

Theory of vibrational overtone line shapes of polyatomic molecules

Donald F. Heller

Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960

S. Mukamel

Department of Chemistry, Rice University, Houston, Texas 77001

(Received 3 July 1978)

We present a general theory for the overtone absorption line shapes of isolated polyatomic molecules. The theory is based on a separation of the molecular vibrational degrees of freedom into: (1) a few relevant CH local modes which interact directly with the radiation field, and (2) the remaining "bath" modes which induce spectral broadening and determine the line shapes. Line shapes are evaluated using the standard Fano-Zwanzig scattering formalism. A simple yet general model is put forth to illustrate some of the features exhibited by polyatomic line shapes. Specific application is made to benzene. The model adequately accounts for the overtone line shapes recently observed by Bray and Berry. Within its context we are able to understand the observed vibrational state and isotopic dependence of the line shape and to predict line shapes for related but as yet unstudied systems. To our knowledge this is the first dynamical application of local mode theories. We discuss their advantages and the extent to which polyatomic line shapes can provide information about intramolecular energy redistribution processes.

I. INTRODUCTION

Studies of the dynamics of isolated, highly vibrationally excited polyatomic molecules are crucial to the detailed understanding of chemical reactions and photodynamics.¹ The development of new experimental techniques has dramatically enhanced the amount of available information regarding the dynamical behavior of polyatomic molecules. To date, some of the most useful techniques include chemical activation,² infrared chemiluminescence,³ molecular beams,⁴ and studies of molecular multiphoton processes.⁵ Unfortunately, these techniques are rarely directed toward obtaining detailed microscopic information about the intramolecular dynamics of highly vibrationally excited molecules.

Recent experiments by Bray and Berry⁶ on the overtone spectroscopy of benzene have yielded extremely valuable information regarding polyatomic intramolecular dynamics on the ground electronic potential energy surface. In these experiments, photoacoustic detection techniques were used to measure the overtone spectra of the CH stretching modes in several isotopically substituted benzenes under gas phase "collision-free" conditions. Absorption line shapes were determined for the observed 0- v transitions for $v=5, 6, 7$ at pressures of a few torr. The principal results of these experiments are:

(1) the $v=5, 6, 7$ overtone spectra of benzene all have well resolved bands. The positions of the band maxima (including the fundamental $v=1$) follow a simple anharmonic model for the levels, i.e.,⁷

$$E_v = \hbar\omega_0(v + \frac{1}{2}) - \hbar\omega_e X_0(v + \frac{1}{2})^2. \quad (1)$$

This behavior is similar to that observed previously by Martin and Kalantar and by Albrecht and co-workers⁷ for the whole $v=1$ through 8 overtone series in liquid benzene. Several other aromatic hydrocarbons (naphthalene, toluene, etc.) exhibit similar overtone bands in the liquid phase.⁸

(2) Each observed overtone ($v=5, 6, 7$) is a structureless band with a (homogeneous) width $\sim 100 \text{ cm}^{-1}$. (For comparison, the fundamental $v=1$ has a (rovibronic) width of 30 cm^{-1} and the overtone spectra in the liquid phase⁶ are much broader having width $\approx 300 \text{ cm}^{-1}$.) This width, which cannot be interpreted as unresolved rotational structure, implies a "lifetime" of roughly 5×10^{-14} sec or 30 vibrational periods.

(3) The 0-5 band is slightly asymmetric, whereas the 0-6, 0-7 bands are symmetric Lorentzians.

(4) The 0- v bands become narrower with increasing v for $v=5, 6, 7$. These widths are 109, 94, and 87 cm^{-1} , respectively.

(5) In deuterated benzenes (H1, H2, H5), the absorption becomes weaker (in rough proportion to the number of H atoms) but the width and peak positions do not change appreciably and observations (1) through (3) hold. Observation (4) holds as well except for the H1 case in which the observed line width increases slightly with v .

(6) The CH stretching overtone bands are accompanied by a continuum of background absorption whose relative intensity increases with the overtone quantum number. The magnitude of this background is uncertain at present.

Observation (4) is one of the most striking results of these experiments. It is very surprising that the width does not grow strongly with v (as might be expected from the rapid increase in density of vibrational states), but rather decreases with increasing v . This behavior is in stark contrast to that observed in optical selection studies of benzene and other molecules⁹ where the rates of intramolecular electronic (nonradiative) relaxation typically increase with the excitation energy (corresponding to broadening of the absorption line with increasing energy). There is additional recent evidence⁸ that similar narrowing behavior also occurs in the C-H stretching overtones of other polyatomics and may well be general

for a rather large class of molecules. Observation (4) together with (3) is very much reminiscent of the motional narrowing phenomena observed in magnetic resonance.^{10,11} There, due to rapid motions of spin systems, complicated line shapes become narrow Lorentzians, e.g., with increasing temperature.

In this paper we present a theory for the overtone line shapes of polyatomic molecules. We use a general energy redistribution (relaxation) model which unifies all the experimental findings⁶ mentioned above and interprets them in terms of molecular parameters. Behavior for as yet unexamined deuterium-substituted benzenes is also predicted. We explore specific coupling schemes to illustrate explicitly how the observed line shape narrowing phenomenon can be understood in terms of the intramolecular interactions (anharmonicities). The present study and especially the discussion of intramolecular dephasing has direct implications for coherent transient spectroscopy of large molecules¹² and for studies of molecular multiphoton processes.^{5,13}

II. THE MOLECULAR HAMILTONIAN AND LOCAL MODES

To study the vibrational overtone spectroscopy of large molecules one must clearly go beyond the harmonic approximation for the molecular (nuclear) Hamiltonian. The obvious reason is that within the harmonic model, overtone spectra (i.e., transitions with changes in quantum number > 1) are strictly forbidden in the electric dipole and crude Born-Oppenheimer approximations.¹⁴ The presence of anharmonicities is thus necessary to induce the overtone spectra, to determine the positions of the unequally spaced absorption lines, and to produce the homogeneous broadening of nondissociative states. In this sense, the overtone line shape problem is much more complicated than the analogous problem of radiationless processes in electronically excited polyatomics^{9,15-17} for which a purely harmonic model suffices to account for the basic processes. Here, any order treatment of the problem must include anharmonicities. On the other hand, the fact that the positions of the overtone lines (up to $\nu = 8$ in benzene) fit fairly well to a simple anharmonic model^{8,18} [Eq. (1)] suggests that one need not go much beyond the harmonic approximation to uncover the important phenomenology.

We consider the following Hamiltonian:

$$H_m = \sum_i -\frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial q_i^2} + \sum_i C_{ii} q_i^2 + \sum_{i \geq j \geq k} C_{ijk} q_i q_j q_k + \sum_{i \geq j \geq k \geq l} C_{ijkl} q_i q_j q_k q_l + \text{higher order terms} \quad (2)$$

which amounts to expanding the potential surface in nuclear displacements. Here, q_i are the (30) normal modes of the molecule. We shall further denote the eigenstates of the harmonic part of H_m [i.e., the first two sums of Eq. (2)] by $|v_1, v_2, \dots, v_{30}\rangle$ where v_j denotes the number of quanta in the j th (normal) mode. Recently, it has been shown that if enough terms are kept in (2) an adequate description of electronic relaxation in small

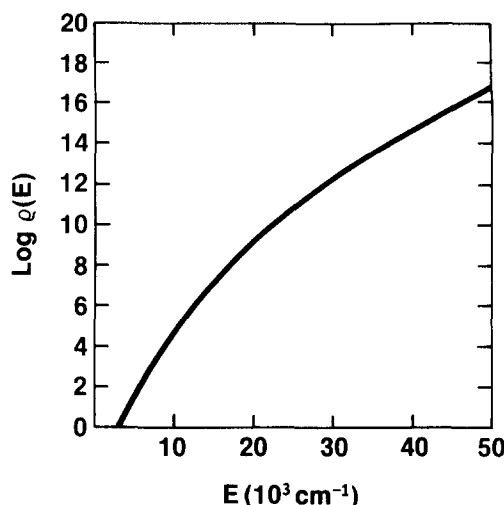


FIG. 1. Benzene density of states. This approximate curve is for a system of identical harmonic oscillators with frequencies equal to benzene's (geometric) mean vibrational frequency (1200 cm^{-1}).

polyatomics can be obtained (albeit tediously) within the normal model approximation.¹⁹ Benzene is much too large to be treated in detail (see below) and we must find a description which permits some substantial simplification.

Having written the molecular Hamiltonian we seek a basis set (i.e., the eigenstates of some zero order Hamiltonian) in which the description of the line shape is most convenient. To this end, it seems desirable to require that within this basis the initial state $|g\rangle$ couples radiatively to only a few zero-order molecular states $\{|s\rangle\}$ with energies $E_s = E_g + \hbar\omega$. Finding such a basis might at first seem hopeless; recall that the benzene molecule has $\sim 10^8$ states/ cm^{-1} in the region of the 5th C-H stretching overtone (see Fig. 1). However, the fact that the overtone bands are so prominent and apparently conform so well to simple anharmonic oscillator position assignments suggests that the initial excitation is strongly localized within the CH stretching motions. The six C-H stretching modes do not seem to be strongly mixed with the other modes by anharmonicities, at least not to the point of gross spectral perturbation.^{14,19} This behavior is understandable in light of the simple fact that the C-H stretching frequencies ($\sim 3000 \text{ cm}^{-1}$) are much higher than all other stretching or bending frequencies ($\sim 2000 \text{ cm}^{-1}$) of the molecule. This frequency mismatch causes the CH motions to be quasi-independent of the other modes. This can be interpreted classically (and recall highly excited states can behave rather classically) in terms of impedance matching arguments or quantum mechanically as arising from the (smaller) off resonant character of interactions between modes of disparate frequencies and the diagonal nature (exact for normal modes, approximate for local modes) of the nuclear kinetic energy matrix.

The molecular state formed by photon absorption (i.e., the doorway state $|s\rangle = \mu |g\rangle$ where μ is the transition dipole operator and $|g\rangle$ is the ground vibrational state) has its energy mainly localized within the CH stretching

motions.¹⁴ Using the harmonic basis set defined above and our separability notion, the v th overtone doorway state may thus be characterized as a linear combination of all the $[(v+5)!/(5!v!)]$ (quasi) degenerate states formed by distributing v quanta among the six CH oscillators. This reduces enormously the size of the problem. For the 6th overtone, say, there are 462 states (out of 10^8 states/cm⁻¹) which are relevant for the description of $|s\rangle$. However, such a basis set is still too large. We can now make use of the experimental observations (1) and (5) in Sec. I, i.e., that the positions of the CH overtones conform very well to a simple anharmonic oscillator and that their intensity is roughly proportional to the number of CH bonds in the molecule. These facts suggest that benzene may well be described by six independent "local modes" associated with the separate C-H bonds. We now wish to construct a zero order Hamiltonian which will reflect this picture. To do this we switch from the purely normal coordinates $\{q\}$ to mixed normal-local coordinates $\{R\}$.¹⁴ Here the set of local coordinates $R_1 \cdots R_6$ are the 6 CH bond displacements. For $i > 6$, $R_i = q_i$. In terms of this set of coordinates, we partition our Hamiltonian (2) as follows:

$$\mathbf{H}_M = \mathbf{H}_M^0(\mathbf{R}) + \mathbf{V}_M(\mathbf{R}) = \sum_{i=1}^6 \mathbf{H}_{\text{Local}}^0(R_i) + \sum_{i=7}^{30} \mathbf{H}_{\text{Normal}}^0(R_i) + \mathbf{V}_M(\mathbf{R}), \quad (3a)$$

where

$$\mathbf{H}_{\text{Normal}}^0 = P_i^2/2m_i + \frac{1}{2}m_i\omega_i^2 R_i^2, \quad i > 6 \quad (3b)$$

$$\mathbf{H}_{\text{Local}}^0 = P_i^2/2m_i + \mathbf{V}_{\text{Local}}(R_i), \quad i \leq 6 \quad (3c)$$

and

$$\begin{aligned} \mathbf{V}_M(\mathbf{R}) &\equiv \mathbf{H}_M(\mathbf{R}) - \mathbf{H}_M^0(\mathbf{R}) \\ &= -\hbar^2 g^{1/4} \sum_{i \neq j \leq 6} (\partial/\partial R_i) g^{-1/2} G_{ij} (\partial/\partial R_j) g^{1/4} \\ &\quad + \sum_{i \neq j \leq 6} d_{ij} R_i R_j + \sum_{i,j} d_{ijk} R_i R_j R_k + \dots \end{aligned} \quad (3d)$$

with \mathbf{G} the usual G matrix and $g = \det[\mathbf{G}]$.²⁰ Here $\mathbf{H}_{\text{Local}}^0$ and $\mathbf{H}_{\text{Normal}}^0$ are the local mode and normal mode zero order Hamiltonians, respectively, and \mathbf{V}_M is the intramolecular coupling consisting of off-diagonal kinetic energy terms²⁰ [the first summation in Eq. (3d)] and potential terms. We further partition \mathbf{V}_M into three types of terms: those describing (1) only local mode interactions (\mathbf{V}_M^{LL}), (2) only normal mode interactions (\mathbf{V}_M^{NN}), and (3) mixed terms involving interactions between local and normal modes (\mathbf{V}_M^{LN}), i.e.,

$$\mathbf{V}_M = \mathbf{V}_M^{\text{LL}} + \mathbf{V}_M^{\text{NN}} + \mathbf{V}_M^{\text{LN}} \quad (3e)$$

Explicit expressions for the contributions to (3e) are given in the Appendix. The eigenstates of \mathbf{H}_M^0 (3a) are products of six local mode states [eigenstates of some anharmonic oscillator (3c)] and 24 normal mode states associated with the other degrees of freedom. These eigenstates will be denoted again by $|v_1, v_2, \dots, v_{30}\rangle$ where $v_1 \cdots v_6$ now refer to the occupation numbers of the CH local modes.

Our choice of zero order Hamiltonian (3a) has the following advantages for the purpose of the line shape calculation:

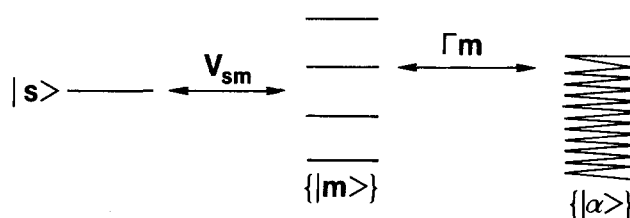


FIG. 2. Simplified energy level diagram. An excited local mode $|s\rangle$ couples more strongly to nearby local mode states $\{|m\rangle\}$ than to other molecular states $\{|\alpha\rangle\}$.

(1) Due to the inclusion of anharmonicities in our zero order Hamiltonian, the degeneracies of the harmonic C-H Hamiltonian are largely removed.

(2) Since we treat the nuclear dipole moment as a single particle operator,¹⁴ the v th overtone doorway state has only six fold degeneracy corresponding to the states $v_i = v$, $v_j = 0$ $i \neq j = 1 \dots 6$, i.e., the initial v th overtone excitation can only put v quanta in a single CH bond.^{8,14}

(3) We can further make use of the molecular symmetry.⁸ From the six-fold degenerate local mode states we can construct symmetrized local mode states, only 1 of which will have E_{1u} symmetry and be radiatively coupled to the ground state.

(4) Perhaps most importantly within this representation it is expected that all zero-order states are only weakly coupled to each other. This permits perturbation theory (at some level) to be of utility. Also, we expect local mode states (and $|s\rangle$ in particular) to be much more strongly coupled amongst themselves than to the normal mode "bath." Thus, the intramolecular coupling situation should be reasonably well described by Fig. 2.

The adoption of a zero order Hamiltonian having some local mode character is an extremely useful conceptual device. It directly accounts for many of the observed spectral features^{6,8} and it has the great advantage of simplifying the description of the "doorway" state to a single eigenstate of H_0 .

III. THE OVERTONE LINE SHAPES

In order to obtain an explicit expression for the overtone line shapes, we have to consider the total Hamiltonian for the molecular system and the radiation field:

$$\mathbf{H} = \mathbf{H}_M + \mathbf{H}_R + \mathbf{V}_{MR} \quad (4)$$

where \mathbf{H}_M is the molecular Hamiltonian (3) and \mathbf{H}_R is the Hamiltonian for the free radiation field

$$\mathbf{H}_R = \sum_k \hbar\omega_k \mathbf{a}_k^\dagger \mathbf{a}_k \quad (5a)$$

$\mathbf{a}_k^\dagger(\mathbf{a}_k)$ being the creation (annihilation) operators for the k th mode with frequency ω_k , the radiation-matter coupling \mathbf{V}_{MR} is assumed to couple only to CH states:

$$\mathbf{V}_{MR} = \mu(R_1, \dots, R_6) \cdot \epsilon \sum_k (\mathbf{a}_k^\dagger + \mathbf{a}_k) \quad (5b)$$

Our Hamiltonian (4) is now partitioned as follows:

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V} \quad (6a)$$

$$\mathbf{H}_0 = \mathbf{H}_{\text{Local}}^0 + \mathbf{H}_{\text{Normal}}^0 + \mathbf{H}_R \quad (6b)$$

$$\mathbf{V} = \mathbf{V}_M + \mathbf{V}_{MR} = \mathbf{V}_M^{\text{LL}} + \mathbf{V}_M^{\text{NN}} + \mathbf{V}_M^{\text{LN}} + \mathbf{V}_{MR} \quad (6c)$$

Since the transition dipole (\mathbf{V}_{MR}) is localized within the CH stretches, the line shape problem is now analogous to the pressure broadening problem of Fano.²¹ We have a system interacting with the radiation field and a (now intramolecular) bath perturbing the system.²² The system in our case is the CH stretches ($R_1 \dots R_6$). The bath is the other molecular degrees of freedom. A schematic representation of this situation is given in Fig. 2.

An appropriate formulation for the line shape is the tetradic scattering formulation of Fano and Zwanzig.²¹ It enables us to perform in a convenient way the trace over the bath's irrelevant degrees of freedom.²¹⁻²³ The derivation of the line shape for the Hamiltonian (6) is done in the Appendix, the final result for the line shape is

$$L(\omega) = \text{Im} \sum_{mm'} \mu_{g'm} G_{mm'}(\omega) \mu_{m'g} \quad (7)$$

Here, the system is assumed to be initially in its ground state $|g\rangle = |000000\rangle$. The states $\{|m\rangle\}$ denote the excited eigenstates of $\mathbf{H}_{\text{Local}}^0$ having energies E_m in the vicinity of $E_g + \hbar\omega$, ω being the photon frequency. The resolvent operator \mathbf{G} can be put into the form

$$\mathbf{G}(\omega) = [\omega - \mathbf{H}_{\text{Local}}^0 - \mathbf{V}_M^{\text{LL}} - \mathbf{R}(\omega)]^{-1} \quad (8)$$

where

$$(\omega - \mathbf{H}_{\text{Local}}^0)_{mm'} = (\omega - E_m) \delta_{mm'} \quad (8a)$$

$$(\mathbf{V}_M^{\text{LL}})_{mm'} = V_{mm'}(1 - \delta_{mm'}) \quad (8b)$$

We have chosen $E_g = 0$. $\mathbf{R}(\omega)$ is a level shift operator whose matrix elements are complex

$$R_{mm'}(\omega) = \left[\Delta_m(\omega) - \frac{i}{2} \Gamma_m(\omega) \right] \delta_{mm'} \quad (9)$$

The damping and level shift matrix elements are given by

$$\Gamma_m(\omega) = \sum_{\substack{m' \\ \alpha, \beta}} \rho(\alpha) |\langle m' \beta | \mathbf{V}_M^{\text{LN}} | m \alpha \rangle|^2 \delta(\omega + E_\alpha - E_{m'} - E_\beta) \quad (10a)$$

and

$$\Delta_m(\omega) = \frac{1}{2} \pi \text{PP} \int_{-\infty}^{\infty} d\omega' \frac{\Gamma_m(\omega')}{\omega - \omega'} \quad (10b)$$

respectively. PP in (10b) indicates that the principal part of the integral is to be taken. The bath states $|\alpha\rangle$, $|\beta\rangle$ are eigenstates of $\mathbf{H}_{\text{Normal}}^0$ and $\rho(\alpha)$ is the equilibrium distribution of the bath states.

Equations (7-10) are quite general and include the possibility that several system states $|m\rangle$ carry oscillator strength from the ground state. We recall from Sec. I that for the benzene line shape problem we need consider only a single (although possibly degenerate) doorway state $|s\rangle = |v00000\rangle$ corresponding to the v th overtone of $\mathbf{H}_{\text{Local}}^0$. Here and in the discussion which follows we drop explicit reference to the bath states—except when required for clarity. In keeping with the Fano-Zwanzig line shape formulation the “irrelevant” bath

states and their couplings are only of interest insofar as they affect the dynamics of the “relevant” CH (local mode) states. The overtone line shape (7) now assumes the form:

$$L(\omega) = |\mu_{gs}|^2 \text{Im} G_{ss}(\omega) \quad (11)$$

where

$$G_{ss}(\omega) = \left[\omega - \tilde{E}_s(\omega) + \frac{i}{2} \tilde{\Gamma}_s(\omega) \right]^{-1} \quad (12)$$

Evaluation of $G_{ss}(\omega)$ requires the inversion of the matrix (8) whose size is determined by the number of relevant local mode states. For C_6H_6 , we recall that the $\{|m\rangle\}$ local mode states closest to $|s\rangle$ are separated from $|s\rangle$ by $\Delta E_{sm} = 2(v-1)\omega_e X_e$. These are states $\{|m\rangle\}$ of the form $|v-1, 1, 0000\rangle$. They are 300 cm^{-1} above $|s\rangle$ for $v=4$. Consequently, we expect the $\{|m\rangle\}$ states to be only weakly coupled to $|s\rangle$, specifically, we expect \mathbf{V}_M^{LL} to be much smaller than $\sqrt{\Delta E_{sm}^2 + \Gamma_s^2}$. Making use of this fact, \tilde{E}_s and $\tilde{\Gamma}_s$ can be evaluated to second order in \mathbf{V}_M^{LL} .

$$\tilde{\Gamma}_s(\omega) = \Gamma_s(\omega) + \sum_{m \neq s} \frac{|\langle \mathbf{V}_M^{\text{LL}} \rangle_{ms}|^2 \Gamma_m(\omega)}{[\omega - E_m - \Delta_m(\omega)]^2 + \frac{1}{4} \Gamma_m(\omega)^2} \quad (13)$$

$$\tilde{E}_s(\omega) = E_s + \Delta_s(\omega) + \sum_{m \neq s} \frac{|\langle \mathbf{V}_M^{\text{LL}} \rangle_{ms}|^2 [\omega - E_m - \Delta_m(\omega)]}{[\omega - E_m - \Delta_m(\omega)]^2 + \frac{1}{4} \Gamma_m(\omega)^2} \quad (14)$$

and the line shape (7) now takes the form

$$L(\omega) = \frac{|\mu_{gs}|^2}{2} \frac{\tilde{\Gamma}_s(\omega)}{[\omega - \tilde{E}_s(\omega)]^2 + \frac{1}{4} \tilde{\Gamma}_s(\omega)^2} \quad (15)$$

For each overtone, we are interested in a narrow ω range (which is of the order of the experimental line-width $|\omega - E_s| \sim 100 \text{ cm}^{-1}$). The Γ_m are not expected to vary rapidly on that frequency scale. We thus have

$$\Gamma_m(\omega) \cong \Gamma_m[E_s(v)] \equiv \Gamma_m \quad (16)$$

We take $\Delta_m = 0$ since we can always include Δ_m by a slight shift of the energies E_m .

Our final expression for the lineshape is thus Eq. (15), with

$$\tilde{\Gamma}_s(\omega) = \Gamma_s + \sum_{m \neq s} \frac{|\langle \mathbf{V}_M^{\text{LL}} \rangle_{sm}|^2 \Gamma_m}{(\omega - E_m)^2 + \frac{1}{4} \Gamma_m^2} \quad (17a)$$

$$\tilde{E}_s(\omega) = E_s + \sum_{m \neq s} \frac{|\langle \mathbf{V}_M^{\text{LL}} \rangle_{ms}|^2 (\omega - E_m)}{(\omega - E_m)^2 + \frac{1}{4} \Gamma_m^2} \quad (17b)$$

and

$$\Gamma_m = \sum_{\substack{m' \neq m \\ \alpha, \beta}} \rho(\alpha) |\langle m' \beta | \mathbf{V}_M^{\text{LN}} | m \alpha \rangle|^2 \delta(E_s + E_\alpha - E_{m'} - E_\beta) + \sum_{\alpha, \beta} \rho(\alpha) |\langle m \beta | \mathbf{V}_M^{\text{LN}} | m \alpha \rangle|^2 \delta(E_s + E_\alpha - E_m - E_\beta) \quad (17c)$$

Equations (15) and (17) form the basis for our discussion and calculation of polyatomic overtone line shapes.

IV. NUMERICAL CALCULATIONS OF THE BENZENE LINE SHAPES

Calculation of the overtone line shapes using equations (15) and (17) requires an evaluation of Γ_s , Γ_m , $\langle \mathbf{V}_M^{\text{LL}} \rangle_{sm}$ and E_m which includes their variation with the overtone quantum number v and with deuteration. To make our discussion concrete, we will make specific reference to

the case of benzene H6. The evaluation procedure for substituted benzenes is virtually identical (the only exception being the substitution of the C–D oscillators for some of the C–H stretching oscillators). We recall that the doorway state $|s\rangle$ for the 0 - v th overtone is given by $|s\rangle = |v0000\rangle$ and its energy is:

$$E_s(v) = \hbar\omega_e(v + \frac{1}{2}) - \hbar\omega_e X_e(v + \frac{1}{2})^2. \quad (18)$$

where ω_e and X_e are the harmonic frequency and anharmonicity, respectively. Similarly, the directly coupled states $\{|m\rangle\}$ are any other local mode (C–H stretching) states

$$|m\rangle = |v_1 \cdots v_6\rangle \quad (19)$$

with energy

$$E_m = \hbar\omega_e \sum_{i=1}^6 (v_i + \frac{1}{2}) - \hbar\omega_e X_e \sum_{i=1}^6 (v_i + \frac{1}{2})^2 \quad (20)$$

The matrix elements coupling $|s\rangle$ to $\{|m\rangle\}$ can be evaluated. For present purposes, it suffices to assume that only the lowest order terms in \mathbf{V}_M^{LL} [cf. Eq. (3d, e) and the Appendix] are important, i.e., all terms which are quadratic in local mode displacements.

$$|V_{sm}|^2 \approx \langle s | \sum_{i>j}^6 d_{ij} R_i R_j | m \rangle|^2. \quad (21)$$

(Inclusion of the kinetic energy coupling terms in (21) will not affect our present estimate).²⁴ If $|s\rangle$ and $|m\rangle$ were products of harmonic (normal) oscillators instead of anharmonic (local) oscillators, only states $|m\rangle$ of the form

$$|m\rangle = |v-1, 10000\rangle \quad (22)$$

would be coupled to $|s\rangle$ and the coupling matrix elements would be

$$|V_{sm}|^2 = \frac{v}{4} \left| \sum_{i>j}^6 d_{ij} \right|^2. \quad (23)$$

Equation (23) shows that for harmonic modes to first order $|V_{sm}|^2$ varies linearly with v with a proportionality constant fixed by the details of the potential surface. Even for anharmonic modes, only states of the form

$$|m\rangle = |v-N, N0000\rangle, \quad N=1, 2, \dots, v \quad (24)$$

can couple to $|s\rangle$ in first order [see Eq. (21)]. Relaxing this first order requirement allows all combination local modes to couple to $|s\rangle$ but since $\{|m\rangle\}$ is a sparse manifold only those few states with energies E_m nearest to E_s are expected to dominate. Given the form of $|s\rangle$ these are states of the form $|m\rangle = |v-1, 10000\rangle$. For such states $|s\rangle$ and $|m\rangle$ it is easy to deduce that $\Delta E_{sm} = 2\hbar\omega_e X_e \times (v-1)$ and that other states are typically much farther away. The first order matrix elements $|V_{sm}|^2$ for these states are again $\propto v$ [for any anharmonic potential (e.g., Morse)] when $vX_e \ll 1$.²⁵

The evaluation of Γ_m is more difficult. Γ_m [Eq. (17c)] has three types of contributions [$\Gamma_m = \Gamma_m^{(1)} + \Gamma_m^{(2)} + \Gamma_m^{(3)}$]:

(1) transitions to states $\{|m'\rangle\}$ having a smaller number of quanta ($< v$) in the CH stretches, e.g., $|v0000\rangle - |v-1, 00000\rangle$;

(2) transitions to states $\{|m^\wedge\rangle\}$ having the same num-

ber (v) of CH quanta, distributed differently among the various CH modes; e.g., $|v-1, 10000\rangle - |v-2, 1, 1, 000\rangle$;

(3) dephasing (“ T_2 ” type) contributions involving no transition within the manifold of C–H stretching states (i.e., $m' = m$). These terms (which appear in the second summation in Eq. (17c) cause broadening of the line without affecting the population of $|m\rangle$.^{21–23}

$\Gamma_m^{(1)}$ involves direct transfer of substantial energy (at least one CH quantum) from the CH stretches to other (low frequency) types of motion. This is expected to be a relatively slow process (at least a few psec corresponding to a linewidth of only 2.5 cm^{-1}).²² $\Gamma_m^{(3)}$ which is a pure dephasing can be much larger than $\Gamma_m^{(1)}$, but since the bath is initially rather cold (i.e., room temperature) it is not expected to be dominant in our case. Similar arguments can be made for the direct decay contributions (Γ_s) to $\tilde{\Gamma}_s$ [cf. Eq. (13)]. Thus, $\Gamma_s^{(1)}$ is not expected to be very large either. “Direct” dephasing of $|s\rangle$ via $\Gamma_s^{(3)}$ is expected to be even smaller than $\Gamma_m^{(3)}$ and transitions between degenerate local mode overtones, e.g., $|v00000\rangle - |0v00000\rangle$ requires high order couplings. However, combination states of the type $|m\rangle = |v-1, 10000\rangle$ may rapidly dephase themselves due to the “hopping” of the single quantum among the five degenerate states. Also, $\Gamma_m^{(2)}$ should be substantial as coupling to $v-2$ type states will be important. Recent classical trajectory calculations by Hase²⁶ indicate that combination states decay significantly faster than pure overtones.

Because dephasing within $\{|m\rangle\}$ (as well as possibly into the bath) and $\Gamma_m^{(2)}$ dominates, we do not expect Γ_m to vary strongly with the overtone quantum number v (the nature of the bath is similar for all the overtones). Therefore, for our calculations, we assume that all contributions to Γ_s except $\Gamma_s^{(2)}$ are negligible and that Γ_m is independent of v . Furthermore, since the $\{|m\rangle\}$ manifold is sparse we assume that the closest $|m\rangle$ level to $|s\rangle$ has the dominant contribution to the line shape.

Within the context of our discussion, $\tilde{\Gamma}_s$ of Eq. (17) now reduces to

$$\tilde{\Gamma}_s(\omega) = \sum_m \frac{|V_{sm}|^2 \Gamma_m}{(\omega - E_m)^2 + \frac{1}{4} \Gamma_m^2} \quad (25a)$$

where $V_{sm} = (\mathbf{V}_M^{LL})_{sm} \propto v^{1/2}$ (v being the overtone quantum number), and $\omega - E_m = (\omega - E_s) + (E_s - E_m) = (\omega - E_s) + 2\hbar\omega_e X_e (v-1)$. We define $\epsilon \equiv (\omega - E_s)$ to reference our energies to the zero order line center and introduce D_m the degeneracy of state $|m\rangle$. Thus,

$$\tilde{\Gamma}_s \approx \frac{D_m |V_{sm}|^2 \Gamma_m}{(\epsilon + \Delta E_{sm})^2 + \frac{1}{4} \Gamma_m^2} \quad (25b)$$

for $|m\rangle = \{|v-1, 1, 0000\rangle\}$. The v dependence of the linewidth $\tilde{\Gamma}_s$ has the following limiting behavior whenever $\epsilon^2 \ll \Delta E_{sm}^2 + \Gamma_m^2/4$.

(1) For $|\Delta E_{sm}| \gg \Gamma_m$,

$$\tilde{\Gamma}_s \approx \frac{D_m (V_{sm})^2 \Gamma_m}{\Delta E_{sm}^2} \propto \frac{1}{v} \quad (26)$$

and we expect narrowing of the lines with the overtone quantum number v .

TABLE I. Benzene overtone linewidths.^a

Overtone (ν)	H1		H2		H5		H6	
	Expt. ^a	Calc. ^b	Expt. ^a	Calc. ^b	Expt. ^a	Calc. ^b	Expt. ^a	Calc. ^b
4	...	70	...	84.5	...	128	...	142.5
		(66)		(79)		(118)		(131)
5	86	87.5	111	93	105	109	109	114
	(78)	(82.5)	(105)	(87)	(99)	(100.5)	(103)	(105)
6	107	105	91	103	97	97	94	95
	(101)	(99)	(84)	(97)	(90)	(90)	(87)	(87.5)
7	...	122.5	...	114	...	90	...	81
		(115.5)		(107)		(83)		(75)

^aData of Bray and Berry (Ref. 6). All linewidths are given in cm^{-1} . Homogeneous (rotationally deconvoluted) linewidths are given in parentheses. Nominal uncertainty $\pm 2 \text{ cm}^{-1}$ except H6 ($\nu=7$) is $\pm 7 \text{ cm}^{-1}$ and H2 ($\nu=5$) which is non-Lorentzian.

^bComputed from Eq. (28) using $A=3.3$ (3.5) and $B=105$ (114) for total (homogeneous) linewidths.

(2) For $\Gamma_m \gg |\Delta E_{sm}|$,

$$\bar{\Gamma}_s \approx \frac{4D_m(V_{sm})^2}{\Gamma_m} \propto \nu \quad (27)$$

and we expect broadening of the lines with ν . Obviously, intermediate behavior (e.g., $\bar{\Gamma}_s$ independent of ν for a small range of ν) is also possible.

We feel that case 1 should be a very good description for benzene H6 at least above the 4th overtone. In this region, $\Delta E_{sm} \gtrsim 500 \text{ cm}^{-1}$ for states $|m\rangle$ of the form $|v-1, 1\rangle$. Other combination local mode states are much farther away (see Swofford, *et al.*, Ref. 8b for a level diagram). Benzene H1 is a different case (in fact, probably case 2 in this energy region). The excited C-H local oscillator can couple (through the same terms in the potential) only to CD modes. These latter modes have lower frequencies and are probably much more strongly coupled to the bath than the corresponding C-H vibrations in H6. Thus, we expect $\Gamma_m^{\text{H1}} > \Gamma_m^{\text{H6}}$. Furthermore, the states nearest to $|s\rangle$ which are still of configuration $|v-1, 1\rangle$ are now much closer (only 250–300 cm^{-1} away) and are energetically below $|s\rangle$ making them easier to dephase via a cold bath. These states grow even closer to $|s\rangle$ with increasing ν . Consequently, even if case 2 applies for H1, broadening is still expected. These simple arguments provide us with an immediate explanation of the observed trends in the line shapes [observations 4 and 5 conform well to Eqs. (26) and (27)]. Turning now to a more quantitative analysis, we can make use of Eqs. (25a), (26), and (27) to obtain the following expression for the width of the ν th overtone in benzene H n (in cm^{-1}):

$$\bar{\Gamma}_s(n, \nu) = A\nu(6-n) + \frac{B}{\nu}(n-1) \quad (28)$$

The first term in (28) is the contribution of the $6-n$ CD local modes and the second is the contribution of the $n-1$ CH local modes (other than the excited local oscillator). In Eq. (28) we assume that only the states $|m\rangle$ of the type $|m\rangle = |v-1, 10000\rangle$ need to be considered and that they are 5-fold degenerate ($n-1$ CH type and $6-n$ CD type). Inhomogeneous (rotational) broadening affects the relative linewidths only slightly ($\gtrsim 3\%$). Thus A and B in (28) can be chosen to fit the observed linewidths as well as the pure homogeneous linewidth. Fitted values for A and B and calculated linewidths are given in Table I. A and B themselves are approximately independent

on ν and n and are given by [compared Eq. (28) with Eqs. (26) and (27)]:

$$A\nu = \frac{4|V_{sm}'|^2}{\Gamma_m} \quad (29a)$$

$$\frac{B}{\nu} = \frac{|V_{sm}|^2 \Gamma_m}{\Delta E_{sm}^2} \quad (29b)$$

where primed (nonprimed) quantities refer to benzene H1 (H6).

For deuterated species, the simple form of Eq. (25a) indicates that contributions to the width $\bar{\Gamma}_s$ from CH and CD oscillators are additive. This give rise to a very general semiempirical equation

$$\bar{\Gamma}_s(n, \nu) = n_{\text{H}} \Gamma^{\text{CH}} + n_{\text{D}} \Gamma^{\text{CD}} \\ = \frac{1}{5} [(n_{\text{H}} - 1) \Gamma_s^{\text{C}_6\text{H}_6} + (6 - n_{\text{H}}) \Gamma_s^{\text{C}_6\text{HD}_5}] \quad (30)$$

which should be less model dependent than (28). Here $n_{\text{H}}(n_{\text{D}})$ are the number of CH (CD) modes coupled to the excited CH mode and $\Gamma^{\text{CH}}(\Gamma^{\text{CD}})$ is the contribution each such mode makes to the total width.

We note that of the nine calculated widths in Table I which can be compared to observed values only the two results for $\text{C}_6\text{H}_6\text{D}_4$ do not agree within experimental error. $\text{C}_6\text{H}_2\text{D}_4$ has the least Lorentzian profile and consequently its width is somewhat ill defined. It is also likely that other factors which have been neglected in our simple model (e.g., noncancelling of interferences due to simultaneous excitation of the two CH stretches) are more important for this case. Additional sophistication to account for some of these effects could be incorporated but only at the cost of introducing additional parameters into the model. Nonetheless, we find the agreement between our two parameter model and experiment extremely encouraging.

Although we could proceed directly to the calculation of the full line shape (25), it is of some interest to consider our description even more seriously (and more speculatively) and attempt to extract the molecular parameters Γ_m and V_{sm} . Equations (29) provide the relationship

$$\left(\frac{|V_{sm}'|^2}{|V_{sm}|^2} \right) (\Gamma_m \Gamma_m')^{-1} = \left(\frac{A}{B} \right) \nu^2 / 4 \Delta E_{sm}^2, \quad (31)$$

where the unprimed and primed quantities refer to C_6H_6 and C_6HD_5 , respectively. Both sides of (31) are essen-

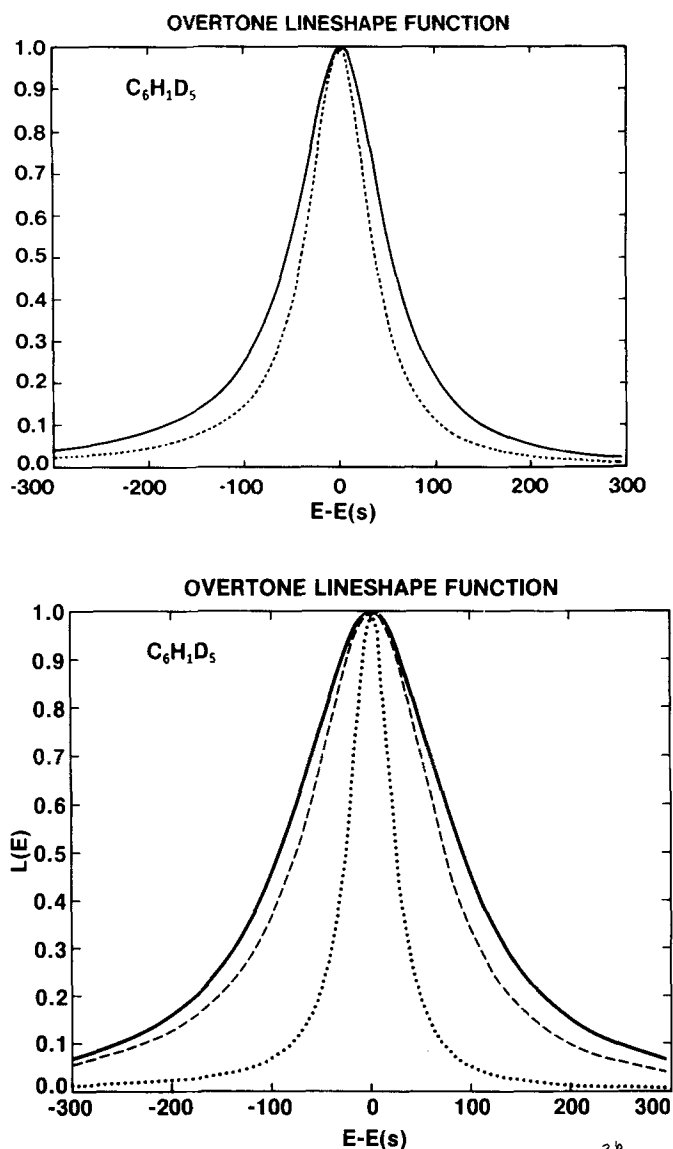


FIG. 3. C_6HD_5 overtone line shapes. Expression (25b) with $d_m=5$, $|V_{sm}| = |V_{sm}|_{C_6H_6}/\sqrt{2}$, $\Gamma_m=1100$ cm^{-1} . (a) For $---$ $v=5$, $—$ $v=6$, compare with observed line shapes in Ref. 6. (b) Predicted line shapes for: \cdots $v=4$, $---$ $v=7$, and $—$ $v=8$.

tially independent of v so other independent relations are needed to untangle the four molecular parameters on the LHS. If the dominant contributions to V_{sm} come from the leading off-diagonal local mode term $R_i R_j$, then (assuming nearly harmonic scaling of the couplings) $|V'_{sm}|^2 = \frac{1}{2} |V_{sm}|^2$ since the prime refers to C_6HD_5 in which coupling is between C-H and C-D oscillators. This gives an expression for the ratio of the widths.

Self consistency with our case (1) and (2) assumptions gives $\Gamma_m \lesssim 500$ cm^{-1} , $\Gamma'_m \gtrsim 1100$ cm^{-1} , and thus $|V_{sm}| \sim 50 v^{1/2}$ cm^{-1} . Line shapes for these particular parametric values are given in Figs. 3 and 4. These line shapes can be compared directly with those obtained by Bray and Berry.⁶ Very similar lineshapes would occur for variations in Γ_m , Γ'_m , and V within a factor of ~ 2 as long as the basic parameters A and B are fixed. As we see linewidth measurements alone are not the most sensitive probes of intramolecular processes governed by

the relaxation rates Γ_m and couplings V_{sm} . We feel that the above estimates of these more fundamental parameters are of the right order for the following reasons:

- (1) $\Gamma_m = 500$ cm^{-1} corresponds to about the fastest timescale on which dephasing (due to interactions with lower frequency modes) can occur (about six vibrational periods),
- (2) one expects Γ'_m to be substantially larger than Γ_m since C-D modes should be more easily dephased by lower frequency vibrations than are the CH modes,
- (3) $|V_{sm}|$ is roughly on the order of the expected off-diagonal anharmonic couplings (10–100 cm^{-1}).

We compute [using Eq. (25b)] the line shapes shown in Figs. 3 and 4 for benzene H1 and H6, respectively. Not only are the gross features of the lines (line positions and widths) correctly reproduced but even the slight asymmetry to the high energy side of the band is obtained (this is chiefly a consequence of $E_m > E_s$). There is also a slight variation in the peak position which is v dependent. Another contribution to the peak position has been neglected [cf., Eq. (13)]. This is the level shift $\Delta_s(E_s) = \Delta E_{sm} |V_{sm}|^2 / (\Delta E_{sm}^2 + \Gamma_m^2/4)$ which has magnitudes of 40 and 25 cm^{-1} , respectively for H6 and H1 (after accounting for the degeneracy of the initial state in H6) for $v=6$. This shift is independent of v for case 1 and goes as v^2 for case 2. However, to some extent, it is absorbed in the definition of ω_s and $\omega_s X_c$.

V. CONCLUDING REMARKS

We have developed a general theory for intramolecular line broadening and applied it to the CH overtone line shapes in benzene. Using our expressions for the line shape, we were able to account for all the qualitative and quantitative features of the experimental line shapes of Bray and Berry.⁶ Our most general line shape function Eq. (15) is Lorentz-like but it can be very much different than a simple Lorentzian since $\bar{\Gamma}_s(\omega)$ and $\bar{\Delta}_s(\omega)$ depend on frequency in a way determined by the intramolecular dynamics. Only in the limit where the frequency dependences of Γ_s and Δ_s can be ignored do the line shapes reduce to simple Lorentzians. This seems to be very nearly the case for the higher overtones which we have considered. In our model, the ω dependence of $\bar{\Gamma}_s$ and $\bar{\Delta}_s$ has the form of a sum of Lorentzians Eq. (17a). [In principle, a more elaborate ω dependence may come about through the explicit dependence of Γ_m and Δ_m on ω Eq. (10).] Assuming Γ_m and Δ_m to be frequency independent over the relevant ϵ range ($\pm \bar{\Gamma}_s$ for a given overtone), we obtain the following condition for $\bar{\Gamma}_s$ to be frequency independent

$$\bar{\Gamma}_s(E_s) < \sqrt{\Delta E_{sm}^2 + \frac{1}{4} \Gamma_m^2} \quad (32)$$

A sufficient condition for (32) to hold is $\Gamma_s(E_s) \ll \Gamma_m$ thus using (25a) we obtain

$$\frac{|V_{sm}|^2}{\Delta E_{sm}^2 + \frac{1}{4} \Gamma_m^2} \ll 1 \quad (33)$$

The same condition guarantees that our perturbative expression for $\bar{\Gamma}_s(\epsilon)$ holds. We have thus a general line shape function Eq. (15) which under the limiting condi-

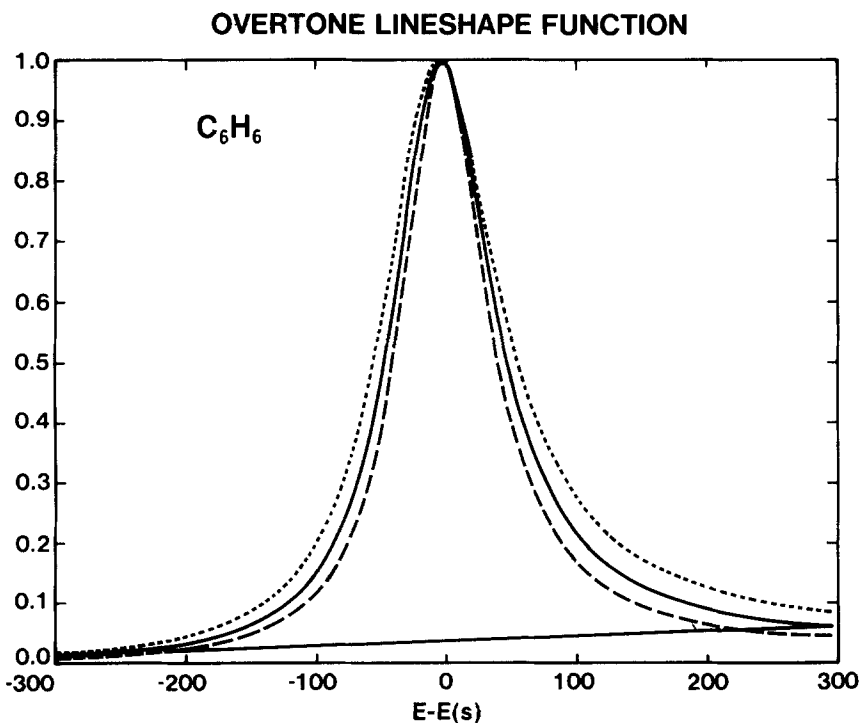
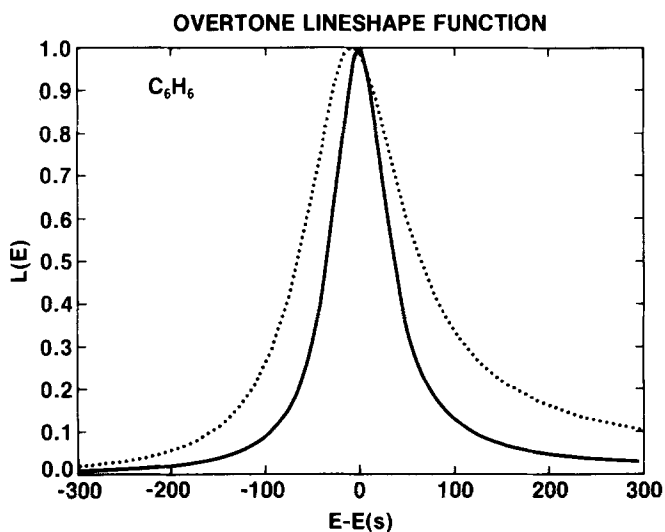


FIG. 4. C_6H_6 overtone line shapes. Expression (25b) with $d_m = 5$, $|V_{sm}| = 50v^{1/2} \text{ cm}^{-1}$, $\Gamma_m = 500 \text{ cm}^{-1}$. (a) For --- $v=5$, — $v=6$, and — · — $v=7$, compare with observed line shapes in Ref. 6. (b) Predicted line shapes for: ··· $v=4$ and — $v=8$.



tion (33) reduces to a simple Lorentzian. This behavior is very much reminiscent of the motional narrowing phenomena in magnetic resonance.¹⁰ There, a general spectral line (usually Gaussian) becomes a narrow Lorentzian when the temperature increases. The reason for this is that at low temperatures the broadening is determined by the dipolar interactions V with the neighboring spins. As the temperature increases, random motions become so fast that typical "bath" correlation times (τ_c) become very short (compared to V). V is thus stochastically averaged on the time scale τ_c , resulting in a narrow Lorentzian line with width $\sim V^2\tau_c$. The narrowing condition is $V\tau_c \ll 1$. Thus, in our model we can view $\Gamma_m/(\Delta E_{sm}^2 + \frac{1}{4}\Gamma_m^2)$ as an effective correlation time of the bath. The asymmetry of the non-Lorentzian line shapes is a natural consequence of couplings to states $|m\rangle$ which are off resonance from the excited

(doorway) state $|s\rangle$. Similarly, the narrowing or broadening of the overtone bands is specifically due to anisotropies of the intramolecular couplings and state spacings. Such features cannot be accounted for by the coupling of an isolated state to a homogeneous bath.

Finally, we note that the continuum underlying the CH bonds can arise from all the Lorentzian tails of the various $|m\rangle$ states (i.e., absorption of the CH modes), alternatively it may arise from direct absorption to other non-CH modes or it may be electronically induced. The present data do not allow us to specify a unique origin for the continuum.

VI. SUMMARY

We have shown that overtone line shapes while complex beasts can be reasonably well understood within a

weak coupling Fano-Zwanzig type formalism in terms of a model which specifically takes into account the anisotropies of intramolecular couplings and level spacings. Successful application requires that one describe the states which are initially prepared by the absorption process. For C-H overtones, local modes appear to provide an adequate zero order description. Local modes do not, however, resemble the true molecular eigenstates except in the crudest sense.¹⁴ It is precisely their nonnegligible couplings to other local CH modes and to the remaining molecular motions which lead to interesting relaxation and dephasing dynamics and to the observed "anomalous" line shape behavior. It seems that an adequate description of the overtone line shape requires that only a few nearly local modes which couple to the prepared oscillator need be considered explicitly. These modes impart a width to the prepared state and receive a bit of oscillator strength in return. Although it is difficult to extract detailed information about the microscopic dynamics of the relaxation process, it is clear that a broad line shape can be compatible with relatively slow energy relaxation within the molecule. In this case, the linewidth measures a dephasing lifetime for the prepared local oscillator. The way in which light "prepares" a local mode is discussed elsewhere.¹⁴

From our analysis most of the gross features thus far exhibited by polyatomic molecules appear understandable. For example, high lying overtones are not observed for low frequency modes even when they are anharmonic enough to couple strongly to absorb light. These modes are typically coupled to many other modes of similar frequency and thus as the overtone quantum number increases they melt (broaden out) into the background continuum. Indeed these processes can be responsible for the continuous background observed in overtone regions and the onset of the celebrated quasicontinuum in multiphoton absorption.

We find it heartening that the dependence of the linewidth on overtone quantum number and degree of deuteration are correctly given by a theory which adequately describes the observed overtone line shape. If the description offered here remains sufficient for interpreting the intramolecular (gas phase) overtone spectra of large molecules one can hope to similarly unravel the comparable intermolecular contributions to the line shapes which occur in neat liquids^{7b} and condensed phases.

ACKNOWLEDGMENTS

We wish to thank Dr. M. J. Berry, Dr. R. G. Bray, and Dr. K. V. Reddy for communicating their experimental results to us and for numerous invaluable discussions during the course of this work.

APPENDIX. TETRADIC FORMULATION OF THE LINE SHAPE

Using the partitioning of the Hamiltonian (6), the line shape problem has been brought into the familiar form of absorption of light by a system perturbed by a bath. The system is now the 6 CH (and CD) stretching modes whereas the bath is the rest of the modes. A formulation of the line shape designed to give closed expressions

for the bath averaged quantities²¹⁻²³ is the tetradic scattering formalism of Fano and Zwanzig.²¹ Let us denote a state of \mathbf{H}_0 by $|i\alpha\rangle$ where $i=g$, m denotes a system quantum number (g is the vacuum phonon state + photon, and $|m\rangle$ are all other system states with no photon). α denotes the bath quantum numbers. The line shape is

$$L(\omega) = \sum_{\alpha, \beta} \rho(\alpha) \langle\langle g\beta, g\beta | \hat{\mathbf{T}}(0) | g\alpha, g\alpha \rangle\rangle \equiv \langle \hat{\mathbf{T}}(0) \rangle \quad (\text{A1})$$

where we are using the familiar double bracket notation to indicate matrix elements of tetradic operators $\hat{\mathbf{O}}$. $\langle \dots \rangle$ denotes averaging over the bath as defined by (A1). The tetradic transition operator is

$$\hat{\mathbf{T}}(E) = \hat{\mathbf{V}} + \hat{\mathbf{V}}\hat{\mathbf{G}}(E)\hat{\mathbf{V}} \quad (\text{A2})$$

where

$$\hat{\mathbf{V}} = [\mu,] \quad (\text{A3})$$

$$\hat{\mathbf{G}}(E) = (E - \hat{\mathbf{L}} + i\epsilon)^{-1} \quad (\text{A4})$$

and

$$\hat{\mathbf{L}} = [\mathbf{H},] \quad (\text{A5})$$

is the Liouville operator, μ is the transition dipole. For the case of a single doorway state $|s\rangle$ carrying oscillator strength from the ground state (g), we have

$$\langle \hat{\mathbf{T}}(0) \rangle = |\mu_{gs}|^2 [\langle \hat{\mathbf{G}}_{gs,gs}(0) \rangle + \langle \hat{\mathbf{G}}_{sg,sg}(0) \rangle] \quad (\text{A6})$$

Using the relation

$$\hat{\mathbf{G}}_{ab,cd}(\omega) = -\hat{\mathbf{G}}_{ba,dc}^*(\omega^*) \quad (\text{A7})$$

we have

$$\langle \hat{\mathbf{T}}(0) \rangle = 2 |\mu_{gs}|^2 \text{Im}[\langle \hat{\mathbf{G}}_{gs,gs}(0) \rangle] \quad (\text{A8})$$

Here

$$\langle \hat{\mathbf{G}}(E) \rangle = [E - \hat{\mathbf{L}}_0^{\text{Local}} - \hat{\mathbf{V}}_M^{\text{Local}} - \langle \hat{\mathbf{R}}(E) \rangle]^{-1} \quad (\text{A9})$$

and

$$(\hat{\mathbf{L}}_0^{\text{Local}} + \hat{\mathbf{V}}_M^{\text{Local}})_{gm, gm'} = (\omega - E_m) \delta_{m, m'} - (\hat{\mathbf{V}}_M^{\text{LL}})_{mm'} \quad (\text{A10})$$

having defined

$$\hat{\mathbf{L}}_0^{\text{Local}} \equiv [\mathbf{H}_{\text{Local}}^0 + \mathbf{H}_R,] \quad (\text{A11})$$

and

$$\hat{\mathbf{V}}_M^{\text{Local}} \equiv [\mathbf{V}_M^{\text{LL}},] \quad (\text{A12})$$

with brackets $[,]$ indicating the usual commutator. The effective local mode coupling operator \mathbf{V}_M^{LL} as well as the effective normal mode (bath) coupling \mathbf{V}_M^{NN} and local mode-normal mode interaction \mathbf{V}_M^{LN} are defined by the decomposition of the intramolecular coupling \mathbf{V}_M [cf. Eqs. (3)] into each subspace. For example, defining the projector \mathbf{P} into the local mode subspace by

all bath states

$$\mathbf{P}\mathbf{O} \equiv \sum_{\alpha} \rho(\alpha) \mathbf{O}_{\alpha\alpha} \quad (\text{A13})$$

where \mathbf{O} is any operator and $\rho(\alpha)$ is the distribution function of the (normal mode) bath and its complement $\mathbf{Q} \equiv \mathbf{1} - \mathbf{P}$ we see that

$$\mathbf{V}_M = \mathbf{P}\mathbf{V}_M\mathbf{P} + \mathbf{Q}\mathbf{V}_M\mathbf{Q} + (\mathbf{P}\mathbf{V}_M\mathbf{Q} + \mathbf{Q}\mathbf{V}_M\mathbf{P}) \quad (\text{A14a})$$

$$\equiv \mathbf{V}_M^{\text{LL}} + \mathbf{V}_M^{\text{NN}} + \mathbf{V}_M^{\text{LN}} \quad (\text{A14b})$$

The level shift operator in (A9) has the matrix elements

$$\langle \hat{\mathbf{R}}(E) \rangle_{g m, g m'} = \sum_{\substack{\alpha, \beta, \gamma \\ m, m'}} \rho(\alpha) \times \frac{\langle \langle g \alpha, m \gamma | \hat{\mathbf{V}} | g \alpha, m' \beta \rangle \rangle \langle \langle g \alpha, m' \beta | \hat{\mathbf{V}} | g \alpha, m' \alpha \rangle \rangle}{E - E_\alpha - E_g - \omega + E_{m'} + E_\beta + i\epsilon}. \quad (\text{A15})$$

Diagonal elements of $\hat{\mathbf{R}}$ (where $m = m'$) are expected to be much larger than the off diagonal due to many cancellations occurring in the sum²¹⁻²³ due to uncorrelated phases of the matrix elements. We thus write

$$\langle \hat{\mathbf{R}}(0) \rangle_{g m, g m'} = \left[\Delta_m(\omega) - \frac{i}{2} \Gamma_m(\omega) \right] \delta_{m m'}, \quad (\text{A16})$$

where

$$\Gamma_m(\omega) = \sum_{m'' \neq \alpha \beta} |\langle m'' \beta | \hat{\mathbf{V}}_M | m \alpha \rangle|^2 \delta(E_\alpha + E_g + \omega - E_{m''} - E_\beta) = \sum_{m'' \neq m} \Gamma_{m'' \rightarrow m} + \bar{\Gamma}_m \quad (\text{A17})$$

$$\Gamma_{m'' \rightarrow m} = \sum_{\alpha \beta} \rho(\alpha) |\langle m'' \beta | \mathbf{V}_M^{\text{LN}} | m \alpha \rangle|^2 \delta(E_\alpha + E_g + \omega - E_{m''} - E_\beta) \quad (\text{A18})$$

$$\bar{\Gamma}_m = \sum_{\alpha \beta} \rho(\alpha) |\langle m \beta | \mathbf{V}_M^{\text{LN}} | m \alpha \rangle|^2 \delta(E_\alpha + E_g + \omega - E_m - E_\beta),$$

with \mathbf{V}_M^{LN} defined by the partitioning of Eq. (6). $\Gamma_{m'' \rightarrow m}$ are T_1 contributions to Γ_m whereas $\bar{\Gamma}_m$ is a purely dephasing (T_2) term which corresponds to no energy relaxation of the state $|m\rangle$. If the bath is initially cold ($T=0$) $\rho(\alpha) = \delta_{\alpha,0}$ and $E_{\alpha=0} = 0$, energy can only be put into the bath. Thus, $\bar{\Gamma}_m$ only contributes when $E_s - E_m > 0$. There will always be states m' such that $E_s - E_{m'} > 0$ permitting contributions through $\Gamma_{m' \rightarrow m}$ to Γ_m . As a result, the generalized width $\Gamma_m(\omega)$ may be skewed significantly to low energies ($\omega < E_s$), however, even at room temperature such skewing will not be substantial over the range $E_s \pm 100 \text{ cm}^{-1}$. Thus, the observed line shape $L(E)$ is not expected to be strongly temperature dependent until $T \lesssim 100 \text{ }^\circ\text{K}$ (although some temperature dependent effects may be observable near room temperature).

¹(a) W. M. Gelbart, S. A. Rice, and K. F. Freed, *J. Chem. Phys.* **57**, 4699 (1972); (b) K. Evans, R. Scheps, D. F. Heller, and S. A. Rice, *J. Chem. Soc. Faraday Trans. II* **69**, 856 (1973); (c) J. D. McDonald and R. A. Marcus, *J. Chem. Phys.* **65**, 2180 (1976); (d) K. F. Freed, *Chem. Phys. Lett.* **42**, 600 (1976); (e) D. J. Zvijac, S. Mukamel, and J. Ross, *J. Chem. Phys.* **67**, 2007 (1971).

²J. D. Rynbrandt and B. S. Rabinovitch, *J. Phys. Chem.* **75**, 2164 (1971).

³J. G. Moehlmann, J. T. Gleaves, J. W. Hudgens, and J. D. McDonald, *J. Chem. Phys.* **64**, 1242 (1976).

⁴J. M. Parson and Y. T. Lee, *J. Chem. Phys.* **56**, 4658 (1972).

⁵(a) J. G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, *Phys. Rev. Lett.* **38**, 1131 (1976); (b) M. J. Coggiola, P. A. Schulz, Y. T. Lee, and Y. R. Shen, *Phys. Rev. Lett.* **38**, 17 (1977); (c) D. F. Heller and J. T. Yardley (to be published).

⁶R. Bray and M. J. Berry, *J. Chem. Phys.* (to be published).

⁷J. W. Ellis, *Phys. Rev.* **32**, 906 (1928); **33**, 27 (1929).

⁸(a) T. E. Martin and A. H. Kalantar, *J. Chem. Phys.* **49**, 235 (1968); (b) R. L. Swofford, M. E. Long, and A. C. Albrecht, *J. Chem. Phys.* **65**, 179 (1976); (c) B. R. Henry, *Accts. Chem. Res.* **10**, 207 (1977).

⁹(a) K. G. Spears and S. A. Rice, *J. Chem. Phys.* **55**, 5561 (1971); (b) A. S. Abramson, K. G. Spears, and S. A. Rice, *J. Chem. Phys.* **56**, 2291 (1972).

¹⁰(a) P. W. Anderson and P. R. Weiss, *Rev. Mod. Phys.* **25**, 269 (1953); (b) R. Kubo, in *Adv. Chem. Phys.* XV, edited by K. E. Shuler, (Wiley, New York, 1969).

¹¹A. Abragam, *The Principles of Nuclear Magnetism*, (Oxford University, London, 1961).

¹²(a) R. G. Brewer and R. L. Shoemaker, *Phys. Rev. Lett.* **27**, 631 (1971); (b) A. H. Zewail, T. E. Orlowski, and D. R. Dawson, *Chem. Phys. Lett.* **44**, 379 (1976).

¹³(a) S. Mukamel, I. Oppenheim, and J. Ross, *Phys. Rev.* **17**, 1988 (1978); (b) S. Mukamel, *Chem. Phys.* **31**, 327 (1978).

¹⁴D. F. Heller, "Molecular Overtones as Local Modes," *Chem. Phys. Lett.* (in press).

¹⁵A. Nitzan and J. Jortner, *J. Chem. Phys.* **55**, 1355 (1971); **56**, 2079 (1972).

¹⁶D. F. Heller, K. F. Freed, and W. M. Gelbart, *J. Chem. Phys.*, **56**, 2309 (1972); I. H. Kühn, D. F. Heller, and W. M. Gelbart, *Chem. Phys.* **22**, 435 (1977).

¹⁷J. Jortner and S. Mukamel, in *The World of Quantum Chemistry*, edited by R. Daudel and R. Pullman, (Reidel, 1973).

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

¹⁹D. F. Heller, M. L. Elert, and W. M. Gelbart, *J. Chem. Phys.* **69**, 4061 (1978).

²⁰E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations*, (McGraw-Hill, New York, 1955).

²¹(a) R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, B. W. Downs, and J. Downs (Interscience, New York, 1961); (b) U. Fano, *Phys. Rev.* **131**, 259 (1963).

²²A. Ben-Reuven, *Adv. Chem. Phys.* **33**, 235 (1974).

²³(a) A. Ben-Reuven and S. Mukamel, *J. Phys. A* **8**, 1313 (1975); (b) S. Mukamel and A. Nitzan, *J. Chem. Phys.* **66**, 2462 (1977).

²⁴(a) R. Wallace, *Chem. Phys.* **11**, 189 (1975); (b) M. L. Elert, P. R. Stannard, W. M. Gelbart, *J. Chem. Phys.* **67**, 5395 (1977).

²⁵(a) H. S. Heaps and G. Herzberg, *Zeit. fur Physik* **133**, 48 (1952); (b) R. C. Hermann and K. E. Shuler, *J. Chem. Phys.* **21**, 373 (1953).

²⁶P. J. Nagy and W. L. Hase, *Chem. Phys. Lett.* **54**, 73 (1978).