

THE UNIVERSITY OF MANITOBA

A LOCAL MODE DESCRIPTION
OF THE
CH-STRETCHING OVERTONE SPECTRA
OF THE ALKANES

by

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I would like to dedicate this work to my wife, Jill, and to my parents in recognition of their invaluable support throughout the duration of my studies. I would like to express my gratitude to Dr. Bryan Henry, not only for his assistance and advice on my project, but more importantly, for his patience with an often frustrating student. Also, I would like to acknowledge the contribution of the computer programs by Dr. R. N. Jones of NRC, Ottawa and thank NRC, the University of Manitoba and the Chemistry Department for financial support.

ABSTRACT

The overtone spectra of the normal alkanes, propane to n-heptane, and several branched alkanes are measured in the liquid or gas phase from 6000 to 15000 Å. Each overtone band is principally composed of peaks corresponding to the different CH oscillator types in the molecule, CH₃, CH₂ or CH. The localized character of the overtone bands increases with increasing energy. The relative intensity of the CH₂ peak to the CH₃ peak correlates with the number of CH₂ hydrogens in the molecule. Combination bands involving CH local modes and a lower frequency normal mode are identified. The relative intensities of the components of these bands parallels that of the pure CH-stretching overtone bands. Combination bands between different CH-stretching local modes are also observed and tentatively assigned. Deconvolution of the main overtone bands for $\Delta v_{\text{CH}} = 3, 4$ and 5 of the normal alkane spectra gives further information about individual local mode peaks, particularly with regard to bandshape and bandwidth. The local mode frequencies, ω_1 , and diagonal local mode anharmonicity constants, X_{11} , for the molecules are obtained from a local mode analysis of both the observed spectral data and deconvolution results. These two parameters form consistent sets for a given CH oscillator type. The CH-stretching overtone spectra of 3-methylpentane are measured for both the liquid and low temperature (77°K glass) solid phases. Calculated diagonal local mode anharmonicity constants show that the local vibrational potential is more harmonic at high viscosity.

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INTRODUCTION

The local mode model has been previously developed (1, 2, 3, 4) to interpret the spectra of highly vibrationally excited molecules. Normal modes, although suitable for the understanding of the fundamental and lower overtone regions of infra-red spectra, have been shown to be inadequate in the description of the higher overtone regions. For example, CH-stretching overtone spectra calculated for dichloromethane, on the basis of anharmonically coupled normal modes, were found to be too complex and resultant bandwidths too large in comparison to the experimentally observed spectra. In that study (4), a general local mode theory was presented and it was concluded that the most prominent spectral features of CH-stretching overtone spectra corresponded to localized modes of vibration, that is, multiple excitation of a single CH oscillator. Many organic molecules contain CH oscillators, however, this study deals specifically with the CH-stretching overtone spectra of the alkanes. Reasons for this choice are outlined later in the Introduction.

The infra-red spectra of the alkanes and their analysis are well documented in the literature (see, for example, references 5, 6, 7 and 8). One of the more important of these studies is the extensive normal mode analysis of the n-alkanes by Snyder and collaborators (8). More relevant to this work is the presentation by Avanesoff and Gaumann of a group model and its application to the analysis of the C-H/C-D valence vibrations of some alkanes (9, 10). The authors employ an experimental model of group frequencies, for methyl and methylene groups, to aid in the assignment of the frequencies.

Only a limited amount of work has been devoted to the CH-stretching overtone spectra of these alkanes. Most recently, the CH-stretching overtone spectra of methane and ethane were interpreted in terms of local modes (11). Prior to that publication was the documentation of the extension of the previously mentioned group model of Avanesoff and collaborators to the observed first and second overtone ($\Delta v_{\text{CH}} = 2$ and 3) spectra of the valence C-H vibrations of alkanes (12). The higher overtones, out to $\Delta v_{\text{CH}} = 6$, were only measured for n-hexane. This later article is particularly interesting. Calculations, based on a normal mode analysis of the valence C-H vibrations of isolated methyl and methylene groups, are compared to observed overtone frequencies. Even this group model, which takes into account the dependence of the observed spectral structure on the CH_3 and CH_2 groups of the molecule, a concept discussed later in this report, is acknowledged by the authors to fail as low as $\Delta v_{\text{CH}} = 3$ to adequately represent the CH-stretching overtone spectra.

The present study comprises a further look at the local-mode character of these CH-stretching overtone spectra. By local mode character I mean the spectral features which have been shown, in the aforementioned paper on dichloromethane (4), to be more readily interpreted in terms of local modes. Before introducing other aspects of this work, a summary of several of the more important characteristics will be given.

The simplicity of CH-stretching overtone spectra has been observed for a wide variety of compounds, including smaller molecules such as dichloromethane (4) and even larger aromatic systems such as naphthalene

(13). It appears that only the most anharmonic normal mode components, that is the ones which correspond to multiple excitation of a single local oscillator, are observed in the higher overtone regions. The highest frequency normal mode components do not seem to contribute at all, which is the reason that the bands are simpler and narrower than expected. The simplicity is not uniform for all overtones, but has been observed to increase with an increase in the vibrational quantum number, v . A normal mode analysis would predict the opposite effect due to an increasing number of symmetry allowed normal mode components.

Although, the pure local mode overtones are the most intense spectral features, combination bands of much less intensity do occur. Two types of combination bands have been previously identified and both are observed to increase in importance for the lower overtones. Indeed, the observed increase in complexity of the lower overtones is largely due to this increase in importance and intensity of these combination bands.

The first type, local mode CH-CH combination bands, appear immediately to the high energy side of a pure local mode overtone band. These local mode CH-CH combination bands are the result of a division of the vibrational quanta among two CH bonds. In local mode terms, such bands are said to be combination bands involving two CH local modes and demonstrate the existence of a small coupling between local modes. However, these local mode CH-CH combination bands can also be interpreted to represent the manifestations of a normal mode pattern in CH-stretching overtones. The other type of combination band is the result of a more direct influence of normal modes on these overtones. This second type

of combination band appears to even higher energy relative to the pure local mode overtone and has been assigned as a combination band between a multiply excited local CH oscillator and a single quantum of a lower frequency normal mode. Both types of combination bands are much less intense and decrease much faster in intensity than related pure local mode overtones, such that by $\Delta\nu_{\text{CH}} = 5$ only a slight broadening of the high energy side of the pure local mode overtone, the result of local mode CH-CH combination activity, is observed.

For $\Delta\nu_{\text{CH}} = 3$ overtones, a much greater influence of normal modes has generally been observed. In the $\Delta\nu_{\text{CH}} = 4$ and 5 regions, the band structures can be described in terms of pure local mode overtones and the two types of combination bands. However, the increased complexity, previously observed in $\Delta\nu_{\text{CH}} = 3$ bands, suggests that normal modes contribute significantly for this overtone. Recent work on the overtone spectra of the dihalomethanes ((14)) has corroborated a previous report by Wallace (15), which indicates that the extent of this normal mode influence, and conversely the applicability of a local mode analysis, is dependent on the mass difference between hydrogen and the moiety to which it is bound.

The alkanes were chosen for this study for several reasons other than availability. Alkanes contain a relative abundance of CH oscillators, which aid in the problem of weak intensities encountered in the overtone region. More importantly, several types of CH oscillator, that is CH_3 , CH_2 and CH, are found in saturated alkanes. The presence of several different CH oscillator types was desired for a further study of another local mode characteristic, the effect of nonequivalent CH

groups.

The effect of nonequivalent CH groups was previously observed in the CH-stretching overtone spectra of benzene, toluene and the xylenes (11). In the benzene spectra, a single peak was observed for each overtone and represented the six equivalent aryl CH bonds. However for toluene and the xylenes, a second peak is resolved to the low energy side of the aryl peak. It appears at an energy comparable to a corresponding transition in ethane and therefore can be identified with an alkyl CH local mode. Thus it has been observed that nonequivalent CH groups are resolved in the overtone region as distinct peaks, reflecting the differences in the nature of the nonequivalent CH bonds. The narrow bandwidths, observed for local mode bands, are instrumental in the resolution of these peaks. However, the difference between the primary, secondary and tertiary CH oscillators of the alkanes (CH_3 , CH_2 and CH groups, respectively) is much less than that between aryl and alkyl CH groups. Therefore, the possible resolution of these CH oscillators was another purpose of this study.

Furthermore, a rough correlation between the number of a given type of CH oscillator and the area of the local mode overtone peak, representing that CH type, has been observed (11, 13, 16). A comparison of the overtone spectra, $\Delta\nu_{\text{CH}} = 3$ to 5, of toluene and benzene has shown a relative decrease in the aryl peak size of the methyl substituted benzene. A second methyl substitution results in a further decrease in the aryl peak size and an approximate doubling in the alkyl peak size in the three xylenes. A similar correlation has been reported for the $\Delta\nu_{\text{CH}} = 6$ overtone transitions of benzene, toluene, m-xylene and

trimethylbenzene, observed by Swofford et al. using the more sensitive technique of thermal lensing spectroscopy (13). A further investigation of the correlation is possible with the alkanes, which present numerous different combinations of three hydrogen types. The concepts of non-equivalent CH groups and the correlation of peak area to the number of a specific CH oscillator type are important for they cannot be explained in terms of normal modes.

The consistency of CH-stretching overtone spectra is another observed local mode characteristic. For example for a given CH oscillator type, corresponding overtone transitions have been observed to occur at approximately the same energy for several compounds. The bandwidths of each overtone are also essentially unchanged for a wide variety of molecules. The consistency of the overtone bands is difficult to explain in terms of normal modes because of the large difference in the predicted number of allowed states of different molecules.

The extent of the applicability of a local mode description to CH-stretching overtones was another concern of this study. To this purpose, a deconvolution^a of experimentally recorded CH-stretching overtone spectra was performed to see how well these spectra could be constructed in terms of the sum of Lorentzian peaks, each corresponding to a different local CH oscillator. The Lorentzian shape has recently been corroborated by the "nearly perfect Lorentzian lineshape" observed in a

^aDeconvolute is used throughout this text to indicate the decomposition of the overtone bands into their component peaks.

dye laser study of the $\Delta v_{\text{CH}} = \text{overtone}$ of gaseous benzene (17). Furthermore, a Lorentzian lineshape is predicted for a transition, in an isolated molecule, to a discrete state, which is coupled to a manifold of nearly degenerate states (18). Here, the given state is coupled anharmonically to other vibrational modes. However, in the liquid phase, intermolecular interactions occur and the peaks broaden substantially. Therefore, there exists the possibility of non-Lorentzian lineshapes.

Deconvolution of the overtone spectra also makes possible the more accurate assignment of peak maxima, usually difficult due to the shifting of the maxima of overlapping peaks. These more accurate maxima are required for the calculation of CH-stretching diagonal local mode anharmonicity constants.

The energy of vibrational states, corresponding to the local CH oscillator, can be expressed as

$$E = E_0 + \sum v_i \omega_i + \sum_{i>j} \sum c_{ij} \omega_{ij} + \sum_{i>j} \sum v_i v_j X_{ij} \quad (1)$$

where v_i and ω_i are the vibrational quantum number and harmonic frequency respectively, associated with local mode i . X_{ij} is the local mode anharmonicity constant and ω_{ij} is a harmonic coupling term of the order of $(\omega_i - \omega_j)$. For a set of nearly degenerate oscillators, such as the alkyl CH oscillator types, the term $(\omega_i - \omega_j)$ is small and the harmonic coupling term can be neglected. Therefore for the excitation of a single oscillator from the vibrational ground state to the state v_i , the transition energy is simply given by

$$\Delta E = v_i \omega_i + v_i^2 X_{ii} \quad (2)$$

A plot of $\Delta E/v_i$ versus v_i will yield, ω_i , the local mode harmonic frequency as the intercept and, X_{ii} , the local mode diagonal anharmonicity constant as the slope.

In summation, this work is divided into three areas of concern. The first section will deal solely with the experimentally obtained CH-stretching overtone spectra of some alkanes. The local mode character of these alkane overtone spectra will be discussed. Secondly, the results of the deconvolution of the spectra will be introduced. This second section will provide a more quantitative look at local mode character in CH-stretching overtone spectra and also be concerned with the extent of the applicability of local modes to such spectra. Finally, CH-stretching local mode diagonal anharmonicity constants, X_{ii} 's, are calculated and discussed.

EXPERIMENTAL

Spectra were obtained for solid, liquid and gas phase samples in this study and, since each phase required specific experimental conditions, these will be discussed separately.

i) Solids

The only solid phase alkane studied was 3-methylpentane, as it forms a clear glass at 77°K. Liquid 3-methylpentane was obtained from the Phillips Petroleum Co. and purified by a modification of the method of Potts (19). For $\Delta v_{CH} = 4, 5$ and 6, the glass was contained in an 8 cm quartz cell fitted in an all quartz dewar (#203908, H. S. Martin & Co., Evanston, Illinois). However for $\Delta v_{CH} = 3$, 3-methylpentane in a 1 cm square Pyrex cell was cooled to 77°K in an Oxford Instrument DN704 optical dewar. The change of cells was necessitated by the requirement of a shorter pathlength.

The samples were cooled gradually over a period of at least one hour. It was observed that the longer pathlength samples were cloudy, probably due to residual water frozen into the glass, and this resulted in a higher background absorbance. At first density gradient filters in the reference beam were required to bring the baseline onto scale. However, it was found that if the cell was turned at a slight angle with respect to the beam, the background absorbance was considerably reduced and the filters not required. No shift in the peak maxima was observed to occur from this procedure.

ii) Liquids

The majority of the alkanes studied were liquids. The sources and purities of these chemicals were as follows: Matheson, Coleman and

Bell, spectroquality (n-hexane, n-heptane, 2-methylbutane, cyclohexane); Fisher Scientific Co., spectranalyzed (n-pentane, cyclohexane); Phillips Petroleum Co., 99 Mol % (3-methylpentane). Because of the intensity of the CH-stretching mode, the long pathlengths of neat liquid, the spectral region observed and other reasons, absorptions due to impurities were not observed and so further purification was not required. These liquid alkane samples were run as neat liquids and contained in 1 cm ($\Delta\nu_{\text{CH}} = 33$) and 10 cm ($\Delta\nu_{\text{CH}} = 4, 5, 6$) quartz cells. Measurement of the $\Delta\nu_{\text{CH}} = 2$ transition for 3-methylpentane required a pathlength less than 1 cm and so a 1 cm divided cell was filled only on one side of the divider. The result was an effective pathlength of approximately 0.5 cm.

iii) Gases

Several gas samples were also studied. These included propane, n-butane and isobutane and all were received from the Phillips Petroleum Co. as lecture bottles of liquified gas in excess of 99.9% in purity. The $\Delta\nu_{\text{CH}} = 4, 5$ and 6 results for these compounds were not acquired on the gaseous samples as originally hoped. Intentions were to use a high pressure gas cell, previously described by Hayward (20), to observe the desired transitions, but pressures of at least 1000 psi are required to obtain a measurable intensity. These samples' pressures are all less than 150 psi. The problem was overcome by effectively distilling these samples into the high pressure gas cell. The gas cylinder's temperature was raised several degrees above room temperature and upon opening the valve, the liquified gas flowed through a connecting system into the high pressure gas cell. The result was an approximately 5 cm pathlength of liquified gas, under pressure.

Recently, a long pathlength, low pressure gas cell (Wilks Scientific Corp., 20 meter variable long pathlength gas cell, Model No. 5720) became available for use. This cell was used to obtain the $\Delta\nu_{\text{CH}} = 3$ gas phase spectra of propane and n-butane. The pathlength for both samples was 2.25 m, but for propane some of the nitrogen, used to flush the cell, was left in the cell and a relatively reduced intensity was observed for that sample.

iv) General Procedures

All spectra were measured using a Cary 14 spectrophotometer, operated in the infra-red mode. Two slidewires were used, a 0 to 2 absorbance slidewire for $\Delta\nu_{\text{CH}} = 3$ and 4 and 0 to 0.2 absorbance, expanded scale slidewire for $\Delta\nu_{\text{CH}} = 5$ and 6. Reference samples were not used, that is the samples were referenced to air. The spectral slit width was never more than 8\AA , and so is negligible when compared to the widths of the observed overtone bands.

Deconvolution studies were performed using slightly modified versions of programs PC-138 (21), PC-116 (22) and PC-122 (22) courtesy of Dr. R. N. Jones. The spectra were digitized and the results converted from wavelength in Angstroms and absorbance, to wavenumbers and transmittance, respectively by program PC-138. The data were read into PC-138 with a given wavelength spacing between the points. Since a direct conversion to wavenumbers would not result in a desired constant wavenumber interval, the authors, Jones et al. employed an interpolation algorithm, using a five point Lagrange formula, to obtain the desired interval between the output data points. The data was then ready for analysis by program PC-116.

A brief explanation of PC-116 will now be given, with an emphasis on aspects more relevant to this work. A more complete discussion for all these programs is given in references 21 and 22. Program PC-116 was written with the analysis of the infra-red spectra of condensed phase systems in mind. It is written, as are the others, in Fortran IV. The program can utilize Lorentz, Gauss, Lorentz-Gauss product or Lorentz-Gauss sum functions as required, for these bandshapes are the most probable in the infra-red spectra of liquid phase samples. PC-116 will, given a set of approximate defining parameters for each peak, an approximate baseline, the number of peaks, the desired bandshape and other input data, optimize the approximate parameters of single or multiple overlapping peaks.

A non-linear least squares method, based on algorithms by Meiron and Marquardt, is used to optimize the parameters. An equation is set up, which adjusts the parameters in iterative steps. The actual adjustments are made by matrices, whose elements are related to the partial derivatives of the differences between the observed and calculated values, f_i , with respect to each parameter, x_k , in other words $\partial f_i / \partial x_k$. Termination of the iterations will occur for several reasons. The most important is, of course, a successful fit of the data by the given function to within a specified tolerance. For this work a significant fit was achieved when the maximum ordinate difference, FM, was less than 0.001 transmittance units. A second reason is slow convergence. In fact, it was slow convergence that terminated all the deconvolutions performed in this study. Slow convergence will result if the minimization of the difference function proceeds too slowly and again is

governed by a specified tolerance limit. A check for slow convergence is performed for every iteration. The sum of the squares of the difference between the observed and calculated results, FSM, is calculated for each iteration. If the ratio of the value of FSM for the previous iteration to its present value was ever less than 1.002 than slow convergence was indicated for these deconvolution studies. If this is the reason for termination, then the optimized parameters, calculated before the tolerance limit was exceeded, are printed out. Even though slow convergence was responsible for the termination of all the deconvolutions, reasonable fits of the data were obtained. Also, although numerous fits were possible for the given data it is noted that the results achieved were physically significant. The comparison of calculated band envelopes to the experimentally observed overtones will be discussed in the results section.

In this study, a Lorentz bandshape was chosen to fit the local mode CH-stretching overtones. Three parameters, x_1 , the maximum peak absorbance, x_2 , the wavenumber position of the peak maximum and x_3 , where $2/x_3$ is the full width at half maximum, are necessary to define a Lorentz band. A fourth parameter in the program is the baseline constant, and it is used to represent a constant background absorbance. For $\Delta\nu_{\text{CH}} = 3$ and 4, this constant background absorbance was able to adequately represent the observed level baseline, but for $\Delta\nu_{\text{CH}} = 5$ the baseline rises sharply toward higher energy. The rising baseline was found to cause difficulties in the deconvolution of the $\Delta\nu_{\text{CH}} = 5$ overtones and comparison of observed and calculated band envelopes revealed large differences.