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## The Local Mode Model and Overtone Spectra: A Probe of Molecular Structure and Conformation

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There is no concept as central to chemistry as the concept of a chemical bond. Generations of chemists have treated Linus Pauling's famous book on the subject<sup>1</sup> with the awe and reverence usually reserved for more theologically oriented tomes. Molecular spectroscopists and crystallographers have measured properties such as bond length to an accuracy that has caused us to examine the very concept itself.<sup>2</sup> A key feature for chemists is the correspondence between structure and reactivity. The length of a chemical bond is associated with its strength and, by implication, with its chemical reactivity.

The lengths of bonds involving hydrogen in large polyatomic molecules have been difficult to determine accurately by experiment. Such bonds are ubiquitous, both in nature and in the laboratory, and play a central role in many areas of chemistry and biochemistry. Recently, *ab initio* methods have been developed<sup>3</sup> that allow the determination of XH bond lengths (X = C, N, O) to 0.001 Å. However, the experimentalist often views such values with suspicion, particularly, when their accuracy is "demonstrated" through a comparison with other theoretical values.

Chemists are interested not only in the lengths of bonds but also in their relative orientation or conformation. In particular, how does a molecular conformation change with time? NMR has been an extremely valuable tool in directly obtaining such information, but on a limited time scale.<sup>4</sup> More recently, picosecond

techniques<sup>5</sup> have been used to probe conformational dynamics, but the experiments are difficult and often their interpretation is not unambiguous.

This Account will describe how the local mode model and overtone spectroscopy can be used to determine XH bond lengths and to investigate molecular conformations. In particular, CH bond length changes that occur upon chemical substitution can be detected with an accuracy of 0.001 Å, i.e., at the same level as *ab initio* approaches. Comparison with *ab initio* values strengthens the physical interpretation of the theoretically derived results. In some cases it can even be used to distinguish between the relative capabilities of these theories. Because of a higher frequency, the overtone experiment can also be used to obtain information on molecular conformations that change on a time scale much shorter than the conventional NMR time scale.

Liquid-phase overtone spectroscopy for XH-stretching transitions is relatively straightforward. All that is required are long path length cells (10–20 cm) and a conventional spectrometer. However, overtone intensity decreases by approximately a factor of 10 at each higher overtone level so the transitions become extremely weak. Laser-based thermal lensing spectroscopy has

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(1) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1948.

(2) For a discussion of the relation between different measures of *r* for CH oscillators, see: Boggs, J. E.; Pang, F.; Pulay, P. *J. Comput. Chem.* 1982, 3, 344 and references therein.

(3) Binkley, J. S.; Frisch, M. J.; Defrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, 1983.

(4) Ōki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Deerfield Beach, FL, 1985.

(5) Hilinski, E. F.; Rentzepis, P. M. *Acc. Chem. Res.* 1983, 16, 224.

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permitted an extension to studies at higher overtones.<sup>6</sup> The problem of intensity is more acute for gas-phase transitions. The higher resolution in the gas phase is generally needed for the bond length/conformational studies described in this Account. Conventional spectroscopy can still be used for the lower overtones ( $\Delta\nu_{\text{CH}} \leq 4$ ), but multiple reflection gas cells and computer data averaging are needed. However, intracavity dye laser photoacoustic spectroscopy has permitted the study of higher overtones ( $\Delta\nu_{\text{CH}} = 5-7$ ) at greatly improved signal-to-noise ratios.<sup>7-9</sup> These higher overtones often provide spectral simplification and greater resolution of peaks corresponding to nonequivalent XH bonds.

It is not the purpose of this Account to review the local mode model.<sup>10,11</sup> Such reviews have appeared previously.<sup>12-16</sup> The model has been used to understand XH-stretching overtone spectra where X is typically C, N, or O. The description<sup>11</sup> that emerges is that these overtone spectra are dominated by transitions to states whose components have the vibrational energy localized in one of a set of equivalent XH oscillators. For example, in a molecule like benzene,<sup>6</sup> the active CH-stretching overtone states correspond primarily to linear combinations of components  $|v,0,0,0,0,0\rangle$ ,  $|0,v,0,0,0,0\rangle$ ,  $|0,0,v,0,0,0\rangle$ , etc. The individual components can be thought of as products of one-dimensional wave functions localized on each of the six CH bonds  $[|v\rangle|0\rangle|0\rangle|0\rangle|0\rangle|0\rangle]$ . These localized wave functions are anharmonic but only weakly coupled. The effective coupling decreases with increasing energy, and the splitting between the various linear combinations also decreases.<sup>11,16</sup> For example, for the dihalomethanes the calculated splitting between the states  $N(|v,0\rangle + |0,v\rangle)$  and  $N(|v,0\rangle - |0,v\rangle)$  decreases from  $\sim 70 \text{ cm}^{-1}$  at  $\Delta\nu_{\text{CH}} = 1$  to less than  $1 \text{ cm}^{-1}$  by  $\Delta\nu_{\text{CH}} = 5$ .<sup>11</sup> Because of the localization, the overtone spectra are extremely sensitive to the properties of these XH bonds. It is this sensitivity that we shall exploit in extracting information about XH bond lengths and molecular conformations.

### Changes in XH Bond Lengths

**Comparison of Overtone and ab Initio Results.** Information about structurally nonequivalent XH bond lengths can be obtained from the fundamental IR spectra by the selective deuteration method of McKean and his collaborators.<sup>17</sup> In this method, all of the hydrogens but one in a molecule are replaced by deuterium. The remaining lone XH stretch is decoupled from the other stretching motions of the molecule as well as from the first overtone of the bending modes. In a sense the XH oscillators in such selectively deuterated

molecules can be thought of as chemically produced local modes. Changes in this isolated XH-stretching fundamental frequency for different molecules correlate remarkably well with changes in XH bond length. For example, for an isolated CH oscillator a shift of  $10 \text{ cm}^{-1}$  corresponds to a bond length change of  $0.001 \text{ \AA}$ .

In 1976, we showed that there was an excellent correlation between this isolated fundamental frequency and CH-stretching frequencies obtained from a local mode analysis of the overtone spectra of the undeuterated molecules.<sup>18</sup> Subsequently, Mizugai and Katayama<sup>19</sup> in liquid-phase studies and Wong and Moore<sup>7</sup> and our group<sup>20,21</sup> in gas-phase studies have demonstrated that changes in CH bond lengths correlate very well with shifts in gas-phase overtone peak positions. These overtone shifts are an extremely sensitive measure of such CH bond length changes. For example, at  $\Delta\nu_{\text{CH}} = 6$  a bond length change of  $0.001 \text{ \AA}$  corresponds to a frequency shift of  $69 \text{ cm}^{-1}$ .<sup>7</sup> These overtone spectral studies are more convenient for such structural investigations in the sense that the difficult synthetic procedures involved with the selective deuteration process<sup>17</sup> are not required. Moreover, the overtone spectra are often easier to interpret than spectra in the fundamental region, particularly when several overtone regions are examined.

Mizugai and Katayama<sup>19</sup> correlated liquid-phase overtone frequency shifts at  $\Delta\nu_{\text{CH}} = 6$  for a number of conjugated heterocyclic molecules with experimental CH bond lengths obtained from microwave spectroscopic studies. Wong and Moore<sup>7</sup> noted a similar correlation for gas-phase overtone frequency shifts of several alkanes and alkenes. However, the correlation improved markedly if the bond lengths from infrared or microwave spectroscopy were replaced by bond lengths obtained from ab initio geometry optimization with a 4-31G basis set. As Wong and Moore noted,<sup>7</sup> the rotational spectroscopic constants are just not very sensitive to the precise location of the hydrogen atoms. However, it was clear that both  $\Delta\nu_{\text{CH}} = 6$  overtone frequency shifts and the ab initio calculations provide a well-correlated measure of CH bond length changes.

In our work in this area we have used the relationship<sup>20</sup>

$$r_{\text{CH}}^{\text{LM}} (\text{\AA}) = 1.084 - (\Delta\bar{\nu}/11\Delta\nu_{\text{CH}})0.001 \quad (1)$$

to determine CH bond lengths from the CH bond length in benzene and the overtone frequency shift ( $\Delta\bar{\nu}$ ) from benzene for a given overtone  $\Delta\nu_{\text{CH}}$ . We express our results in terms of absolute bond lengths, but it is important to realize that what the overtone spectral shifts measure are bond length changes. These are the quantities that we compare to the ab initio calculations. Typically, the results are averaged over two or more overtones.

We have summarized the results of our studies in Table I for the fluorobenzenes,<sup>20</sup> toluene and the xylenes,<sup>21</sup> and the fluorotoluenes.<sup>24</sup> Examples of overtone spectra are shown in Figure 1 for the gas-phase overtone spectra of *o*-, *m*-, and *p*-fluorotoluene at  $\Delta\nu_{\text{CH}} = 5$ .<sup>24</sup>

(18) Hayward, R. J.; Henry, B. R. *Chem. Phys.* 1976, 12, 387.

(19) Mizugai, Y.; Katayama, M. *Chem. Phys. Lett.* 1980, 73, 240.

(20) Gough, K. M.; Henry, B. R. *J. Am. Chem. Soc.* 1984, 106, 2781.

(21) Gough, K. M.; Henry, B. R. *J. Phys. Chem.* 1984, 88, 1298.

(22) Gough, K. M. Ph.D. Thesis, The University of Manitoba, Winnipeg, Canada, 1984.

(6) Swofford, R. L.; Long, M. E.; Albrecht, A. C. *J. Chem. Phys.* 1976, 65, 179.

(7) Wong, J. S.; Moore, C. B. *J. Chem. Phys.* 1982, 77, 603.

(8) Reddy, K. V.; Heller, D. F.; Berry, M. J. *J. Chem. Phys.* 1982, 76, 2814.

(9) Fang, H. L.; Meister, D. M.; Swofford, R. L. *J. Phys. Chem.* 1984, 88, 410.

(10) Hayward, R. J.; Henry, B. R. *J. Mol. Spectrosc.* 1975, 57, 221.

(11) Mortensen, O. S.; Henry, B. R.; Mohammadi, M. A. *J. Chem. Phys.* 1981, 75, 4800.

(12) Henry, B. R. *Vib. Spectra Struct.* 1981, 10, 269.

(13) Henry, B. R. *Acc. Chem. Res.* 1977, 10, 207.

(14) Sage, M. L.; Jortner, J. *Adv. Chem. Phys.* 1981, 47, 293.

(15) Child, M. S.; Halonen, L. *Adv. Chem. Phys.* 1984, 57, 1.

(16) Child, M. S. *Acc. Chem. Res.* 1985, 18, 45.

(17) McKean, D. C. *Chem. Soc. Rev.* 1978, 7, 399; *J. Mol. Struct.* 1984, 113, 251.

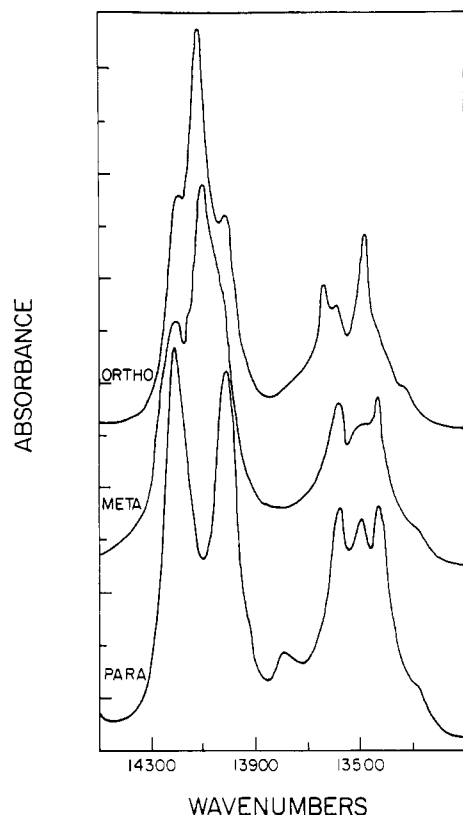


Figure 1. Gas-phase overtone spectra of *o*-, *m*-, and *p*-fluorotoluene in the region of  $\Delta\nu_{\text{CH}} = 5$ . The spectra were detected photoacoustically in a 10 cm path length cell at sample pressures corresponding to the room-temperature vapor pressure.<sup>24</sup>

These spectra were obtained by intracavity dye laser photoacoustic spectroscopy. Two sets of peaks are evident. The set at higher frequency,  $\sim 14\,000\text{ cm}^{-1}$ , corresponds to aryl CH bonds. The set at lower frequency,  $\sim 13\,000\text{ cm}^{-1}$ , corresponds to the methyl CH bonds. The methyl regions all display structure which we can understand in terms of contributions from conformationally nonequivalent methyl CH bonds. We will discuss this structure in detail in the next section.

The spectrum of *p*-fluorotoluene can serve as an illustrative example to demonstrate the resolution of structurally nonequivalent CH bonds.<sup>24</sup> The aryl region of the spectrum consists of a clear doublet with peaks of nearly equal intensity. These peaks can be associated with the two types of nonequivalent CH bonds. Their splitting increases with overtone level in accord with eq 1. At  $\Delta\nu_{\text{CH}} = 3$ , the two peaks are split by  $\sim 120\text{ cm}^{-1}$ , which increases to  $\sim 200\text{ cm}^{-1}$  (Figure 1) at  $\Delta\nu_{\text{CH}} = 5$ . The higher frequency peak corresponds to the CH bonds ortho to the fluorine substituent. The combined effects of  $\sigma$ -electron withdrawal and  $\pi$ -electron donation by fluorine substituents cause aryl CH bonds to shorten.<sup>20</sup> The effects of methyl substitution are less pronounced but cause a lengthening of aryl CH bonds.<sup>21</sup> Thus, the lower frequency peak appears at slightly lower energy than the corresponding peak in benzene.<sup>8</sup>

Often peaks due to structurally nonequivalent CH bonds are not as clearly resolved as in the case of the aryl CH bonds of *p*-fluorotoluene (e.g., aryl regions of the spectra of *o*- and *m*-fluorotoluene). In these latter cases, the bands can be decomposed into component Lorentzian peaks which can be associated with the individual bonds.

Table I.  
Comparison of CH Bond Lengths Obtained from *ab Initio* Calculations and from Local Mode Overtone Spectra

| molecule  | assignmt    | $r_{\text{CH}}^{\text{LM}}, \text{ \AA}$ | $r_{\text{CH}}^{4-21\text{G}}, \text{ \AA}$ |
|---|-------------|--|---|
| fluorobenzene <sup>a</sup>                              | H(2)        | 1.081                                    | 1.081 <sup>b</sup>                          |
|   | H(3)        | 1.083                                    | 1.083 <sup>b</sup>                          |
|   | H(4)        | 1.083                                    | 1.083 <sup>b</sup>                          |
| 1,2-difluorobenzene <sup>a</sup>                        | H(3)        | 1.081                                    | 1.082 <sup>c</sup>                          |
|   | H(4)        | 1.082                                    | 1.083 <sup>c</sup>                          |
| 1,3-difluorobenzene <sup>a</sup>                        | H(2)        | 1.079                                    | 1.079 <sup>b</sup>                          |
|   | H(4)        | 1.080                                    | 1.081 <sup>b</sup>                          |
| 1,4-difluorobenzene <sup>a</sup>                        |             | 1.082                                    | 1.083 <sup>b</sup>                          |
|   |             | 1.081                                    | 1.081 <sup>c</sup>                          |
| 1,3,5-trifluorobenzene <sup>a</sup><br>toluene          | aryl H(2)   | 1.086 <sup>d</sup>                       | 1.085 <sup>e</sup>                          |
|   | aryl H(3,5) | 1.084 <sup>d</sup>                       | 1.084 <sup>e</sup>                          |
|   | aryl H(4)   | 1.084 <sup>d</sup>                       | 1.084 <sup>e</sup>                          |
|   | aryl H(6)   | 1.086 <sup>d</sup>                       | 1.087 <sup>e</sup>                          |
|   | methyl 0°   | 1.093 <sup>d</sup>                       | 1.094 <sup>e</sup>                          |
|   | methyl 60°  | 1.096 <sup>d</sup>                       | 1.096 <sup>e</sup>                          |
|   |             |  |   |
| <i>o</i> -xylene  | aryl H(3)   | 1.086 <sup>d</sup>                       | 1.085 <sup>f</sup>                          |
|   | aryl H(4)   | 1.084 <sup>d</sup>                       | 1.084 <sup>f</sup>                          |
|   | methyl 0°   | 1.093 <sup>d</sup>                       | 1.095 <sup>f</sup>                          |
| <i>m</i> -xylene  | methyl 60°  | 1.096 <sup>d</sup>                       | 1.097 <sup>f</sup>                          |
|   | aryl H(2)   | 1.087 <sup>d</sup>                       | 1.087 <sup>f</sup>                          |
|   | aryl H(4)   | 1.085 <sup>d</sup>                       | 1.085 <sup>f</sup>                          |
| <i>p</i> -xylene  | aryl H(5)   | 1.084 <sup>d</sup>                       | 1.085 <sup>f</sup>                          |
|   | methyl 0°   | 1.093 <sup>d</sup>                       | 1.095 <sup>f</sup>                          |
|   | methyl 60°  | 1.096 <sup>d</sup>                       | 1.097 <sup>f</sup>                          |
| <i>o</i> -fluorotoluene <sup>f</sup><br>(Me = 1; F = 2) | aryl        | 1.086 <sup>d</sup>                       | 1.085 <sup>f</sup>                          |
|   | methyl 60°  | 1.093 <sup>d</sup>                       | 1.095 <sup>f</sup>                          |
| <i>m</i> -fluorotoluene <sup>f</sup><br>(Me = 1; F = 3) | aryl H(3)   | 1.082                                    | 1.082                                       |
|   | aryl H(4)   | 1.083                                    | 1.083                                       |
|   | aryl H(5)   | 1.083                                    | 1.083                                       |
|   | aryl H(6)   | 1.085                                    | 1.084                                       |
|   | methyl 0°   | 1.091                                    | 1.094                                       |
|   | methyl 60°  | 1.094                                    | 1.096                                       |
| <i>p</i> -fluorotoluene <sup>f</sup><br>(Me = 1; F = 4) | aryl H(2)   | 1.082                                    | 1.083                                       |
|   | aryl H(4)   | 1.081                                    | 1.081                                       |
|   | aryl H(5)   | 1.082                                    | 1.084                                       |
|   | aryl H(6)   | 1.084                                    | 1.084                                       |
|   | methyl 0°   | 1.092                                    | 1.095                                       |
|   | methyl 60°  | 1.095                                    | 1.097                                       |

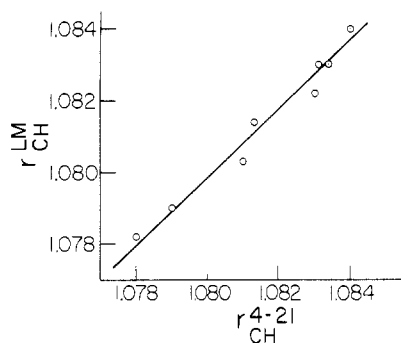
<sup>a</sup> From ref 20. <sup>b</sup> From ref 2. <sup>c</sup> From ref 22. <sup>d</sup> From ref 21. <sup>e</sup> From ref 23. <sup>f</sup> From ref 24.

The results of Table I,  $r_{\text{CH}}^{\text{LM}}$ , are obtained from the correlation given by eq 1 and the measured frequency shifts relative to the corresponding overtone peak in benzene.<sup>8</sup> These results are compared to geometry-optimized *ab initio* molecular orbital values at the 4-21G level (4-31G for toluene). The split valence results are scaled as recommended by Boggs et al.<sup>2</sup>

We have also calculated bond lengths with a minimal STO-3G basis.<sup>20,23,24</sup> However the STO-3G bond lengths do not model small bond length changes nearly as well as the 4-21G calculations. The excellent correlation of the 4-21G results is illustrated in Figure 2 for the fluorinated benzenes.<sup>20</sup> The correlation appears to be accurate to within 0.001 Å. The 4-21G calculations also account for the bond length increase between the aryl and methyl CH bonds, although agreement for the

(23) Gough, K. M.; Henry, B. R.; Wildman, T. A. *J. Mol. Struct.* 1985, 124, 71.

(24) Sowa, M. G.; Gough, K. M.; Henry, B. R., manuscript in preparation.



**Figure 2.** Correlation between CH bond lengths in fluorinated benzenes, which are obtained from frequency shifts in the overtone spectra, and CH bond lengths from ab initio molecular orbital calculations at the 4-21G level.<sup>2</sup> From ref 20.

absolute methyl bond lengths is not quite as good as for the aryl CH bonds. However, the calculations accurately reflect the bond length difference between the planar and out-of-plane methyl CH bonds (vide infra).

The overall message of this section is clear. A remarkably consistent correlation exists between frequency shifts of overtone peaks associated with non-equivalent CH bonds and ab initio predicted bond length changes. In fact, overtone spectra provide the best currently available experimental technique to determine these CH bond lengths at the level of accuracy provided by ab initio molecular orbital theories.

**Basis for Frequency Shift–Bond Length Correlation.** Theoretically, it is somewhat of a puzzle why the correlation between overtone frequency shifts and bond lengths should be so good. If we consider the local CH oscillator as a diatomic fragment, we would expect the shape of the potential curve to determine the frequency and the position of the potential curve minimum to determine the equilibrium internuclear distance. However, such correlations are well-known for diatomic molecules where several relations have been proposed to connect bond lengths and vibrational spectroscopic constants.<sup>25–34</sup> Many of these diatomic relations can be summarized in the following form

$$k_e(r_e - d_{ij})^n = c_{ij} \quad (2)$$

where  $k_e$  is the force constant,  $r_e$  is the equilibrium bond length, and  $c_{ij}$  and  $d_{ij}$  are constants that depend on the rows of the periodic table corresponding to the constituent atoms. The most successful of these relations is Badger's<sup>25,26</sup> rule where  $n = 3$ , but other relations of this form have been proposed with  $n = 2$ – $6$ .<sup>27–34</sup>

Although there have been a number of attempts to explain these relations theoretically, in our view there was no satisfactory theoretical rationalization. What would be desirable would be a simple formula connecting  $r_e$  and spectroscopic constants, with a minimum

number of adjustable parameters and based on a physically realistic potential. One of the most successful attempts was by Huggins,<sup>27,28</sup> but his approach was based on a potential that did not go to infinity but had a finite value at  $r = 0$ .

Recently, we have used a modified Morse potential, in particular one that approaches infinity as  $r$  approaches zero, to derive the following relationship between  $r_e$  and the harmonic frequency  $\omega_e$ <sup>35</sup>

$$(r_e - r_a)\omega_e = 2\hbar(D_e/2\mu)^{1/2} \ln \{1 + [(V_a/D_e) + 1]^{1/2}\} \quad (3)$$

where  $D_e$  is the bond dissociation energy,  $\mu$  is the reduced mass, and  $V_a$  is the potential energy at the hard-sphere distance of closest approach  $r_a$  of the two bonded atoms. Our approach provides a theoretical basis for the observed correlation of overtone frequency shifts and changes in equilibrium bond lengths. It also provides an explanation for the apparent success of the various empirical relationships between  $r_e$  and spectroscopic constants that have been proposed for diatomics. We tested the validity of our approach by using it to calculate values for  $r_e$  from  $\omega_e$  and the anharmonicity  $\omega_e x_e$  for diatomic molecules and for CH local oscillators in several polyatomic molecules. A comparison of these results<sup>35</sup> with experiment and with results obtained on the basis of Badger's rule<sup>25,26</sup> or by Huggins' method<sup>27,28</sup> showed that our results were better, for both the diatomic and polyatomic cases. Thus, it appears that our modified potential is physically realistic and that our derived results have general validity.

### Conformationally Nonequivalent Bonds

**Historical Perspective.** The first indication that overtone spectroscopy and the local mode model could be used to study molecular conformations occurred with our liquid-phase studies of the spectra of hexamethylbenzene<sup>36</sup> and the cyclic alkanes.<sup>37</sup> Instead of observing a single peak at the various CH stretching overtones of hexamethylbenzene, two peaks were observed with a 2:1 intensity ratio. It appeared that the rotation of the methyl groups was sufficiently restricted by the close proximity of neighboring groups to freeze the motion of the methyl groups on the time scale of the overtone experiment. The spectra can be interpreted most straightforwardly<sup>23,36</sup> in terms of a conformer where one methyl CH lies approximately in the plane of the benzene ring and two lie at approximately 60°. The stronger in-plane methyl CH bond is associated with the higher frequency, lower intensity peak, and the lower frequency, higher intensity peak is associated with the two methyl CH bonds at 60°.

Similar effects were observed in our studies of the liquid-phase spectra of the cyclic alkanes and cyclic alkenes.<sup>37</sup> Not only were we able to resolve two peaks corresponding to axial and equatorial hydrogens in the overtone spectrum of cyclohexane, but similar structure was observed in cyclopentane where pseudorotation interconverts the CH bonds on a rapid time scale. However, we were able to demonstrate that even very fast pseudorotation is too slow to average the spectral splitting in cyclopentane and that the spectral structure

(25) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128.

(26) Badger, R. M. *J. Chem. Phys.* **1935**, *3*, 710.

(27) Huggins, M. L. *J. Chem. Phys.* **1935**, *3*, 473.

(28) Huggins, M. L. *J. Chem. Phys.* **1936**, *4*, 308.

(29) Sutherland, G. B. B. M. *J. Chem. Phys.* **1940**, *8*, 161.

(30) Linnett, J. W. *Trans. Faraday Soc.* **1940**, *36*, 1123.

(31) Linnett, J. W. *Trans. Faraday Soc.* **1942**, *38*, 1.

(32) Varshni, Y. P. *J. Chem. Phys.* **1958**, *28*, 1078.

(33) Varshni, Y. P. *J. Chem. Phys.* **1958**, *28*, 1081.

(34) Goodisman, J. *Diatom Interaction Potential Theory*; Academic: New York, 1975; Vol. 1, 2 and references therein.

(35) Swanton, D. J.; Henry, B. R. *J. Chem. Phys.* **1987**, *86*, 4801.

(36) Henry, B. R.; Greenlay, W. R. A. *J. Chem. Phys.* **1980**, *72*, 5516.

(37) Henry, B. R.; Hung, I. F.; MacPhail, R. A.; Strauss, H. L. *J. Am. Chem. Soc.* **1980**, *102*, 515.

reflects the static distribution of CH bond types. Analogous considerations were used in the analysis of conformational contributions in the liquid- and solution-phase overtone spectra of *cis*- and *trans*-decalin(l) and adamantane(sol).<sup>38</sup>

The observations for the cyclic alkanes and alkenes were extended to the gas phase by Wong et al.<sup>39</sup> The resolution of the conformationally nonequivalent CH bonds is improved, but the basic spectral features remain unchanged from the liquid-phase studies. Wong and Moore<sup>7</sup> investigated the gas-phase overtone spectra of several alkanes and alkenes. Features due to conformationally nonequivalent CH bonds associated with the methyl groups were clearly resolvable.

Fang and Swofford and their collaborators have extensively examined the gas-phase overtone spectra of a series of molecules including alcohols, aldehydes, ketones, ethers, esters, sulfides, and amines.<sup>9,40-45</sup> In the spectra of many of these molecules in which the methyl group is in a conformationally anisotropic environment, two distinct methyl peaks are observed. For example, in acetaldehyde,<sup>9,45</sup> two methyl peaks are clearly resolved. The higher frequency peak corresponds to the methyl CH bond lying in the plane of the carbonyl group, whereas the lower frequency peak corresponds to the two methyl bonds lying out of that plane. These spectral features have been explained theoretically<sup>45</sup> on the basis of a local mode coupled oscillator theory.<sup>46</sup> Hanazaki et al.<sup>47</sup> have reached similar conclusions in their study of the splitting of the methyl CH overtones in the gas-phase spectra of acetone and acetaldehyde.

**Methyl Group Conformation in Aromatic Molecules.** We have observed overtone spectral structure which arises from a methyl group in a conformationally anisotropic environment in a series of molecules in which the methyl group is attached to a benzene ring.<sup>21,24,48</sup> An example is shown in Figure 1 for the spectra of the fluorotoluenes at  $\Delta\nu_{\text{CH}} = 5$ .<sup>24</sup> We have observed similar spectra in the overtone regions corresponding to  $\Delta\nu_{\text{CH}} = 3$  and 6. The methyl regions of these spectra are very similar to the methyl regions of the spectra of the corresponding xylenes and to the spectra of toluene.<sup>21</sup>

In geometry-optimized ab initio calculations on toluene with STO-3G, 4-21G, and 4-31G basis sets,<sup>21,23</sup> we find, in agreement with calculations by Pang et al.,<sup>49</sup> that a methyl CH bond is shortest when it is in the ring plane and increases by  $\sim 0.002$  Å to a maximum length when it lies at 90° to the ring plane. The source of this

bond length change is an angular dependence of non-bonded, antibonding interactions between the ring carbons and the methyl hydrogens.<sup>21</sup> Thus, the strength of the methyl CH bond is a function of its angle with respect to the benzene ring.

We expect that overtone spectral structure will reflect the symmetry of the lowest energy molecular conformation. The spectra which are most straightforward to interpret are those of *o*-xylene.<sup>21</sup> Two peaks are observed in the methyl region with an area ratio (low to high frequency) of approximately 2:1. The barrier to internal methyl rotation in *o*-xylene is very high, and the most stable conformer is planar with one methyl CH in the plane of the benzene ring and two at 60°. <sup>50</sup> The lower intensity, higher frequency peak is associated with the planar methyl CH, and the lower frequency peak is associated with the two methyl CH bonds at 60°. <sup>21</sup>

A similar spectrum is observed for *o*-fluorotoluene in the methyl region, except that now there is a third relatively low intensity central methyl peak.<sup>24</sup> The barrier to internal rotation in *o*-fluorotoluene<sup>51</sup> is less than half of that in *o*-xylene. The most stable conformation for the methyl group is also planar as in *o*-xylene.<sup>51</sup> Once again we associate the two outside methyl peaks with the planar (highest frequency) and out-of-plane (lowest frequency) methyl hydrogens.

The spectral splitting between these two methyl peaks corresponds to a bond length difference of 0.003 Å for both *o*-xylene and *o*-fluorotoluene.<sup>21,24</sup> Our ab initio calculations with a 4-21G basis set<sup>24</sup> predict bond length differences of  $\sim 0.002$  Å for both molecules.

The situation for toluene, *m*- and *p*-xylene, and *m*- and *p*-fluorotoluene is not as clear. The methyl regions of the overtone spectra of all of these molecules are essentially the same, with three peaks. For toluene and *m*- and *p*-xylene, the frequencies of the lowest and highest energy peaks are almost the same as the frequencies of the two methyl peaks in *o*-xylene. The barrier to internal rotation in toluene,<sup>23,52</sup> and presumably in the meta and para molecules, is extremely low, but it appears that the time scale of the overtone experiment is short enough to interrogate conformational preferences for methyl groups that must be nearly free rotors.

The correspondence of the frequencies of the two outside peaks in toluene and *m*- and *p*-xylene to the two peaks in *o*-xylene suggests that these outside peaks arise from a planar methyl conformer. By analogy, the same assignment would hold for the outside peaks in the spectra of *m*- and *p*-fluorotoluene. Thus, the spectral splitting between the highest frequency peak, which arises from the in-plane methyl CH, and the lowest frequency peak, which arises from the two methyl CH bonds at 60°, once again corresponds to a bond length difference of 0.003 Å for all five molecules. Our ab initio calculations with a 4-21G basis set (see Table I) predict bond length differences of 0.002 Å for all five molecules.<sup>23,24</sup>

Why is there a central peak in the methyl regions of the spectra of *o*-fluorotoluene, toluene, and the meta and para molecules, and why is such a peak apparently

(38) Henry, B. R.; Thomson, J. A. *Chem. Phys. Lett.* 1980, 69, 275.

(39) Wong, J. S.; MacPhail, R. A.; Moore, C. B.; Strauss, H. L. *J. Phys. Chem.* 1982, 86, 1478.

(40) Fang, H. L.; Swofford, R. L. *Appl. Opt.* 1982, 21, 55.

(41) Fang, H. L.; Swofford, R. L. *Chem. Phys. Lett.* 1984, 105, 5.

(42) Fang, H. L.; Swofford, R. L.; Compton, D. A. *Chem. Phys. Lett.* 1984, 108, 539.

(43) Fang, H. L.; Meister, D. M.; Swofford, R. L. *J. Phys. Chem.* 1984, 88, 405.

(44) Fang, H. L.; Swofford, R. L.; McDevitt, M.; Anderson, A. B. *J. Phys. Chem.* 1985, 89, 225.

(45) Findsen, L. A.; Fang, H. L.; Swofford, R. L.; Birge, R. R. *J. Chem. Phys.* 1986, 84, 16.

(46) Watson, I. A.; Henry, B. R.; Ross, I. G. *Spectrochim. Acta, Part A* 1981, 37, 857.

(47) Hanazaki, I.; Baba, M.; Nagashima, U. *J. Phys. Chem.* 1985, 89, 5637.

(48) Ahmed, M. K.; Henry, B. R. *J. Phys. Chem.* 1986, 90, 1737.

(49) Pang, F.; Boggs, J. E.; Pulay, P.; Fogarasi, G. *J. Mol. Struct.* 1980, 66, 281.

(50) Rudolph, H. D.; Walzer, K.; Krutzik, I. *J. Mol. Spectrosc.* 1973, 47, 314.

(51) Susskind, J. *J. Chem. Phys.* 1970, 53, 2492.

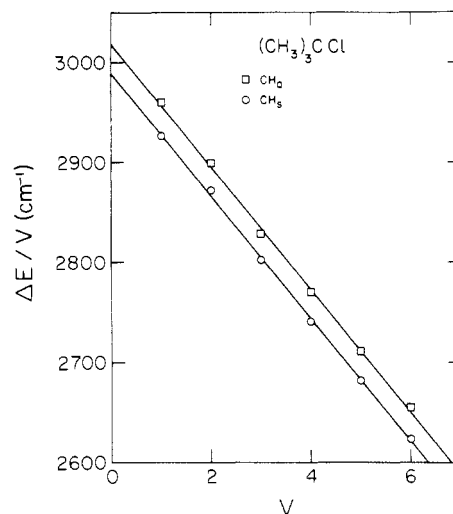
(52) Kreiner, W. A.; Rudolph, H. D.; Tan, B. T. *J. Mol. Spectrosc.* 1973, 48, 86.

absent in the spectrum of *o*-xylene? We have tentatively assigned these central peaks<sup>21,24</sup> to transitions which originate from rotational states above the very low barrier to methyl internal rotation. Such "free rotor" peaks have also been assigned in the fundamental region of the spectra of several related molecules by Cavagnat and Lascombe<sup>53</sup> and by McKean et al.<sup>54,55</sup>

Further support for this interpretation comes from overtone spectral studies of the trimethylbenzenes.<sup>48</sup> We have observed the gas-phase overtone spectra of the three trimethylbenzenes in the region of  $\Delta\nu_{\text{CH}} = 3$ .<sup>48</sup> Two peaks are observed in the methyl regions of the spectra of 1,2,3-trimethylbenzene with peak positions and relative intensities virtually the same as the corresponding features in the spectrum of *o*-xylene. Similarly, the methyl regions of the spectra of 1,3,5-trimethylbenzene are essentially the same as the corresponding features in the spectra of *m*-xylene. These spectra indicate methyl group conformations for 1,2,3- and 1,3,5-trimethylbenzene that are virtually identical with the corresponding conformations in *o*-xylene and *m*-xylene, respectively.

The methyl region of the spectrum of 1,2,4-trimethylbenzene appears to be a superposition of the methyl regions of the spectra of toluene and *o*-xylene. The relative intensity of the central peak is significantly lower here than in *m*-xylene or in 1,3,5-trimethylbenzene. Thus, the spectra indicate an orientation of the two adjacent methyl groups which is the same as in *o*-xylene. The methyl group in the 4-position will be the only one to give rise to the central peak corresponding to transitions from rotational levels above the rotational barrier. In summary, the results for the three trimethylbenzenes<sup>48</sup> provide further support for our interpretation of the methyl regions of the spectra of all of these aromatic molecules<sup>21,24,48</sup> in terms of contributions from states characteristic of the lowest energy conformation as well as from "free rotor" states. However, many unanswered questions remain. In particular, what is the effect of a change in the rotational barrier between the ground and excited vibrational states?

**Methyl Group Conformations in  $(\text{CH}_3)_3\text{CX}$  Molecules.** We have observed a striking manifestation of the resolution of contributions from conformationally nonequivalent methyl CH bonds in the gas- and liquid-phase overtone spectra of 2-chloro-2-methylpropane [ $(\text{CH}_3)_3\text{CCl}$ ] and chlorotrimethylsilane [ $(\text{CH}_3)_3\text{SiCl}$ ].<sup>56</sup> The expected structure of these molecules<sup>57,58</sup> involves three equivalent  $\text{CH}_\beta$  bonds lying trans to the chlorine and in  $\sigma_v$  planes that contain the methyl carbon, the central carbon, and chlorine. The remaining six equivalent  $\text{CH}_\alpha$  bonds exist in pairs on opposite sides of each plane. The overtone spectra<sup>56</sup> are dominated by two well-resolved peaks which correspond to these two types of conformationally nonequivalent CH bonds. In agreement with the ordering predicted by gas-phase fundamental studies of the deuteriated molecule  $(\text{CD}_3)_2(\text{CD}_2\text{H})\text{CCl}$ <sup>58</sup> and by ab initio MO calculations,<sup>56</sup> the overtone frequencies indicate that the  $\text{CH}_\beta$  bonds



**Figure 3.** Plots of the vibrational energy equation of a single Morse oscillator for the nonequivalent CH bonds of liquid-phase  $(\text{CH}_3)_3\text{CCl}$ . From ref 56.

trans to the C–Cl (Si–Cl) bonds are longer than the  $\text{CH}_\alpha$  bonds.

We have successfully analyzed these spectra by treating the two  $\text{CH}_\alpha$  oscillators as harmonically coupled local modes.<sup>11</sup> In this analysis, the stretching motion of the unique  $\text{CH}_\beta$  bond is assumed to be uncoupled from the stretching motions of the two  $\text{CH}_\alpha$  bonds. The validity of this simple model is demonstrated by the very good agreement between the calculated and observed energies of the CH-stretching peaks.<sup>56</sup> It is also illustrated in Figure 3,<sup>56</sup> which displays a plot of the equation

$$\Delta E = \nu\omega - (\nu + \nu^2)\omega x \quad (4)$$

for the energies of the  $\text{CH}_\alpha$  and  $\text{CH}_\beta$  peaks in the spectra of  $(\text{CH}_3)_3\text{CCl}$ . In eq 4 for CH-stretching overtones,  $\nu$  is the vibrational quantum number ( $= \Delta\nu_{\text{CH}}$ ),  $\omega$  is the harmonic local mode frequency, and  $\omega x$  is the diagonal local mode anharmonicity. Although there is some evidence for weak coupling at the lower overtones ( $\Delta\nu_{\text{CH}} = 2$  and 3), despite the fact that they are bonded to a common carbon, these conformationally nonequivalent methyl CH bonds appear to be essentially uncoupled at the higher overtones ( $\Delta\nu_{\text{CH}} \geq 4$ ).

**Distinct Conformational Species.** Overtone spectroscopy and the local mode model have also been used to study conformationally nonequivalent bonds, not within the same molecule but in two distinct conformational species. Peaks in the overtone spectra of 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane are decidedly asymmetric with the asymmetry more pronounced in the bromo-substituted molecule.<sup>59</sup> The structure arises from the presence of two rotational conformers, trans and gauche. The trans conformer is the more stable, and its dominance is more pronounced in tetrabromoethane than in tetrachloroethane. Accordingly, the ratio of the trans spectral component to the less intense gauche component is greater in tetrabromoethane than in tetrachloroethane. On the basis of the assumption that the transition dipole is the same in both conformations, the relative intensities of the two spectral components were used to determine the energy

(59) Henry, B. R.; Mohammadi, M. A. *Chem. Phys.* 1981, 55, 385.

(53) Cavagnat, D.; Lascombe, J. J. *Mol. Spectrosc.* 1982, 92, 141.

(54) McKean, D. C.; Watt, R. A. *J. Mol. Spectrosc.* 1976, 61, 184.

(55) McKean, D. C.; Becher, H. J.; Bramslepe, F. *Spectrochim. Acta, Part A* 1977, 33, 951.

(56) Ahmed, M. K.; Henry, B. R. *J. Phys. Chem.* 1987, 91, 3741.

(57) Lide, D. R. *J. Chem. Phys.* 1960, 33, 1519.

(58) McKean, D. C.; Biedermann, S.; Burger, H. *Spectrochim. Acta, Part A* 1974, 30, 845.

difference between the trans and gauche conformers.

In a recent study of the overtone spectra of liquid-phase benzal chloride and benzal bromide, we have also found evidence for equilibria between conformationally distinct species.<sup>60</sup> The alkyl regions of the overtone spectra of  $C_6H_5CHBr_2$  are single symmetric peaks which can be described by single Lorentzian functions. However, the alkyl regions of the overtone spectra of  $C_6H_5CHCl_2$  are asymmetric bands which can be fitted with two Lorentzian functions. We have analyzed our results by proposing that the  $-CHBr_2$  group of benzal bromide exists in a single conformation, while both planar and orthogonal conformations of the  $-CHCl_2$  group are present in liquid benzal chloride. Our results for benzal chloride are in accord with Raman studies, which also indicate the existence of two conformers,<sup>61,62</sup> but they are in apparent disagreement with ab initio studies which indicate the existence of a single planar conformer.<sup>60,63</sup> It is conceivable, as pointed out by Schaefer and Penner,<sup>63</sup> that intermolecular interactions could stabilize the orthogonal conformer in the liquid phase.

Often it is difficult to study such conformational equilibria by other methods. Microwave techniques are limited to relatively small molecules, and for molecules the size of the tetrahaloethanes, the spectra can be complex due to effects such as quadrupolar couplings and differing isotopes. Often IR spectra in the fundamental region are ambiguous because of the large number of transitions and the corresponding difficulty of unambiguously assigning the peaks to different conformers. In many instances, a local mode inter-

pretation of overtone spectra may prove to be the simplest and most effective method of investigating such conformational equilibria.

## Conclusion

Overtone spectroscopy and the local mode model provide a valuable probe of molecular structure and molecular conformation. The recent development of techniques like intracavity dye laser photoacoustic spectroscopy has produced dramatic improvements in resolution and applicability. The highly sensitive determination of bond length changes has already led to an understanding of substituent effects on CH bonds in aryl systems<sup>20,21</sup> and to an elucidation of the trans lone-pair effect.<sup>9,43</sup> Further, applications to the investigation of both chemistry and reactivity are likely. Moreover, the very short time scale makes these overtone techniques ideally suited to study the conformational properties of XH bonds.

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(60) Ahmed, M. K.; Swanton, D. J.; Henry, B. R. *J. Phys. Chem.* **1987**, *91*, 293.

(61) Ribeiro-Claro, P. J. A.; Teixeira-Dias, J. J. C. *J. Raman Spectrosc.* **1984**, *15*, 224.

(62) Ribeiro-Claro, R. J. A.; Rocha Gonsalves, A. M. D'A.; Teixeira-Dias, J. J. C. *Spectrochim. Acta, Part A* **1985**, *41*, 1055.

(63) Schaefer, T.; Penner, G. H. *J. Raman Spectrosc.* **1985**, *16*, 353.