SPECTRAL LINESHAPES OF MOLECULAR CLUSTERS

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The electronic spectral lineshape of an impurity molecule in a cluster is calculated. Both a rigid (solid-like) and a non-rigid (droplet-like) model for the cluster are considered and compared. The spectrum is calculated using the spectral density $J(\omega)$ which is related to the correlation function of the time-dependent energy gap between the two electronic states. Our calculations demonstrate how the information regarding individual eigenstates is lost under the broadened lineshape envelope in large clusters.

Recent progress in the spectroscopic studies of molecular and atomic clusters in supersonic beams creates the need for the development of efficient theoretical methods towards the calculation and interpretation of these spectra [1–4]. The spectroscopy of clusters is of great interest since it provides a unique means of interpolating between isolated molecules and solvated molecules in condensed phases. It is, of course, possible to approach the calculation of spectra of clusters from the small-molecule limit, by calculating eigenstates, as is done in traditional molecular spectroscopy. However, as the cluster size increases and line broadening sets in, the information regarding individual eigenstates is gradually eroded and it seems natural to adopt methods commonly used in *macroscopic* theories of line broadening rather than focus on individual eigenstates [5–7]. In this letter, we report some model calculations of the electronic spectrum of an impurity molecule in a rare gas cluster. The calculation is done by considering the energy gap U between the two electronic states and evaluating its correlation function which gives the *spectral density* [8–10]. The latter is then used to calculate the absorption spectrum. Both rigid (solid-like) and a non-rigid (droplet-like) models for the cluster are considered [11]. Our model system con-

sists of a molecule with two electronic states, embedded in a cluster. The Hamiltonian is:

$$H = |a\rangle[H_a(Q) - \tfrac{1}{2}i\gamma_a]\langle a|$$
$$+ |b\rangle[\omega_{ba} + H_b(Q) - \tfrac{1}{2}i\gamma_b]\langle b|. \tag{1}$$

where

$$H_a = T_Q + V_a(Q). \tag{1a}$$

$$H_b = T_Q + V_b(Q). \tag{1b}$$

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 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 our two states. We further assume that the molecule interacts with the radiation field via the dipole interaction.

$$\mu = D(|a\rangle\langle b| + |b\rangle\langle a|)E(t), \tag{2}$$

E being an external electromagnetic field, and D is the electronic dipole operator which for convenience is taken to be independent on the nuclear coordinates Q. (This assumption may be easily relaxed without a major complication.) The absorption lineshape may be expressed in terms of the spectral density $J(\omega)$ which is related to the correlation function of the energy gap between the two electronic states, i.e.

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$$U = V_b - V_a - \langle V_b - V_a \rangle, \tag{3}$$

$$J(\tau) = \langle U(0)U(\tau) \rangle$$

$$= \text{tr}[U \exp(iH_a\tau)U \exp(-iH_a\tau)\rho], \tag{4a}$$

$$J(\omega) = (1/2\pi) \int_{-\infty}^{\infty} d\tau \exp(-i\omega\tau)J(\tau). \tag{4b}$$

Here ρ is the equilibrium canonical density matrix, i.e.

$$\rho = \exp(-H_a/kT)/\text{tr} \exp(-H_a/kT). \tag{5}$$

The absorption lineshape (within the second-order cumulant expansion) is then given by [9]:

$$I(\Delta) = \pi^{-1} \text{Re} \int_0^{\infty} d\tau \exp[-i\Delta\tau - \tfrac{1}{2}(\gamma_a + \gamma_b)\tau$$

$$- g(\tau)], \tag{6}$$

where:

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

$$= \int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega^2} [\exp(i\omega\tau) - i\omega\tau - 1], \tag{7}$$

$$\Delta \equiv \omega - \omega_{ba} - \langle V_b - V_a \rangle, \tag{8}$$

ω is the radiation-field frequency and $\langle V_b - V_a \rangle$ is a static level shift. Within the spectral density formalism, the lineshape is therefore calculated by first calculating the spectral density $J(\omega)$ and then, using eqs. (6)–(8) we obtain the lineshape. $J(\omega)$ may be calculated, of course, by solving for the eigenstates of H_a but other methods (e.g. semi-classical) exist which enable us to get $J(\omega)$ directly from the Hamiltonian without calculating the cluster eigenstates [8,12].

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. Our model for V_a and V_b is therefore:

$$V_a = \tfrac{1}{2}k \sum_{i=1}^{N} (X_{i+1} - X_i)^2, \tag{9a}$$

$$V_b = V_a + \tfrac{1}{2}\Delta k [(X_s - X_{s-1})^2 + (X_{s+1} - X_s)^2]. \tag{9b}$$

Here, X_i is the cartesian displacement of the ith atom (absorber or perturber) from its equilibrium position and $i = s = \tfrac{1}{2}N + 1$ is the absorber (we take N to be even). We have assumed that the force constant (k) between the absorber and its neighbors changes upon excitation to $k + \Delta k$. For this model we have:

$$J(\omega) = \sum_{i,j} A_{ij}\omega_i\omega_j[(\bar{n}_i + 1)(\bar{n}_j + 1)\delta(\omega - \omega_i - \omega_j)$$

$$+ 2(\bar{n}_i + 1)\bar{n}_j\delta(\omega - \omega_i + \omega_j)$$

$$+ \bar{n}_i\bar{n}_j\delta(\omega + \omega_i + \omega_j)], \tag{10}$$

where ω_j are the normal mode frequencies

$$\omega_j = \bar{\omega} \sin[j\pi/(2N + 2)], \quad j = 1, 2, ..., N, \tag{10a}$$

with

$$\bar{\omega} = 2(k/m)^{1/2}, \tag{10b}$$

and

$$\bar{n}_j = [\exp(\hbar\omega_j/kT) - 1]^{-1}, \tag{10c}$$

$$A_{ij} = \left(\frac{\Delta k}{k}\right)^2 \frac{2\omega_i^2\omega_j^2}{(N+1)^2\bar{\omega}^4}, \qquad i,j \text{ even},$$

$$= \left(\frac{\Delta k}{k}\right)^2 \frac{2(\bar{\omega}^2 - \omega_i^2)(\bar{\omega}^2 - \omega_j^2)}{(N+1)^2\bar{\omega}^4}, \qquad i,j \text{ odd},$$

$$= 0, \qquad \text{else}. \tag{10d}$$

In the thermodynamic limit ($N \to \infty$) we can switch the summation in eq. (10) to integration and get

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

$$\times \{3F(\omega', \omega)/[\exp(-\beta\hbar\omega) - \exp(-\beta\hbar\omega')]\}$$

$$\times \{F(\omega', -\omega)/[\exp(-\beta\hbar(\omega + \omega')) - 1]\}, \tag{11}$$

where

$$F(\omega', \omega) = [(\omega' - \omega)^3(2\omega'^3 - \omega'\bar{\omega}^2)$$

$$+ \omega'\bar{\omega}^2(\omega' - \omega)(\bar{\omega}^2 - \omega'^2)]$$

$$\times (\bar{\omega}^2 - \omega'^2)^{-1/2}[\bar{\omega}^2 - (\omega' - \omega)^2]^{-1/2}. \tag{11a}$$

We next turn to a non-rigid (droplet-like) cluster. We consider a one dimensional box of length L con-

taining the absorber + N perturbers. We further assume that the perturbers do not interact with each other, but merely interact with the absorber via a repulsive interaction which depends exponentially

on the internuclear separation Q between the absorber and the perturber, i.e.

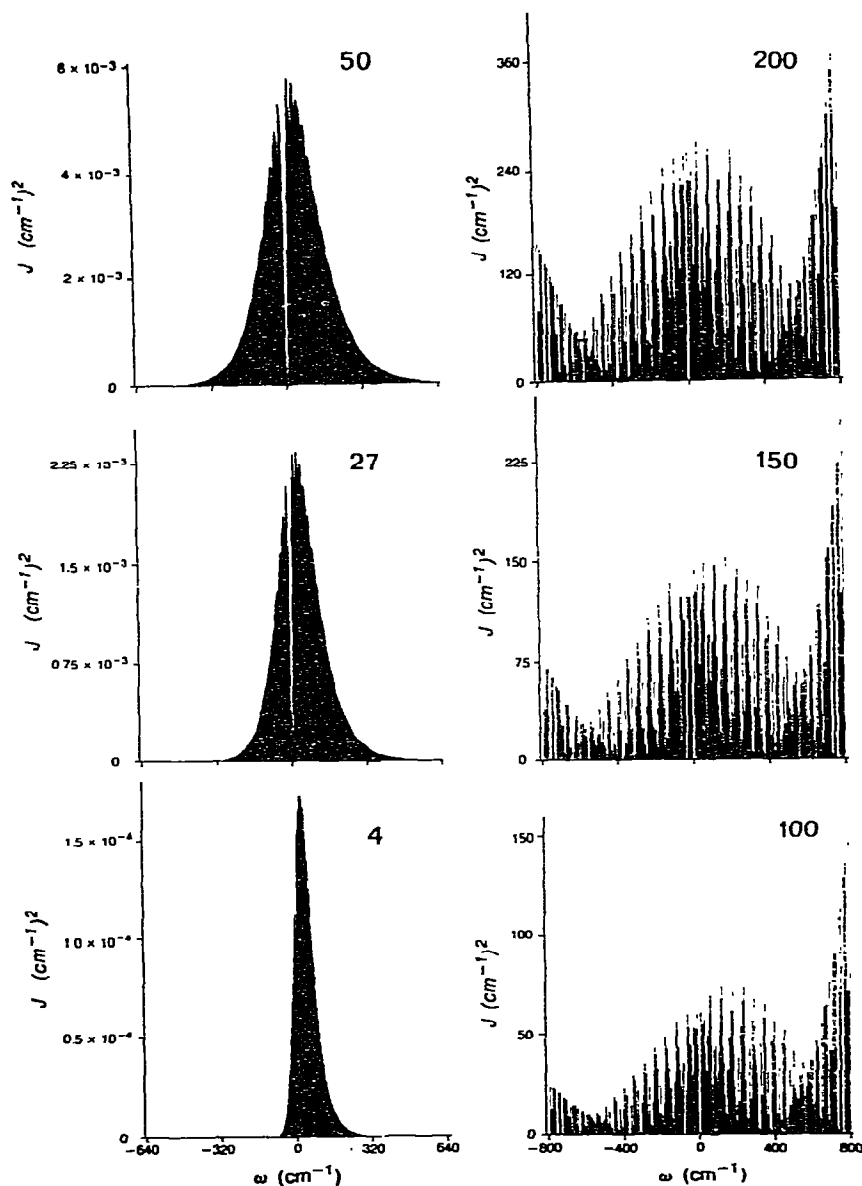$$V_a = A_a \exp(-\alpha Q), \tag{12a}$$

Fig. 1. The spectral density $J(\omega)$ for a two-level absorber in a non-rigid cluster of 8 perturbers (left column) and in a rigid cluster of 20 perturbers (right column). The temperature T (in K) is indicated in each panel. For the non-rigid cluster: $\mu = 20$ amu, $\alpha = 2.5$ A^{-1}, $L = 2$ A, $c = 0.1$. For the rigid cluster: $\Delta k/k = 0.2$, $\bar{\omega} = 401.5$ cm^{-1} are used. Shown are the coefficients of the δ functions in rhs of eqs. (10) and (13).

and

$$V_b = A_b \exp(-\alpha Q).$$ (12b)

For this model, denoting the reduced mass of the absorber and perturber by μ, we have:

$$J(\omega) = N \sum_{n \neq m} P_n |U_{nm}|^2 \delta(\omega - \omega_{mn}),$$ (13)

where

$$U_{nm} = (\pi c \alpha \hbar^2 / 16 \mu L)[q_n q_m \sinh(\pi q_n)\sinh(\pi q_m)]^{1/2}$$

$$\times (q_n^2 - q_m^2)/[\cosh(\pi q_n) - \cosh(\pi q_m)],$$ (13a)

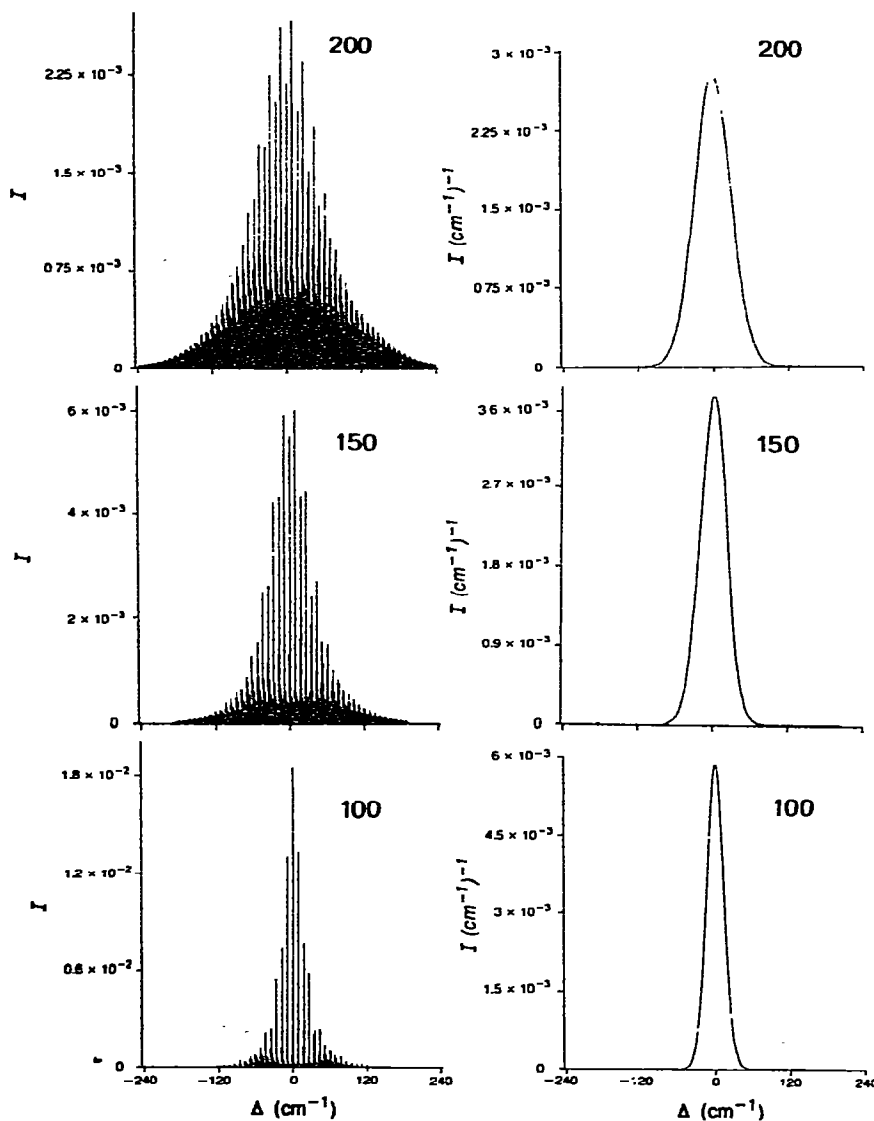$$P_n = \exp(-\beta E_n)\left(\sum_n \exp(-\beta E_n)\right)^{-1}.$$ (13b)

Fig. 2. The absorption lineshape $I(\Delta)$ [eq. (6)] for a two-level absorber in a rigid cluster. The temperature (in K) is indicated in each panel. The left column is for $N = 20$, uses $J(\omega)$ of fig. 1 and is normalized as $\Sigma I_i = 1$. For clarity, we have omitted the large component at $\Delta = 0$. The right column is for $N = \infty$, $J(\omega)$ was calculated using eq. (11) with the same parameters of the left column and the lineshape is normalized as $\int I(\Delta)d\Delta = 1$. $\gamma_a = \gamma_b = 0$.

$$\omega_{mn} = (\pi h/4\mu L^2)(m^2 - n^2), \tag{13c}$$

and

$$c = (A_b - A_a)/A_a.$$

In the thermodynamic limit ($N \to \infty$, $L \to \infty$, $\rho = N/L$ finite) we get:

$$J(\omega) = (\rho c^2 \omega^2/\alpha^4 h^2)(2\pi\beta\mu^3)^{1/2} \int_0^\infty d\epsilon \, \exp(-\beta\epsilon)$$

$$\times \frac{\sinh(\sigma\epsilon^{1/2})\sinh[\sigma(h\omega + \epsilon)^{1/2}]}{\{\cosh[\sigma(h\omega + \epsilon)^{1/2}] - \cosh(\sigma\epsilon^{1/2})\}^2}, \tag{14}$$
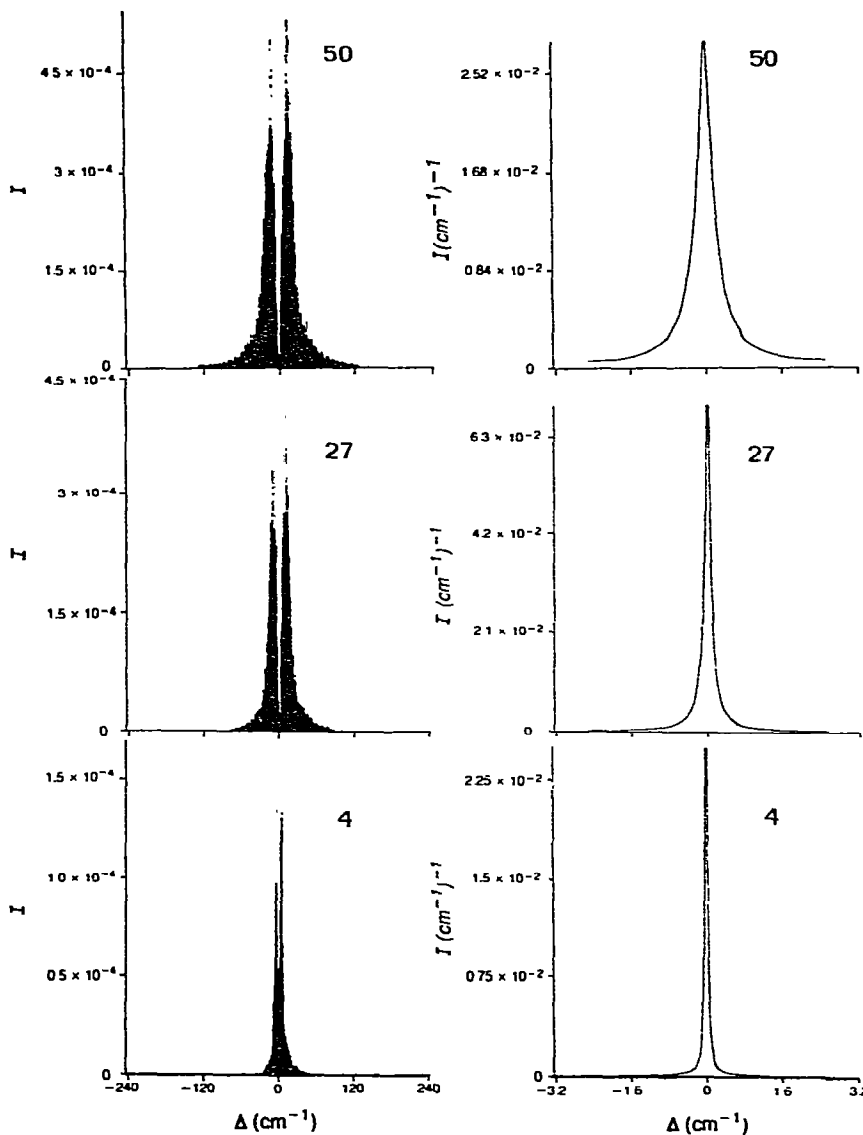
where

Fig. 3. The absorption lineshape $I(\Delta)$ [eq. (6)] for a two-level absorber in a non-rigid cluster. The temperature (in K) is indicated in each panel. The left column is for $N = 8$, uses $J(\omega)$ of fig. 1 and is normalized as $\Sigma I_i = 1$. For clarity we have omitted the large component at $\Delta = 0$. The right column is for $N = \infty$. $J(\omega)$ was calculated using eq. (14) with the same parameters of the left column and the lineshape is normalized as $\int I(\Delta)d\Delta = 1$. $\gamma_a = \gamma_b = 0$.

$$\sigma = (8\pi^2\mu/\alpha^2\hbar^2)^{1/2}. \tag{14a}$$

We have calculated the spectral density $J(\omega)$ as well as the lineshape function for the rigid and non-rigid models. In fig. 1 we show $J(\omega)$ for these two models as a function of temperature. The right column represents a rigid cluster of 20 perturbers and the left column represents a non-rigid cluster with 8 perturbers. Each J was calculated for several temperatures which are indicated in each panel (in K). Note how the eigenstates are grouped together to form a smooth envelope. We further note that $J(\omega)$ becomes more symmetric at higher temperatures. This is due to the fluctuation–dissipation relation:

$$J(-\omega) = \exp(-\hbar\omega/kT)J(\omega). \tag{15}$$

In fig. 2 we show the lineshapes for the rigid clusters of fig. 1 (left column). The right column gives for comparison the lineshape for an infinite cluster. This was done using eq. (11). Fig. 3 shows the corresponding lineshapes for the non-rigid cluster. The left column is for $N = 8$ using $J(\omega)$ of fig. 1. The right column was calculated for $N = \infty$ using eq. (14). It is clear that as the cluster size or the temperature increase, the information regarding individual eigenstates is eroded and the only relevant information is contained in the envelopes which may be obtained relatively easily using semiclassical methods [7,8,12]. We also note that the infinite cluster (matrix) lineshapes are simply Lorentzians in both cases, and all the structural information contained in the small

clusters is averaged [8,9]. The full-width half-maximum of the lineshape in this case is simply $2\pi J(\omega = 0)$.

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