Use of Local Modes in the Description of Highly Vibrationally Excited Molecules

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The existence of normal modes of vibration is elegantly demonstrated in a film by Crawford and Overend.[1] A loosely coupled eccentric motor excites a ball and spring model of the carbon dioxide molecule. As the frequency of rotation of the motor increases, the chaotic motions of the excited "atoms" are resolved into a coherent bending motion. A further increase in the frequency of the motor again procedures chaos until, at some higher frequency, the symmetric stretching motion appears and finally, at even higher frequency, the antisymmetric stretch. Thus we see directly that at these "natural" frequencies each "atom" in the "molecule" is moving with the same frequency and phase so that each "atom" reaches its position of maximum displacement at the same time and each "atom" passes through its equilibrium position at the same time.

These are the familar characteristics of normal modes and they arise analytically from the assumption that vibrational motion in polyatomic molecules follows a harmonic force law. In terms of the normal coordinates, Q_i, along which normal-mode motion occurs, both the potential and kinetic energies are diagonal in the harmonic approximation (eq 1). Thus the molecule can be considered as being made up of $3N - 6(5)$ uncoupled harmonic normal modes.

$$2T = \sum_{i=1}^{3N-6} \dot{Q}_i^2$$

$$2V = \sum_{i=1}^{3N-6} k_{ii} Q_i^2 \qquad (1)$$

This description takes us a long way in understanding the fundamental and lower overtone regions of the infrared spectrum of molecules. However, on purely physical grounds it cannot be valid under all conditions. If we continually pump energy into the vibrational motions of a molecule, we will produce dissociation, a distinctly nonharmonic phenomenon! Moreover, intuition suggests that the molecule will follow low-energy pathways to dissociation. These pathways are unlikely to be those along normal coordinates. Consider, for example, the CH stretching motions of benzene. Dissociation along the Q_i associated with, say, the totally symmetric stretching mode requires the simultaneous breaking of all six CH bonds, a prohibitively high-energy process. The rupture of one or two CH bonds is more likely. Expressed in terms of a normal-mode basis, the coordinate corresponding to the rupture of one or two CH bonds involves the coupling of several normal modes. For example, the in-phase superposition of the symmetric (a_{1g}) CH stretching and the antisymmetric (b_{1u}) CH stretching modes involves motion of only three CH bonds. Further coupling of the normal modes can lead to the motion of fewer bonds.

Deviation from the harmonic approximation is generally referred to as anharmonicity. Anharmonicity then must account for the fact that at large internuclear distances the vibrational potential varies more slowly than quadratically with distance and eventually becomes constant at the dissociation energy of the oscillator. The effects of anharmonicity will be to reflect this change in potential and, as a result, to destroy the purely Hermite polynominal character of the vibrational wave functions. If the actual wave functions are expressed in terms of normal modes, the latter are now strongly coupled. The physical manifestations of anharmonicity are that transitions, forbidden in a purely harmonic approximation, become allowed to some extent. Also, dissociation and chemical reactions involving bond breaking become possible.

This Account discusses attempts by ourselves and others to develop a model for highly vibrationally excited molecules. We will ask how far the harmonic approximation and the normal modes resulting from this approximation will take us. We will first show how evidence for normal-mode coupling can be obtained from relatively high-energy vibrational overtone spectra. A precise analysis of band shapes and band widths will demonstrate the limitations of a normal-mode description of transitions, for example, as low in energy as $\Delta v = 3$ in CH stretching. We will then show how an alternative, simplified description in terms of local coordinates leads to a correct description of the properties of overtone spectra and to interesting predictions about the spectral properties of wide classes of molecules.

This ability to account for overtone spectra is in itself a sufficient rationale for the development of a general description of highly vibrationally excited molecules. However, such a description will find application in a number of other areas of physics and chemistry. Radiationless transitions between molecular electronic states involve the conversion of the electronic energy difference between two states into vibrational energy of the lower state. The transitions most extensively studied to date are those with the ground state as the lower state. In general, this state contains a large amount of molecular vibrational energy. Thus, a correct theoretical description of a radiationless transition must account for the vibrational properties of this terminal

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[1] B. Crawford, Jr., and J. Overend, Molecular Spectroscopy, Chemistry Study Film, Modern Learning Aids, New York, N.Y.

state. Another area in which highly vibrationally excited molecules are of importance is in the understanding of unimolecular reactions. In particular, an understanding of the pathways of energy flow in a molecule that ultimately lead to fragmentation requires a description of the vibrational states involved. At the conclusion of the paper we will give a very brief account of how the model might be applied in these areas.

Overtone Spectra—Evidence for Normal-Mode Coupling

The conventional description of overtone spectra maintains symmetry adapted normal modes, but introduces anharmonicity as a perturbation. Cubic and quartic terms now occur in the potential-energy expression, and these terms contain products involving different normal coordinates:

$$V = \sum_{i} k_{ii} Q_i^2 + \sum_{i,j,k} \alpha_{ijk} Q_i Q_j Q_k + \sum_{i,j,k,l} \beta_{ijkl} Q_i Q_j Q_k Q_l \qquad (2)$$

where

$$\alpha_{ijk} = \left. \frac{\partial^3 V}{\partial Q_i \partial Q_j \partial Q_k} \right|^0$$

$$\beta_{ijkl} = \left. \frac{\partial^4 V}{\partial Q_i \partial Q_j \partial Q_k \partial Q_l} \right|^0$$

Perturbation theory can then be used to calculate the modifications of the vibrational states caused by the additional terms. This approach is straightforward in principle but tedious in application. A more fundamental criticism is that the perturbations can be large enough to vitiate the assumptions of second-order perturbation theory.

In practice, the energy is often fitted to an equation of the form

$$E = E_0 + \sum_{K} v_K \hbar \omega_K + \sum_{K \geqslant L} v_K v_L X_{KL} \qquad (3)$$

The α's and β's can be related to the X's through perturbation theory, but for larger molecules (>6 atoms) this equation is often used empirically. Even this greatly simplified approach is fraught with difficulties. There is a large number of the X's and, because they are expressed in terms of normal modes, it is difficult to relate them to molecular structure and to know when a reasonable set has been found.

Let us qualitatively describe what one might expect for the general structure of an overtone spectrum arising from a set of nearly degenerate anharmonic normal modes. Consider the four CH stretching modes of benzene, A, B, C, and D (symmetric stretching, antisymmetric stretching, and the two degenerate stretching modes, respectively). If, for the moment, we neglect degeneracy, there are ten anharmonicity constants, X_{AA}, X_{BB}, X_{AB}, etc. The character of the $\Delta v_{CH} = n$ group of transitions is obtained from the following analysis. The n quanta are first distributed over the four modes. Then, those distributions are selected which correspond to wave functions with the allowed symmetry to interact with electric dipole radiation. The states have different energies because the anharmonic constants, X_{KL}, in eq 3 are unequal. The number of such "allowed" states increases rapidly as n increases. There are 3 for n = 2 and 75 (doubly degenerate) states for n = 6. Thus one might expect, for the higher and higher overtones, a complicated series of bands, or an increasingly broad single band if the components are not resolvable. As we shall see, although this description appears valid for lower overtones (Δv = 2, 3), it does not agree with experimental observations for the higher overtones.

Let us, at the outset, restrict our attention to XH stretching transitions. Their high frequency allows the modes involved in these transitions to be considered separately from the other vibrational modes. Moreover, because of their relatively high intensity and energy, the XH stretching overtone transitions are particularly easy to identify in the overtone spectrum.

It we consider the OH stretching overtone spectrum of water, there is enough experimental information to obtain values for the anharmonicity constants involving the symmetric (A) and the antisymmetric (B) stretching modes:[2] $X_{AA} = -43.9$ cm^{-1}, $X_{BB} = -46.4$ cm^{-1}, and $X_{AB} = -155.1$ cm^{-1}. As pointed out by Siebrand and Williams,[3] the diagonal values can be explained on the basis of the Morse relation for diatomic molecules, eq 4,

$$X = \frac{-\omega^2}{4D} \qquad (4)$$

which relates X to the dissociation energy. Because dissociation according to either of the normal modes of water requires rupture of two OH bonds, X_{AA} and X_{BB} should equal about one-half the value of X for the OH radical ($X_{OH} = -82.8$ cm^{-1} [4]). On the other hand, the off-diagonal normal-mode anharmonicity is twice as large as the anharmonicity constant of the OH radical. Superposition of the two normal modes yields a mode in which only one OH bond is stretched. Because the anharmonic content of the vibrational energy increases as the square of the quantum number, n, the pairwise coupling of normal modes must strengthen at increased vibrational energies. In consequence, the vibrational pattern will display an increasing local character as n increases.

The discrepancy beteen diagonal and off-diagonal normal-mode anharmonicity constants will be more pronounced the greater the number of equivalent bonds. If we again consider the CH stretching vibrations of benzene, there are six CH oscillators. Thus we might expect the diagonal normal-mode anharmonicity constants to be quite small and the off-diagonal or coupling constants to carry even greater relative weight than they do in water.

Normal modes are based on infinitesimal motions. Let us choose modes associated with the other extreme, that is bond breakage, and call the vibration associated with single bond breakage a local mode. The vibrational energy in terms of these modes is given by eq 5,

$$E = E_0 + \sum_{i} v_i \hbar \omega_i + \sum_{i>j} c_{ij} \omega_{ij} + \sum_{i \geqslant j} v_i v_j X_{ij} \qquad (5)$$

where the ω_{ij} are harmonic coupling terms, which depend on the frequency differences between the local modes. For a series of CH oscillators, as in benzene, there terms are small and can be neglected. Because

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(2) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945.

(3) W. Siebrand and D. F. Williams, *J. Chem. Phys.*, **49**, 1860 (1968).

(4) G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed., Van Nostrand-Reinhold Co., New York, N.Y., 1950.

it takes less energy to dissociate along a local coordinate than along a normal coordinate, the previous arguments mean that the diagonal anharmonicity constant is larger in a local-mode representation than in a normal-mode representation. A comparison of eq 3 and 5 shows that the off-diagonal normal-mode anharmonicities, that is, those that couple the normal modes, must be substantially greater than the off-diagonal local-mode anharmonicities. Thus, for a set of equivalent bonds, as anharmonicity becomes more and more important with increasing vibrational amplitude, the vibrational energy becomes increasingly more diagonal in a local-mode representation than in a normal-mode representation.

These local-mode ideas can be used to obtain the normal-mode anharmonicity constants X_{KL}, and thus to describe the spectrum in terms of the components of anharmonically coupled normal modes. We have carried out such an analysis for benzene[5,6] and for ammonia and methane.[7] Let us consider benzene as an example and briefly outline the method.

We first use the equivalence of the energies in eq 3 and 5 to express the normal-mode anharmonicity constants (X_{KL}) in terms of the local-mode anharmonicity constants (X_{ij}). The diagonal local-mode anharmonicity X_{11} can be obtained by analogy with the relationship for Morse oscillators[6] (eq 4). If one assumes that off-diagonal local-mode coupling is negligible, numerical values for the normal-mode anharmonicities can be found. Given these normal-mode anharmonicities and the fundamental frequencies, we can calculate the energy of each allowed normal-mode component within a given overtone band. The components are assigned a weighting based on their anharmonicity. Because it is the departure from harmonicity that allows overtones to occur at all, it is reasonable that the more anharmonic components will contribute more to the intensity. Taking the energy of a component as an abscissa and its calculated intensity as an ordinate, we can generate Lorentzian bands for each component. The bands are summed and an overall band maximum is obtained for each overtone band out to $\Delta v = 8$.[5,6]

The results are in essentially exact agreement with the experimental spectrum of Ellis[8] for transitions with $\Delta v_{\mathrm{CH}} \geq 4$. The generated set of normal-mode anharmonicity constants is: $X_{\mathrm{AA}} = -9.6\ \mathrm{cm}^{-1}$; $X_{\mathrm{CC}} = -19.2\ \mathrm{cm}^{-1}$; $X_{\mathrm{CD}} = -86.3\ \mathrm{cm}^{-1}$; $X_{\mathrm{AC}} = -183.5\ \mathrm{cm}^{-1}$; and $X_{\mathrm{AB}} = -57.5\ \mathrm{cm}^{-1}$. The paramount importance of off-diagonal coupling in the normal-mode representation is clearly evident. Essentially the same results were obtained for ammonia and methane, although there was some evidence for off-diagonal local-mode coupling in these molecules.[7]

In summary it appears that this method, which uses the concept of weakly coupled local modes, can successfully account for the average energies of XH stretching overtone spectra. The spectra are described in terms of the components of highly coupled anharmonic normal modes. However, a closer examination of the characteristics of the spectral bands reveals two difficulties. In general, the observed spectral width of the overtone bands is much smaller than expected on the basis of the calculated energies of the anharmonic normal-mode components. Moreover, the spectra seem simpler than expected, and any traces of structure due to the different symmetry-allowed normal-mode components seems to rapidly disappear.

It is as if the description of the excited state in terms of a linear combination of normal modes is breaking down for a highly vibrationally excited molecule. Furthermore, the presumption that all of the symmetry-allowed normal-mode combinations will be excited seems to be invalid. It appears that the radiation field only sees a specific group of the symmetry-allowed normal-mode components. In fact, as we shall see, these components are the ones that contain the most anharmonicity. Because for normal modes most of the anharmonicity is contained in off-diagonal or coupling anharmonicity constants, the components selected by the radiation field are those in which the normal modes are most strongly coupled. These are just single local modes. Thus, for high vibrational excitations, we do not expect the large number of "allowed" states predicted by a normal-mode analysis, but instead the relatively small number corresponding to the multiple excitation of local modes.

However, the analysis given above is capable of providing accurate numerical predictions of band maxima, despite its description of the spectrum in terms of anharmonic normal-mode components. In order to understand its success, given the apparent unsuitability of a normal-mode representation, we examine in some detail the experimental band shapes and band widths in the CH stretching overtone spectrum of a particularly simple molecule, dichloromethane. We will demonstrate how these transitions, in particular, and XH stretching contributions to overtone spectra, in general, can be understood solely in terms of local-mode concepts without any recourse to normal-mode components.

CH Stretching Overtone Spectrum of Dichloromethane—A General Local Mode Theory

A detailed examination of the general patterns in overtone spectra and band shapes shows clearly that the method just described overlooks an overall simplicity characteristic of all the XH stretching overtone spectra observed to date. The effects mentioned at the end of the last section show up clearly in dichloromethane. The overtone spectrum of this liquid out to $\Delta v_{\mathrm{CH}} = 6$ exhibits a series of relatively narrow CH stretching overtone bands which lack structure.[9] Combination activity appears between $\Delta v_{\mathrm{CH}} = 3$ and $\Delta v_{\mathrm{CH}} = 4$, and again between $\Delta v_{\mathrm{CH}} = 4$ and $\Delta v_{\mathrm{CH}} = 5$.

It is extemely straightforward to apply the technique described earlier for benzene and to analyze this overtone spectrum in terms of the components of anharmonically coupled normal modes. There are only two nondegenerate CH stretching modes, so that eq 3 and 5 immediately yield equivalence relations between the diagonal and single off-diagonal normal-mode anharmonicity constants, on the one hand, and the corresponding local-mode anharmonicities, on the other. If we take the diagonal local-mode constant from

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(5) B. R. Henry and W. Siebrand, *J. Chem. Phys.*, **49**, 5369 (1968).

(6) R. J. Hayward, B. R. Henry, and W. Siebrand, *J. Mol. Spectrosc.*, **46**, 207 (1973).

(7) R. J. Hayward and B. R. Henry, *J. Mol. Spectrosc.*, **50**, 58 (1974).

(8) J. W. Ellis, *Trans. Faraday Soc.*, **25**, 888 (1929).

(9) R. J. Hayward and B. R. Henry, *J. Mol. Spectrosc.*, **57**, 221 (1975).

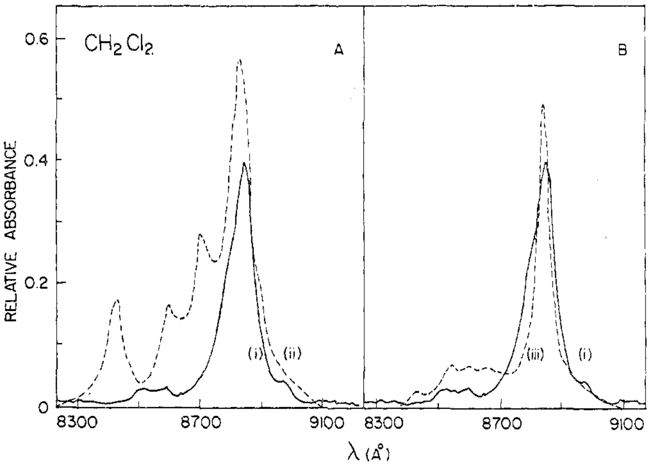

Figure 1. Taken from Figure 5 of ref 9, copyright Academic Press. Calculated and observed CH stretching overtone band of dichloromethane corresponding to $\Delta v_{\mathrm{CH}} = 4$. (A) (- - - -) Calculated curve based on anharmonic normal-mode components; (—) low-resolution experimental spectrum; (B) (- - - -) computed spectrum of overtones and combinations of the modes with frequency and anharmonicity 2991 (−55), 2991 (−55), and 1429 (0) cm^{-1} with a weighting of the fundamental local-mode overtone 50 times that of a combination band of the same degeneracy. All computed components were assigned a band width of 80 cm^{-1}.

methane[10] and, as we did in benzene, set the off-diagonal or coupling local-mode constant equal to zero, we can obtain the numerical values of the normal-mode anharmonicity constants and thus calculate the energies of the normal-mode components for any given overtone band.[9] If these components are weighted according to their anharmonicity and the total overtone band is constructed as a sum of Lorentzians (as in the case of benzene), one obtains the results displayed on the left-hand side of Figure 1 for the $\Delta v_{\mathrm{CH}} = 4$ transition. The solid curve corresponds to an experimental spectrum of slightly lower resolution than is optimally possible under our experimental conditions,[9] and the dotted curve corresponds to what is calculated on the basis of anharmonic normal-mode components.

It is clear from a comparison of the two curves why this method can successfully predict band maxima. Because the components are weighted by their anharmonicity, the lower frequency components are given the most weight. It is also clear why the method overestimates spectral width. The highest frequency normal-mode components, which correspond in normal-mode language to pure normal-mode overtones (e.g., 4 quanta of A_1), do not seem to contribute much at all. In fact, if we examine the whole series of experimental CH stretching overtone peaks out to $\Delta v_{\mathrm{CH}} = 6$, we find generally that the observed overtone progression resembles the series of the most anharmonic normal-mode components.[9] These are the components for which anharmonic coupling between the normal modes is greatest and which, as indicated previously, correspond to the multiple excitation of a single local oscillator. Thus there is evidence that the radiation field and the molecule interact in such a way that the field selectively drives states of local excitation.

It is possible to reproduce the observed band shape on the basis of the local-mode model. Two degenerate CH local oscillators are assigned a frequency lying between the two normal-mode frequencies and a diagonal local-mode anharmonicity the same as for methane.[10] These modes, along with a single harmonic CH bending normal mode (1429 cm^{-1} [2]), are entered in an anharmonic modification of a computer-programmed state counting algorithm described by Beyer and Swinehart and by Stein and Rabinovitch.[11] The program generates all possible combination and overtone states of the input modes. The dotted curve on the right of Figure 1 is obtained by weighting those generated components with all of the energy localized in a single CH stretching oscillator 50 times as compared to other combination components. Lorentzians are then constructed for each component and are summed to obtain the resultant curve. The weighting is a parameter, and actually a value of 80 gives the best fit, but the curves of Figure 1 illustrate the nature of the result. The agreement of the experimental and calculated curve is very good and suggests the following selection rules:[9] (*1*) *Local-mode overtones involving high frequency oscillators are the most intense, but decrease rapidly in intensity with increasing* Δv. (*2*) *Combination bands involving degenerate oscillators of high frequency and combination bands involving modes of high and low frequency appear with much less intensity than pure local-mode overtones.*

A similar pattern is observed for higher overtone bands. For the $\Delta v_{\mathrm{CH}} = 5$ band, the calculated normal-mode components again span a wider energy range than does the observed band. However, it is possible to account for the band shape and width on the basis of the same three modes used to describe $\Delta v_{\mathrm{CH}} = 4$, except that here the "pure local-mode overtone" is assigned a weight 200 times that of a combination band of the same degeneracy. Lower ratios than this give wings to the spectrum that are not observed experimentally. The successful description of this band suggests a third selection rule:[9] (*3*) *Combination bands fall off more quickly in intensity than the local-mode overtone bands.*

In other words, this effective weighting of pure local-mode overtones relative to combinations increases with increasing Δv. This result is heartening in the sense that, for lower overtones, the relative intensities of these combination bands will increase, and this is what is required at lower Δv for convergence to the more traditional normal-mode overtone combination pattern. This latter description generally does fit the data in the first and second overtone regions of many molecules. A similar analysis for $\Delta v_{\mathrm{CH}} = 6$ shows that the structural aspects of this band correspond to just those expected for single oscillator excitation lacking any discernible combination component.[9]

An investigation, at somewhat higher resolution, of the region between the CH overtones has been carried out for dichloromethane and for chloroform.[12] These transitions are generally weaker than the pure overtone transitions, and they vanish for higher overtones. The two spectra show marked similarities. The presence of the extra CH oscillator in dichloromethane gives rise to a well-resolved combination band of the two local CH modes, which appears just to the high energy side of the

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(10) The experimental dissociation energy for $CH_2Cl_2 \rightarrow CHCl_2 + H$, which is needed to obtain X_{11} from the Morse relation via eq 4, is not known.

(11) S. E. Stein and B. S. Rabinovitch, *J. Chem. Phys.*, **58**, 2438 (1973).

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

$\Delta v_{CH} = 4$ overtone. In keeping with the trend noted in selection rule 3, no local-mode combination band is resolved for $\Delta v_{CH} = 5$ of dichloromethane. Its presence is suggested by a slight asymmetry on the high-energy side of the band.

The other combination bands in the region between $\Delta v_{CH} = 4$ and $\Delta v_{CH} = 5$, for both chloroform and dichloromethane, can be assigned to the multiple excitation of a local CH oscillator with the addition of 1 quantum of a lower frequency normal mode.[12] Thus, for chloroform the major combination bands at 1155 cm^{-1} and 747 cm^{-1} to the high-energy side of $\Delta v_{CH} = 4$ correspond to coupling of the local-mode overtone with the normal CH bend (1205 cm^{-1} [2]) and CCl stretch (760 cm^{-1} [2]). The spectrum is somewhat more congested in dichloromethane due to the presence of the local-mode combination band, but the observed peaks at 726, 886, and 1095 cm^{-1} from $\Delta v_{CH} = 4$ most probably correspond to coupling of the local-mode overtone with the normal mode[2] CCl stretch (737 cm^{-1}), the rocking mode (899 cm^{-1}), and the torsional mode (1155 cm^{-1}).

The presence of local-mode combinations shows that off-diagonal coupling between local modes is not zero. Similarly, the combination bands involving local modes and lower frequency normal modes demonstrate couplings between these modes as well. However, the magnitude of both these couplings appears small in comparison to the diagonal CH local-mode anharmonicities.

Other Molecules and the Effect of Nonequivalent CH Groups

The situation where a single molecule contains nonequivalent CH groups has interesting ramifications within the local-mode model. A parameter, $\omega_{CH}{}^{D}$, is useful in a discussion of the differences between the overtone spectra of different molecules and of the structure within overtone transitions of molecules with nonequivalent CH groups. $\omega_{CH}{}^{D}$ is the CH stretching frequency in a molecule in which all the hydrogens but one are replaced by deuterium. This deuterium-decoupled CH stretching frequency should reflect the nature of the individual CH bond in the undeuterated molecule. In fact, one finds that this parameter directly relates to the energies of the CH stretching overtone transitions of a whole series of molecules.[12]

We have examined the overtone spectra in the region from $\Delta v_{CH} = 3$ to $\Delta v_{CH} = 6$ for benzene, toluene, and the three xylenes.[12] The $\Delta v_{CH} = 4, 5, 6$ transitions in benzene are all single peaks corresponding to the overtones of an aryl CH local mode. In toluene a clearly resolvable peak appears to the low-energy side of the aryl peak and at the same energy observed for the corresponding transition in ethane. This alkyl CH peak is more intense for the three xylenes than for toluene, and there is actually a rough correlation of relative peak areas and the relative numbers of aryl and alkyl hydrogens. A similar pattern is observed for the $\Delta v_{CH} = 3$ transition, although we begin to see the complications expected as the normal-mode pattern begins to assert itself. The difference in $\omega_{CH}{}^{D}$ between benzene and ethane is about 100 cm^{-1}, and we would expect this difference to be multiplied by approximately n for a $\Delta v_{CH} = n$ transition. On this basis we would predict that the transitions due to the two groups would be resolvable and appear in the spectrum as two distinct local-mode bands, as they clearly do. The measured frequency separation between the alkyl and aryl peaks does decrease from $\Delta v_{CH} = 5$ to 4 to 3 (e.g., for p-xylene, ω(aryl) − ω(alkyl) goes from 495 to 395 to 297 cm^{-1}, respectively).[12] Such a direct magnification of $\omega_{CH}{}^{D}$ is only expected, even in a local-mode model, if off-diagonal local-mode couplings are small.

The $\Delta v_{CH} = 6$ overtone transitions of benzene and of three methyl-substituted benzenes have been observed by Swofford et al. using thermal lensing spectroscopy.[13] This technique has greater sensitivity than direct absorption and has also permitted the authors to study the $\Delta v_{CH} = 6$ transitions of benzene, naphthalene, and anthracene dissolved in CCl_4. The observations follow the familiar pattern expected on the basis of a local-mode model. The energy of the transition corresponding to $\Delta v_{CH} = 6$ for the aryl CH stretching mode and its full width at half-maximum are relatively unchanged from molecule to molecule. Methyl substitution gives rise to an intensity drop in the aryl peak and the appearance of an alkyl peak at lower energy. It is interesting that, in anthracene, a high-energy shoulder on the peak may be due to a different energy for the CH stretching local modes at the 9,10 positions. The unchanging spectral width is especially notable given the large difference in the predicted number of allowed states for the different molecules; however, it is expected on the basis of selection rules two and three. The authors provide a formal justification of the constant width by showing that, for a model consisting of a set of uncoupled local modes, only one state is spectroscopically allowed for $\Delta v_{CH} = n$. In benzene, this is the sixfold degenerate state $(n,0,0,0,0,0)$, $(0,n,0,0,0,0)$ etc., where all the vibrational energy exists in a single local mode.

A similar point had been made by Wallace in a discussion of the CH overtone spectrum of benzene.[14] In this paper, the author describes the vibrational states of H_2O in terms of two Morse oscillators and of a harmonic bending mode. Analytic solutions to the eigenvalue problem are obtained and the intensities expected from the various contributions to the overtone transitions are calculated. However, when benzene is treated as a collection of CH stretching Morse oscillators, the zero-coupling approximation is maintained and the results are equivalent to those obtained by the approaches discussed earlier.[9,13]

Both Wallace[14] and Swofford et al.[13] use symmetry-adapted combinations of local-mode functions $(n,0,0...)$ in their calculations. If local-mode coupling is neglected, the numerical results are equivalent to those obtained from the local mode functions themselves $(n,0,0...)$. The conceptual role of symmetry in a local-mode description is one that will likely continue to be the subject of lively debate.

A significant application of the local coordinate concept has been made recently by Bron and Wallace.[15] They have developed a theory which calculates the anharmonic correction to the ground rotational–vibrational energy of a polyatomic molecule. They have assumed that the anharmonic contributions to vibration are solely associated with bond-stretching coordinates

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

(14) R. Wallace, *Chem. Phys.*, 11, 189 (1975).

(15) J. Bron and R. Wallace, submitted for publication.

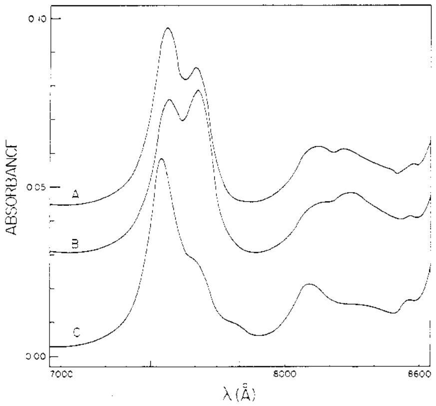

Figure 2. The experimental liquid phase room temperature overtone spectra in the region of $\Delta v_{\mathrm{CH}} = 5$ for (A) *n*-pentane, (B) *n*-heptane, and (C) 3-methylpentane. Path length 10 cm. The absorbance of curves A and B have been off set by 0.04 and 0.02 absorbance unit, respectively.

and that such bond stretchs follow a Morse potential. Such an approach greatly simplifies the calculation of this correction, which is necessary to obtain the correct partition functions for such systems.

We have studied the high-pressure gas- or liquid-phase overtone spectra out to $\Delta v_{\mathrm{CH}} = 6$ of the normal alkanes from methane to heptane, as well as the spectra of several branched alkanes.[16] The spectra clearly reflect the features expected on the basis of a local-mode model. Some of these features are illustrated in Figure 2 where we have presented the spectra of three typical molecules in the region of $\Delta v_{\mathrm{CH}} = 5$. $\omega_{\mathrm{CH}}{}^{\mathrm{D}}$ is greater by about 50 cm^{-1} for a hydrogen in a CH_4 environment, as in methane, than for a hydrogen in a CH_3 environment, as in ethane. Qualitatively, we expect this trend to continue to CH_2 and CH hydrogens. This expectation is borne out by the spectra. Throughout the series, the resolution of the CH_3 and CH_2 peaks is evident, with the CH_3 peak higher in energy. The CH peak appears at even lower energy than the CH_2 peak. Thus we associate a different diagonal local-mode anharmonicity and a different "harmonic" frequency with each of these three types of CH bonds. The intensity of the CH_2 peak relative to that of the CH_3 peak increases in a regular way from ethane to heptane. This is clearly illustrated in Figure 2 for pentane and heptane. In a similar fashion to the xylene results, the spacing between the two alkyl components, CH_2 and CH_3, increases from $\Delta v_{\mathrm{CH}} = 3$ to 4 to 5.

As in the overtone spectrum of dichloromethane, combination bands involving a local-mode overtone plus one quantum of a lower frequency normal mode are present in these spectra. In the spectra of Figure 2, the peak on the low-energy side of $\Delta v_{\mathrm{CH}} = 5$ is such a combination band involving the local-mode overtone $\Delta v_{\mathrm{CH}} = 4$. Throughout the series, and as evidenced in particular by a comparison of pentane and heptane in Figure 2, the doublet structure and the relative intensities of the doublet components in the combination band parallel that in the pure CH stretching overtone band. Although it is not evident in the $\Delta v_{\mathrm{CH}} = 5$ transition, in the $\Delta v_{\mathrm{CH}} = 4$ overtone the spectra show a small peak just to the high-energy side of the band. This small peak corresponds to a local-mode combination band.

There is a striking similarity between all these spectra especially in spectral band width. These similarities become more pronounced in the higher overtone regions. In fact, there are marked similarities of these spectra to the spectra of benzene, dichloromethane, and chloroform. Moreover the common features among the spectra are not entirely limited to the pure CH overtones. Although I have just outlined the qualitative features of the alkane spectra (a more quantitative treatment is to be found in ref 16), it is clear, even from this discussion, that these spectra demand a local-mode type of interpretation. Any attempt to describe them in terms of normal modes, with the predicted vast differences in both the number and types of vibrational states from molecule to molecule, is doomed to failure. Thus the local-mode and normal-mode models are complementary. The normal-mode approach is appropriate for the fundamental and to a lesser degree for the $\Delta v = 2$ region, but the local-mode model is required for $\Delta v \geq 3$ if we are considering XH stretching motions.

Two areas of current investigation, with reference to these spectra, are worth noting. In the development of a theory of the intermolecular perturbation of molecular potentials,[17] Dellinger and Kasha have suggested that the inhibition of large-amplitude vibrations in high-viscosity matrices may result in a change in anharmonicity for molecular vibrations describable by a Morse potential. We are currently investigating this possibility by an observation of the $\Delta v_{\mathrm{CH}} = 3$, 4, 5, and 6 CH stretching overtones for the CH_3 hydrogens in 3-methylpentane.[18] The preliminary results show that the diagonal local-mode anharmonicity decreases in magnitude from -60 to -54 cm^{-1} on going from the room temperature liquid to the glass at 77 K. It appears that intermolecular forces in the solid phase directly shape the molecular vibrational potential and render it more harmonic. These investigations are continuing and will be extended to a comparison of the gas and liquid phases.

Secondly, the structure in the $\Delta v_{\mathrm{CH}} = 4$ band of methane is very similar to the rotational structure observed for similar bands in simpler molecules such as acetylene;[12] in other words, it appears to have the features of the rotational structure of a single vibrational transition. The local-mode approach predicts that the single vibrational character of the transitions should become more pronounced at higher overtones. Thus we should see a concurrent simplification of the rotational structure. Such a possibility is currently under investigation in a study of the overtone transitions of the lighter alkanes at low pressures in a long pathlength cell.

Applications in Other Areas—Some Future Studies

As indicated in the introduction, the description of highly vibrationally excited molecules is of primary importance in the study of radiationless transitions, particularly of those transitions to the ground state where a large amount of vibrational energy is involved. The studies of Siebrand and others[19] have shown the

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critical importance of Franck–Condon factors in controlling the rates of these transitions. Much effort has been expended in constructing models and in attempts at accounting for the transition properties in various classes of molecules.[19] However, almost all the work has employed the harmonic approximation and thus used normal modes. In this Account, we have shown that the interpretation of high-energy overtone spectra requires a local-mode description. Firstly, we have shown that for high-energy CH stretching modes the couplings between normal modes are very large and that a local-mode representation leads to a more diagonal form of the energy matrix. Secondly, evidence has been presented to show that the radiation field selectively excites states of local character. In high-energy radiationless transitions, the CH stretching modes are of primary importance. However, the radiation field is not directly involved in the selection of the terminal state for a radiationless transition, and thus the second reason for preferring a local-mode representation does not apply. Nevertheless, the greater diagonality of a local-mode representation suggests that these modes are more in accord with physical reality than normal modes and thus should prove a better starting point in a representation of the terminal state in a radiationless process. We are currently investigating the effect of local modes on the calculation of Franck–Condon factors for radiationless transitions in specific molecules.

If local-mode states are closely related to the stationary states of the molecular Hamiltonian, we might expect a difference between the effective lifetime of a pure local-mode state and a combination state involving a local-mode overtone and 1 quantum of a lower frequency normal mode. One might also expect a somewhat longer time for vibrational "spreading" from a high-energy pure local-mode state than had heretofore been expected on the basis of a normal-mode description of such a high-energy vibrational state. We have recently determined the overtone spectrum of liquid guaiazulene.[20] This molecule is useful because the low energy of its first excited singlet state (S_1) provides the possibility of sequentially exciting that state in a biphotonic process via the intermediate overtone state. A pure local-mode overtone state and a combination state are spectrally placed and sufficiently isolated in this molecule so as to allow the possibility of such a process through either state. Thus with synchronized picosecond laser pulses, it should be possible to directly observe the dynamics of the vibrational state by monitoring the change in Franck–Condon factors for absorption into S_1. Such a possibility is currently under investigation.

A fundamental assumption of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory of unimolecular reactions is that only the energy of an initial state is important in the prediction of the time rate of molecular dissociation.[21] This assumed complete communication between highly excited vibrational states dictates that their mode of preparation will not affect their mode of decay. However, the description of local-mode overtones suggests that such states are only weakly coupled to other vibrations in the molecule. Such modes are unlikely to satisfy the rapid statistical redistribution conditions of RRKM theory. Moreover, small changes in energy are associated with distinctly different vibrational states, e.g., the difference between aryl and alkyl excited local-mode states. Recent molecular beam experiments involving the decomposition of C_2H_4F indicate a nonstatistical energy distribution.[22] Similarly, experiments on the laser-induced dissociation of $CClF_3$ and CCl_3F indicate that the energy distribution of the laser-activated reacting molecules is decidedly nonstatistical.[23] In fact, the results suggest that the primary process occurs with the excitation energy still in the vibrational mode into which it was absorbed.[23] These results are expected on the basis of a local-mode theory. As lasers become increasingly available, studies of the variation in the yield of photochemical products as a function of wavelength may well become common. These studies may provide convincing demonstrations of the limitations of this fundamental assumption of RRKM theory.

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