Scaling of Overtone Line Broadening with Molecular Size

Shaul Mukamel

Department of Chemistry, University of Rochester, Rochester, New York 14627 (Received: August 15, 1983; In Final Form: January 9, 1984)

The scaling of the line widths of overtone transitions with the molecular size is discussed by exploring the analogy with macroscopic theories of line broadening. A general argument shows that, in the large molecule limit, the line width should become independent of the molecular size. The density of vibrational states is therefore irrelevant under these conditions, for the same reasons that the spectrum of an impurity in a solid matrix does not depend on the size of the matrix. Our argument explains recent experimental and theoretical results and holds both for \( T_1 \) and \( T_2 \) (dephasing) mechanisms for the line broadening. A simple model is proposed for treating the overtone line width in terms of purely \( T_2 \) processes.

The conventional formulations of intramolecular relaxation processes are based on the Fermi golden rule, i.e.,

\[
\Gamma = 2\pi|\mathcal{V}|^2\rho
\]

(1)

Here \( \Gamma \) is the rate of the process under consideration (radiationless transitions, intramolecular vibrational redistribution, etc.). \(|\mathcal{V}|^2\rho \) is an average coupling matrix element and \( \rho \) is the density of states in the final channel. This formula may be misinterpreted to imply that \( \Gamma \) should necessarily increase as \( \rho \) increases. The density of states \( \rho \) plays an important role in the common chemical intuition and many qualitative arguments in intramolecular dynamics and chemical kinetics are based on the behavior of the density of states as a function of energy, \( \rho(E) \). It is expected, e.g., that the intramolecular dynamics of large molecules are extremely fast since the density of states is very high, and that the rates should increase rapidly with the available energy. It is also expected that for a series of molecules with the same "active site" (e.g., an overtone line shape) and increasing size, \( \Gamma \) should be proportional to \( \rho \) since the relevant coupling \( |\mathcal{V}| \) is similar. This type of "intuition" contradicts the common wisdom of researchers working on macroscopic relaxation and line shape problems. If we consider, e.g., an impurity in a solid matrix then the density of modes in the host medium is proportional to the size of the sample (and the density of states increases even much more rapidly with the size). Obviously the size of the sample is irrelevant in the thermodynamic limit of a large sample, and we do not expect the line width of the impurity to grow with the volume of the sample. The reason is that usually \( V \) represents a localized interaction with a macroscopic range. As the size of the system increases, more degrees of freedom become relevant but the projection of each on the microscopic \( V \) decreases in exactly the same fashion, so that in the thermodynamic limit of large size \( |\mathcal{V}|^2\rho \) becomes independent of the size. Another way of viewing this is by realizing that \(|\mathcal{V}| \) and \( \rho \) cannot be considered to be independent parameters. That is, when we vary the molecular size, we always change both \(|\mathcal{V}| \) and \( \rho \), and it is virtually impossible to imagine a controlled intramolecular experiment where we vary \(|\mathcal{V}| \) and \( \rho \) separately. In fact for large systems they usually vary with molecular size in an opposite manner, such that the product \(|\mathcal{V}|\rho \) is invariant. Similar arguments may be given also regarding the dependence of the overtone line width on the degree of excitation (i.e., the overtone quantum number \( n \)). Any argument that is based on the density of states alone is therefore meaningless under these circumstances.

The idea that the rates of intramolecular relaxations in large molecules should become size independent was introduced and discussed at length in the context of line broadening in the quasicontinuum of molecular multiphoton processes. It was shown how the resulting reduced equations of motion obey exactly the scaling behavior discussed above. Recent experimental results

1 Alfred P. Sloan Fellow, Camille and Henry Dreyfus Teacher Scholar.

as well as theoretical calculations\(^6\) of the line width of the CH overtone transitions provide further evidence for this argument. The line width of the overtone transitions is insensitive to the molecular size or to the overtone quantum number \(n\). The density of vibrational states \(\rho\) on the other hand grows very rapidly with \(n\) and with the number of degrees of freedom \(N\) \((\rho \sim n^N)\). The purpose of this Letter is to point out that the arguments given earlier\(^4\) apply also to the overtone line shapes so that this size independence is not at all surprising. We shall consider two possible mechanisms: \(T_1\), i.e., the relaxation of energy from the CH mode to other molecular modes\(^5,9,13\) and a \(T_2\) mechanism in which the width is associated with fluctuations in the frequency of the overtone transition and does not correspond to population changes of the overtone state.\(^10,12\) We shall show that the same scaling behavior is common to both models: When the molecule is sufficiently large the resulting width is expected to be invariant with the molecular size.

### A. \(T_1\) Relaxation Model

We consider a model Hamiltonian consisting of a single local-mode coordinate \((R)\) and a harmonic bath\(^6\) with \(N\) coordinates \(Q,\ v = 1, 2, \ldots, N,\ i.e.,\)

\[
H = H_L(R) + H_B(Q) + V(R,Q) \tag{2}
\]

Here \(H_L\) is the local-mode Hamiltonian which can be taken to be a Morse oscillator:\(^{13}\)

\[
H_L(R) = \frac{P^2}{2M} + D[1 - \exp[-a(R - R_c)]^2] \tag{3}
\]

\(H_B\) is the bath Hamiltonian

\[
H_B = \sum_{\nu} \hbar \omega_\nu(P_{\nu}^2 + Q_{\nu}^2) \tag{4}
\]

where \(P_{\nu}\) and \(Q_{\nu}\) are the dimensionless momenta and coordinates. \(V\) is a coupling which could be kinetic energy or potential coupling, or both. Let us further denote the eigenstates of \(H_L\) and \(H_B\) by \(|n\rangle\) and \(|\alpha\rangle\), respectively

\[
H_L|n\rangle = E_n|n\rangle \tag{5a}
\]

\[
H_B|\alpha\rangle = E_\alpha|\alpha\rangle \tag{5b}
\]

Here

\[
E_n = \omega_n(n + \frac{1}{2}) - X(n + \frac{1}{2})^{12} \tag{6a}
\]

\[
\omega_n = \hbar a(2D/M)^{1/2} \tag{6b}
\]

and

\[
X = \hbar^2a^2/2M \tag{6c}
\]

\(\alpha\) stands for the collection of all bath harmonic quantum numbers. The relaxation rate of state \(|n\rangle\) to \(|n'\rangle\) (usually \(n' = n - 1\)) is given by

\[
\Gamma_{nm} = 2\pi \sum_\alpha \rho_\alpha |\langle n'|V|\alpha\rangle|^{2}\delta(\omega_{nm} - \omega_{\alpha}) = 2\pi |V|^2\rho \tag{7}
\]

This rate is the \(T_1\) contribution to the overtone line width. For the sake of our subsequent discussion it will be more convenient to rewrite eq 7 in the form of a Fourier transform of a correlation function of the coupling \(V\), i.e.,

\[
\Gamma_{nm} = \int_{-\infty}^{\infty} d\tau \left< V(\tau)V(0) \right> \tag{8a}
\]

where

\[
\left< V(\tau)V(0) \right> = \left< \rho_\alpha \right> \left< H_B(\tau)V \right> \tag{8b}
\]

Here \(\rho_\alpha\) is the canonical equilibrium density matrix

\[
\rho_\alpha = \exp(-H_B/kT)/\text{tr} \left[ \exp(-H_B/kT) \right] \tag{9}
\]

### B. A Dephasing \((T_2)\) Model for the Line Broadening

Dephasing of a spectral line arises from time-dependent fluctuations in its frequency which do no result in relaxation of population.\(^{10,12}\) Although the partitioning of \(H\) (eq 2) can be used to describe dephasing as well, by considering elements of \(V\) which are diagonal in \(n\), i.e., \((n\|V|\alpha\rangle)\),\(^{11}\) it is more convenient to adopt the following model Hamiltonian:

\[
H = H_L(R,Q) + H_B(Q) \tag{10}
\]

Here, the local-mode Hamiltonian is assumed to depend on the bath coordinates \(Q\). As a simple model we may assume that \(H_B\) is given by eq 3 but that the parameters \(D\) and \(a\) depend on the bath coordinates, i.e., \(D = D(Q)\), and \(a = a(Q)\). For this model the frequency of the \(n\)th overtone is given by

\[
\Delta E_{n,0} = (\omega_n - X)n - Xn^2 \tag{11}
\]

where \(\omega_n\) and \(X\) depend on the bath coordinates \(Q\). It will now be convenient to split \(D\) and \(a\) into their equilibrium value where the bath is in the equilibrium configuration \(Q_0\), and a fluctuation part, i.e.,

\[
D(Q) = D + \delta D(Q) \tag{12a}
\]

\[
a(Q) = a + \delta a(Q) \tag{12b}
\]

where \(D = D(Q_0)\), \(\delta \equiv a(Q_0)\). Equation 12 is nothing but a definition of \(\delta D\) and \(\delta a\). Upon the substitution of eq 6 and 12 in eq 11 we get

\[
\Delta E_{n,0} = \Delta E_{n,0} + U(Q) \tag{13}
\]

where

\[
\Delta E_{n,0} = (\omega_n - X)n - Xn^2 \tag{14}
\]

and

\[
U(Q) = A \frac{\delta a(Q)}{a} - B \frac{\delta D(Q)}{D} \tag{15}
\]

Here \(\omega_n\) and \(X\) are given by eq 6 with \(D\) and \(a\) replaced by \(\delta D\) and \(\delta a\), respectively, \(\Delta E_{n,0}\) is the frequency of the overtone transition when all other nuclei are in their equilibrium position, and \(A = \omega_n - 2X(n + n^2)\), \(B = \frac{1}{2}J\omega_n\). This model, in the Markovian limit whereby the time scales of the bath are fast compared with the line width, predicts a Lorentzian line shape whose dephasing width is given by\(^12\)

\[
\Gamma = \int_{-\infty}^{\infty} d\tau \left< U(\tau)U(0) \right> \tag{16a}
\]

where

\[
\left< U(\tau)U(0) \right> = \text{tr} \left( \exp(iH_B\tau)U \exp(-iH_B\tau)\rho_\alpha \right) \tag{16b}
\]

Upon the substitution of eq 15 in eq 16 we finally get

\[
\left< U(\tau)U(0) \right> = A^2 \frac{(\delta a\tau)(\delta a(0))}{\delta a} + B^2 \frac{(\delta D\tau)(\delta D(0))}{\delta D} + \frac{AB}{\delta a\delta D} \frac{(\delta a\tau)(\delta D(0)) + (\delta D\tau)(\delta a(0))}{\delta D} \tag{17}
\]

Within this model the line width is therefore attributed to fluctuations in time of the Morse potential parameters \(D\) and \(a\) which cause the overtone frequency to fluctuate. No energy transfer from the local mode to the other degrees of freedom occurs in this picture.

Equations 8 and 16 show that both the \(T_1\) and the \(T_2\) line widths are given by an integral of a correlation function of a bath operator (either \(V\) or \(L\)). In the following analysis we shall consider the correlation function \(\left< V(\tau)V(0) \right>\) but all our arguments hold for \(\left< U(\tau)U(0) \right>\) as well. An important property of \(V\) is that it is local in nature (i.e., depends on the coordinates of the atoms in the immediate vicinity of the local mode). Let us assume first that
$V$ is linear in some bond distance $q$ which in turn is a linear combination of the bath normal modes $Q_n$, i.e.

$$V = \bar{a}q = \sum_{i=1}^{N} c_i Q_n$$

(18)

So that

$$\langle V(\tau)V(0) \rangle = \sum_{i=1}^{N} c_i^2 \langle Q_i(\tau)Q_i(0) \rangle$$

(19)

The correlation function $\langle V(\tau)V(0) \rangle$ may be characterized by two parameters: (i) its value at $\tau = 0$

$$\Omega^2 = \langle V^2 \rangle = \sum_{i=1}^{N} c_i^4$$

(20)

and (ii) its typical time scale $\gamma^{-1}$. The value of $\Gamma$ (eq 8a or eq 16a) is therefore

$$\Gamma \sim \frac{2n}{\gamma}$$

(21)

Let us imagine a series of molecules with the same local mode but with increasing size of the bath. Since $c_i$ is the projection of a bond coordinate on the $i$th normal mode, it is scaled with the number $N$ of bath degrees of freedom as

$$c_i \sim 1/N^{1/2}$$

(22)

c2 therefore scales as 1/N. There are, however, $N$ terms in eq 20 so that $\Omega^2$ is expected to become independent of $N$ for large $N$. This argument will not change if the dependence of $V$ on $q$ is nonlinear. Let us assume for example that $V \sim \bar{a}q^2$. In such a case there will be typically $N^2$ terms in the expression of $\Omega^2$ but each one will be of the order of $c_i^2$ and will scale as $N^{-1}$. Therefore, again $\Omega^2$ is independent of $N$. $\gamma$ is roughly given by the frequency spread of the molecular modes. As $N$ increases, we usually have more frequencies of each type but their spread does not change significantly. Thus, $\gamma$ is also expected to go to a fixed value as $N \rightarrow \infty$. We have thus shown why $\Omega^2, \gamma$, and consequently the width $\Gamma$ become size independent. The previous argument was given in terms of states (rather than modes) and led to the same result. In conclusion we note the following:

1) We have shown that the width of overtone line shapes may be written as

$$\Gamma = 2\pi|\Omega|^2 \rho = 2\pi \Omega^2 / \gamma$$

(23)

It is interesting to note the connection between the parameters $|\Omega|^2, \rho$ and $\gamma$. Using a complete set of bath states $|\alpha\rangle, |\beta\rangle$, we have

$$|\Omega|^2 = \sum_{\alpha} P(\alpha) |\langle \alpha | \Omega | \beta \rangle|^2$$

(23a)

whereas

$$\Omega^2 = \sum_{\alpha,\beta} P(\alpha) |\langle \alpha | \beta \rangle|^2$$

(23b)

Thus, if the number of bath states contributing to eq 23 is $d$ then

$$\Omega^2 = |\Omega|^2 d$$

(24)

Similarly, since $\gamma$ is the spread of effectively coupled levels, $\rho$ is their density, and $d$ is their number, we have

$$\gamma = d \rho^{-1}$$

(25)

As the molecular size increases, $d$ increases, $|\Omega|^2$ and $\rho$ will both change but $\Omega^2$ and $\gamma$ will not change appreciably. It may be therefore advantageous to discuss intramolecular dynamics in terms of $\Omega$ and $\gamma$ rather than $|\Omega|^2$ and $\rho$ since $\Omega$ and $\gamma$ are independent and they both have a finite limit as $d \rightarrow \infty$. In the same limit $|\Omega|^2 \rightarrow 0$ and $\rho \rightarrow \infty$ and only the product $|\Omega|^2 \rho$ is significant. Furthermore, as shown in the reduced equation of motion for multiphoton processes, $\Omega^{-1}$ and $\gamma^{-1}$ (and not $\Omega^{-1}$ and $\rho$) are the two relevant molecular time scales in the problem.

2) The invariance of $\Gamma$ with size is not surprising if we think of an overtone as an "impurity" in a host. In the latter case the size of the host and the boundary conditions are, of course, immaterial.

3) The same conclusion will hold for line broadening of an impurity in a nonrigid cluster where the bath particles are free to move within the cluster. In the limit of large clusters this will reduce to the problem of pressure broadening and the line width will depend only on the density of particles within the cluster and not on its size.12

4) The present arguments are not restricted to the Markovian limit where the line is Lorentzian and they hold equally well any non-Markovian line shapes.

5) Finally, we wish to reiterate that, as noted earlier,11,15 the distinction between intramolecular $T_1$ and $T_2$ type processes is not absolute. The same terms in the Hamiltonian may be considered as $T_1$ or $T_2$ type depending on the partitioning of the Hamiltonian and on the basis set. The eigenstates $|n\rangle$ of $H_1(R,Q)$ (eq 10) depend parametrically on the bath coordinates $Q$ and are thus fluctuating in time. The eigenstates of $H_1(R)$ (eq 2), on the other hand, are fixed. This is analogous to adopting an adiabatic vs. a crude adiabatic basis set.16 The same terms which cause dephasing in the former basis set may cause relaxation of population ($T_2$) in the latter. It is therefore the convenience and simplicity in the description which will determine which kind of picture we want to adopt.

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