Resonance optical response of small dielectric clusters

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The optical response of small clusters made of two-level molecules is investigated with particular emphasis on the near-resonance region. It is seen that the dielectric-function concept is still useful for describing first-order properties such as particle polarizability and particle-absorption profile; however, near resonance the dielectric response is strongly affected by dephasing and by the energy-level shifts resulting from clustering of molecules in space. Finite-size effects on the dielectric response are also more pronounced near resonance. Second-order response (light scattering) cannot be described by the dielectric function if dephasing processes are important (as they usually are near resonance) and different response functions must be used for different observables. For a cluster of N molecules the light-scattering cross section is made of two contributions: a coherent part (proportional to N^2) which may be described by the dielectric-function concept and an incoherent part (proportional to N). Implications for surface effects on the optical properties of molecules adsorbed on such clusters are considered.

I. INTRODUCTION

The response of small dielectric particles to an incident electromagnetic field has long been a subject of considerable interest.[1] Research in this subject has mounted recently with the discovery of a number of unusual electromagnetic phenomena associated with small particles, such as enhanced absorption, Raman scattering and fluorescence of molecules adsorbed on such particles,[2] unusual behavior of fluorescence by molecules embedded in such particles,[3] and enhanced far-infrared absorption by small metallic particles.[4,5]

Theoretical treatments of these problems have taken one of the following two routes: The first is to associate with the particle a dielectric function $\epsilon(\omega)$, taken either to be identical to that of the bulk material, or otherwise corrected (for metallic particles) by adding an imaginary contribution to ϵ due to finite-size effect (scattering of the electrons of the walls). The second route is to treat the particle as a microscopic quantum-mechanical system and to evaluate its dielectric properties from first principles. This second route has so far been followed only for metallic particles, modeling them as systems of free electrons subject to the constraint that they remain within a finite volume. Such studies have been carried out mostly with regard to the far-infrared absorption by small metallic particles.[5]

In this paper we investigate some other aspects of the dielectric response of small particles. We consider the particle to be a cluster of two-level atoms or molecules interacting with each other via the usual dipole-dipole interaction operator. The usual approach to the dielectric response of such a system consists of the following steps:

(a) Consider each atom to be represented by a classical polarizable point particle with polarizability $\alpha(\omega)$.

(b) Solve (for $\vec{\mu}_j$) the system of coupled equations

$$\vec{\mu}_j = \alpha(\omega)\left[\vec{E}_{ex}(r_j,\omega) + \sum_{j'} \overset{\leftrightarrow}{M}_{jj'}\cdot\vec{\mu}_{j'}\right], \quad (1.1)$$

where $\vec{\mu}_j$ is the dipole induced on the atom j at position r_j, $\vec{E}_{ex}(\vec{r}_j,\omega)$ is the ω component of the external radiation field at position $\vec{r}_j$

$$\vec{E}_{ex}(\vec{r}_j,t) = \int d\omega\, e^{-i\omega t}\vec{E}_{ex}(\vec{r}_j,\omega), \quad (1.2)$$

and where $\overset{\leftrightarrow}{M}_{jj'}$ is the dipole-dipole interaction tensor. In the long-wavelength (electrostatic) limit, where the linear size of the cluster is small relative to the radiation wavelength, the $\vec{r}_j$ dependence of $\vec{E}_{ex}$ may be disregarded and $\overset{\leftrightarrow}{M}_{jj'}$ is given by

$$\overset{\leftrightarrow}{M}_{jj'} = \frac{3\hat{u}_{jj'}\hat{u}_{jj'} - \overset{\leftrightarrow}{I}}{|r_{jj'}|^3}, \quad (1.3)$$

where $\vec{r}_{jj'} = \vec{r}_j - \vec{r}_j{}'$, $\hat{u}_{jj'} = \vec{r}_{jj'}/|r_{jj'}|$, and where $\overset{\leftrightarrow}{I}$ is the unit tensor. Unless otherwise stated we assume in what follows that the long-wavelength limit is valid. We also omit the notation concerning the ω dependence of the calculated quantities.

(c) Having found $\vec{\mu}_j$ for all sites j, the average polarization in the cluster is

$$\vec{P} = \frac{1}{\mathscr{V}}\sum_j \vec{\mu}_j \equiv \overset{\leftrightarrow}{K}\cdot\vec{E}_{ex}, \quad (1.4)$$

where $\mathscr{V}$ is cluster volume. The response tensor $\overset{\leftrightarrow}{K}$ is defined from this equation. Note that $\vec{P}$ and $\overset{\leftrightarrow}{K}$ depend in principle on all the positions $\{r_j\}$.

(d) Find a relation between the average field $\vec{E}$ in the particle and the incident field $\vec{E}_{ex}$. For clusters of ellipsoidal shape such a relation may be found from the identity[6]

$$\vec{E}=\vec{E}_{ex}-4\pi\overset{\leftrightarrow}{L}\cdot\vec{P} \; . \tag{1.5}$$

For an ellipsoid with axes a,b,c in the x, y, and z directions, L (the depolarization tensor) is diagonal and is given by

$$L_w=\tfrac{1}{2}abc\int_0^\infty ds\frac{1}{R(s)}\times\begin{cases}(s+a^2)^{-1}, & w=x\\(s+b^2)^{-1}, & w=y\\(s+c^2)^{-1}, & w=z\end{cases} \tag{1.6}$$

where

$$R(s)=[(s+a^2)(s+b^2)(s+c^2)]^{1/2} \; . \tag{1.7}$$

The factors L_j satisfy $\sum_j L_j=1$. For a sphere $L_j=\tfrac{1}{3}$. Equations (5) and (4) lead to

$$\vec{E}=(\overset{\leftrightarrow}{I}-4\pi\overset{\leftrightarrow}{L}\cdot\overset{\leftrightarrow}{K})\cdot\vec{E}_{ex} \; . \tag{1.8}$$

(e) Average Eqs. (4), (5), and (7) over the positions $\vec{r}_j$ of all atoms subject to any given constraint on these positions. Denote the average quantities by $\langle\vec{P}\rangle$, $\langle\vec{E}\rangle$, and $\langle\overset{\leftrightarrow}{K}\rangle$. In terms of these, Eqs. (1.4) and (1.8) take the forms

$$\langle\vec{P}\rangle=\langle\overset{\leftrightarrow}{K}\rangle\cdot\vec{E}_{ex} \; , \tag{1.4'}$$

$$\langle\vec{E}\rangle=(\overset{\leftrightarrow}{I}-4\pi\overset{\leftrightarrow}{L}\cdot\langle\overset{\leftrightarrow}{K}\rangle)\cdot\vec{E}_{ex} \; , \tag{1.8'}$$

which together imply

$$\langle\vec{P}\rangle=\overset{\leftrightarrow}{\chi}\cdot\langle\vec{E}\rangle \tag{1.9}$$

with the susceptibility $\overset{\leftrightarrow}{\chi}$ given by

$$\overset{\leftrightarrow}{\chi}=\langle\overset{\leftrightarrow}{K}\rangle\cdot(\overset{\leftrightarrow}{I}-4\pi\overset{\leftrightarrow}{L}\cdot\langle\overset{\leftrightarrow}{K}\rangle)^{-1} \; . \tag{1.10}$$

(f) The dielectric tensor $\overset{\leftrightarrow}{\epsilon}$ is now obtained from

$$\overset{\leftrightarrow}{\epsilon}=1+4\pi\overset{\leftrightarrow}{\chi}=1+4\pi\langle\overset{\leftrightarrow}{K}\rangle\cdot(\overset{\leftrightarrow}{I}-4\pi L\langle\overset{\leftrightarrow}{K}\rangle)^{-1} \; . \tag{1.11}$$

The following points should be made in connection with this derivation:

(1) The Clausius-Mossotti (CM) [or the equivalent Maxwell-Garnett (MG)] approximation for $\overset{\leftrightarrow}{\epsilon}$ is obtained by considering a sphere geometry ($\overset{\leftrightarrow}{L}=\tfrac{1}{3}\overset{\leftrightarrow}{I}$) and by taking $\langle\overset{\leftrightarrow}{K}\rangle=n\alpha\overset{\leftrightarrow}{I}$, where n is the number density and α is the polarization of the atoms. It should be noted that taking $\overset{\leftrightarrow}{K}=n\alpha\overset{\leftrightarrow}{I}$ in (4) is equivalent to assuming $\sum_j\overset{\leftrightarrow}{M}_{jj'}\cdot\vec{\mu}_{j'}=0$ in (1). This is the same assumption used in the Lorentz local-field argument.

(2) The above procedure for evaluating ϵ is used in a very similar form to evaluate the dielectric response of molecular films or of metal island films. The main difference lies in the fact that instead of Eq. (1.5) one must relate $\vec{E}$ to $\vec{E}_{ex}$ by a different procedure.

(3) While for infinite three-dimensional systems the as-

sumption $\sum_{j'}\overset{\leftrightarrow}{M}_{jj'}\cdot\vec{\mu}_{j'}=0$ may hold approximately (exactly for an infinite cubic lattice) due to cancellation of contributions of opposing signs, for finite particles (as well as for films) it is no longer applicable.

(4) The fact that $\sum_{j'}M_{jj'}\cdot\mu_{j'}\neq0$ for small clusters suggests that the dielectric tensor ϵ may depend on the cluster shape. This in turn implies that for small clusters of polarizable atoms or molecules the response tensor $\overset{\leftrightarrow}{K}$ (polarizability per unit volume of the cluster) is a more fundamental quantity than $\overset{\leftrightarrow}{\epsilon}$. $\overset{\leftrightarrow}{K}$ may be calculated directly from the equation describing the coupled dipoles [Eq. (1)] and its knowledge enables us to calculate the absorption and scattering cross-sections associated with the particle. These are given by

$$\sigma_a=\frac{4\pi}{c}\omega\mathscr{V}\,\mathrm{Im}(\hat{e}_I\cdot\overset{\leftrightarrow}{K}\cdot\hat{e}_I) \; , \tag{1.12}$$

$$\frac{d}{d\Omega}\sigma_{sc}=\left[\frac{\omega}{c}\right]^4\mathscr{V}^2|\hat{e}_s\cdot\overset{\leftrightarrow}{K}\cdot\hat{e}_I|^2 \; , \tag{1.13}$$

where $\hat{e}_I$ and $\hat{e}_s$ are unit vectors associated with the incident and scattered polarizations, c is the speed of light, and $\mathscr{V}$ is the cluster's volume.

A large body of work now exists[7] which studies several effects that lead to corrections to the procedure described above. The main effort has been directed towards studying the implications of nonisotropic polarizabilities (as is usually the case with molecules), of the presence of permanent dipole moments on the molecules, and of rotational relaxation associated with such permanent dipoles. In the present work we address other effects which become important when the incident radiation is close to resonance with a characteristic atomic or molecular absorption frequency. While a naive approach will use the same formalism described above with the resonance condition entering through the ω dependence of the polarizability (and in fact this is often done in works on molecular films[8]), there are several effects which become important near resonance which lead to both quantitative and qualitative difference from the off-resonance behavior. These are as follows:

(a) Clustering (or grouping together) of the atoms within the cluster under consideration leads to statistical broadening of the resonance. Every group of atoms considered separately will have a set of resonance frequencies (due to splitting of levels) which depends on the configuration. The response of the whole system corresponds to a superposition of such contributions. This is a configurational randomness effect.

(b) Dephasing due to rapid modulations of the resonance frequency resulting from local thermal interactions becomes important near resonance. Thus during the relatively long time delay associated with the atomic response near resonance, the atoms may get out of phase with each other and the cluster under study will respond more as a collection of independent atoms than as a dielectric body. This is a temporal randomness effect.

The two effects discussed here have long been recognized as important factors in theories of optical line shapes[9]. They are not always appreciated in theories of

optical response which use the dielectric function approach. In particular dephasing phenomena are not built into the usual theory of dielectric response. The present calculation takes account of both the dephasing and the atomic clustering effects within the model defined in Sec. II. We obtain shape- and size-dependent corrections to the Clausius-Mossotti theory of the dielectric function due to formation of atomic pairs [Eqs. (3.22), (3.24), and (3.27)]. We show that in the presence of dephasing the mean dielectric function has the same form as in the absence of dephasing, the only difference being that the atomic decay rate γ is replaced by the total atomic linewidth $\Gamma = \gamma + \kappa$ (κ is the dephasing rate). We further show that this mean dielectric function is useful only for calculating first-order processes such as light absorption by the cluster and that other response functions should be employed for higher-order processes. We calculate the response function that is appropriate for light scattering and show [cf. Eqs. (4.9) and (4.12)] that the cross section for light scattering is made of two contributions: an incoherent ("fluorescence") part which is proportional to κ and to the number of atoms in the cluster N, and a coherent part which, for clusters small relative to the radiation wavelength, is proportional to N^2. This leads to the ratio $N\gamma/\kappa$ between the coherent and incoherent response of a cluster of size N [cf. Eq. (4.20)] and to an estimate for the minimum cluster size ($N \sim 10^3 - 10^4$) for which the coherent response is larger, indicating a possibility of enhancing electromagnetic processes associated with molecules absorbed near such clusters.

This paper is organized as follows. In Sec. II we define our model. In Sec. III we consider the average dielectric function and the absorption line shape of small molecular clusters. In Sec. IV we consider the problem of light scattering by small molecular clusters and obtain expressions for the coherent and incoherent scattering components. Our conclusions are summarized in Sec. V.

II. THE MODEL

Our model is a cluster made of N polarizable particles ("atoms") with isotropic polarizabilities $\alpha(\omega)$. We take these polarizabilities to correspond to the Drude's model for the dipole induced on the atom

$$\ddot{\vec{\mu}} + \omega_0^2 \vec{\mu} + \gamma \dot{\vec{\mu}} = \alpha_0 \omega_0^2 \vec{E}_{ex}(t) , \qquad (2.1)$$

where $\vec{E}_{ex}(t)$ is the external electric field at the position of the atom, α_0 is the static polarizability, γ is the friction, and ω_0 is the resonance frequency of the atoms. Equation (2.1) implies

$$\alpha(\omega) = \frac{\omega_0^2 \alpha_0}{\omega_0^2 - \omega^2 - i\omega\gamma} . \qquad (2.2)$$

The atoms are located at positions $\vec{r}_j$ ($j = 1, \ldots, N$) and interact with each other as point dipoles [Eq. (1.3)]. Since we are interested in the near-resonance response of the system we may simplify Eq. (2.1) by considering its equivalent in the rotating-wave approximation (RWA)

$$\dot{\vec{\mu}} + (i\omega_0 + \tfrac{1}{2}\gamma)\vec{\mu} = \tfrac{1}{2} i\omega_0\alpha_0 \vec{E}_{ex}(\omega)e^{-i\omega t} , \qquad (2.3)$$

where we have now specified a particular external field frequency and where $\vec{E}_{ex}(\omega)$ now denotes the corresponding amplitude. Equation (2.3) is valid for $\omega \sim \omega_0$.

Dephasing effects are introduced by replacing ω_0 by the time-dependent frequency

$$\omega_0 \rightarrow \omega_0 + \phi_j(t) , \qquad (2.4)$$

where $\{\phi_j(t)\}$ are taken to be δ-correlated Gaussian random variables

$$\begin{aligned} \langle \phi_j(t) \rangle &= 0 , \\ \langle \phi_j(t)\phi_{j'}(t') \rangle &= \kappa \delta_{jj'}\delta(t-t') . \end{aligned} \qquad (2.5)$$

The equations of motion for the atomic dipoles are now

$$\dot{\vec{\mu}}_j + [i\omega_0 + i\phi_j(t) + \tfrac{1}{2}\gamma]\vec{\mu}_j = \tfrac{1}{2} i\omega_0\alpha_0 \left[\vec{E}_{ex}(\omega)e^{-i\omega t} + \sum_{\substack{j' \\ (j' \neq j)}} \overleftrightarrow{M}_{jj'} \cdot \vec{\mu}_{j'} \right] , \quad j = 1, \ldots, N . \qquad (2.6)$$

Equations (2.6) constitute one possible starting point for evaluating the optical response of the cluster. We note that the Drude model is known to account well for the optical response of a two-level system in the weak-field (absence of saturation effects) limit. We also use an alternative approach based on the quantum-mechanical equation of motion for the relevant elements of the density matrix of the coupled atom-radiation field system. We now describe this model.

Consider first a system consisting of N noninteracting two-level atoms. The ground and excited states of the jth atom are denoted by $|g_j\rangle$ and $|b_j\rangle$, respectively. The ground state $|G\rangle$ and a singly excited state $|B_j\rangle$ of the whole system are $\prod_j |g_j\rangle$ and $|b_j\rangle \prod_{j' (\neq j)} |g_{j'}\rangle$; the latter is N-fold degenerate. The state of the incident photon with wave vector $\vec{k}$ is denoted $|\vec{k}\rangle$ while that of the scattered photon is denoted $|\vec{k}'\rangle$. We take these notations to implicitly contain also the polarizations of the photons. These photons correspond to the incident and scattered frequencies $\omega = ck$ and $\omega' = ck'$. We are interested in light absorption and scattering by the cluster in the weak-field limit. In this limit it is sufficient to consider these processes in the lowest order in the cluster-field coupling. In this case the only states of the combined cluster-field system which are relevant are

$$|I\rangle = |\vec{k}\rangle \prod_j |g_j\rangle , \qquad (2.7)$$

$$|F\rangle = |\vec{k}'\rangle \prod_j |g_j\rangle , \qquad (2.8)$$

and

$$|B_j\rangle = |0\rangle \, |b_j\rangle \prod_{j'\neq j} |g_{j'}\rangle \; . \tag{2.9}$$

$|0\rangle$ denotes the vacuum state of the radiation field.

In the limited Hilbert space which is spanned by the set $|I\rangle$, $|F\rangle$, $\{|B_j\rangle\}$, the Hamiltonian may be written in the form

$$H = \hbar\omega_I |I\rangle\langle I| + \hbar\omega_F |F\rangle\langle F| + \hbar\omega_B |B\rangle\langle B| + \hbar V_{IB} \sum_j |I\rangle\langle B_j| \, e^{i\vec{k}\cdot\vec{r}_j} + \hbar V_{BI} \sum_j |B_j\rangle\langle I| \, e^{-i\vec{k}\cdot\vec{r}_j}$$

$$+ \hbar V_{FB} \sum_j |F\rangle\langle B_j| \, e^{i\vec{k}'\cdot\vec{r}_j} + \hbar V_{BF} \sum_j |B_j\rangle\langle F| \, e^{-i\vec{k}'\cdot\vec{r}_j} + \hbar \sum_j \sum_{\substack{j'\\ j'\neq j}} W_{jj'} |B_j\rangle\langle B_{j'}| \; , \tag{2.10}$$

where

$$\hbar\omega_I = E_g + \hbar\omega_k \; , \tag{2.11}$$

$$\hbar\omega_F = E_g + \hbar\omega_{k'} \; , \tag{2.12}$$

$$\hbar\omega_B = E_b \tag{2.13}$$

(E_g and E_b being the ground-state and singly excited-state energies of the cluster of noninteracting atoms), and where $V_{IB} = V_{BI}^*$ and $V_{FB} = V_{BF}^*$ are matrix elements of the atom–radiation-field coupling. The Hamiltonian (2.10) also includes interatomic coupling which we have modeled for simplicity as a term which only couples between the singly excited states of the system (coupling elements $W_{jj'}$) and thus causes transfer of excitation between the atoms.

The corresponding density operator is

$$\rho = \rho_{II} |I\rangle\langle I| + \rho_{FF} |F\rangle\langle F| + \sum_j \rho_{jj} |j\rangle\langle j| + \sum_j (\rho_{Ij} |I\rangle\langle B_j| + \rho_{jI} |B_j\rangle\langle I|)$$

$$+ \sum_j (\rho_{Fj} |F\rangle\langle B_j| + \rho_{jF} |B_j\rangle\langle F|) + \rho_{FI} |F\rangle\langle I| + \rho_{IF} |I\rangle\langle F| + \sum_j \sum_{\substack{j'\\ j'\neq j}} \rho_{jj'} |B_j\rangle\langle B_{j'}| \; . \tag{2.14}$$

Note that we use ρ_{Ij} as a shorthand notation for ρ_{I,B_j}, etc. The equation of motion for the density operator

$$\dot{\rho} = -\frac{i}{\hbar}[H,\rho] \tag{2.15}$$

yields equations for the evolution of the matrix elements ρ_{mn}. These are simplified by disregarding terms which lead to higher than lowest order (in V) contributions to the absorption and scattering processes. Furthermore, these equations are supplemented by adding terms describing relaxation (T_1) and dephasing (T_2) processes. The resulting equations of motion are as follows:

$$\dot{\rho}_{II} = -2\,\mathrm{Im}\left[V_{BI} \sum_j \rho_{ij} e^{-i\vec{k}\cdot\vec{r}_j}\right] \; , \tag{2.16a}$$

$$\dot{\rho}_{FF} = -2\,\mathrm{Im}\left[V_{BF} \sum_j \rho_{Fj} e^{-i\vec{k}'\cdot\vec{r}_j}\right] \; , \tag{2.16b}$$

$$\dot{\rho}_{jj} = -2\,\mathrm{Im}(V_{IB}\rho_{jI} e^{i\vec{k}\cdot\vec{r}_j})$$

$$+ i \sum_{\substack{j'\\ j'\neq j}} (W_{j'j}\rho_{jj'} - W_{jj'}\rho_{j'j}) - \gamma\rho_{jj} \; , \tag{2.16c}$$

$$\dot{\rho}_{Ij} = -i\omega_{IB}\rho_{Ij} + iV_{IB}\rho_{II} e^{i\vec{k}\cdot\vec{r}_j}$$

$$+ i \sum_{\substack{j'\\ j'\neq j}} W_{j'j}\rho_{Ij'} - \tfrac{1}{2}(\Gamma+\eta)\rho_{Ij} \; , \tag{2.16d}$$

$$\dot{\rho}_{Fj} = -i\omega_{FB}\rho_{Fj} + iV_{IB}\rho_{FI} e^{i\vec{k}\cdot\vec{r}_j} - iV_{FB} \sum_{j'} \rho_{j'j} e^{i\vec{k}'\cdot\vec{r}_{j'}}$$

$$+ \sum_{\substack{j'\\ j'\neq j}} W_{j'j}\rho_{Fj'} - \tfrac{1}{2}(\Gamma+\eta)\rho_{Fj} \; , \tag{2.16e}$$

$$\dot{\rho}_{FI} = -i\omega_{FI}\rho_{FI} - iV_{FB} \sum_j \rho_{jI} e^{i\vec{k}'\cdot\vec{r}_j} - \eta\rho_{FI} \; , \tag{2.16f}$$

$$\dot{\rho}_{j'j} = -iV_{BI} e^{-i\vec{k}\cdot\vec{r}_{j'}}\rho_{Ij} + iV_{IB} e^{i\vec{k}\cdot\vec{r}_j}\rho_{j'I}$$

$$-iW_{j'j}(\rho_{jj} - \rho_{j'j'})$$

$$+ i \sum_{\substack{j_1\\ j_1\neq j,j'}} (W_{j_1 j}\rho_{j'j_1} - W_{j'j_1}\rho_{j_1 j}) - \Gamma\rho_{j'j}$$

$$(j'\neq j) \; . \tag{2.16g}$$

In these equations γ is the (T_1) relaxation rate of the excited atomic level (which includes, in principle, radiative and nonradiative contributions) and $\Gamma = \gamma + \kappa$ is the sum of T_1 (relaxation) and T_2 (dephasing) rates associated with the atomic states (the dephasing rate associated with the excited atomic states is denoted by κ; that associated with the ground state is denoted by η). We note again that in obtaining Eqs. (2.16) from (2.10), (2.14), and (2.15) we have neglected terms that lead to contributions of higher order in the cluster–radiation-field coupling.

Equations (2.16) provide an alternative to Eqs. (2.6) as a starting point for our problems. Note that Eqs. (2.6) are

written with the assumption that the cluster is much smaller than the radiation wavelength [so that no phase factors of the form $\exp(i\vec{k}\cdot\vec{r}_j)$ appear], while Eqs. (2.16) are not limited in this way. In the following sections we shall use both approaches in discussing different aspects of our problem.

III. THE MEAN DIELECTRIC FUNCTION

A. Effect of dephasing

Starting from Eq. (2.6) as a near-resonance approximation to Eq. (2.1), we calculate the average of the total dipole induced in our system by the field $\vec{E}_{ex}$. This is

$$\langle \vec{\mu}_{tot}(t) \rangle = \left\langle \sum_j \vec{\mu}_j(t) \right\rangle \equiv \mathcal{V} P , \tag{3.1}$$

where $\mathcal{V}$ is the volume and P the averaged polarization. Rewrite Eq. (2.6) in the form

$$\dot{\underline{\mu}} + [\underline{\overset{\leftrightarrow}{\Lambda}} + i\underline{\overset{\leftrightarrow}{\Phi}}(t)]\cdot\underline{\mu} = \vec{\underline{F}}(t) . \tag{3.2}$$

Here and below we use arrows ($\rightarrow$, $\leftrightarrow$) to indicate vectors or tensors in the three-dimensional coordinate space. Single underlines denote vectors and double underlines denote matrices in the atoms space. $\underline{\overset{\leftrightarrow}{\Lambda}}$ is a constant matrix of dimension $3N \times 3N$ given by

$$\underline{\overset{\leftrightarrow}{\Lambda}} = \left[i\omega + \frac{\gamma}{2} \right]\underline{\overset{\leftrightarrow}{I}} - \frac{1}{2}i\omega_0\alpha_0\underline{\overset{\leftrightarrow}{M}} \tag{3.3}$$

with $\underline{\overset{\leftrightarrow}{I}}$ being the $3N \times 3N$ unit matrix and $\underline{\overset{\leftrightarrow}{M}}$ a $3N$-dimensional matrix constructed from the $\overset{\leftrightarrow}{M}_{jj'}$ diadics

$$\underline{\overset{\leftrightarrow}{M}} = \begin{bmatrix} \overset{\leftrightarrow}{0} & \overset{\leftrightarrow}{M}_{12} & \overset{\leftrightarrow}{M}_{13} & \cdots \\ \overset{\leftrightarrow}{M}_{21} & \overset{\leftrightarrow}{0} & \overset{\leftrightarrow}{M}_{23} & \cdots \\ \overset{\leftrightarrow}{M}_{31} & \overset{\leftrightarrow}{M}_{32} & \overset{\leftrightarrow}{0} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix} . \tag{3.4}$$

Also in Eq. (3.2), $\underline{\overset{\leftrightarrow}{\Phi}}(t)$ is the diagonal matrix

$$\underline{\overset{\leftrightarrow}{\Phi}}(t) \equiv \begin{bmatrix} \Phi_1\overset{\leftrightarrow}{I} & & & \\ & & & 0 \\ & \Phi_2(t)\overset{\leftrightarrow}{I} & & \\ 0 & & \cdots & \\ & & & \Phi_N(t)\overset{\leftrightarrow}{I} \end{bmatrix} , \tag{3.5}$$

and $\underline{\mu}(t)$ and $\vec{\underline{F}}(t)$ are the column vectors defined by

$$\underline{\mu}(t) \equiv \begin{bmatrix} \vec{\mu}_1(t) \\ \vec{\mu}_2(t) \\ \vdots \\ \vec{\mu}_N(t) \end{bmatrix} \tag{3.6}$$

and

$$\vec{\underline{F}}(t) \equiv \frac{1}{2}\alpha_0\omega_0 e^{-i\omega t}\vec{E}_{ex}(\omega) \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix} . \tag{3.7}$$

With this notation we can formally solve Eq. (3.2) for $\underline{\mu}$, average the solution over the random process $\underline{\overset{\leftrightarrow}{\Phi}}$, and look for the equations of motion satisfied by the resulting $\langle \underline{\mu} \rangle$. This procedure is described in the Appendix. The resulting equation is

$$\langle \dot{\underline{\mu}} \rangle + \left[\left[i\omega + \frac{\Gamma}{2} \right]\underline{\overset{\leftrightarrow}{I}} - \frac{1}{2}i\omega_0\alpha_0\underline{\overset{\leftrightarrow}{M}} \right]\langle \underline{\mu} \rangle = \vec{\underline{F}}(t) , \tag{3.8}$$

where $\Gamma = \gamma + \kappa$. Comparing this to our starting point, Eq. (3.2), we see that as long as we are interested only in the average dipole induced in the system, we may consider the dephasing process as inducing an additional damping rate. This result is well known for a single oscillator or a two-level system and was generalized here for a system of interacting atoms.

B. Effect of clustering

Having taken care of the dephasing effects, we now consider spatial fluctuations. In what follows we start from Eq. (2.1) with $\Gamma = \gamma + \kappa$ replacing γ. The amplitude of the dipole satisfies

$$\vec{\mu}_j(\omega) = \alpha(\omega)\left[E_{ex}(\omega) + \sum_{\substack{j'=1 \\ j' \neq j}}^{N} \overset{\leftrightarrow}{M}_{jj'}\vec{\mu}_{j'}(\omega) \right] , \tag{3.9}$$

where

$$\alpha(\omega) = \frac{\alpha_0\omega_0^2}{\omega_0^2 - \omega^2 - i\omega\Gamma} . \tag{3.10}$$

As discussed in the Introduction, clustering of atoms is expected to have a strong effect on the dielectric response near resonance. This cannot be seen in the Clausius-Mossotti level of treatment. We therefore consider a density (virial) expansion of the induced dipole moment using a procedure developed by van Kranendonk.[10] The total dipole $\vec{\mu}_{tot}(\vec{r}_1, \ldots, \vec{r}_N)$ induced in the N-atom system may be written as a sum of reduced dipoles $\vec{D}(\vec{r}_1, \ldots, \vec{r}_j)$ in the form [using the notation $(\vec{r}_1, \ldots, \vec{r}_N) \rightarrow (1, \ldots, N)$, etc.]

$$\vec{\mu}_{tot}(1, \ldots, N) = [\vec{D}(1) + \cdots + \vec{D}(N)]$$
$$+ [\vec{D}(1,2) + \vec{D}(1,3) + \cdots + \vec{D}(N-1,N)]$$
$$+ \cdots + \vec{D}(1, \ldots, N) , \tag{3.11}$$

where[10]

$$\vec{D}(1) = \vec{\mu}_{tot}(1) , \tag{3.12a}$$

$$\vec{D}(1,2) = \vec{\mu}_{tot}(1,2) - \vec{\mu}_{tot}(1) - \vec{\mu}_{tot}(2) , \tag{3.12b}$$

$$\vec{D}(1,2,3) = \vec{\mu}_{tot}(1,2,3) - \vec{\mu}_{tot}(1,2) - \vec{\mu}_{tot}(1,3)$$
$$- \vec{\mu}_{tot}(2,3) + \vec{\mu}_{tot}(1) + \vec{\mu}_{tot}(2) + \vec{\mu}_{tot}(3) , \tag{3.12c}$$

and so on. A $\vec{D}$ function of any order depends only on $\vec{\mu}_{\rm tot}$ functions of this and lower orders. Any $\vec{D}$ function of two or more atoms vanishes if any of the coordinates is brought to infinity.

Using Eq. (3.9) for systems of one and two atoms, we get

$$\vec{\mu}_{\rm tot}(1)=\alpha(\omega)\vec{E}_{\rm ex}(\omega) \tag{3.13}$$

and

$$\vec{\mu}_{\rm tot}(1,2)=2\alpha\left[\frac{\overleftrightarrow{I}}{1+\alpha/r^3}\right.$$
$$\left.+\frac{3\alpha}{r^3}\frac{\hat{u}\hat{u}}{(1+\alpha/r^3)(1-2\alpha/r^3)}\right]\cdot\vec{E}_{\rm ex} \tag{3.14}$$

whence [using Eq. (3.12b)]

$$\vec{D}(1,2)=\frac{2\alpha^2}{r^3}\frac{1}{1+\alpha/r^3}\left[-\overleftrightarrow{I}+\frac{3\hat{u}\hat{u}}{1-2\alpha/r^3}\right]\cdot\vec{E}_{\rm ex}\ .$$
$$\tag{3.15}$$

The polarization

$$\vec{P}=\frac{1}{\mathscr{V}}\langle\vec{\mu}_{\rm tot}(1,\ldots,N)\rangle$$
$$=\frac{1}{\mathscr{V}}\int f(1,\ldots,N)\vec{\mu}_{\rm tot}(1,\ldots,N)$$
$$\times d\vec{r}_1,\ldots,d\vec{r}_N \tag{3.16}$$

[where $f(1,\ldots,N)$ is the N-body distribution for the N-atom cluster] may be expanded in terms of the D functions using Eqs. (3.12). We get

$$\vec{P}=\frac{1}{\mathscr{V}}\left[N\int f(1)\vec{D}(1)d\vec{r}_1\right.$$
$$+\frac{N(N-1)}{2}\int f(1,2)\vec{D}(1,2)d\vec{r}_1 d\vec{r}_2$$
$$+\frac{N(N-1)(N-2)}{6}\int f(1,2,3)\vec{D}(1,2,3)$$
$$\left.\times d\vec{r}_1 d\vec{r}_2 d\vec{r}_3\cdots\right]\ .$$
$$\tag{3.17}$$

Equations (3.17) and (3.15) now lead to

$$\overleftrightarrow{K}=n\alpha\overleftrightarrow{I}+\frac{N(N-1)}{2\mathscr{V}^2}\int f(2\mid 1)\overleftrightarrow{T}(1,2)d\vec{r}_1 d\vec{r}_2+\cdots\ ,$$
$$\tag{3.18}$$

where $f(2\mid 1)$ is the conditional probability distribution to find an atom at $\vec{r}_2$ given that another atom occupies the position $\vec{r}_1$, and where

$$\overleftrightarrow{T}(1,2)=\frac{2\alpha^2/r^3}{1+\alpha/r^3}\left[-\overleftrightarrow{I}+\frac{3}{1-2\alpha/r^3}\hat{u}\hat{u}\right]\ . \tag{3.19}$$

We note that the first term in $\hat{\mu}_{\rm tot}$ implied by (3.18) is just $n\alpha E_{\rm ex}(n=N/\mathscr{V})$ and is independent of any characteristic of the cluster. The highest-order terms depend in general on the cluster size and shape. In what follows we consider in some detail the second-order contribution.

Focusing first on the case of an infinite uniform and isotropic system, we get from Eqs. (3.18) and (3.19)

$$\overleftrightarrow{K}=\overleftrightarrow{I}\left[n\alpha+8\pi(n\alpha)^2\alpha\right.$$
$$\times\int_0^\infty dr\,g(r)[r^4(1+\alpha/r^3)(1-2\alpha/r^3)]^{-1}\Big]$$
$$+O((n\alpha)^3)\ , \tag{3.20}$$

where $g(r)$ is the pair correlation function. For the particular case of hard-sphere interactions [$g(r)=0$ for $r<2r_0$, $g(r)=1$ for $r\geq 2r_0$], (3.20) leads to

$$\overleftrightarrow{K}=n\alpha\overleftrightarrow{I}\left[1+\frac{8\pi}{9}n\alpha\ln\frac{r_0^3+\alpha}{r_0^3-\alpha}\right]+O((n\alpha)^3)\ . \tag{3.21}$$

Having found $\overleftrightarrow{K}$, the dielectric tensor may be evaluated from (1.11). For an infinite isotropic medium we use the Clausius-Mossotti procedure [choosing $\overleftrightarrow{L}=\frac{1}{3}\overleftrightarrow{I}$ in (1.11)] to get

$$\frac{\epsilon-1}{\epsilon+2}=\frac{4\pi}{3}K\ . \tag{3.22}$$

This leads to a density ("virial") expansion of the dielectric function. Equation (3.21), if further expanded for small α/r_0^3, results in the conventional[11] virial expansion for ϵ.

Returning now to Eqs. (3.18) and (3.19) we consider the case of a spheroidal cluster. Choosing a system of coordinates such that the symmetry axis of the spheroid is in the z direction and taking the length of the symmetry axis and the normal axis to be $2a$ and $2b$, respectively, we obtain

$$\overleftrightarrow{K}=\begin{bmatrix}K_x & & 0\\ & K_y & \\ 0 & & K_z\end{bmatrix}\ , \tag{3.23}$$

where (for $w=x,z$)

$$K_w=n\alpha\left[1+\frac{gn\alpha}{4\pi}J_w\right]\ , \tag{3.24a}$$

$$J_w=\int_0^1 dz_1\int_0^{(1-z_1^2)^{1/2}}dr_1\int_0^{2\pi}d\phi\int_{-1}^1 dz_2\int_0^{(1-z_2^2)^{1/2}}dr_2(r_1 r_2 I_w)\ , \tag{3.24b}$$

$$I_w=-g(r_{12})\frac{\mathscr{V}/(r_{12})^3}{1+\alpha/r_{12}^3}\left[-1+\frac{3}{1-2\alpha/r_{12}^3}C_w\right]\ , \tag{3.24c}$$

$$C_w=\begin{cases}(z_{12}/r_{12})^2, & w=z\\ \frac{1}{2}[1-(z_{12}/r_{12})^2], & w=x\end{cases} \tag{3.24d}$$

and where

$$z_{12} = a(z_1 - z_2) ,$$ (3.25a)

$$r_{12} = [b^2(r_1^2 + r_2^2 - 2r_1 r_2 \cos\phi) + z_{12}^2]^{1/2} ,$$ (3.25b)

and

$$\mathscr{V} = \frac{4\pi}{3} ab^2 .$$ (3.26)

For a sphere of finite volume the integral in Eq. (3.24b) may be reduced further. For this case we get

$$K = n\alpha(1 + 9n\alpha J) ,$$ (3.27a)

$$J = \int_0^1 dr \int_0^{1+r} dy \, r^2 y^2 g(ay) F_1(y) F_2(y) ,$$ (3.27b)

$$F_1(y) = \min\left\{ \frac{1 - (r-y)^2}{2ry}, 2 \right\} ,$$ (3.27c)

$$F_2(y) = \frac{\mathscr{V}}{\alpha} \frac{[\alpha/(ay)^3]^2}{[1 + \alpha/(ay)^3][1 - 2\alpha/(ay)^3]} ,$$ (3.27d)

with $\mathscr{V} = (4\pi/3)a^3$, a being the sphere radius.

To demonstrate the dependence of the dielectric response on the cluster size and on the statistics of the atom distribution we show in Figs. 1—4 the functions $k(\omega)$ [which is proportional to the absorption profile per unit volume; cf. Eq. (1.12)] and $\mathrm{Re}\,\epsilon(\omega)$ obtained from Eq. (3.22). These are shown for spheres of different radii and a given density of atoms. The model (3.2) was used for the polarizability and the density was chosen so that $n|\alpha| < 0.1$ at the peak value of $|\alpha|$. These results are obtained by numerically integrating Eqs. (3.27). In Figs. 1 and 2 hard-sphere interactions were taken (with hard-sphere radius r_0). In Figs. 3 and 4 we used
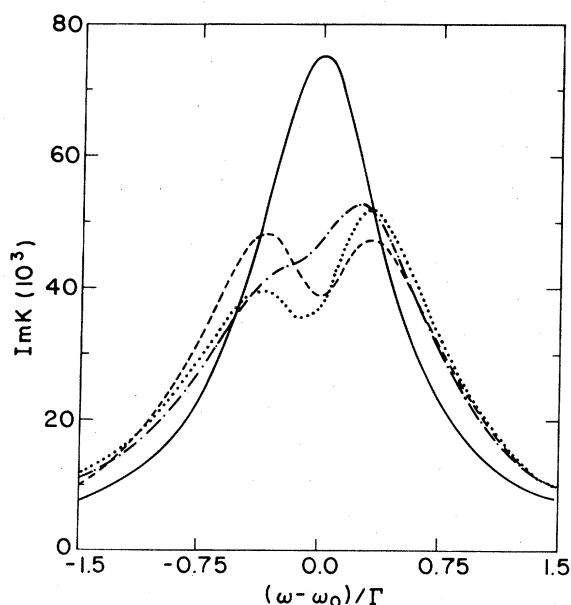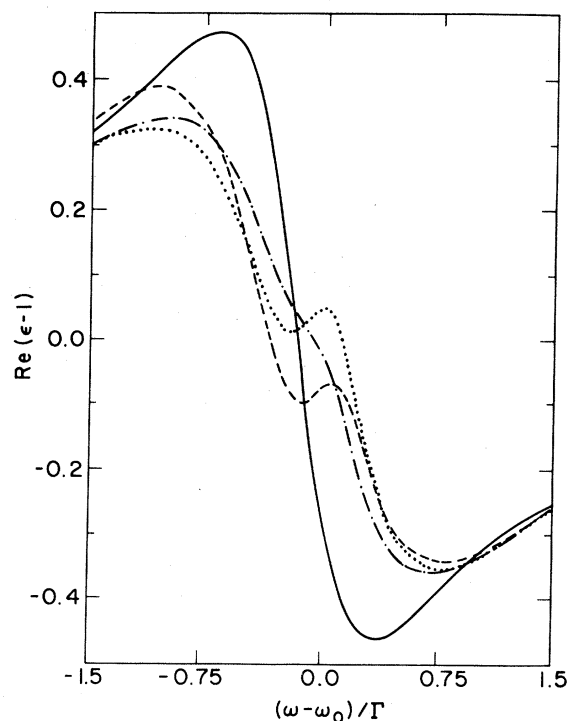

FIG. 2. $\mathrm{Re}[\epsilon(\omega) - 1]$ as a function of frequency for the cases considered in Fig. 1. Notation is the same as in Fig. 1.

$$g(r) = \exp[-v(r)/kT]$$ (3.28)

with

$$v(r) = \begin{cases} \infty, & r \leq r_0 \\ 4D\left[\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^6\right], & r > r_0 . \end{cases}$$ (3.29)

FIG. 1. $\mathrm{Im}K(\omega)$ as a function of frequency. Solid line: the Clausius-Mossotti approximation ($K = n\alpha$). Dashed line: the infinite medium result, Eq. (3.33). Dotted line: sphere of radius 150 Å. Dotted-dashed line: sphere of radius 15 Å. The density n is 1.25×10^{-3} Å^{-3}, and the molecular parameters used are $\alpha_0 = 2.0$ Å^3, $\Gamma = 0.033\omega_0$, and $r_0 = 3$ Å. The ordinate has been multiplied by 10^3.
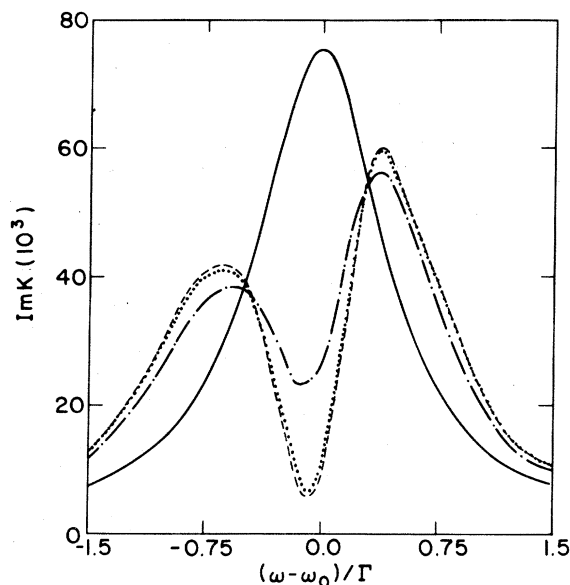

FIG. 3. Same as Fig. 1 with attractive intramolecular interaction. The Ar-Ar interaction parameters $D = 145$ K and $\sigma = 3.8$ Å were used in Eq. (3.41). Other parameters and the line notation are the same as in Fig. 1. The temperature is 100 K.
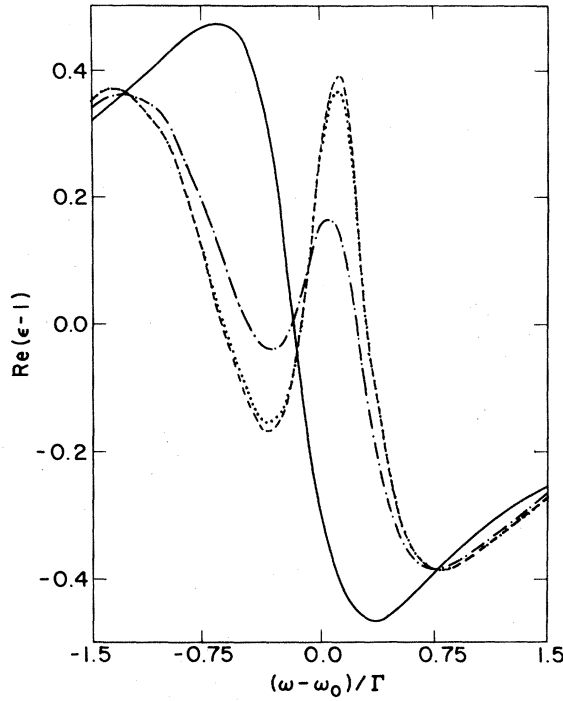
FIG. 4. Same as Fig. 2 with the parameters of Fig. 3.

We see from these results that the size of the cluster and the statistical distribution of molecules in the cluster are factors affecting the optical response and other dielectric properties of the cluster. These effects, which become considerable near resonance, are disregarded if one uses the bulk Clausius-Mossotti expression for the dielectric function. Several other points concerning these results should be made:

(a) The broadening of the resonance peak (relative to the Clausius-Mossotti value) results, as discussed above, from clustering together of several molecules. This broadening effect is observed also in numerical simulations of random distributions of interacting polarizable particles.[12] It is also related to the (configuration-dependent) splitting of resonance lines obtained in the calculated dielectric response of clusters of interacting polarizable particles.[13]

(b) The double-peak nature of the results displayed in Figs. 1 and 3 results from the fact that, to order $(n\alpha)^2$ considered here, pair formation is the dominant form of atom clustering. The more pronounced splitting in Fig. 3 corresponds to higher pair density obtained under the effect of attractive interaction between the atoms.

(c) The dielectric response of small clusters is expected to depend also on the cluster shape (as indeed observed by the dependence on configuration of the results of Ref. 13). However, an integration of Eq. (3.24b), which should show this effect, is prohibitively expensive.

(d) As mentioned above and as seen from the structure of Eqs. (3.21), (3.24a), and (3.27a), these results constitute a virial expansion for the response function K, with the Clausius-Mossotti result constituting the zero-order approximation. This expansion breaks down for $n |\alpha|$ too large. For this reason we had to limit ourselves to rela-

tively low densities in the calculations of Figs. 1–4. These results should be viewed as demonstrations of the effects discussed above which undoubtedly become more pronounced at higher densities.

IV. LIGHT SCATTERING

Light scattering by small dielectric particles is usually discussed using the theory of Mie.[14] The input for this theory is the dielectric function ϵ of the material making the cluster. As noted in Sec. I, when discussing small clusters in terms of the optical properties of their constituent atoms it is more convenient to use other response functions, the choice of which depends on the observable under study. $\langle K(\omega)\rangle$, the polarizability per unit volume, averaged over spatial disorder and over rapid temporal phase fluctuations, is directly related to the absorption by an ensemble of independent clusters. The corresponding $\langle \epsilon(\omega)\rangle$ may also be used, provided one keeps in mind that it depends on cluster size and shape. In discussing light scattering in the presence of dephasing, we avoid the dielectric function concept and instead proceed in calculating directly the scattering cross section.

One way to proceed is as follows. Start from Eq. (A1):

$$\vec{\mu}(t) = \int_{-\infty}^{t} dt' \overset{\leftrightarrow}{\underline{\mathbf{L}}}(t,t') \cdot \vec{\mathbf{F}}(t') , \qquad (4.1)$$

$$\overset{\leftrightarrow}{\underline{\mathbf{L}}}(t,t') = \overset{\leftrightarrow}{\underline{\mathbf{U}}}(t) \cdot \overset{\leftrightarrow}{\underline{\mathbf{U}}}^{-1}(t') , \qquad (4.2)$$

where $\vec{\mathbf{F}}$ and $\overset{\leftrightarrow}{\underline{\mathbf{U}}}$ are defined in Sec. III and in the Appendix. The total instantaneous dipole induced in the system is

$$\vec{\mu}_{\text{tot}}(t) = \sum_j \vec{\mu}_j(t) . \qquad (4.3)$$

The total steady-state power radiated at frequency ω' is given by the classical formula

$$I_{\text{sc}}^{\text{tot}} = \frac{1}{3} \frac{(\omega')^4}{c^3} |\mu_{\text{tot}}(\omega')|^2 , \qquad (4.4)$$

where

$$\vec{\mu}_{\text{tot}}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \vec{\mu}_{\text{tot}}(t) . \qquad (4.5)$$

Thus to calculate the scattered power or the scattering cross section $(=I_{\text{sc}}/[(c/8\pi) |E_{\text{ex}}|^2])$ for the model (2.6) we must evaluate $\langle |\vec{\mu}_{\text{tot}}(\omega')|^2 \rangle$, the average taken over all temporal and spatial randomness. From Eq. (4.1) we see that the response function of interest is

$$\langle \overset{\leftrightarrow}{\underline{\mathbf{L}}}(t_1',t_1,t,t')\rangle \equiv \langle (\overset{\leftrightarrow}{\underline{\mathbf{U}}}^\dagger)^{-1}(t_1') \cdot \overset{\leftrightarrow}{\underline{\mathbf{U}}}^\dagger(t_1) \cdot \overset{\leftrightarrow}{\underline{\mathbf{U}}}(t) \cdot \overset{\leftrightarrow}{\underline{\mathbf{U}}}^{-1}(t')\rangle .$$

$$(4.6)$$

The average in (4.6) may be evaluated using the time-ordering and cumulant expansion technique described in the Appendix. We have succeeded in carrying out this procedure for a dilute system where the dipole-dipole interaction is neglected. Rather than providing the (rather involved) details of this method, we proceed in a different but equivalent route based on the quantum-mechanical approach, Eq. (2.16). For noninteracting atoms the latter

route results in an expression for the scattering cross section [Eq. (4.9)] identical to that obtained from the classical approach. The quantum-mechanical approach may also be carried out for a particular model of interacting atoms.

Consider first the case of noninteracting atoms, setting $W_{jj'}=0$ for all j,j' in Eqs. (2.16). Consider further a steady-state situation in which Eqs. (2.16a) and (2.16b) are supplemented by pumping and escape terms

$$\dot{\rho}_{II} = -2\,\mathrm{Im}\left[V_{BI}\sum_j \rho_{Ij}e^{-i\vec{k}\cdot\vec{r}_j}\right] + (\dot{\rho}_{II})_{\mathrm{pump}}\,,\qquad(4.7a)$$

$$\dot{\rho}_{FF} = -2\,\mathrm{Im}\left[V_{BF}\sum_j \rho_{Fj}e^{-i\vec{k}'\cdot\vec{r}_j}\right] - (\dot{\rho}_{FF})_{\mathrm{out}}\,.\qquad(4.7b)$$

The term $(\dot{\rho}_{II})_{\mathrm{pump}}$ represents the rate of pumping due to the incident field, while $(\dot{\rho}_{FF})_{\mathrm{out}}$ represents the escape of the scattered photons. At steady state (SS) all the elements of $\dot{\rho}$ are zero, and the scattered intensity (with wave vector k') is proportional to $(\dot{\rho}_{FF})_{\mathrm{out}}$ given by

$$(\dot{\rho}_{FF})_{\mathrm{out,SS}} = -2\,\mathrm{Im}\left[V_{BF}\sum_j \rho_{Fj}e^{-i\vec{k}'\cdot\vec{r}_j}\right]\,.\qquad(4.8)$$

This must be evaluated in terms of ρ_{II}. Setting the left-hand side (lhs) of Eqs. (2.16c)–(2.16g) to zero and solving the resulting set of algebraic equations, taking also for simplicity $\eta\rightarrow 0$ (no dephasing in the ground state), we obtain

$$(\dot{\rho}_{FF})_{\mathrm{out,SS}} = 2\pi\frac{|V_{IB}|^2|V_{FB}|^2}{\omega_{IB}^2+(\tfrac{1}{2}\Gamma)^2}$$

$$\times\left[\delta(\omega_{FI})\left|\sum_{j=1}^{N}e^{-i(\Delta\vec{k})\cdot\vec{r}_j}\right|^2\right.$$

$$\left.+N\frac{\Gamma/2\pi}{\omega_{FB}^2+(\tfrac{1}{2}\Gamma)^2}\frac{\Gamma-\gamma}{\gamma}\right]\rho_{II}\,,\qquad(4.9)$$

where

$$\Delta\vec{k}=\vec{k}'-\vec{k}\,.\qquad(4.10)$$

When dipole-dipole interactions are present, the mathematical problem represented by (2.16) becomes much more difficult. A simple solution may be still obtained at the cost of choosing a very simple model for the interactions $V_{jj'}$. If, rather than taking the dipolar coupling matrix elements we invoke the model

$$V_{jj'}=V \text{ independent of } j \text{ and } j'\qquad(4.11)$$

we obtain, for the small cluster case (where $\Delta\vec{k}\cdot\vec{r}_j=0$ for all j) the result

$$(\dot{\rho}_{FF})_{\mathrm{out,SS}} = 2\pi\frac{|V_{IB}|^2|V_{FB}|^2}{\bar{\omega}_{IB}^2+(\tfrac{1}{2}\Gamma)^2}$$

$$\times\left[N^2\delta(\omega_{FI})+N\frac{\Gamma/2\pi}{\bar{\omega}_{FB}^2+(\tfrac{1}{2}\Gamma)^2}\frac{\Gamma-\gamma}{\gamma}\right]\rho_{II}\,,$$

$$(4.12)$$

where

$$\bar{\omega}_{IB}=\omega_{IB}-V(N-1)\,,$$

$$\bar{\omega}_{FB}=\omega_{FB}-V(N-1)\,,\qquad(4.13)$$

which is identical to (4.9) in this small-cluster limit with the only exception being the shifted frequencies. Equation (4.12) is obtained from (2.16) (under steady-state conditions, $\dot{\rho}=0$) by replacing all the phase factors $\exp(i\vec{k}\cdot\vec{r})$ by unity, and by evaluating first the auxiliary quantities $\sum_j\rho_{Fj}$, $\sum_j\rho_{Ij}$, $\sum_j\rho_{jj}$, and $\sum_j\sum_{j'}\rho_{jj'}$.

Several points regarding the results (4.9) and (4.12) are in order.

(a) For a single atom ($N=1$) we obtain

$$(\dot{\rho}_{FF})_{\mathrm{out,SS}} = 2\pi\frac{|V_{IB}|^2|V_{FB}|^2}{\omega_{IB}^2+(\tfrac{1}{2}\Gamma)^2}$$

$$\times\left[\delta(\omega_{FI})+\frac{\Gamma/2\pi}{\omega_{FB}^2+(\tfrac{1}{2}\Gamma)^2}\frac{\Gamma-\gamma}{\gamma}\right]\rho_{II}\,,$$

$$(4.14)$$

which is familiar in the theory of thermal redistribution effects in resonance light scattering.[15] Note that as seen in Sec. II, $\Gamma-\gamma=\kappa$ is identical to the dephasing rate defined in Sec. III, and that $\omega_{IB}=\omega_0-\omega$, $\omega_{FB}=\omega_0-\omega'$, where ω_0 is the atomic resonance frequency and ω,ω' are the incident and scattered frequencies. Also note that V_{IB} and V_{FB} are products of atomic and radiation field matrix elements.

(b) In the absence of dephasing ($\Gamma=\gamma$) we obtain the familiar[16] expression proportional to the factor $|\sum_j\exp(i\Delta\vec{k}\cdot\vec{r}_j)|^2$. For a cluster small relative to the radiation wavelength we may take $\Delta\vec{k}\cdot\vec{r}_j\simeq 0$ for all r_j, and we get a factor of N^2. For a larger isotropic system with a random distribution of atoms we get

$$\left\langle\left|\sum_j e^{i\Delta\vec{k}\cdot\vec{r}_j}\right|^2\right\rangle=n^2\mathcal{V}\int d^3r\,e^{-i\Delta\vec{k}\cdot\vec{r}}g(r)\,,\qquad(4.15)$$

where $g(r)$ is the pair correlation function.

(c) In the small-cluster limit we may get a more transparent form of Eq. (4.9) by making the following correspondence between quantum and classical quantities:[17]

$$|V_{FB}|^2\rho(\omega_0)\leftrightarrow\frac{\alpha_0}{3\pi}\frac{\omega_0^4}{c^3}\,,\qquad(4.16a)$$

$$\hbar\omega_0\rho_{II}|V_{IB}|^2\leftrightarrow\frac{\alpha_0\omega_0^2}{8}|E_{\mathrm{ex}}(\omega)|^2\,,\qquad(4.16b)$$

where $\rho(\omega_0)$ in Eq. (4.16a) is the density of photons states (per unit frequency) at the frequency ω_0 (while ρ_{II} is an element of the density matrix). Multiplying Eq. (4.9) by $\hbar\omega'\rho(\omega')$ (to get the energy outflow per unit time and per unit frequency range) and dividing by the incident energy flux $(c/8\pi)|E_{\mathrm{ex}}(\omega)|^2$, we get an expression for the scattering cross section per unit frequency range of the N-atom cluster

$$\frac{d\sigma_{sc}^{(N)}}{d\omega'} \simeq \frac{8\pi}{3} \frac{\omega_0}{c} |\alpha(\omega)|^2$$

$$\times \left[\delta(\omega - \omega')N^2 + \frac{\Gamma/2\pi}{(\omega' - \omega_0)^2 + (\frac{1}{2}\Gamma)^2} \frac{\Gamma - \gamma}{\gamma} N \right],$$

(4.17)

where [see Eq. (2.3)]

$$\alpha(\omega) = \frac{\frac{1}{2} i \alpha_0 \omega_0}{i(\omega_0 - \omega) + (\frac{1}{2}\Gamma)^2}.$$

(4.18)

To get (4.17) we have also used $\omega_{IB} = \omega - \omega_0$, $\omega_{FB} = \omega' - \omega_0$, and $\omega_{FI} = \omega' - \omega$, where ω and ω' are the incident and scattered frequencies.

If, in (4.17), we put $N = 1$ and $\Gamma = \gamma$ and integrate over ω', we get the scattering cross section of a single atom in the absence of dephasing

$$\sigma_{sc}^{(1)}(\text{no dephasing}) = \frac{8\pi}{3} \left[\frac{\omega_0}{c} \right]^4 |\alpha(\omega)|^2.$$

(4.19)

This is indeed the familiar classical result.[18]

(d) Equations (4.9), (4.12), or (4.17) gives the light scattering by the cluster as a sum of two terms: a coherent term, proportional to N^2 in the small-cluster limit, and an incoherent term proportional to N. The latter is also characterized by a redistributed final photon energy: Energy conservation $\omega = \omega'$ is not strictly obeyed but only approximately within the uncertainty of the resonance width. This incoherent term may be identified with resonance fluorescence by the cluster atoms. In order to estimate the relative contribution of the coherent and incoherent contributions consider the integrated cross sections. Equation (4.17) yields

$$\frac{\sigma_{sc,coh}^{(N)}}{\sigma_{sc,incoh}^{(N)}} = \frac{N\gamma}{\kappa} = \frac{NT_2}{T_1},$$

(4.20)

where $\kappa = \Gamma - \gamma$ is the dephasing rate, while T_1 and T_2 are the population relaxation time and the (proper) dephasing time of the atom. In condensed phases $T_2/T_1 \sim 10^{-3} - 10^{-4}$, so that incoherent response is predicted to dominate for clusters made of less than ~ 1000 atoms (or molecules). In clusters containing more than 10^4 atoms coherent response will dominate unless the cluster size is larger than the radiation wavelength. In the latter case the factor N^2 is replaced by (4.15), which is proportional to N unless $g(r)$ is long ranged (relative to the cluster size). Incoherent response will usually dominate in such large clusters unless for ordered lattices $\vec{\Delta k}$ is equal to a reciprocal-lattice vector.

(e) The result (4.12) shows that Eq. (4.19) is valid also in the presence of long-range interatomic coupling. We find this surprising since we have intuitively expected that stronger interatomic coupling should imply increase of the coherent relative to the incoherent response. In view of this result, it seems worthwhile to study this question further in order to elucidate the effect of particle-particle interaction on the yield of coherent versus noncoherent response. It is possible that this behavior results from the

special model of interaction used and more realistic models should be investigated.

(f) It is of interest to speculate on the effect that particles of the kind studied in this paper may have on the optical properties of molecules adsorbed on their surface. It should be noted that an important contribution to surface enhanced Raman scattering[2] (SERS) is the interaction of the molecule with resonance excitations in the substrate surface. While practically all SERS phenomena so far have been observed on metal surfaces and particles, molecular clusters of the kind discussed here[19] may be prepared in supersonic beams. Alternatively, small polymer particles with embedded dye molecules may be used.[20] The results of this section indicate that in order for SERS (and other enhanced optical processes) to be observed for molecules absorbed on molecular clusters, the coherent contribution in (4.17) has to be dominant. This part of the response is associated with the formation of a coherent giant dipole on the cluster, which is the source of the electromagnetic mechanism of surface enhanced electromagnetic processes.

V. CONCLUSIONS

Many physical properties of small clusters are known to be different from the corresponding properties of bulk materials. In this paper we have investigated two aspects related to the resonance optical response of small molecular clusters. We have seen that resonance absorption and light scattering, which are sensitive both in the bulk and in finite clusters to the nature of the molecular distribution within the medium, show a marked dependence on the cluster size and shape. This dependence becomes smaller further from resonance. We have also seen that the relative yield of coherent (Rayleigh and Raman) versus noncoherent responses of a cluster made of noninteracting molecules strongly depends on the cluster size. We were surprised to find that a simple model which takes intermolecular interaction into account gives a result for the coherent relative to the noncoherent yields which does not depend on the intermolecular interaction and have concluded that his point deserves further study.

Even though our model uses two-level atoms or molecules, it is expected to be realistic also for clusters of larger molecules. This results from our focusing on near-resonance situations. The main new feature that should be taken into account for such cases is the fact that the incident and scattered or emitted radiation may be in different spectral regions. Another point that may influence the optical properties of clusters of larger molecules is the possible effect of molecular clustering on the radiationless damping of molecular electronic energy due to transfer to low-frequency vibrations (cluster phonons). Cluster-size dependence of this effect is expected to occur mainly for small size $(N \lesssim 100)$ clusters.

Surface enhanced electromagnetic processes involving molecules absorbed on molecular particles may be observed when the incident radiation is close to resonance with the dipolar excitation of the particle and when the coherent response is dominant.

ACKNOWLEDGMENTS

APPENDIX

The formal solution to Eq. (3.2) is

$$\vec{\mu}(t) = \int_{-\infty}^{t} dt' \overleftrightarrow{\underline{U}}(t) \cdot \overleftrightarrow{\underline{U}}^{-1}(t') \cdot \vec{F}(t') , \tag{A1}$$

where $\overleftrightarrow{\underline{U}}(t)$ may be expressed as the time-ordered exponential[21]

$$\overleftrightarrow{\underline{U}}(t) = T \exp\left[-\int_{-\infty}^{t} [\overleftrightarrow{\underline{A}} + i\overleftrightarrow{\underline{\Phi}}(t')] dt' \right] . \tag{A2}$$

The time-ordering operator T implies that all operators on its right should be ordered so that later time appears to the left. Averaging over the random process $\overleftrightarrow{\underline{\Phi}}$ we get

$$\langle \vec{\mu}(t) \rangle = \int_{-\infty}^{t} dt' \langle \overleftrightarrow{\underline{L}}(t,t') \rangle \vec{F}(t') , \tag{A3}$$

where the kernel $\langle \overleftrightarrow{\underline{L}}(t,t') \rangle$ is defined by

$$\langle \overleftrightarrow{\underline{L}}(t,t') \rangle \equiv \left\langle \overline{T} \exp\left[-\int_{-\infty}^{t} dt_1 [\overleftrightarrow{\underline{A}} + i\overleftrightarrow{\underline{\Phi}}(t_1)] \right. \right.$$
$$\left. \left. + \int_{-\infty}^{t'} dt_2 [\overleftrightarrow{\underline{A}} + i\overleftrightarrow{\underline{\Phi}}(t_2)] \right] \right\rangle . \tag{A4}$$

The time-ordering prescription denoted symbolically by $\overline{T}$ is as follows: When the exponent is expanded we get products of integrals involving t_1, t_1', t_1'', ..., etc. originating from the t_1 integral, and integrals involving $t_2, t_2', t_2'', \ldots$ originating from the t_2 integral in (A4). Those integrals involving the t_1 labels always stand to the left of those involving t_2 labels. The t_1 labels themselves are ordered so that leftward-standing labels depict later times. The t_2 labels are ordered so that rightward-standing labels depict later times.

By employing this ordering technique it is possible to apply the cumulant expansion method[22] to affect the averaging in Eq. (A4). Since by our assumption [Eq. (2.5)] $\overleftrightarrow{\underline{\Phi}}(t)$ is a diagonal matrix whose elements are Gaussian random variables, only the first two cumulants are nonvanishing. Thus we find

$$\langle \overleftrightarrow{\underline{L}}(t,t') \rangle = \overline{T} \exp\left[-\overleftrightarrow{\underline{A}}(t-t') - \frac{1}{2}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_1' \langle \overleftrightarrow{\underline{\Phi}}(t_1) \cdot \overleftrightarrow{\underline{\Phi}}(t_1') \rangle - \frac{1}{2}\int_{-\infty}^{t'} dt_2 \int_{-\infty}^{t'} dt_2' \langle \overleftrightarrow{\underline{\Phi}}(t_2) \cdot \overleftrightarrow{\underline{\Phi}}(t_2') \rangle \right.$$
$$\left. + \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t'} dt_2 \langle \overleftrightarrow{\underline{\Phi}}(t_1) \cdot \overleftrightarrow{\underline{\Phi}}(t_2) \rangle \right] . \tag{A5}$$

With the use of Eq. (2.5) all averages in (A5) result in a scalar multiplying a unit matrix. At this stage the presence of $\overline{T}$ is of no consequence. We get

$$\langle \overleftrightarrow{\underline{L}}(t,t') \rangle = \exp[-\overleftrightarrow{\underline{A}}(t-t') - \frac{1}{2}\kappa(t-t')\overleftrightarrow{\underline{I}}] . \tag{A6}$$

With the use of Eqs. (3.3) and (A3) this leads to

$$\langle \vec{\mu}(t) \rangle = [i(\omega_0 - \omega + \frac{1}{2}i\Gamma)\overleftrightarrow{\underline{I}} - \frac{1}{2}i\alpha_0\omega_0\overleftrightarrow{\underline{M}}]^{-1}\vec{F}(t) , \tag{A7}$$

where we have defined the full width Γ as

$$\Gamma = \gamma + \kappa . \tag{A8}$$

κ may now be identified as the dephasing rate. Equation (A7) is equivalent to Eq. (3.8).

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