

A PURE-DEPHASING MODEL FOR OVERTONE LINESHAPES

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A model is developed for calculating the pure-dephasing (T_2) contribution to overtone lineshapes in isolated molecules. The linewidth is attributed to time-dependent fluctuations in the frequency of the overtone transition, resulting from the vibrational motions in the molecule, and no transfer of energy (intramolecular vibrational distribution) occurs in this picture. Numerical calculations for 2,3,5,6-paradeuterobenzene are presented.

The observation of overtone lineshapes in medium size molecules (e.g. benzene and benzene derivatives) [1–7] has triggered a considerable attention in recent years [8–17]. Many of the high overtone lineshapes of aromatic C–H stretches have a characteristic width of $\approx 100 \text{ cm}^{-1}$. The simplest way to interpret this width is in terms of a “doorway state” picture in which the zero-order overtone state is coupled to a manifold of states whereby the vibrational energy is redistributed among the other modes of the molecule [8]. In this picture we have,

$$\Gamma = 2\pi |V|^2 \rho, \quad (1)$$

where V denotes the coupling strength, ρ is the density of states in the manifold and Γ is the fwhm of the resulting lineshape. This model was first suggested [8] following the pioneering experiments of Bray and Berry [1]. In this picture, the linewidth is associated with the inverse lifetime (vibrational redistribution rate) of the doorway state or in the language of relaxation theory a “ T_1 process”. Considerable progress was subsequently made in identifying the nature of the final states and the coupling strength [14].

It was suggested, however, that there exists an alternative mechanism to account for these lineshapes, namely a pure dephasing “ T_2 processes”

[9,10,18]. In this mechanism, the linewidth is attributed to time-dependent fluctuations of the overtone transition frequency resulting from the motions of the other molecular degrees of freedom. This mechanism can induce line broadening without changing the lifetime of the excited overtone state. In other words, the inverse linewidth Γ^{-1} is not associated with any intramolecular vibrational redistribution rate but rather with the magnitude and the time scale of the frequency fluctuations. Dephasing mechanisms are common in macroscopic lineshapes (e.g. pressure broadening [18,19], impurity spectra [20], and magnetic resonance [21]), but their significance in intramolecular lineshapes was not explored in detail.

A specific model was proposed recently towards the calculation of dephasing contributions to overtone lineshapes [10]. We consider a single local mode q (e.g. a C–H stretch) in a molecule whose normal modes are denoted Q . (Q should exclude the C–H stretch to avoid double counting.) The molecular Hamiltonian will be partitioned as follows:

$$H = H_L(q; Q) + H_N(Q), \quad (2)$$

where

$$H_L = -(\hbar^2/2\mu) \partial^2/\partial q^2 + D \{1 - \exp[-a(q - \bar{q})]\}^2 \quad (2a)$$

and

$$H_N = \sum_i \hbar \omega_i (P_i^2 + Q_i^2). \quad (2b)$$

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Here H_L denotes the local mode Hamiltonian which is taken to have a Morse potential. μ , D , a and \bar{q} are the reduced mass, the dissociation energy, inverse range and the equilibrium position of the local mode. H_N represents the other molecular normal modes where P_i and Q_i are the dimensionless momentum and coordinate of the i th mode, respectively. The coupling between the local mode and the rest of the molecule is represented by the parametric dependence of H_L on Q . We assume that the Morse parameters D and a depend on Q . (We could assume that \bar{q} also depends on Q , but this dependence will not contribute to the line broadening within our model.) We thus have

$$D(Q) \equiv \bar{D} + \delta D(Q), \quad a(Q) \equiv \bar{a} + \delta a(Q), \quad (3)$$

where \bar{D} and \bar{a} are the values of D and a when all other nuclei are in their equilibrium positions ($Q_i = 0$) and δD and δa represent the fluctuations in these quantities. If we ignore these fluctuations, we have the eigenvalues of H_L :

$$\bar{E}_n = \bar{\omega}_e(n + \frac{1}{2}) - \bar{x}(n + \frac{1}{2})^2, \quad (4)$$

where

$$\bar{\omega}_e = \hbar \bar{a} (2\bar{D}/\mu)^{1/2} \quad (4a)$$

and

$$\bar{x} = \hbar^2 \bar{a}^2 / 2\mu. \quad (4b)$$

The frequency of the n th overtone transition is therefore:

$$\bar{\Delta E}_{n,0} = (\bar{\omega}_e - \bar{x})n - \bar{x}n^2. \quad (5)$$

When the fluctuations δD and δa are taken into account, $\Delta E_{n,0}$ will be given by eqs. (4) and (5) where \bar{D} and \bar{a} replaced by D and a respectively. Performing a Taylor expansion, we get to lowest order in δD and δa

$$\Delta E_{n,0} = \bar{\Delta E}_{n,0} + U(Q), \quad (6)$$

where

$$U(Q) = (\partial \Delta E_{n,0} / \partial a) \delta a + (\partial \Delta E_{n,0} / \partial D) \delta D. \quad (7)$$

Making use of eqs. (4)–(7) we get

$$U(Q) = A \delta a / \bar{a} + B \delta D / \bar{D}, \quad (8)$$

where

$$A \equiv \bar{\omega}_e n - 2\bar{x}(n + n^2) \quad (8a)$$

and

$$B \equiv \frac{1}{2} \bar{\omega}_e n. \quad (8b)$$

Since the coordinates Q are dynamical variables which depend on time, eq. (6) implies that the frequency of the n th overtone is modulated in time. The resulting lineshape, within the second-order cumulant expansion is then [19]

$$I(\Delta) = \pi^{-1} \text{Re} \left(\int_0^\infty d\tau \exp[-i\Delta\tau - g(\tau)] \right), \quad (9)$$

where

$$\Delta = \omega - \bar{\Delta E}_{n,0}, \quad (9a)$$

$$g(\tau) = \int_0^\tau d\tau_1 (\tau - \tau_1) \langle U(0)U(\tau_1) \rangle \quad (9b)$$

and

$$\langle U(0)U(\tau) \rangle = \text{Tr} [U \exp(iH_N\tau) U \exp(-iH_N\tau) \rho_N]. \quad (9c)$$

ρ_N is the canonical density matrix of the normal modes, i.e.

$$\rho_N = \exp(-H_N/kT) / \text{Tr} [\exp(-H_N/kT)]. \quad (10)$$

The lineshape is given therefore in terms of the correlation function of the frequency fluctuations $\langle U(0)U(\tau) \rangle$. Alternatively, we can define the spectral density function

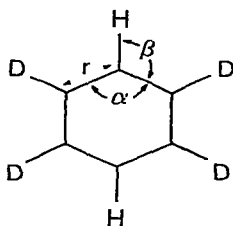
$$J(\omega) = (2\pi)^{-1} \int_{-\infty}^\infty d\tau \langle U(0)U(\tau) \rangle \exp(-i\omega\tau), \quad (11)$$

resulting in

$$g(\tau) = \int_{-\infty}^\infty d\omega \omega^{-2} J(\omega) [\exp(i\omega\tau) - i\omega\tau - 1]. \quad (12)$$

We shall now specify the model for 2,3,5,6-para-deuterobenzene. It is reasonable to assume that the local mode Hamiltonian H_L is most affected by the configuration of nuclei in the immediate vicinity of the local mode. We therefore take δD and δa to depend on the internal coordinates α , β and r , shown on the

following scheme:



Let us introduce the following dimensionless rectilinear internal coordinates

$$R_r \equiv (r - r_0)/r_0, \quad R_\alpha \equiv \alpha - \alpha_0, \quad R_\beta \equiv \beta - \beta_0, \quad (13)$$

Here, r_0, α_0, β_0 are the equilibrium values of these coordinates. We now expand δD and δa in these coordinates, i.e.

$$\delta D/\bar{D} = \sum_{\nu, \mu = \alpha, \beta, r} h_{\nu\mu}^{(D)} R_\nu R_\mu + \dots, \quad (14a)$$

$$\delta a/\bar{a} = \sum_{\nu, \mu = \alpha, \beta, r} h_{\nu\mu}^{(a)} R_\nu R_\mu + \dots \quad (14b)$$

The h being dimensionless coupling constants. The rectilinear coordinates may be expressed in terms of the normal modes, i.e.

$$R_\nu = \sum_i L_{\nu i} Q_i. \quad (15)$$

The transformation matrix \mathbf{L} was calculated using the relations

$$\mathbf{S} = \mathbf{U}\mathbf{R}, \quad \mathbf{S} = \mathbf{L}\mathbf{Q}, \quad (16)$$

i.e.

$$\mathbf{L} = \mathbf{U}^\dagger \mathbf{L}, \quad (17)$$

Here \mathbf{S} is the set of symmetry coordinates. \mathbf{U} and \mathbf{L} were taken from Albrecht [22] and Whiffen [23–25]. Making use of eqs. (8), (14) and (15) we finally get:

$$U(Q) = \sum_{ij} \eta_{ij} Q_i Q_j, \quad (18)$$

where

$$\eta_{ij} = \sum_{\nu\mu} (A h_{\nu\mu}^{(a)} + B h_{\nu\mu}^{(D)}) L_{\nu i} L_{\mu j}. \quad (19)$$

The spectral density (eq. (11)) may then be calculated using standard techniques:

$$\begin{aligned} J(\omega) &= (2\pi)^{-1} \int_{-\infty}^{\infty} d\tau \langle U(0)U(\tau) \rangle \exp(-i\omega\tau) \\ &= \sum_{i,j} \frac{1}{2} |\eta_{ij}|^2 [\bar{n}_i(\bar{n}_j + 1) \delta(\omega - \omega_i + \omega_j) \\ &\quad + (\bar{n}_i + 1)(\bar{n}_j + 1) \delta(\omega - \omega_i - \omega_j) \\ &\quad + \bar{n}_i \bar{n}_j \delta(\omega + \omega_i + \omega_j)], \end{aligned} \quad (20)$$

where \bar{n}_i is the occupation number of the i th oscillator,

$$\bar{n}_i = [\exp(\hbar\omega_i/kT) - 1]^{-1}. \quad (21)$$

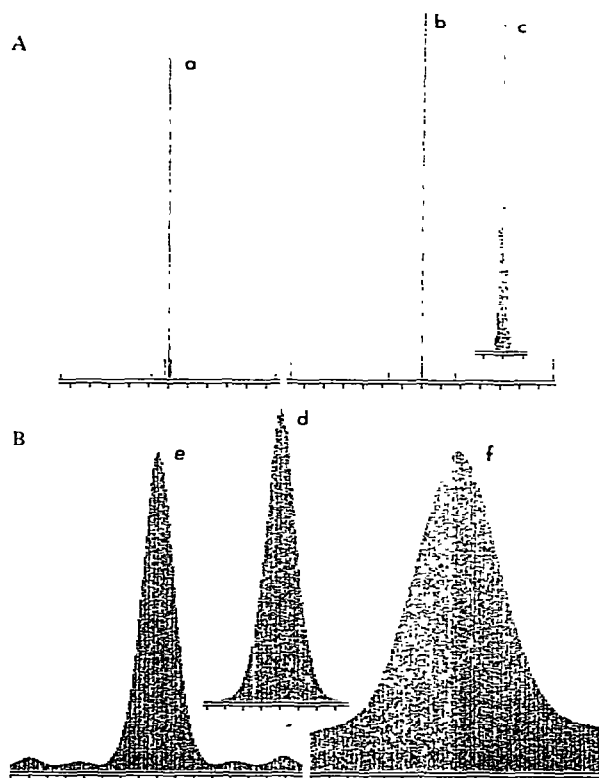


Fig. 1. Comparison of the contribution of the various rectilinear coordinates to the overtone line broadening. Shown is the lineshape $I(\Delta)$ (eq. (9)) for $n = 6, T = 300$ K. The spacing between divisions on the frequency axis is 20 cm^{-1} . (A) Diagonal coupling terms: (a) $h_{\alpha\alpha}^{(a)} = h_{\alpha\alpha}^{(D)} = 0.25$; (b) $h_{\beta\beta}^{(a)} = h_{\beta\beta}^{(D)} = 0.25$; (c) $h_{rr}^{(a)} = h_{rr}^{(D)} = 0.25$. (B) Mixed coupling terms: (d) $h_{\alpha r}^{(a)} = h_{\alpha r}^{(D)} = 0.25$; (e) $h_{\beta r}^{(a)} = h_{\beta r}^{(D)} = 0.25$; (f) $h_{\alpha\beta}^{(a)} = h_{\alpha\beta}^{(D)} = 0.25$. All the other h are taken to be zero.

The first term on the rhs of eq. (20) contains some contributions of frequencies ω around $\omega = 0$, and these will play the dominant role in the dephasing mechanism by forming "clumps" of lines around $\omega = 0$. The other two terms contain high frequencies $\omega = \pm(\omega_i + \omega_j)$ which will contribute to some weak combination bands but not to the broadening of our overtone transition of interest. The absorption lineshape was calculated by taking $J(\omega)$ (eq. (20)), calculating $g(\tau)$ (eq. (12)) which was then substituted in eq. (9). In figs. 1–4, we display the results of the numerical calculations. The only free parameters in the calculation are the dimensionless coupling constants h (eq. (14)). All the other information was taken from the force field of Albrecht [22,23]. We have included the 21 in-plane vibrations in the calculation. We first tested the effects of individual couplings $h_{\nu\mu}$. In fig. 1 we show a series of lineshapes in which one particular pair of coordinates $\nu\mu$ was taken to have $h_{\nu\mu}^{(a)} = h_{\nu\mu}^{(D)} = 0.25$ and all the other h were taken to be zero. It is clear that the mixed terms $h_{\alpha r}$, $h_{\beta r}$ and in particular $h_{\alpha\beta}$ (fig. 1B) are most effective in inducing the line broadening, whereas the diagonal terms $h_{\alpha\alpha}$, $h_{\beta\beta}$ and h_{rr} (fig. 1A) are much less effective. The effect of the coupling strength is shown in fig. 2 whereby we have taken a specific choice of h

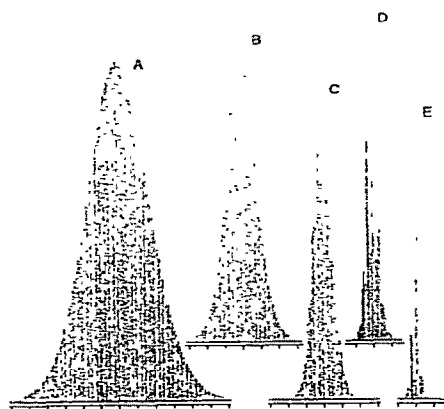


Fig. 2. Effect of the coupling strength (h) on the overtone lineshapes. Shown are $J(\Delta)$ for $n = 6$, $T = 300$ K. The spacing between divisions on the frequency axis is 20 cm^{-1} . (A) $h_{\alpha\alpha}^{(a)} = h_{\alpha\alpha}^{(D)} = h_{\alpha\beta}^{(a)} = h_{\alpha\beta}^{(D)} = 0.1$, $h_{\beta\beta}^{(a)} = h_{\beta\beta}^{(D)} = h_{\alpha\beta}^{(a)} = h_{\alpha\beta}^{(D)} = 0.1$, $h_{\alpha r}^{(a)} = h_{\alpha r}^{(D)} = h_{\beta r}^{(a)} = h_{\beta r}^{(D)} = h_{rr}^{(a)} = h_{rr}^{(D)} = h_{rr}^{(D)} = 0.2$; (B) same as (A) but all h divided by 2; (C) same as (A) but all h divided by 3; (D) same as (A) but all h divided by 5; (E) same as (A) but all h divided by 8.

Table 1

The major contributions to $J(\omega)/\omega^2$ for the parameters of fig. 2A. Shown are the largest contributions to $J(\omega)/\omega^2$ where $\omega = \omega_i - \omega_j$ (The first term on the rhs of eq. (20))

$\omega \text{ (cm}^{-1}\text{)}$	$\omega_i \text{ (cm}^{-1}\text{)}$	$\omega_j \text{ (cm}^{-1}\text{)}$	$J(\omega)/\omega^2$
0.8	960.9	960.1	0.79
3.4	588.6	585.2	42.2
4.3	1568.5	1564.2	0.50
5.2	818.6	813.4	4.03
17.7	977.8	960.1	0.22
48.9	867.5	818.6	0.054

and scaled all of them down gradually. The h parameters of the lineshape A were chosen such that the $\text{fwhm} \approx 85 \text{ cm}^{-1}$ will agree with the experiment [1]. As the couplings h are scaled down by factors of 2, 3, 5 and 8, the picture changes drastically and the lineshape E contains just a few lines. In table 1 we show the dominant terms in $J(\omega)/\omega^2$ and their origin (i.e. from which particular $\omega_i - \omega_j$ pair they arise). It is clear that a few low frequencies 3.4, 5.2, 0.8 and 4.3 cm^{-1} dominate. The dependence of the width on n is shown in fig. 3. In general, the coupling strength U (eq. (8)) and consequently the linewidth grow with n . This is not always the case in the experimental lineshapes [1], which implies that the dephasing is not the only broadening mechanism. Finally, in fig. 4 we show the dependence of the lineshapes

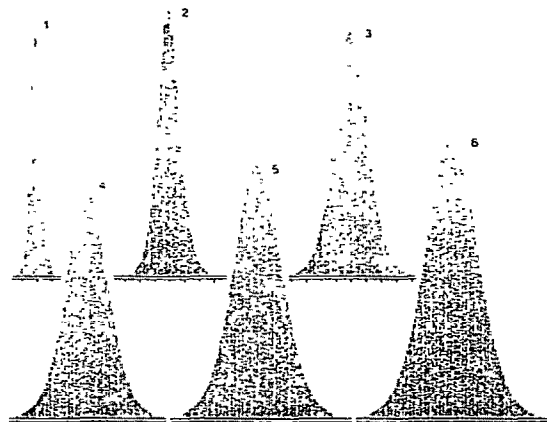


Fig. 3. The dependence of the lineshape on the overtone quantum number n . $T = 300$ K. The spacing between divisions on the frequency axis is 20 cm^{-1} . Other parameters same as fig. 2A. The value of n is indicated on each lineshape. The fwhm of these lineshapes are 33, 36, 53, 66, 77 and 85 cm^{-1} for $n = 1-6$, respectively.

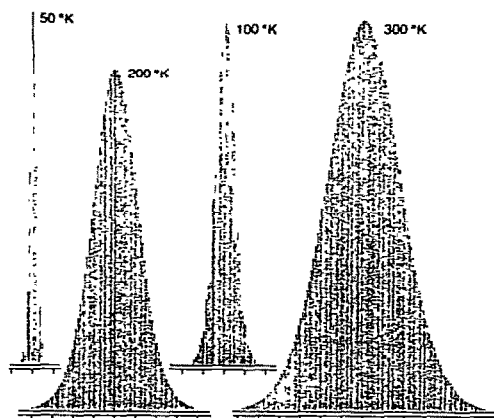


Fig. 4. Temperature dependence of the overtone lineshape, $n = 6$. The spacing between divisions on the frequency axis is 20 cm^{-1} . Other parameters same as fig. 2A.

on the temperature. There is a strong dependence at low temperatures and the broadening eventually vanishes at zero temperature. This dependence may be used to distinguish between the dephasing and the T_1 (intramolecular vibrational redistribution) mechanisms. The latter is expected to exhibit a much weaker temperature dependence and will have a finite contribution even at zero temperature. There exists one example (tetramethyldeoxetane) [12] which showed a very weak temperature dependence in the range 4–300 K suggesting that in this case T_1 is probably the dominant mechanism.

In summary, we have shown that a pure dephasing mechanism can be significant in inducing line broadening of overtone lineshapes. More studies are needed in order to evaluate the $h_{\nu\mu}$ parameters and determine the absolute magnitude of the resulting broadening and what fraction of the observed linewidth is accounted for by the present dephasing mechanism. This may be achieved either by monitoring the temperature dependence of the linewidth or by time-resolved double resonance experiments which probe directly the intramolecular vibrational redistribution processes.

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