

Applications of the Local Mode Model to CH Bond Length Changes, Molecular Conformations and Vibrational Dynamics

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The theoretical basis for the local mode model is reviewed. The model is applied to gas phase overtone spectra of aromatic molecules to investigate both substituent induced CH bond length changes and conformationally inequivalent hydrogens. The dynamic implications of the local mode model are discussed.

INTRODUCTION

The local mode model has been highly successful in explaining the high energy ($\Delta v_{\text{XH}} \geq 3$) XH-stretching overtone spectra of a wide variety of molecules.¹ The model in its present form was proposed in 1975.² Subsequently several calculations, frequently carried out for the vibrational states of water, have provided a substantial theoretical basis for the model.^{3–10}

In order to examine the features of the model, let us consider the OH-stretching vibrational states of water. We will neglect the bending motion and assume that each of the OH bonds can be described by a Morse potential.¹⁰ Appropriate zero order states are then simple product states of Morse oscillator wavefunctions, one for each bond (e.g., the state $|5, 0\rangle$ corresponds to five quanta in one Morse oscillator and none in the other). For example, at $\Delta v = 5$, the six zero order states will have zero order energies determined simply by differences

in anharmonicity. The states $|5, 0\rangle$ and $|0, 5\rangle$ lie lowest, then, 647 cm^{-1} higher, are the states $|4, 1\rangle$ and $|1, 4\rangle$, and, 970 cm^{-1} higher, are the states $|3, 2\rangle$ and $|2, 3\rangle$. Interaction between these zero order states is only significant if a given one of the two Morse oscillators differs in excitation by a single quantum. Therefore interaction of the state $|5, 0\rangle$ with the state $|0, 5\rangle$ occurs only indirectly, via the coupling route $|5, 0\rangle \leftrightarrow |4, 1\rangle \leftrightarrow |3, 2\rangle \leftrightarrow |2, 3\rangle \leftrightarrow |1, 4\rangle \leftrightarrow |0, 5\rangle$. The two lowest energy eigenfunctions, after full diagonalization, are well approximated by the in-phase and out-of-phase combination of these two lowest energy zero order states

$$(v, 0)_{\pm} \cong \frac{1}{\sqrt{2}}[|v, 0\rangle \pm |0, v\rangle]$$

The energy splitting of these two lowest energy eigenfunctions is due principally to the interaction between $|v, 0\rangle$ and $|0, v\rangle$. As v increases the coupling between $|v, 0\rangle$ and $|0, v\rangle$ becomes more indirect and the two lowest energy eigenfunctions will tend to become degenerate. For example, at $\Delta v = 5$ this splitting is only 0.03 cm^{-1} .¹⁰ Intensity calculations predict that the intensity should become increasingly concentrated in these two lowest levels as v increases. Therefore one might expect that as v increases the most intense overtone transition should become narrower.

At high v , what the radiation field excites is not $(v, 0)_{+}$ or $(v, 0)_{-}$ separately, but both of them together. Such a superposition is equivalent to exciting the nonstationary states $|v, 0\rangle$ or $|0, v\rangle$, with the vibrational quanta localized in one or the other of the chemical bonds.

Lawton and Child have illustrated this situation in their calculations on water.⁹ In this work⁹, they point out that the splitting between $(v, 0)_{+}$ and $(v, 0)_{-}$ is a measure of the time it takes to transfer the v quanta of vibrational energy from one bond to the other. At $\Delta v = 8$ in water, the splitting between these states is so small that such energy transfer will occur on a nanosecond timescale,⁹ which is clearly an extremely long time on a vibrational timescale.

The coupling between these zero order states is evident in the low energy overtone spectrum at $\Delta v = 2$. In the spectra of the dihalomethanes, three main peaks are present in this region.¹¹ They are readily assignable as $(2, 0)_{+}$, $(2, 0)_{-}$ and $(1, 1)$. At $\Delta v = 3$, one peak dominates the absorption. It corresponds to unresolved transitions to $(3, 0)_{+}$ and $(3, 0)_{-}$. (Remember that $|3, 0\rangle$ and $|0, 3\rangle$ are only

indirectly coupled.) Two much lower intensity peaks can be assigned as $(2, 1)_+$ and $(2, 1)_-$. We expect to observe this splitting since $|2, 1\rangle$ and $|1, 2\rangle$ are coupled in first order.

In summary, therefore, it appears that when a radiation field interacts with a molecule in the high energy XH-stretching region of the overtone spectrum, it effectively deposits all of its energy in a single one of a set of equivalent XH oscillators. The spectra then should be extremely sensitive to the properties of the bonds themselves. There has been a great deal of work which has exploited these local oscillators as probes of the chemical and the physical environment of the XH bond.¹ The next section discusses two examples, characteristic of recent work in this area.

CH BOND LENGTH CHANGES

McKean and his collaborators have examined the fundamental IR spectra of molecules where all of the hydrogens but one have been replaced by deuterium.¹² In a sense one can think of the CH oscillators in these molecules as chemically produced local modes. One application of this work has been the observation of a change in this isolated CH-stretching frequency with chemical substitution in the remainder of the molecule¹². It has been found that, over a wide range of molecules, a shift of $\sim 10 \text{ cm}^{-1}$ in this isolated CH-stretching frequency corresponds to a change in CH bond length of 0.001 \AA . Not surprisingly, a similar correlation has been observed in overtone spectra. Both Mizugai and Katayama,¹³ and Wong and Moore,¹⁴ have noted such a correlation at $\Delta v = 6$. In this region, a CH bond length change of 0.001 \AA corresponds to a shift of 69 cm^{-1} in the gas phase overtone spectrum.¹⁴ In the present work, we will adopt the correspondence of $11\Delta v \text{ cm}^{-1}$, for $\Delta v = 3, 4$ and 5 , to a bond length change of 0.001 \AA .

Recently we have examined the gas phase overtone spectrum of 1,3-difluorobenzene. (Further details on this work, as well as on the gas phase spectra of several other fluorobenzenes will be published shortly.¹⁵) The spectrum shows three unresolved peaks at $\Delta v = 5$ (Figure 1). Similar spectra have been observed for $\Delta v = 3$ and 4 . When these spectra were deconvoluted, with a Nicolet 1280 curve analysis program, we obtained an area ratio of $1:2:1$ for the three

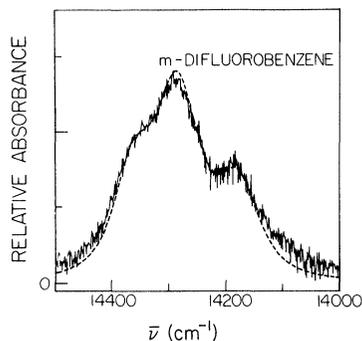


FIGURE 1 The gas phase overtone spectrum of 1,3-difluorobenzene at 86°C in the region of $\Delta\nu_{\text{CH}} = 5$.

peaks for all three overtones. These peaks can be identified with the three inequivalent hydrogens. On the basis of intensities, we would assign the higher intensity center peak to the two hydrogens at positions four and six (H(4) and H(6)). Fluorine withdraws sigma electrons and this effect causes the aryl CH bonds to shorten. Qualitatively we expect this effect to be most pronounced for H(2) and least pronounced for H(5). Thus H(2) should have the shortest CH bond, and therefore should be associated with the highest frequency peak, whereas H(5) should be associated with the lowest frequency peak.

From the frequency shifts relative to a CH oscillator in benzene, we can calculate the expected bond length changes.

$$r_0^{\text{CH}} (\text{\AA}) = 1.084 - (\Delta\bar{\nu}/11\Delta\nu)0.001$$

1.084 is the CH bond length in benzene¹⁶ and $\Delta\bar{\nu}$ is the frequency shift for a given overtone $\Delta\nu$. The changes in bond length are remarkably consistent for the three overtones. Δr_0^{CH} values in thousandths of an \AA are 5.2, 5.3 and 5.2 from $\Delta\nu = 3, 4$ and 5 for H(2). The corresponding values for the other hydrogens are 4.1, 3.8 and 3.8 for H(4) and H(6), and 2.3, 1.5 and 1.9 for H(5).

The CH bond lengths, calculated from the averaged frequency shifts and the above equation, are given in Table I, where they are compared to CH bond lengths calculated in a recent geometry optimized *ab initio* 4-21G calculation.¹⁷ The correspondence is very good.

Similar results have been obtained in our study of the gas phase overtone spectra of toluene and the three xylenes (further details

TABLE 1
CH bond lengths in 1,3-difluorobenzene obtained from overtone
frequency shifts and from 4-21G calculations^a

Bond	r_0^{CH} (4-21G) ^a (Å)	r_0^{CH} (overtone) (Å)
H(2)	1.079	1.079
H(4, 6)	1.081	1.080
H(5)	1.083	1.082

^a Taken from Ref. 17.

of this study will be published shortly¹⁸). The gas phase spectrum of *o*-xylene in the region of $\Delta v = 3$ is given in Figure 2. The higher frequency doublet corresponds to the aryl CH bonds and the lower frequency one to the methyl CH bonds. The two aryl peaks correspond to the two types of inequivalent aryl CH bonds. The spectrum of toluene in the aryl region is similar, with two peaks. The methyl region in toluene is not quite as clear due to interference from what is probably a combination band.¹⁸

In toluene the frequency separation between the aryl peaks at $\Delta v = 3$ is 72 cm^{-1} . A computer deconvolution gives the ratio of the area of the high frequency peak to that of the low frequency one as 3:2. Boggs and his collaborators have also carried out 4-21G calculations for toluene¹⁶. They predict that the two ortho CH bonds are longer by 0.001 to 0.002 Å than the meta and para bonds. The spectral splitting of 72 cm^{-1} corresponds to a bond length difference of

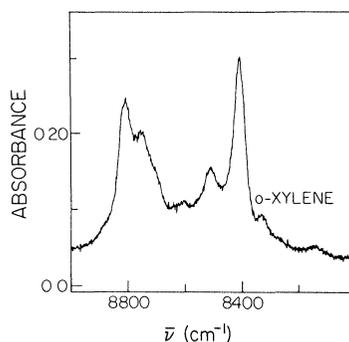


FIGURE 2 The gas phase overtone spectrum of *o*-xylene at 86°C in the region of $\Delta v_{\text{CH}} = 3$.

$\sim 0.002 \text{ \AA}$. Thus, both on the basis of relative area and predicted bond length changes, the higher frequency aryl peak in toluene corresponds to the meta and para CH bonds and the lower frequency one to the ortho bonds.

The areas of the two aryl CH peaks in *o*-xylene are approximately equal. There are no geometry optimized M.O. calculations available for *o*-xylene. However, by analogy to toluene, it seems reasonable to assign the higher frequency aryl peak to H(3) and H(4) and the lower frequency one to H(5) and H(6). The overall result, both with toluene and the xylenes, and with 1,3-difluorobenzene, is that a beautifully consistent picture can be obtained correlating overtone frequency shifts, relative areas and bond length changes.

MOLECULAR CONFORMATIONS

We can understand the doublet structure in the methyl peak of *o*-xylene (Figure 2) in terms of contributions from conformationally inequivalent hydrogens. The first applications of overtone spectroscopy to the study of molecular conformations occurred in examinations of the liquid phase spectra of hexamethylbenzene¹⁹ and of the cyclic alkanes.²⁰ At both $\Delta v = 3$ and 4, the spectrum of hexamethylbenzene is a doublet. The intensity ratio of the doublet components is 2:1. The spectrum reflects a molecular conformation²¹ in which the methyl groups are arranged around the ring in a cogwheel fashion. One methyl group will have two hydrogens above the plane and one below, while the next methyl will have one above and two below, etc. The net result will be two types of conformationally inequivalent hydrogens in a two to one ratio, exactly as reflected by the overtone spectrum.

Both cyclohexane and cyclopentane also show doublet overtone bands from $\Delta v = 3$ to 7.²⁰ The splitting in cyclohexane can be understood on the basis of the axial and equatorial CH bonds in the stable chair conformation. These bonds are interconverted by the inversion of the chair. This inversion occurs at a rate of about 10^3 s at room temperature.²² Given the splitting of 100 to 200 cm^{-1} observed in the overtone spectrum, inversion is too slow to motionally average the two peaks. Thus the observed splitting corresponds to the static difference between the two types of CH bonds.

At room temperature, cyclopentane does not exist in a single stable conformation. Rather it moves among a large number of conformations through pseudorotation.²³ Pseudorotation gives rise to inter-conversion of axial, equatorial and eclipsed CH bond types on a time scale of $\sim 4 \times 10^{-13}$ s. However, even fast pseudorotation is too slow to average the spectral splitting and we have accounted for the spectral band shape on the basis of contributions which reflect the static distribution of the CH bonds.²⁰

Wong *et al.*²⁴ have determined the spectra of the cyclic alkanes in the gas phase with photoacoustic intracavity dye laser techniques. The gas phase bands are narrower for the higher overtones and thus resolution of these conformationally inequivalent hydrogens is improved.

Wong and Moore¹⁴ have also obtained gas phase spectra of the alkanes which they have used in a discussion of conformational properties. The point with all of these experiments is that on the time scale of the overtone experiment, information about conformational features can be obtained which is inaccessible by slower techniques like NMR.

Although it is not in the gas phase, recent work on durene in the crystalline phase at low temperature²⁵ is also relevant to the present discussion. Partly on the basis of polarization data, the authors attribute the spectral splittings in the methyl overtones to methyl local modes split by the molecular and crystal fields.

In the gas phase spectrum of *o*-xylene (Figure 2), the ratio of the areas of the two methyl peaks is close to 2:1. A similar ratio is found in the toluene spectrum if correction is made for the combination band. In *o*-xylene, the most stable conformer is likely to be "planar" with one methyl CH bond in the plane of the ring and two at 60° to the ring.²⁶ A similar observation has been made by Nakagaki and Hanazaki based on the liquid phase *o*-xylene overtone spectrum.²⁷ The most stable conformer in toluene is either the corresponding "planar" one or an "orthogonal" conformer with one methyl CH bond perpendicular to the ring. For either conformer of toluene, as with *o*-xylene, if the methyl hydrogens are resolved, the spectrum should show two methyl peaks with an area ratio of 2:1, which is just what is observed.

4-21G calculations for toluene predict the methyl CH in-plane bond to be shorter by about 0.002 Å than the two bonds at 60°.¹⁶

This is in accord with the overtone spectrum, where the higher frequency peak is the least intense and the frequency separation of $\sim 100 \text{ cm}^{-1}$ corresponds to a bond length difference of $\sim 0.003 \text{ \AA}$. This agreement, coupled with the similarity of the methyl regions of the *o*-xylene and toluene spectra, support the "planar" rather than the "orthogonal" conformer as the stable species in toluene.

DYNAMIC IMPLICATIONS

In this section we discuss, albeit in a somewhat speculative fashion, the dynamic implications of a local mode description. The prime question of interest has been "Can we observe selective bond photochemistry from highly excited local mode states?" The answer to this question, and our very ability to answer it, will be found in the answers to two other questions:

- 1) What processes determine the time evolution of an initially prepared local mode state, i.e., what are the coupling routes?
- 2) To what extent can we gain information about these processes from observable spectroscopic parameters, e.g., overtone bandwidths?

The local mode model maintains that the initial state prepared in the high energy overtone region is a nonstationary state $|v, 0\rangle$. (We now generalize the notation and identify $|v, 0\rangle$ with a state which corresponds to all v quanta in a single one of a set of equivalent XH oscillators and zero quanta in all of the rest.) Let us identify the possible processes in the time evolution of such a state.

- 1) $|v, 0\rangle \rightarrow |0, v\rangle$. This process would involve the transfer of all v vibrational quanta from one local oscillator to another equivalent local oscillator.
- 2) Off-resonance coupling of $|v, 0\rangle$ to a higher energy state $|v-1, 1\rangle$, where now one quantum has been transferred to another equivalent local mode. The state $|v-1, 1\rangle$ has higher energy due to its lower anharmonicity. This process has been considered in detail for benzene by Heller and Mukamel.²⁸
- 3) Direct resonant coupling of $|v, 0\rangle$ to the full set of molecular vibrational states. This process has been considered by Sage and Jortner.²⁹

4) Resonant coupling of $|v, 0\rangle$ to a subset of molecular vibrational states of the type $|v-1, 0; nm\rangle$, where the lower frequency normal modes are excited to the degree required to produce an approximately degenerate state. This process could be followed by sequential coupling of these states to $|v-2, 0; nm\rangle$ and eventually to the full vibrational bath. Such a process has been considered by Stannard and Gelbart.³⁰

The first process differs in nature from the last three. The last three processes all represent vibrational energy redistribution whereas the first process is simply an energy hopping or exciton-like process. For higher energy vibrational excitation, we have already noted, from the water example in the introduction, that this process will be relatively slow. Let us therefore neglect it.

Of the remaining processes, for reasonably large molecules, in our view, the most likely is process four. Therefore we shall examine the implications of this process in further detail.

The rate of this process, and therefore its ability to compete with the other processes, will depend both on the size of the molecule and on the level of excitation. At a given level of excitation, we could imagine limiting cases analogous to those found in the theory of radiationless transitions.³¹ For small molecules there will be few states of the type $|v-1, 0; nm\rangle$, near the energy of $|v, 0\rangle$ i.e., a sparse coupling limit. For large molecules the states $|v-1, 0; nm\rangle$ will effectively provide a continuum, i.e., the statistical limit.

Now consider a gas phase overtone spectrum, where line broadening due to intermolecular perturbations can be neglected. In the large molecule limit, the broadening due to coupling to the resonant $|v-1, 0; nm\rangle$ states will be much larger than any rotational spacing. Therefore a Lorentzian line should be observed whose width will be determined by the rate of the redistribution process. Such band-shapes have been observed in the photoacoustic gas phase overtone spectra of benzene and related molecules, as measured by Berry and his co-workers.³²

In the small molecule limit, we could envisage a case where the rotational spacing is larger than the intrinsic redistribution width, both because of the smaller molecular mass and the slower rate of the redistribution process in the sparse coupling limit. In this case we should see rotational fine structure associated with transitions to symmetrized local mode states analogous to $(v, 0)_{\pm}$. In the limit, when

the splitting between such states is small, we should observe rotational fine structure associated with the nonstationary state $|v, 0\rangle$.

In a recent reinvestigation of the overtone spectrum of acetylene,³³ we have pointed out that the most natural description of the spectrum is in terms of the local mode model. Transitions to states with $\Delta v \geq 3$, show a regular rotational pattern similar to those associated with a single vibrational state.

However, our recent work on the gas phase overtone spectrum of neopentane³⁴ raises some puzzling questions with regard to the interpretation of high energy overtone spectra. The spectrum of neopentane shows overtone bandwidths that are uncharacteristically narrow. For benzene, at a pressure of 70 torr, Berry and his coworkers have observed a bandwidth of 109 cm^{-1} at $\Delta v = 5$.³² However, for neopentane, at a pressure of 200 torr, we have observed a bandwidth of 64 cm^{-1} .³⁴

At first sight, both a local mode coupling model²⁸ and a statistical coupling model²⁹ should be more efficient in neopentane than in benzene. In neopentane, the three hydrogens of the methyl group are bound to a common carbon. Therefore they should be much more strongly coupled than in benzene and redistribution between these local CH modes should be more rapid in neopentane. Neopentane has 17 atoms compared to only 12 for benzene. Therefore the overall density of vibrational states will be greater in neopentane and any statistically governed process should be more rapid.

We have recently obtained the gas phase overtone spectrum of tetradeuteroneopentane, $(\text{CH}_2\text{D})_4\text{C}$.³⁵ Contrary to our expectations, the bandwidth at $\Delta v = 5$ ($88 \pm 5 \text{ cm}^{-1}$) is significantly broader than in neopentane itself.

One possible explanation of all of these seemingly conflicting observations is that the overtone bandwidth is not determined solely by intramolecular vibrational energy redistribution. Possibly, for the high amplitude excursions associated with these overtones, the spectral perturbations associated with intermolecular interactions become much more important than for lower energy transitions. Thus high energy overtone spectra may have to be observed at extremely low pressures before the limit is reached where the lineshape is determined by purely intramolecular vibrational energy redistribution. However, it should also be noted that the recent experiments by West *et al.* on tetramethyldioxetane seem to indicate that the overtone bandwidth

is virtually unchanged on going from room temperature to a cooled supersonic beam.³⁶

Are we any closer to the answer to the question raised at the beginning of this section? In our view, if the $|v-1, 0; nm\rangle$ coupling route is the dominant one, and if the sequential coupling of these states to the full, vibrational bath is relatively slow, then, although selective bond photochemistry would not be observed, it should be possible to see nonstatistical photochemistry as the bulk of the vibrational energy would remain effectively trapped in a subset of the full set of molecular vibrational states.

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