

Line broadening in rigid and nonrigid clusters and molecular electronic spectra. The spectral density formalism

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The spectral density formalism is used to solve for intramolecular line broadening in simple model systems corresponding to rigid (solid-like) and nonrigid (droplet-like) clusters of varying sizes. Both quantum mechanical and classical techniques are used to calculate the spectral density $J(\omega)$, which subsequently yields the absorption spectrum. Our calculations demonstrate how the averaging of molecular information takes place in the broadened line shapes. This occurs in two steps: The molecular eigenstates are grouped to form the spectral density $J(\omega)$, and the line shape in turn averages the information contained in $J(\omega)$. The semiclassical approximation for $J(\omega)$ is excellent for rigid clusters of any size. For nonrigid clusters it holds only when the cluster size is large enough. The present approach may be used also towards the calculation of molecular electronic spectra and overtone line shapes.

I. INTRODUCTION

Spectroscopic studies of intermediate size systems, e.g., polyatomic molecules, metal clusters, and van der Waals clusters of molecules and atoms are currently yielding novel type of information regarding intramolecular dynamics and relaxation processes.¹⁻⁹ When the system is small enough and at low degrees of excitation, the spectrum consists of well-resolved narrow lines. The spectroscopic information is then static in nature and consists of the level positions and their transition dipole matrix elements. In intermediate size and large systems the picture is, however, quite different. The observed spectra often consist of a series of broadened spectral features with well characterized widths and shapes. Under the envelope of each broadened feature there are, of course, many individual lines. Although in relatively small systems it is possible to resolve these individual lines, this task becomes formidable as the molecular size increases. The relevant spectroscopic information becomes therefore the positions and line shapes of these broadened features. This level of information is greatly reduced compared with a detailed study of individual levels. Nevertheless, it contains an extremely interesting amount of dynamical information regarding motions and relaxation processes in large molecules. The extraction of this information can be made by developing a reduced description of molecular dynamics using statistical methods. In such descriptions, we directly follow the behavior of correlation functions of key dynamical variables and do not attempt to consider individual eigenstates. Such procedures are common in the theoretical treatments of line shapes in *macroscopic* systems (e.g., pressure broadening of spectral lines,^{10,12} line broadening in condensed phases, etc.).¹³⁻¹⁷ It was recently shown how these ideas may be implemented in the calculation of spectra of isolated large molecules.^{18,19} In this paper, we demonstrate how macroscopic methods and in particular the spectral density approach can be used to calculate spectra of isolated molecules or molecular clusters. In Sec. II, we introduce the spectral density $J(\omega)$ and show how molecular spectra may be expressed in terms

of this quantity. In Sec. III, we present two expansion schemes towards the approximate calculation of $J(\omega)$: A perturbation theory and a density (cluster) expansion. In each case, we present a simple model for which the lowest order in the expansion is exact. Electronic spectra of molecules with linearly displaced harmonic surfaces are given exactly by a second-order perturbation theory for $J(\omega)$. The Anderson-Talman model of collisional broadening results in an exact expression for $J(\omega)$ which is first order in the density of perturbers. All higher order terms vanish identically in both cases. These examples demonstrate the power of the spectral density formalism in the calculation of molecular spectra. In Sec. IV, we construct a model of a rigid cluster (small solid) and develop the expression for $J(\omega)$ as a function of the cluster size. Both quantum and classical techniques are used. In Sec. V, we make a similar calculation for a nonrigid cluster with repulsive intermolecular force. Finally, in Sec. VI, we present numerical calculations for both models and discuss their significance.

II. THE SPECTRAL DENSITY FORMALISM

A variety of molecular line shape problems are defined in terms of the following two-state model^{12,17,18}

$$H = |a\rangle \left[H_a(Q) - \frac{i}{2}\gamma_a \right] \langle a| + |b\rangle \left[\omega_{ba} + H_b(Q) - \frac{i}{2}\gamma_b \right] \langle b|, \quad (1)$$

where

$$H_a = T_Q + V_a(Q), \quad (1a)$$

$$H_b = T_Q + V_b(Q). \quad (1b)$$

Here Q is the collection of nuclear coordinates, T_Q is the nuclear kinetic energy, and V_a and V_b are two potential functions corresponding to the ground ($|a\rangle$) and an electronically excited ($|b\rangle$) states, respectively, ω_{ba} is the frequency of the ab transition and γ_a and γ_b are the inverse lifetimes of these states. We further assume that the system interacts

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with the radiation field via the dipole coupling,

$$\mu = D(Q)(|a\rangle\langle b| + |b\rangle\langle a|)E(t), \quad (2)$$

E being an external electromagnetic field and $D(Q)$ is the electronic dipole operator. The Hamiltonian [Eq. (1)] applies to the electronic spectrum of polyatomic molecules whenever only one electronically excited state need to be considered. It also applies to spectra of clusters of e.g., a molecule + several rare gas atoms, as obtained in supersonic beams. It was recently shown²⁰ that this Hamiltonian may also apply to overtone spectra (such as CH stretches) in polyatomic molecules. In this case $|a\rangle$ and $|b\rangle$ are two "local mode" states of the CH stretch and Q are all other nuclear coordinates. Throughout this paper we shall make use of the usually weak dependence of D on the nuclear coordinates Q and simply set $D = 1$. This assumption may be easily relaxed without a major complication. Making use of this assumption, the normalized absorption line shape of a photon with frequency ω is given by¹⁰⁻¹⁸

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty d\tau \times \exp[-i(\omega - \omega_{ba})\tau - \frac{1}{2}(\gamma_a + \gamma_b)\tau] I(\tau), \quad (3)$$

where $I(\tau)$ is the dipole correlation function,

$$I(\tau) \equiv \langle \mu_{ab}(0)\mu_{ba}(\tau) \rangle = \operatorname{Tr}[\exp(iH_b\tau)\exp(-iH_a\tau)\rho_a], \quad (4)$$

i.e.,

$$I(\tau) \equiv \langle \exp(iH_b\tau)\exp(-iH_a\tau) \rangle, \quad (5)$$

where we have introduced the notation

$$\langle A \rangle \equiv \operatorname{Tr}(A\rho_a), \quad (6)$$

and ρ_a is the equilibrium molecular density matrix in the $|a\rangle$ electronic state, i.e.,

$$\rho_a = \exp(-\beta H_a) / \operatorname{Tr} \exp(-\beta H_a). \quad (7)$$

Here $\beta = 1/k_B T$, k_B is Boltzmann's constant, and T is the temperature. Using elementary manipulations, we can rewrite Eq. (5) in the form^{12,18}:

$$I(\tau) = \exp[i\langle V_b - V_a \rangle \tau] \left\langle \exp_- \left[i \int_0^\tau d\tau_1 U(\tau_1) \right] \right\rangle, \quad (8)$$

where

$$U \equiv V_b - V_a - \langle V_b - V_a \rangle, \quad (9)$$

$$U(\tau) = \exp(iH_a\tau)U\exp(-iH_a\tau), \quad (10)$$

and \exp_- is the negative time ordered exponential

$$\begin{aligned} \exp_- \left[i \int_0^\tau d\tau_1 U(\tau_1) \right] \\ \equiv 1 + i \int_0^\tau d\tau_1 U(\tau_1) + i^2 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 U(\tau_2)U(\tau_1) + \dots \end{aligned} \quad (11)$$

We note that $U(\tau)$ (the time dependent energy gap of the two electronic states) is the key quantity which determines the resulting line shape. It is common in macroscopic theories of line broadening to calculate the logarithm of $I(\tau)$ rather than $I(\tau)$ itself. This is done by introducing the spectral density $J(\omega)$ [Eq. (12)]. The introduction of $J(\omega)$, of course, does not affect the results when the calculation is exact. However, once approximations are made (e.g., perturbation theory,

cluster expansion, semiclassical approximations, etc.) it has a significant impact on the efficiency and the accuracy of the calculation. In this paper, we shall show how the spectral density is useful also for intermediate systems (clusters and polyatomic molecules). To that end we introduce the *molecular spectral density* $J(\omega)$ define as follows:

$$J(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \exp(-i\omega\tau)J(\tau), \quad (12a)$$

where

$$J(\tau) \equiv -\frac{d^2}{d\tau^2} \ln I(\tau) = -\frac{d^2}{d\tau^2} \ln \left\langle \exp_- \left[i \int_0^\tau d\tau_1 U(\tau_1) \right] \right\rangle. \quad (12b)$$

The absorption line shape [Eq. (3)] may then be expressed in terms of the latter quantity as follows^{12,18}:

$$I(\Delta) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty d\tau \exp[-i\Delta\tau - \frac{1}{2}(\gamma_a + \gamma_b)\tau - g(\tau)], \quad (13)$$

where

$$g(\tau) = -\int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega^2} [\exp(i\omega\tau) - i\omega\tau - 1], \quad (13a)$$

$$\Delta \equiv \omega - \omega_{ba} - \langle V_b - V_a \rangle, \quad (13b)$$

$\langle V_b - V_a \rangle$ is a static level shift. $J(\omega)$ is responsible for another contribution to the level shift as well as for the line broadening. Alternatively, we may express $g(\tau)$ in terms of $J(\tau)$ as follows:

$$g(\tau) = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 J(\tau_2) = -\ln \left\langle \exp_- \left[i \int_0^\tau d\tau_1 U(\tau_1) \right] \right\rangle, \quad (14)$$

and

$$J(\tau) = \frac{d^2 g(\tau)}{d\tau^2}. \quad (15)$$

Eqs. (8)–(15) may be easily derived using Eqs. (1)–(5). Our procedure for the calculation of molecular line shapes consists therefore of two steps: We first calculate the spectral density $J(\omega)$ and then, using Eq. (13), we get the spectrum. We shall show that $J(\omega)$ has several interesting properties and that we can easily develop efficient methods toward its calculation.

III. MICROSCOPIC CALCULATION OF THE SPECTRAL DENSITY

In this section, we shall develop two approximation schemes towards the calculation of the spectral density $J(\omega)$. A perturbation theory in U , and a density expansion which applies to line broadening in clusters. For each case, we shall present a simple microscopic model for which the expansion truncates rigorously at the lowest order.

A. Perturbation theory

The spectral density $J(\tau)$ may be expanded perturbatively in U . This corresponds to the cumulant expansion and may be achieved by rewriting Eq. (14) in the form¹²:

$$g(\tau) = -\ln \left\{ 1 + \left\langle \exp_- \left[i \int_0^\tau d\tau_1 U(\tau_1) \right] - 1 \right\rangle \right\}. \quad (16)$$

Upon expanding Eq. (16) and collecting terms according to the power of U we get:

$$g(\tau) = g_1(\tau) + g_2(\tau) + \dots, \quad (17)$$

where the g_i terms contain all the contributions to i th order in U . In order to write the expressions for g_i let us introduce the moments:

$$m_n(\tau_1, \tau_2, \dots, \tau_n) \equiv \langle U(\tau_1)U(\tau_2)\dots U(\tau_n) \rangle. \quad (18)$$

Note that by Eq. (9) we have

$$m_1(\tau) = \langle U \rangle = 0. \quad (19)$$

We then get:

$$g_1 = 0, \quad (20a)$$

$$g_2 = i^2 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 m_2(\tau_2, \tau_1), \quad (20b)$$

$$g_3 = i^3 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 m_3(\tau_3, \tau_2, \tau_1), \quad (20c)$$

$$g_4 = i^4 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \\ \times [m_4(\tau_4, \tau_3, \tau_2, \tau_1) - m_2(\tau_4, \tau_3)m_2(\tau_2, \tau_1) \\ - m_2(\tau_4, \tau_2)m_2(\tau_3, \tau_1) - m_2(\tau_4, \tau_1)m_2(\tau_3, \tau_2)]. \quad (20d)$$

The spectral density may then be obtained via Eq. (15). We shall consider now a simple model for which the perturbation expansion for J truncates exactly in second order. Let us take a harmonic molecule with linearly displaced potential surfaces,¹⁸ i.e.,

$$V_a(Q) = \sum_{\nu} \frac{1}{2} m_{\nu} \omega_{\nu}^2 Q_{\nu}, \quad (21a)$$

$$V_b(Q) = V_a(Q) + \sum_{\nu} \Delta_{\nu} Q_{\nu}. \quad (21b)$$

For this model

$$J(\tau) = \sum_{\nu} \Delta_{\nu}^2 \langle Q_{\nu}(0)Q_{\nu}(\tau) \rangle$$

$$= \sum_{\nu} \Delta_{\nu}^2 [\bar{n}_{\nu} \exp(-i\omega_{\nu}\tau) + (\bar{n}_{\nu} + 1) \exp(i\omega_{\nu}\tau)], \quad (22)$$

$$\bar{n}_{\nu} = \frac{1}{\exp(\beta\hbar\omega_{\nu}) - 1} \quad (23)$$

and

$$g(\tau) = \sum_{\nu} \frac{\Delta_{\nu}^2}{\omega_{\nu}^2} \{ (\bar{n}_{\nu} + 1) [\exp(i\omega_{\nu}\tau) - 1 - i\omega_{\nu}\tau] \\ + \bar{n}_{\nu} [\exp(-i\omega_{\nu}\tau) - 1 + i\omega_{\nu}\tau] \}. \quad (24)$$

This is a common model in molecular spectra and radiationless transitions.

B. The density (cluster) expansion

We consider a two-level system interacting with N structureless perturbers confined to a volume Ω . The potentials of interaction are taken to be pairwise additive, i.e.¹²:

$$V_a = \sum_p V_a^{sp} + \sum_{p>p'} V^{pp'}, \quad (25a)$$

$$V_b = \sum_p V_b^{sp} + \sum_{p>p'} V^{pp'}, \quad (25b)$$

Here V_v^{sp} denotes the system-perturber interaction which depends on the state of the system $v = a, b$, $V^{pp'}$ is the perturber-perturber interaction. We shall be interested in large clusters for which both N and Ω are large but the density of perturbers $n \equiv N/\Omega$ is finite. The density expansion is obtained by a successive solution of the line shape for clusters of increasing size. Denoting the dipole correlation function I [Eq. (5)] for a system consisting of the absorber + k perturbers by $I_k(\tau)$ we have

$$I_1(\tau) \equiv 1 + \frac{1}{\Omega} \chi_1(\tau), \quad (26a)$$

$$I_2(\tau) \equiv 1 + \frac{2}{\Omega} \chi_1(\tau) + \frac{1}{\Omega^2} \chi_2(\tau), \quad (26b)$$

and in general¹²

$$I_k(\tau) = 1 + \sum_{q=1}^k \binom{k}{q} \frac{1}{\Omega^q} \chi_q(\tau). \quad (26c)$$

Here χ_q represents the contribution of clusters of the system + q perturbers. The $1/\Omega^q$ terms represent the likelihood for the formation of such a cluster. χ_k as defined by Eqs. (26) are independent on the volume when $\Omega \rightarrow \infty$. The actual line shape in the thermodynamic limit ($N \rightarrow \infty$, $\Omega \rightarrow \infty$, $n = N/\Omega$ finite) can then be written in the form of Eq. (13) where

$$g(\tau) = \sum_{q=1}^{\infty} \frac{n^q}{q!} g_q(\tau), \quad (27)$$

and where

$$g_1(\tau) = \chi_1(\tau) = \Omega [I_1(\tau) - 1], \quad (27a)$$

$$g_2(\tau) = \chi_2(\tau) - \chi_1^2(\tau), \text{ etc.} \quad (27b)$$

It should be emphasized that to q th order in density we need consider clusters containing q perturbers at most.

We shall consider now a simplified model for which the expansion [Eq. (27)] truncates rigorously to first order in density. This is the Anderson Talman model of line broadening obtained from Eq. (25) by setting $V^{pp'} = 0$, i.e., we assume that the perturbers do not interact with each other but merely interact with the system.¹² We then take

$$V_a(Q) = \sum_p V_a(Q_p) \quad (28a)$$

and

$$V_b(Q) = \sum_p V_b(Q_p). \quad (28b)$$

(We assume that the two level impurity is fixed at the origin.) We then have

$$U = \sum_p U_p, \quad (29)$$

$$\rho_a = \prod_p \rho_a(Q_p). \quad (30)$$

Let us consider a system with one perturber only. It is then

clear that

$$I_1(\tau) = 1 - \frac{1}{\Omega} g_1(\tau), \quad (31)$$

where

$$g_1(\tau) = -\Omega \langle \exp(i\bar{H}_b \tau) \exp(-i\bar{H}_a \tau) - 1 \rangle, \quad (32)$$

where \bar{H}_a and \bar{H}_b correspond to the system + one perturber. The contribution of the single perturber is $O(1/\Omega)$ and $g_1(\tau)$ is $O(1)$. In this simple case, if we consider a cluster with N perturbers, we simply have

$$I(\tau) = \left[1 - \frac{1}{\Omega} g_1(\tau) \right]^N, \quad (33)$$

so that

$$g(\tau) = -N \ln \left[1 - \frac{1}{\Omega} g_1(\tau) \right]. \quad (34)$$

In the thermodynamic limit we get

$$g(\tau) = n g_1(\tau), \quad (35a)$$

$$J(\tau) = -n \frac{d^2}{d\tau^2} \langle \exp(i\bar{H}_b \tau) \exp(-i\bar{H}_a \tau) \rangle. \quad (35b)$$

For this model thus $g(\tau) = g_1(\tau)$ and the expansion truncates rigorously at first order, i.e.,

$$g_2 = g_3 = \dots = 0. \quad (36)$$

IV. LINE BROADENING IN RIGID CLUSTERS

As a first model for line broadening in clusters. We consider a "rigid cluster" i.e., a small harmonic crystal with one two-level absorber + N perturbers. We adopt a one dimensional model whereby the absorber is at the center of the crystal. Upon excitation, the force constant of the absorber and its two neighbors change by an amount Δk . Our model for H_a and H_b is therefore:

$$H_a = \sum_{i=1}^{N+1} \frac{p_i^2}{2m} + \frac{k}{2} \sum_{i=1}^N (X_{i+1} - X_i)^2, \quad (37a)$$

$$H_b = H_a + \frac{\Delta k}{2} [(X_s - X_{s-1})^2 + (X_{s+1} - X_s)^2]. \quad (37b)$$

Here, X_i is the Cartesian displacement of the i th atom (absorber or perturber) from its equilibrium position, and $s = (N/2) + 1$ is the absorber (we take N to be even). The normal modes of the crystal Q_i are given by

$$X_j = \sum_i B_{ji} Q_i, \quad i, j = 1, 2, \dots, N, \quad (38)$$

where

$$B_{ji} = \left(\frac{2}{N+1} \right)^{1/2} \cos \left[\frac{(i-1)j\pi}{N+1} \right]. \quad (39)$$

Introducing the frequencies,

$$\omega_j = \bar{\omega} \sin \left[\frac{j\pi}{2(N+1)} \right], \quad (40)$$

where

$$\bar{\omega} = 2\sqrt{k/m}, \quad (41)$$

we then have:

$$H_a = \sum_{j=1}^N \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{Q_j^2} + \frac{m}{2} \omega_j^2 Q_j^2 \right), \quad (42)$$

$$V_b - V_a \equiv H_b - H_a = \sum_{i,j=1}^N c_{ij} Q_i Q_j, \quad (43)$$

where

$$c_{ij} = \frac{\Delta k}{k} \cdot \frac{m}{N+1} \times [1 + (-1)^{i+j}] \omega_i \omega_j \sin \left(\frac{iN\pi}{2N+2} \right) \sin \left(\frac{jN\pi}{2N+2} \right). \quad (44)$$

The absorption line shape will be calculated using the second order perturbation theory. Upon truncating the expansion [Eq. (17)] we get:

$$g(\tau) = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 J(\tau_2), \quad (45)$$

and

$$J(\tau) = \langle U(0)U(\tau) \rangle. \quad (46)$$

We are now in a position to evaluate the correlation function $\langle U(0)U(\tau) \rangle$ and $J(\omega)$. To that end we make use of the relation which holds for harmonic systems²¹:

$$\langle Q_i Q_j Q_k Q_l \rangle = \langle Q_i Q_j \rangle \langle Q_k Q_l \rangle + \langle Q_i Q_k \rangle \langle Q_j Q_l \rangle + \langle Q_i Q_l \rangle \langle Q_j Q_k \rangle \quad (47)$$

resulting in

$$\begin{aligned} \langle U(0)U(\tau) \rangle &= \sum_{i,j=1}^N A_{ij} \omega_i \omega_j \\ &\times \{ (\bar{n}_i + 1)(\bar{n}_j + 1) \exp[i(\omega_i + \omega_j)\tau] \\ &+ 2(\bar{n}_i + 1)\bar{n}_j \exp[i(\omega_i - \omega_j)\tau] \\ &+ \bar{n}_i \bar{n}_j \exp[-i(\omega_i + \omega_j)\tau] \}, \quad (48) \end{aligned}$$

where

$$A_{ij} = \begin{cases} \left(\frac{\Delta k}{k} \right)^2 \frac{2\omega_i^2 \omega_j^2}{(N+1)^2 \bar{\omega}^4} & i, j \text{ even} \\ \left(\frac{\Delta k}{k} \right)^2 \frac{2(\bar{\omega}^2 - \omega_i^2)(\bar{\omega}^2 - \omega_j^2)}{(N+1)^2 \bar{\omega}^4} & i, j \text{ odd} \\ 0 & \text{else.} \end{cases} \quad (50)$$

\bar{n}_i is the mean occupation number of the i th oscillator, i.e.:

$$\bar{n}_i = [\exp(\hbar\omega_i/kT) - 1]^{-1}. \quad (50a)$$

Making use of Eqs. (46) and (12a) we get

$$\begin{aligned} J(\omega) &= \sum_{i,j} A_{ij} \omega_i \omega_j [(\bar{n}_i + 1)(\bar{n}_j + 1) \delta(\omega - \omega_i - \omega_j) \\ &+ 2(\bar{n}_i + 1)\bar{n}_j \delta(\omega - \omega_i + \omega_j) \\ &+ \bar{n}_i \bar{n}_j \delta(\omega + \omega_i + \omega_j)]. \quad (51) \end{aligned}$$

In the thermodynamic limit ($N \rightarrow \infty$) we can switch to inte-

gration and get

$$J(\omega) = \left(\frac{\Delta k}{k}\right)^2 \frac{8}{\pi^2 \bar{\omega}^4} \int_0^{\bar{\omega}} d\omega' \times \frac{1}{\exp(\beta \hbar \omega') - 1} \left[\frac{3F(\omega', \omega)}{\exp(-\beta \hbar \omega) - \exp(-\beta \hbar \omega')} - \frac{F(\omega' - \omega)}{\exp[-\beta \hbar(\omega + \omega')] - 1} \right], \quad (52)$$

where

$$F(\omega', \omega) = \frac{(\omega' - \omega)^3 (2\omega'^3 - \omega' \bar{\omega}^2) + \omega' \bar{\omega}^2 (\omega' - \omega) (\bar{\omega}^2 - \omega'^2)}{(\bar{\omega}^2 - \omega'^2)^{1/2} [\bar{\omega}^2 - (\omega' - \omega)^2]^{1/2}}. \quad (53)$$

Equations (51) and (52) constitute our final quantum mechanical expressions for $J(\omega)$. We shall turn now to a semiclassical method for evaluating the spectral density.^{18,22} The procedure goes as follows: We start at a given point in phase space and solve the classical equations of motion to get $U(\tau) \equiv U[Q(\tau)]$. We next perform a Fourier transform of $U(\tau)$ i.e.,

$$U(\tau) \equiv \sum_n U_n [\exp(i\omega_n \tau) + \exp(-i\omega_n \tau)], \quad (54)$$

and get

$$J_c(\tau) = \sum_n |U_n|^2 [\exp(i\omega_n \tau) + \exp(-i\omega_n \tau)], \quad (55)$$

so that

$$J_c(\omega) = \sum_n |U_n|^2 [\delta(\omega - \omega_n) + \delta(\omega + \omega_n)]. \quad (56)$$

Finally, we have to average $J(\omega)$ over ensemble of trajectories which span the initial distribution $\rho_a(P, Q)$. For a harmonic system, one trajectory is sufficient and we get

$$J_c(\omega) = (k_B T)^2 \sum_{i,j} A_{ij} [\delta(\omega - \omega_i - \omega_j) + 2\delta(\omega - \omega_i + \omega_j) + \delta(\omega + \omega_i + \omega_j)]. \quad (57)$$

We note that for this perturbative calculation

$$J_c(-\omega) = J_c(\omega). \quad (58)$$

This is a general property of classical correlation functions. Quantum mechanically, however, we have

$$J_c(-\omega) = \exp(-\beta \hbar \omega) J_c(\omega). \quad (59)$$

This is a manifestation of the fluctuation-dissipation theorem.^{18,23} A standard way to get an improved semiclassical formula for J is by taking the symmetric function obtained classically [Eq. (56)] and introducing the correct asymmetry required by the fluctuation dissipation theorem.^{18,23} To that end we define

$$\kappa(\omega) \equiv [1 + \exp(-\beta \hbar \omega)]^{-1}. \quad (60)$$

The semiclassical approximation for $J(\omega)$ which satisfies the fluctuation dissipation theorem is then

$$J_{sc}(\omega) = \kappa(\omega) J_c(\omega). \quad (61)$$

Equation (56) together with Eq. (61) is our final semiclassical approximation for $J(\omega)$. In Sec. VI we shall present some numerical calculations for $J(\omega)$ and the line shape $I(\Delta)$ using

the expressions derived in this section. It should be noted that $J(\omega)$ may be solved exactly for general two harmonic potentials V_a and V_b including linear coordinate displacements frequency changes as well as Duschinsky rotations. Numerical calculation using these more general expressions will be presented elsewhere.²⁴

V. LINE BROADENING IN NONRIGID CLUSTERS

We consider a one dimensional box of length L containing the absorber + N perturbers. Using the Anderson-Talman model, we assume that the perturbers do not interact with each other, but merely interact with the absorber. We further assume a repulsive exponential potential of interaction between the system and the perturbers, i.e.,

$$V_a^{sp} = A_a \exp(-\alpha Q_{sp}) \quad (62a)$$

and

$$V_b^{sp} = A_b \exp(-\alpha Q_{sp}). \quad (62b)$$

To lowest order in density, we need consider a system consisting of one absorber and one perturber. Denoting $Q = Q_{sp}$ we have

$$H_a = -\frac{\hbar^2}{2\mu} \frac{d^2}{dQ^2} + A_a \exp(-\alpha Q), \quad (63a)$$

$$H_b = -\frac{\hbar^2}{2\mu} \frac{d^2}{dQ^2} + A_b \exp(-\alpha Q), \quad (63b)$$

μ being the reduced mass of the absorber and perturber pair

$$\frac{1}{\mu} = \frac{1}{m_s} + \frac{1}{m_p}. \quad (64)$$

For this model we have

$$U \equiv V_b - V_a - \langle V_b - V_a \rangle = cA_a [\exp(-\alpha Q) - \langle \exp(-\alpha Q) \rangle], \quad (65)$$

where

$$c \equiv A_b/A_a - 1, \quad (66)$$

represents the coupling strength (when $c = 0$ there will be no line broadening). Assuming that the absorber is located at the origin ($Q_s \equiv 0$), the eigenfunctions and eigenvalues of H_a are given by²⁵

$$\psi_n(Q) = \left[\frac{q_n \sinh(\pi q_n)}{\pi L} \right]^{1/2} K_n(\theta), \quad (67a)$$

$$K_n(Q) = \int_0^\infty du \exp[-Q \cosh(u)] \cos(q_n u), \quad (67b)$$

$$q_n = \left(\frac{8\mu E_n}{\alpha^2 \hbar^2} \right)^{1/2}, \quad (67c)$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2\mu L^2}, \quad n = 1, 2, \dots \quad (67d)$$

We have taken the eigenvalues to be identical with those of a free particle in a box (ignoring the potential V_a). This is a good approximation when $\alpha L \gg 1$. The matrix elements of $(V_b - V_a)$ are then given by

$$(V_b - V_a)_{nm} = \frac{\pi c \alpha \hbar^2}{16 \mu L} [q_n q_m \sinh(\pi q_n) \sinh(\pi q_m)]^{1/2} \times \frac{q_n^2 - q_m^2}{\cosh(\pi q_n) - \cosh(\pi q_m)}, \quad (68)$$

and

$$\langle U(0)U(\tau) \rangle = \sum_{n \neq m} P_n |U_{nm}|^2 \exp(i\omega_{mn}\tau) + \frac{c^2}{\alpha^2 L^2} [\langle E^2 \rangle - \langle E \rangle^2], \quad (69)$$

$$P_n = \exp(-\beta E_n) / \sum_n \exp(-\beta E_n), \quad (70)$$

$$\omega_{mn} = \frac{\pi \hbar}{4 \mu L^2} (m^2 - n^2). \quad (71)$$

Neglecting the second (time independent) term of Eq. (69) and using Eq. (46) we get

$$J(\omega) = N \sum_{n \neq m} P_n |U_{nm}|^2 \delta(\omega - \omega_{mn}). \quad (72)$$

In the thermodynamic limit ($N \rightarrow \infty$, $L \rightarrow \infty$, $n = N/L$ finite) we have¹⁵

$$J(\omega) = \frac{nc^2\omega^2}{\alpha^4 \hbar^2} (2\pi \beta \mu^3)^{1/2} \int_0^\infty d\epsilon \exp(-\beta\epsilon) \times \frac{\sinh(\sigma\sqrt{\epsilon}) \sinh \sigma\sqrt{(\hbar\omega + \epsilon)}}{[\cosh \sigma\sqrt{(\hbar\omega + \epsilon)} - \cosh(\sigma\sqrt{\epsilon})]^2}, \quad (73)$$

where

$$\sigma = (8\pi^2 \mu / \alpha^2 \hbar^2)^{1/2}. \quad (74)$$

Equations (72) and (73) are our final quantum mechanical expressions for $J(\omega)$.

Let us turn now to a semiclassical calculation of the spectral density. To that end, we need to solve the classical equations of motion for our particle with the Hamiltonian H_a . The solution is²⁵

$$\exp(-\alpha Q) = \operatorname{sech}^2[(\epsilon/2\mu)^{1/2} \alpha \tau], \quad (75)$$

ϵ being the kinetic energy and at $\tau = 0$ we assume that the particle is at the turning point. Using Eqs. (65) and (75) we get

$$U(\tau) = c\epsilon \operatorname{sech}^2[(\epsilon/2\mu)^{1/2} \alpha \tau] - \langle U \rangle. \quad (76)$$

Taking the Fourier transform of Eq. (76) (excluding the time independent $\langle U \rangle$ term) we get

$$\chi(\omega, \epsilon) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} U(\tau) \exp(-i\omega\tau) d\tau = \frac{\mu c}{\alpha^2} \frac{\omega}{\sinh(\pi\omega/2b)}, \quad (77)$$

$$b = \alpha \sqrt{\frac{\epsilon}{2\mu}}. \quad (78)$$

The microcanonical correlation function of U (for a given ϵ) is then given by²¹

$$\hat{J}(\omega, \epsilon) = \pi \frac{|\chi(\omega, \epsilon)|^2}{T(\epsilon)}, \quad (79)$$

$T(\epsilon)$ being the time between collisions

$$T(\epsilon) = \frac{2L}{(2\epsilon/\mu)^{1/2}}. \quad (80)$$

The classical canonical correlation function is then obtained

by averaging Eq. (79) over ϵ , i.e.,

$$J_c(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega\tau) \langle U(0)U(\tau) \rangle d\tau = \pi \int_0^\infty \frac{|\chi(\omega, \epsilon)|^2}{T(\epsilon)} P(\epsilon) d\epsilon, \quad (81)$$

where

$$P(\epsilon) = \frac{1}{2} \left(\frac{\beta}{\pi\epsilon} \right)^{1/2} \exp(-\beta\epsilon). \quad (82)$$

Upon the substitution of Eqs. (78), (80), and (82) in Eq. (81) we get¹⁷

$$J_c(\omega) = \frac{nc^2\omega^2}{\alpha^4 \hbar^2} (\pi \beta \mu^3 / 8)^{1/2} \int_0^\infty d\epsilon \times \exp(-\beta\epsilon) \operatorname{cosh}^2[\pi\omega/\alpha(2\epsilon/\mu)^{1/2}]. \quad (83)$$

$J_c(\omega)$ is in this case continuous and does not depend on the cluster size, but only depends on the perturber density $n \equiv N/L$. We can get an improved semiclassical approximation for J by invoking the fluctuation-dissipation theorem; similar to what we did for the rigid clusters, i.e.,

$$J_{sc}(\omega) = \kappa(\omega) J_c(\omega), \quad (84)$$

where $\kappa(\omega)$ is given by Eq. (57). Numerical calculations using Eqs. (69), (73), (83), and (84) will be presented in the next section.

VI. DISCUSSION

In this paper we have developed the spectral density method towards the calculation of electronic spectra of polyatomic molecules and molecular clusters. The calculation is done in two steps: First, we calculate the spectral density $J(\omega)$. The absorption line shape is subsequently obtained by substituting $J(\omega)$ in Eq. (13) and carrying a Fourier transform using a standard fast Fourier transform program. This method is common in macroscopic line shape problems (e.g., impurities in condensed phases, pressure broadening) and its advantages for intramolecular line broadening were discussed recently.¹⁸ It was further extended towards the studies of two photon (fluorescence) and multiphoton spectra.^{12,26} Useful approximations for $J(\omega)$ may be obtained by using perturbation theory, the density expansion and semiclassical methods. These approximate techniques enable us to calculate the spectra directly without having to consider the exact vibronic eigenstates of the system. In the perturbative approach, e.g., we need to calculate the vibronic eigenstates of the ground electronic state $|a\rangle$ only (and not of $|b\rangle$!). Moreover, we can formulate the expansion in a different way such that we shall need the vibronic eigenstates of a chosen reference potential [e.g., $(V_a + V_b)/2$] instead.¹⁸ The cluster expansion allows us to consider smaller systems and to build the spectrum as an expansion in density. Finally, the semiclassical technique uses only classical trajectories and totally avoids the calculation of any quantum eigenstates.

We have calculated the electronic spectra of an impurity molecule in a cluster consisting of perturbers which do not interact directly with the radiation field, as a function of cluster size. The model applies, for example, to the supersonic beam spectra of van der Waals clusters of polyatomic

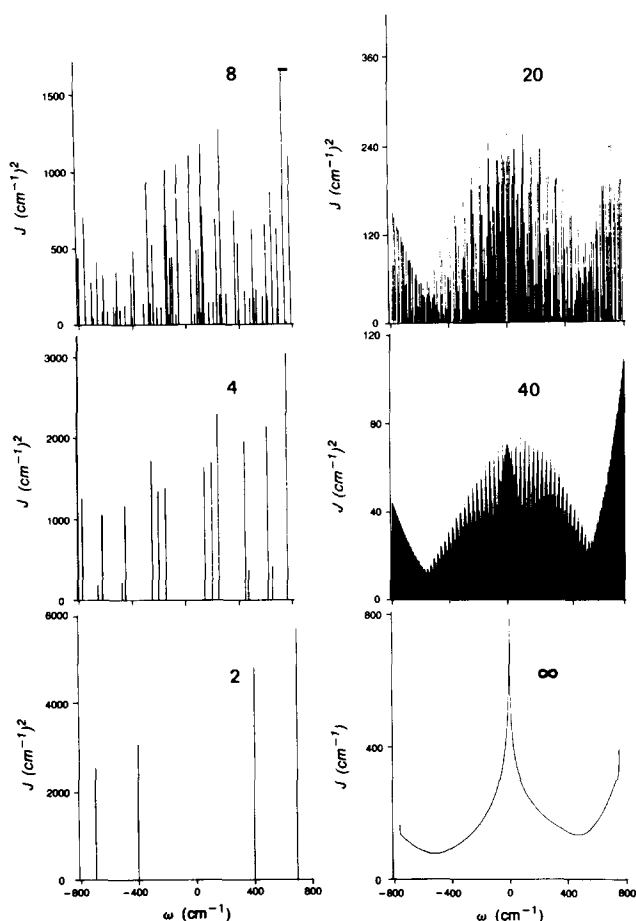


FIG. 1. The spectral density $J(\omega)$ [Eq. (51)] for a two-level absorber in a rigid cluster. The cluster size (N) is indicated in each panel. $T = 200$ °K, $\Delta k/k = 0.2$, $\bar{\omega} = 401.5$ cm^{-1} . Shown are the coefficients of the δ functions in the right-hand side of Eq. (51). The lower right panel ($N = \infty$) was calculated using Eq. (52).

molecules with rare gas perturbers.³ Both rigid (solid-like) and nonrigid (droplet-like) models for the clusters were considered. The thermodynamic properties of rigid and nonrigid clusters were considered recently²⁷ and our calculations compare the spectroscopic implications of the rigid vs the nonrigid structure. In Fig. 1 we show the spectral density $J(\omega)$ for rigid clusters with various sizes (2, 4, 8, 20, 40, and infinite numbers of perturbers). The finite size calculations were made using Eq. (51) together with Eq. (50), whereas the infinite cluster calculation was made using Eqs. (52) and (53). In Fig. 2 we show the corresponding line shape functions obtained by substituting $J(\omega)$ in Eq. (13). In Fig. 3 we display $J(\omega)$ for the nonrigid (drop-like) clusters with 2, 4, 8, 20, and infinite number of perturbers. The finite size calculations were made using Eq. (72) together with Eqs. (68) and (70). The infinite cluster (matrix) spectral function was calculated using Eq. (73). We also show the semiclassical calculation (which does not depend on cluster size). This was made using Eq. (84) together with Eq. (83). In Fig. 4 we show the corresponding line shapes $I(\Delta)$, obtained by substituting $J(\omega)$ of Fig. 3 in Eq. (13).

A close examination of Figs. 1–4 results in the following observations: For small clusters both $J(\omega)$ and $I(\Delta)$ consist of a series of isolated discrete lines. In these cases, the informa-

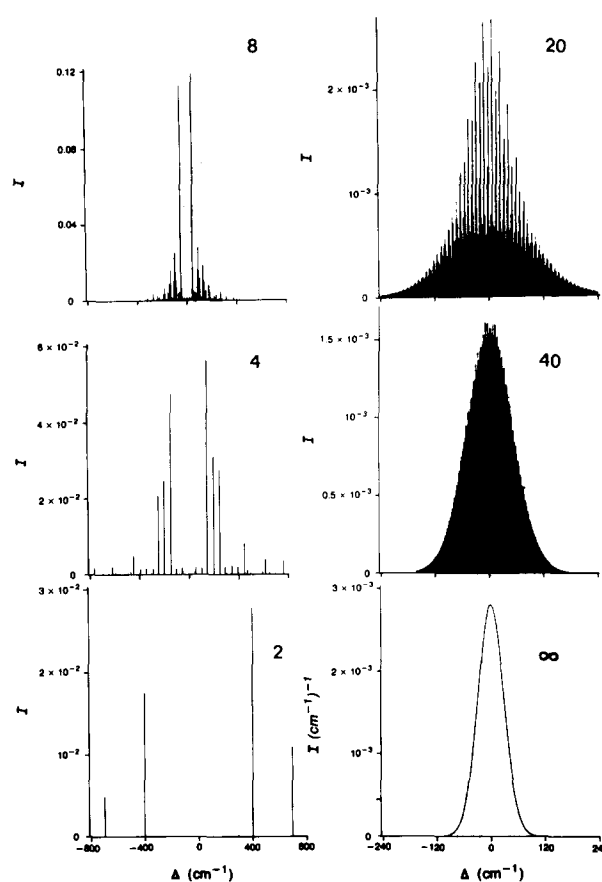


FIG. 2. The absorption line shape $I(\Delta)$ for a two-level absorber in a rigid cluster. The calculations were made using Eq. (13) and $J(\omega)$ of Fig. 1. $\gamma_b = \gamma_a = 0$. The finite size line shapes are normalized as $\sum_i I_i = 1$, and for clarity we omitted the large component at $\Delta = 0$. The $N = \infty$ line shape is normalized as $\int I(\Delta) d\Delta = 1$.

tion content of the spectra is simply the line positions and their strength (dipole matrix elements). This is the traditional way of analyzing molecular spectra. As the cluster size increases, however, there is a gradual loss of information and the spectrum probes global properties (envelopes consisting of many transitions) rather than individual lines. Our calculations enable us to monitor how this loss of information takes place. First, the molecular eigenstates are grouped together to form $J(\omega)$, and for large clusters $J(\omega)$ becomes practically continuous. The traditional spectroscopic information is then coarse grained and lost under the envelope of $J(\omega)$. Moreover, the spectrum $I(\Delta)$ is not always sensitive to the details of $J(\omega)$. An extreme example is the Markovian limit¹² in which the observed linewidth of $I(\Delta)$ is much narrower than the spectral width of $J(\omega)$. [See, e.g., the infinite cluster in Figs. 3 and 4 where the linewidth of $I(\Delta)$ is ~ 0.4 cm^{-1} , whereas the spectral width of $J(\omega)$ is ~ 200 cm^{-1} .] In this case, we have (on the time scale relevant for the line broadening)

$$J(\tau) \equiv \hat{\Gamma} \delta(\tau), \quad (85)$$

where

$$\hat{\Gamma} = \pi J(\omega = 0). \quad (86)$$

So that

$$g(\tau) = \hat{\Gamma} \tau, \quad (87)$$

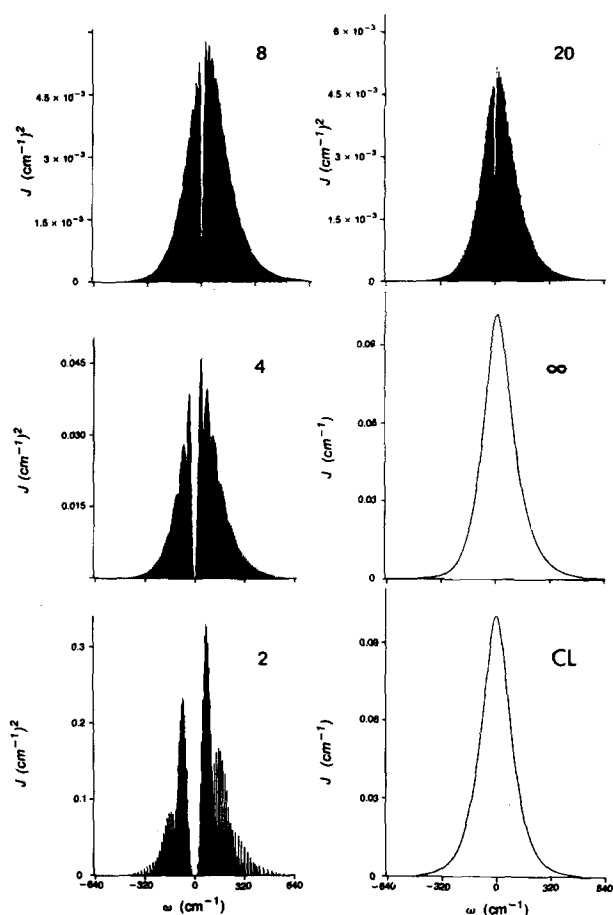


FIG. 3. The spectral density $J(\omega)$ [Eqs. (67), (68), (70), and (72)] for a two-level absorber in a nonrigid cluster. The cluster size (N) is indicated in each panel. $T = 50$ °K, $\mu = 20$ amu, $\alpha = 2.5$ Å⁻¹, $L/N = 2$ Å, $c = 0.1$. Shown are the coefficients of the δ functions in the right-hand side of Eq. (72). The $N = \infty$ curve was calculated using Eq. (73) and the semiclassical calculation [denoted (CL)] was made using Eq. (84) together with Eq. (83).

and

$$I(\Delta) = \frac{\Gamma}{\Delta^2 + \Gamma^2}, \quad (88)$$

where

$$\Gamma \equiv \frac{1}{2}(\gamma_a + \gamma_b) + \hat{\Gamma}. \quad (89)$$

The loss of information is in this case enormous, since the line shape is a simple Lorentzian and its information content is basically two numbers: $\hat{\Gamma}$ which is related to the zero frequency component of $J(\omega)$ [Eq. (86)], and the line position. In the Markovian limit which is quite common in macroscopic line broadening $I(\Delta)$ carries therefore very little information. It is clear from our calculations that the spectral density method is particularly useful for large clusters where many eigenstates contribute to the spectrum and the loss of information is substantial. In these cases calculating individual eigenstates becomes impractical and unnecessary. Finally, let us consider the semiclassical approximations for $J(\omega)$. At high temperature they become exact, however, the interest in cluster spectroscopy lies mainly at low temperatures whereby these spectra can be obtained such as in supersonic beams. The fluctuation dissipation theorem enabled us to use the classical correlation functions to construct useful

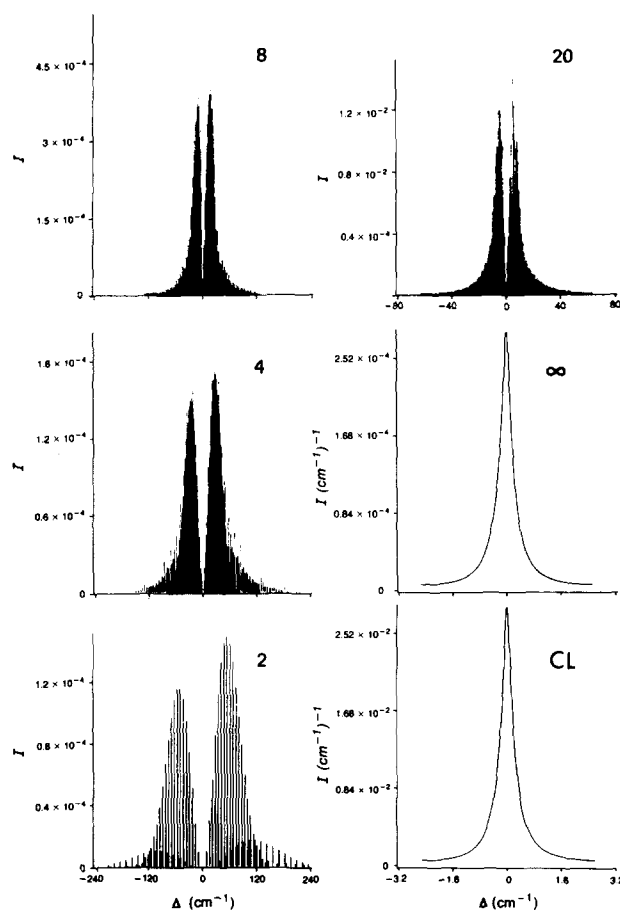


FIG. 4. The absorption line shape $I(\Delta)$ for a two-level absorber in a nonrigid cluster with N perturbbers. The calculations were made using Eq. (13) together with $J(\omega)$ of Fig. 3. $\gamma_a = \gamma_b = 0$. The line shapes are normalized as in Fig. 2.

quantum mechanical approximations for $J(\omega)$. It should be noted however, that $J(\omega)$, as defined in Eqs. (12) does not obey the fluctuation dissipation theorem. Only the second order perturbative expression [Eq. (46)] obeys it rigorously. Further attention should be given to this point in the future. We have carried out semiclassical calculations of $J(\omega)$ using the same parameters of Figs. 1 and 3. In the rigid case, the semiclassical results were almost identical with the quantum and we did not reproduce them here. For the nonrigid clusters, however, the semiclassical approximation does not depend on size and yields the infinite size even for $N = 2$. The reason is that in this case $J(\omega)$ is given by the frequency of collisions times the contribution of a single collision. For our model both of these are independent on size. The semiclassical approximation is therefore very poor for small nonrigid clusters and improves as the size increases. For the infinite cluster, it is identical with the quantum calculation as can be seen in Figs. 3 and 4.

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