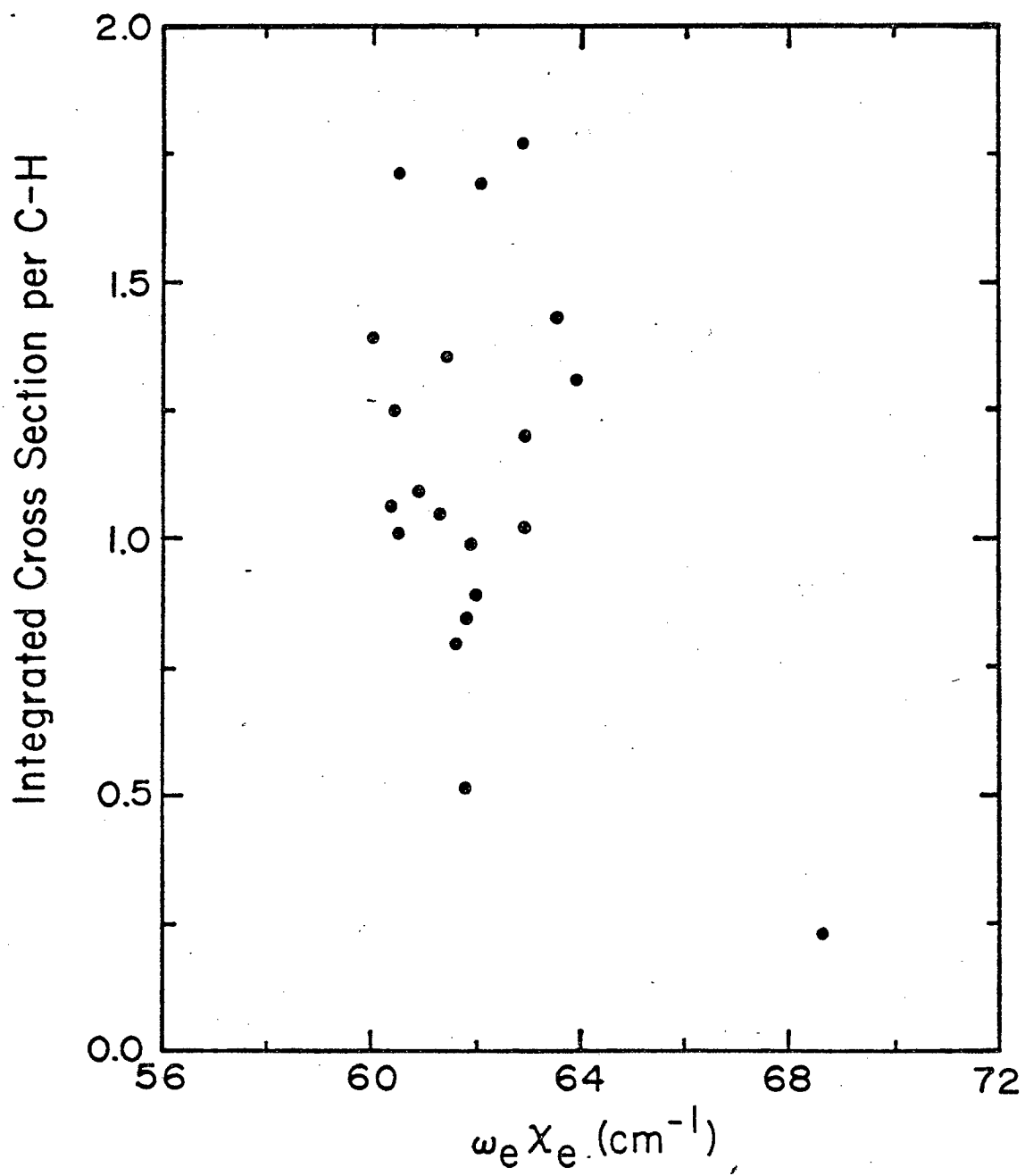


Fig. 12

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

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