

# The effect of small cluster environment on molecular oscillator strengths and spectra

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In this paper, we present an electrostatic theory of the effect of small atomic cluster environment on molecular oscillator strengths and spectra. The molecular dipole is represented by a classical oscillating charge distribution and the cluster atoms by spherical polarizable particles. From our general theoretical results, we calculate the effect of cluster size and geometry on the molecular radiative lifetime and the spectral shift. These properties exhibit a considerable sensitivity to the cluster and molecular geometry, i.e., the cluster size and structure, the molecule-atom(s) distance(s), the spatial size of the molecular transition dipole, and molecular orientation within the cluster. The reduced plot of the relative change in the oscillator strength vs the relative frequency shift seems to have universal character and is useful in analyzing and predicting experimental trends. Available experimental results are consistent with the theoretical predictions.

## I. INTRODUCTION

The study of solvent effects on the electronic absorption spectrum and on the electronic oscillator strength of solvated molecules has been a subject of considerable experimental and theoretical interest.<sup>1-3</sup> While specific chemical interactions can never be ruled out, in many systems the solvent-induced electromagnetic interactions can be identified as a major source of the effect. The implications of the solvent polarizability on spectral shifts of solvated molecules were elucidated in the pioneering work of Longuett-Higgins and Pople.<sup>1</sup> Of particular interest is a recent paper by Myers and Birge,<sup>3</sup> who have shown that the effects of solvent polarization on molecular electronic oscillator strengths are sensitive to the local geometry, being determined by the shape of the solute molecule and the direction, relative to this shape, of the molecular transition dipole. Thus, for a long thin molecule, whose shape can be approximated by a cylinder, the transition moment is predicted to decrease or increase, with increasing solvent refractive index, according to whether the transition dipole is parallel or perpendicular to the cylinder axis; these predictions are reversed for a low flat cylinder. These prognostications are borne out by experimental data for solvent effects on the oscillator strengths of some spin-allowed electronic transitions of  $\beta$ -carotene and pyrazine.

The recent surge of interest in properties of small molecular clusters, which was initiated by remarkable experimental progress in the production and the interrogation of cluster beams,<sup>4</sup> has raised interesting questions concerning the effect of such solvent clusters on the optical properties of a heterocluster containing a guest molecule embedded in it. These questions constitute part of the general intriguing problem of the transition from a single molecule property to the behavior of the macroscopic bulk. While most of the current conducted studies deal with the questions pertaining to pure materials, the comparison between a bulk solvent and the physical and chemical properties of solute molecules in solvent clusters of different sizes and shapes is of no less importance. In addition, the observation that the solvent ef-

fect on the solute optical properties is sensitive to the local geometry raises the interesting possibility that such studies may yield information on a mixed cluster structure.

Extensive experimental information concerning microscopic solvent shifts on the energetics of electronic excitations of a guest molecule in large van der Waals molecules<sup>5</sup> and clusters<sup>6</sup> is emerging. However, only scanty information regarding microscopic solvent effects on the oscillators strengths and pure radiative lifetimes of large guest molecules embedded in clusters is available. Such information can be inferred from the combination of experimental lifetimes  $\tau$  and absolute fluorescence quantum yields  $Y$  from photoselected electronic-vibrational excitation of large molecules and their van der Waals complex in supersonic jets. The pure radiative lifetime  $\tau_r$  is obtained from the relation  $\tau_r = \tau/Y$ . The available information for the electronic origin of the first spin-allowed  $S_1$  electronic excitation of some large molecules, e.g., 9-cyanoanthracene and tetracene and their complexes with rare-gas atoms is summarized in Table I. From these results, it is apparent that the pure radiative lifetime of the short axis polarized excitation is lengthened by about  $\sim 10\% \pm 5\%$  due to complexing with an Ar atom and by  $\sim 20\% \pm 10\%$  due to complexing with a Xe atom, both of these rare-gas atoms being located at 3.5–4.0 Å above the aromatic ring.<sup>5</sup>

In this paper, we present a study of clustering effects on molecular oscillator strengths and energy levels. We focus on the electromagnetic (local field) issue, so that this work should be seen as an application of the concepts formerly advanced for bulk solvents<sup>1-3</sup> to the case of van der Waals molecules and clusters. It should be emphasized that specific chemical interactions (e.g., heavy atom effects on intersystem crossing) are not taken into account. Unlike the work of Myers and Birge,<sup>3</sup> which rests on first-order perturbation expansion of the molecular wave functions in the presence of the molecule-solvent interaction, the present treatment is based on classical electrostatics. In the next section we will show that the two approaches are completely equivalent, provided that the interaction between solvent molecules is

TABLE I. Fluorescence lifetimes ( $\tau$ ), quantum yields ( $Y$ ), pure radiative lifetimes ( $\tau_r$ ), and spectral shifts ( $\Delta\omega$ ) of the lowest  $\pi\pi^*$  electronic origin of some aromatic molecules and their van der Waals complexes.

Molecule	$\tau$ (ns)	$Y$	$\tau_r$ (ns)	$\Delta\omega$ ( $\text{cm}^{-1}$ ) <sup>s</sup>	$\Delta\omega/\omega_0^h$
Tetracene	$20 \pm 1^a$	$0.40 \pm 1^e$	$50 \pm 2$	0	0
Tetracene Ar	$29^b$	$0.45 \pm 0.05$	$64 \pm 10$	$-41^i$	$-0.0018$
9-Cyanoanthracene	$28.0 \pm 0.2^c$	$1.00 \pm 0.03^e$	$28 \pm 1$	$0^c$	0
9-Cyanoanthracene Ar	$26.9 \pm 0.5^d$	$0.84 \pm 0.03^f$	$32 \pm 3$	$-51^f$	$-0.0019$
9-Cyanoanthracene Xe	$30.0 \pm 0.5^d$	$0.85 \pm 0.03^f$	$35 \pm 3$	$-122^f$	$-0.0047$

<sup>a</sup> A. Amirav, U. Even, and J. Jortner, J. Chem. Phys. **75**, 3770 (1981).

<sup>b</sup> A. Amirav, U. Even, and J. Jortner, J. Chem. Phys. **75**, 2481 (1981).

<sup>c</sup> A. Amirav, J. Jortner, S. Okajima, and E. C. Lim, Chem. Phys. Lett. **126**, 487 (1986).

<sup>d</sup> S. Hirayama, K. Shobatake, and K. Tobayashi, Chem. Phys. Lett. **121**, 228 (1985).

<sup>e</sup> M. Sonnenschein, A. Amirav, and J. Jortner, J. Phys. Chem. **88**, 4214 (1984).

<sup>f</sup> A. Amirav and J. Jortner, Chem. Phys. Lett. **132**, 335 (1986).

<sup>g</sup> A negative sign of  $\Delta\omega$  refers to spectral red shifts.

<sup>h</sup>  $\omega_0$ —energy of electronic transition of the bare molecule.

<sup>i</sup> A. Amirav and J. Jortner, Chem. Phys. **85**, 19 (1984).

disregarded. The simplicity of the classical electrostatic approach makes it possible to include this interaction with little additional effort. The neglect of this interaction, which for bulk solvents leads to the Clausius Mossotti (Lorentz-Lorentz) relation between the solvent molecule polarizability and its refractive index, is not always justified for the treatment of electrostatic interactions in the vicinity of an impurity molecule, and is even less justified for the case of microscopic solvent effects in clusters.

After establishing the equivalence of the perturbative quantum mechanical and the classical electrostatic approaches, we use the latter approach to calculate the effect on molecular lifetimes of clustering with rare-gas atoms. We find that this effect is structure dependent and trace this dependence to the structure dependence of the reaction field induced by the solvent atoms. The simplicity of the classical electrostatics approach makes it also possible to depart from the conventional approximation of representing the molecular transition dipole as a point dipole and enables us also to study the effect of finite molecular size. Our results are discussed in the light of available experimental data.

## II. QUANTUM PERTURBATION THEORY AND CLASSICAL ELECTROSTATICS

In this section we demonstrate the equivalence of the quantum mechanical perturbation theory calculation of the solvent effect on molecular oscillator strengths to the classical electrostatic approach. We shall apply the model by Myers and Birge<sup>3</sup> and consider solute and solvent molecules which have no permanent dipole moments in their ground or excited states. Orbital overlap between molecules is neglected so that the total wave function for the system is written as a simple product of single-molecule wave functions. Furthermore, interaction between solvent molecules is neglected so that it is sufficient to consider a single solvent molecule. For the solute molecule A, we consider only two states, i.e., the ground state  $|A_0\rangle$  and the excited state  $|A_I\rangle$ . For the solvent molecule B, we consider the ground state  $|B_0\rangle$  and the set of excited state ( $|B_k\rangle$ ). The unperturbed ground state of the system is

$$|g^0\rangle \equiv |A_0B_0\rangle = |A_0\rangle|B_0\rangle. \quad (1)$$

The unperturbed excited state in which the molecule has been promoted to the  $I$  state is

$$|e^0\rangle \equiv |A_I B_0\rangle = |A_I\rangle|B_0\rangle. \quad (2)$$

These states are the eigenstates of  $H_0$ , and the zero-order Hamiltonian of the solute-solvent system which neglects the dipolar interactions. They interact with other zero-order states, namely ( $|A_0B_k\rangle$ ) and ( $|A_I B_k\rangle$ ). Under our model assumptions, the first-order perturbation theory expressions for the ground ( $|g^1\rangle$ ) and excited ( $|e^1\rangle$ ) states of the system are given by

$$|g^1\rangle = |A_0B_0\rangle - \sum_{k \neq 0} |A_I B_k\rangle \frac{\langle A_I B_k | H' | A_0 B_0 \rangle}{E_B^k + E_A^I} \quad (3)$$

and

$$|e^1\rangle = |A_I B_0\rangle - \sum_{k \neq 0} |A_0 B_k\rangle \frac{\langle A_0 B_k | H' | A_I B_0 \rangle}{E_B^k - E_A^I}, \quad (4)$$

where  $E_B^k$  is the energy of molecule B in state  $k$ , etc. All the energies are chosen relative to the energy of the  $A_0B_0$  state, which is taken to be zero.  $H'$  is the dipolar interaction operator

$$H' = \frac{3(\boldsymbol{\mu}_A \cdot \hat{n})(\boldsymbol{\mu}_B \cdot \hat{n}) - (\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B)}{R^3}, \quad (5)$$

where  $\boldsymbol{\mu}_A$  and  $\boldsymbol{\mu}_B$  are dipole moment operators for molecules A and B,  $\hat{n}$  is a unit vector in the direction from A to B, and  $R = |R_{AB}|$ . Thus,

$$\begin{aligned} \langle A_I B_k | H' | A_0 B_0 \rangle &= \langle A_0 B_k | H' | A_I B_0 \rangle \\ &= \frac{1}{R^3} [3(\boldsymbol{\mu}_A^{(I)} \cdot \hat{n})(\boldsymbol{\mu}_B^{(k)} \cdot \hat{n}) \\ &\quad - (\boldsymbol{\mu}_A^{(I)} \cdot \boldsymbol{\mu}_B^{(k)})], \end{aligned} \quad (6)$$

where  $\boldsymbol{\mu}_A^{(I)}$  and  $\boldsymbol{\mu}_B^{(k)}$  denote the matrix elements

$$\boldsymbol{\mu}_A^{(I)} = \langle A_I | \boldsymbol{\mu}_A | A_0 \rangle \quad (7)$$

and

$$\boldsymbol{\mu}_B^{(k)} = \langle B_k | \boldsymbol{\mu}_B | B_0 \rangle. \quad (8)$$

The total transition moment of the solute-solvent system is

$$\mu_{\text{tot}} = \langle g^1 | \mu_A + \mu_B | e^1 \rangle. \quad (9)$$

Using Eq. (3), and keeping the terms only up to first order, lead to

$$\begin{aligned} \mu_{\text{tot}} = & \mu_A^{(j)} - \sum_{k \neq 0} \frac{2E_B^k}{(E_B^k)^2 - (E_A^I)^2} \\ & \times \frac{3(\mu_A^{(j)} \cdot \hat{n})(\mu_B^{(k)} \cdot \hat{n}) - \mu_A^{(j)} \cdot \mu_B^{(k)}}{R^3} \mu_B^{(k)}. \end{aligned} \quad (10)$$

This result can be recast in the form

$$\mu_{\text{tot}} = \mu_A^{(j)} - \mathbf{a} \frac{3(\mu_A^{(j)} \cdot \hat{n})\hat{n} - \mu_A^{(j)}}{R^3}, \quad (11)$$

where the tensor  $\mathbf{a}$  is given by

$$\mathbf{a} = \sum_{k \neq 0} \frac{2E_B^k}{(E_B^k)^2 - (E_A^I)^2} \mu_B^{(k)} \mu_B^{(k)}. \quad (12)$$

Equation (12) is recognized as the perturbation theory expression for the dynamical polarizability tensor of the molecule B at frequency  $\omega = E_A^I/\hbar$ .<sup>7</sup> Accordingly, Eq. (11) is of the same form as the classical electrostatics result, expressing the total dipole as the sum of the dipole on A and the dipole induced on B by the field of the dipole A. We have thus shown that classical electrostatics can be used on this level of approximation. This result is not actually surprising because it is well known that low-order time dependent perturbation theory treatment of a forced two-level system yields results equivalent to the Drude model, which represents such a system as a classical damped forced harmonic oscillator.<sup>8</sup> The above result is another manifestation of this same equivalence.

An immediate consequence of the equivalence of the first-order quantum mechanical perturbation theory and classical electrostatics in the present context is the possibility to derive optical properties of solute molecules in a cavity of a given geometry surrounded by the solvent, where the latter is represented as a continuous dielectric of a given dielectric function  $\epsilon(\omega)$  using purely classical electrostatics arguments. Such a formal derivation was outlined by Gersten and Nitzan<sup>9</sup> and its application to the present problem will be given elsewhere.

In the next section we present the results of classical electrostatics calculation of the optical response of a molecule embedded in a cluster of polarizable atoms, which are characterized by their polarizability. Again, these results are expected to be at least as reliable as those based on quantum mechanical perturbation theory.

### III. ELECTROSTATIC CALCULATION OF THE OPTICAL PROPERTIES OF A MOLECULE IN A CLUSTER OF POLARIZABLE ATOMS

Classical electrostatics can be used to evaluate optical properties of systems, whose size is much smaller than relevant electromagnetic wavelengths. Relevant wavelengths satisfy  $\lambda \sim 2\pi c/\omega$ , where  $\omega$  is a characteristic frequency of the system. Classical electrostatics can then be applied to a continuous system characterized by a given dielectric function  $\epsilon(\omega)$ , to a system of particles characterized by their

polarizabilities or to a combination of both. The method and its application to a molecule located in the vicinity of dielectric particles (representing colloidal particles or surface island film) has been described previously.<sup>10</sup> Here, instead of dielectric particles, we have  $N$  atoms which, for our purposes, may be represented by point polarizable particles with polarizabilities  $\alpha_j$  ( $j = 1, 2, \dots, N$ ). The molecule is represented by a charge distribution  $\rho(\mathbf{r})$ , oscillating (for the transition under discussion) with the molecular transition frequency  $\omega$  and with a space dependent amplitude  $\rho(\mathbf{r})$ .  $\rho(\mathbf{r})$  satisfies (for a neutral molecule)  $\int d^3r \rho(\mathbf{r}) = 0$  and is related to the molecular transition dipole  $\mu$  by

$$\mu = \int d^3r \mathbf{r} \rho(\mathbf{r}). \quad (13)$$

Let  $\Gamma_R^{(f)}$  be the radiative decay rate of the free molecule. The radiative rate of the molecule in the cluster is given by<sup>10</sup>

$$\Gamma_R = \frac{|\mu^{\text{tot}}|^2}{|\mu|^2} \Gamma_R^{(f)}, \quad (14)$$

where  $\mu^{\text{tot}}$  is the amplitude of the total oscillating dipole, at the frequency  $\omega$ , which consists of the sum of the molecular transition dipole  $\mu$  and the dipole induced in the cluster by  $\mu$ . A modified form of Eq. (13) which takes into account the possible frequency shift is

$$\Gamma_R = \left( \frac{\omega}{\omega_0} \right)^3 \frac{|\mu^{\text{tot}}|^2}{|\mu|^2} \Gamma_R^{(f)}. \quad (15)$$

The problem of cluster effect on the molecular radiative lifetime is thus reduced to the electrostatic problem of evaluating the ratio  $|\mu^{\text{tot}}|^2/|\mu|^2$  between the total dipole in the system and the source dipole associated with the molecular charge distribution  $\rho(\mathbf{r})$ . We note in passing that this ratio depends only on molecular properties and on the geometry of the cluster, but not on the absolute magnitude of  $\rho(\mathbf{r})$ , as the multiplication of  $\rho$  by a constant will not affect Eq. (15).

The evaluation of  $\mu^{\text{tot}} = \mu + \sum_{j=1}^N \mu_j$  is a simple exercise in classical electrostatics. Let  $\mathbf{E}(\mathbf{r})$  be the field at  $\mathbf{r}$  associated with the molecular charge distribution

$$\mathbf{E}(\mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}. \quad (16)$$

Then the dipoles induced on the surrounding atoms are obtained from the following set of coupled equations:

$$\mu_j = \alpha_j \left[ \mathbf{E}(\mathbf{r}_j) + \sum_{\substack{k=1 \\ k \neq j}}^N \mathbf{M}_{jk} \cdot \mu_k \right]; \quad j = 1, 2, \dots, N, \quad (17)$$

where  $\mathbf{M}_{jk}$  is the dipole-dipole interaction tensor

$$\mathbf{M}_{jk} = \frac{3\hat{n} \cdot \hat{n} - 1}{|\mathbf{r}_k - \mathbf{r}_j|}. \quad (18)$$

Here,  $\mathbf{l}$  is the unit tensor and  $\hat{n} = (\mathbf{r}_k - \mathbf{r}_j)/|\mathbf{r}_k - \mathbf{r}_j|$ . The set of equations (17) is easily solved numerically for any given cluster geometry and assumed molecular charge distribution. Note that Eq. (17) explicitly takes into account the dipole-dipole coupling between the dipoles induced on the atoms. This coupling is neglected in the standard quantum mechanical calculation.

The frequency shift for the same model is derived from the Drude model, taking the transition dipole as a classical damped harmonic oscillator<sup>11</sup>

$$\dot{\mu} + \omega_0^2 \mu + \Gamma_R^{(f)} \dot{\mu} = \alpha \omega_0^2 E_r, \quad (19)$$

where  $\omega_0$  is the "bare" molecular transition frequency and  $\alpha$  is the polarizability associated with the transition dipole.  $\alpha$  is related to the radiative decay rate of the free molecule by<sup>9</sup>

$$\alpha = \frac{3}{2} \frac{\Gamma_R^{(f)}}{\omega_0} \left( \frac{c}{\omega_0} \right)^3. \quad (20)$$

The field  $E_r$  in Eq. (19) is the reaction field (in the direction of the molecular transition) due to the medium surrounding the molecules. For our problem, it is given by a sum over the surrounding atoms

$$E_r = E_{0r} e^{-i\omega t - \frac{1}{2}\Gamma_R t}, \quad (21)$$

$$E_{0r} = \epsilon \sum_{k=1}^N M_{0k} \cdot \mu_k. \quad (22)$$

In Eq. (21),  $\omega$  and  $\Gamma_R$  are the actual frequency and decay rate associated with the transition. In Eq. (22),  $\epsilon$  is the polarization vector of the molecular transition and the indices 0 and 1, 2, ...,  $N$  denote the molecular dipole and the  $N$  surrounding atoms, respectively. The magnitudes of  $\mu_k$  are calculated from Eq. (17). Inserting Eq. (21) and

$$\mu = \mu_0 e^{-i\omega t - \frac{1}{2}\Gamma_R t} \quad (23)$$

into Eq. (19) leads to<sup>12</sup>

$$\omega - \omega_0 = -\frac{(\Gamma_R^{(f)})^2}{8\omega_0} - \frac{\alpha\omega_0}{2\mu_0} \text{Re}[E_{0r}]. \quad (24)$$

For an isolated molecule Eq. (24) implies that  $\omega = \omega_0 - (\Gamma_R^{(f)})^2/(8\omega_0)$ . The frequency shift due to the surrounding atoms therefore satisfies

$$\frac{\Delta\omega}{\omega_0} = -\frac{\alpha}{2\mu_0} \text{Re}[E_{0r}]. \quad (25)$$

Here [as well as in Eq. (15)] the difference between the bare frequency  $\omega_0$  and the actual frequency of the isolated molecule will be disregarded.

It should be noted that the same formalism can provide the nonradiative decay rate, due to energy transfer from the molecule to the surrounding medium, if the reaction field  $E_r$  (i.e., the medium polarizabilities  $\alpha_k$ ) have dissipative (imaginary) components. This approach can also yield corrections to the radiative lifetime but only when used beyond the electrostatic approximation of Eq. (22).<sup>12</sup> In the situation investigated in Ref. 12 (a molecule near a dielectric surface) this leads to essentially the same result as given by Eq. (15). In the following discussion, we limit ourselves to the nondissipative situation which is relevant to a molecule in a rare-gas cluster. Equations (15) and (25) together with the solutions to Eq. (17) then provide the desired decay rate and frequency shift.

The results of model calculations for the ratio of the decay rates, Eq. (14), of a molecule in a cluster of Ar atoms are presented in Figs. 1–4. The atomic arrangement around the molecule is shown in the inset of the figures. These figures show the ratio  $\Gamma_R/\Gamma_R^{(f)}$  between the radiative rates associated with the clustered and the free molecule for various geometries as a function of the distance between the centers of the nearest atoms. The argon polarizability is taken to be

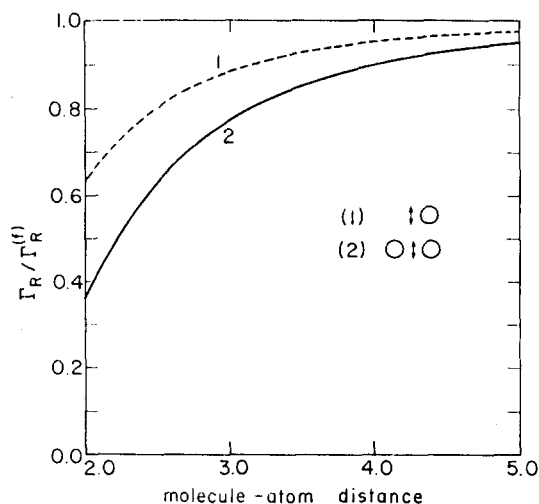


FIG. 1. The ratio between radiative decay rates of a clustered and free molecule as a function of molecule-atom distance. The molecule is represented by a point dipole whose direction is perpendicular to the molecule-atom axis. Full line—two atom cluster. Dashed line—one atom cluster. All distances are in units of the atomic radius.

$1.64 \times 10^{-24} \text{ cm}^3$ . In Figs. 1–4, the molecule is represented by a point dipole. The ratio  $\Gamma_R/\Gamma_R^{(f)}$  does not depend on the magnitude of this dipole. In Figs. 5 and 6, we examine the effect of the finite spatial spread of the molecular dipole. For this purpose, we represent the molecule by two charges  $+Q$  and  $-Q$  separated by a distance  $l$  along the direction of the molecular dipole, such that  $Ql = \mu$ . In these figures,  $\mu$  is kept constant as the interchange distance  $l$  is varied.

The results in Figs. 1–6 are based on Eq. (14) and should be further corrected by the numerical factor  $(\omega/\omega_0)^3$ . The ratio of the corrected decay rates, Eq. (15), can also be identified with the ratio of the oscillator strengths of the clustered and the free molecule. The frequency shifts  $(\Delta\omega/\omega_0)$  where  $\Delta\omega = (\omega - \omega_0)$  are portrayed in Figs. 7 and 8. From these results, we conclude the following:

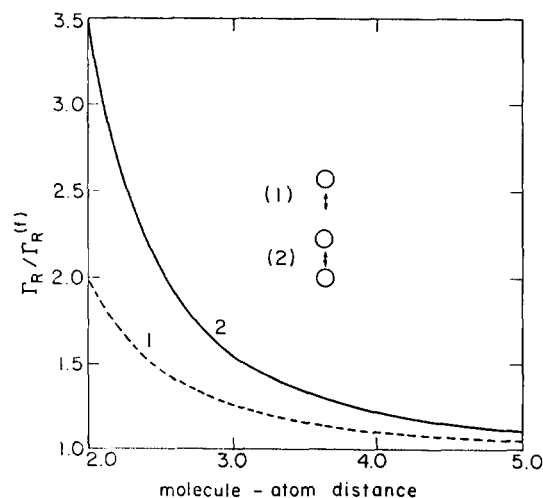


FIG. 2. Same as Fig. 1, with the molecular dipole parallel to the molecule-atom axis.

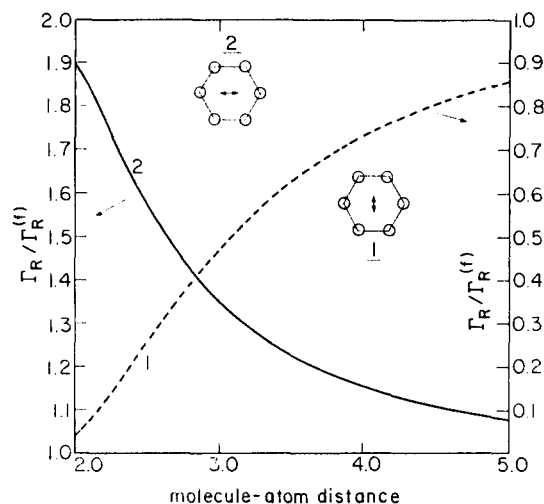


FIG. 3. Same as Figs. 1 and 2 where the molecule is in the center of a hexagon with six Ar atoms at its corner. Full line—molecular dipole in the hexagon plane (the inset shows this case). Dashed line—molecular dipole normal to the hexagon plane.

(a) The radiative decay rate of a clustered molecule is sensitive to the cluster geometry and, in particular, to the positions of the solvent atoms relative to the direction of the molecular transition dipole. It is seen (Figs. 1 and 2) that, when the solvent atom(s) approach the molecule along a line parallel to the direction of the transition dipole, the decay rate increases. In the reverse case, when the direction of approach is perpendicular to the transition dipole, the radiative decay rate decreases for a closer atomic approach. This observation is in accord with the observation by Myers and Birge<sup>3</sup> that the oscillator strength is lowered for long and thin molecules with a transition dipole parallel to the molecular axis because of interaction with polarizable solvent molecules. The cause for this observed trend is clear for the geometries described by the insets in Figs. 1 and 2. For the perpendicular geometry (i.e., dipole orientation is perpen-

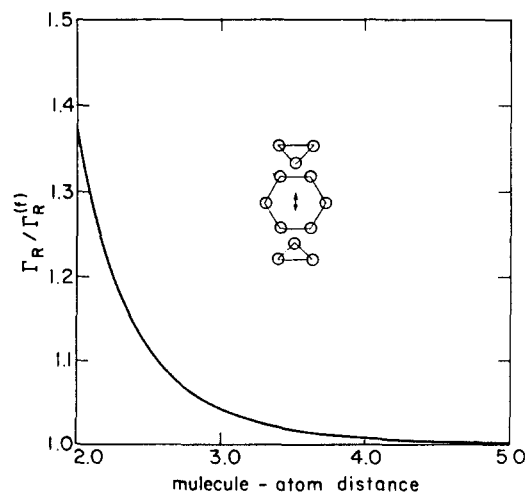


FIG. 4. Same as Figs. 1–3, with the molecule in the center of a 12 atom cluster in the position of an octahedral interstitial site.

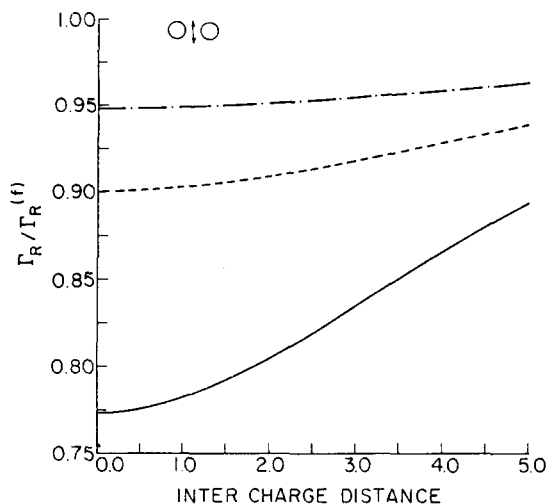


FIG. 5. The ratio  $\Gamma_R/\Gamma_R^{(f)}$  as a function of dipole size  $l$  (in units of atomic radius), for a molecule between two Ar atoms in the configuration of Fig. 1. Full, dashed, and dashed-dotted lines correspond to molecule center-atom center distances of 3, 4, and 5, respectively.

dicular to the molecule-atom axis), the dipole moments induced on the neighboring atoms are opposite in sign to the inducing molecular dipole, so that the overall cluster dipole  $|\mu^{\text{tot}}|$  is smaller than  $\mu$ . Hence, by Eqs. (14) or (15), the oscillator strength is reduced in the cluster. The reverse situation occurs in the parallel geometry, where the induced dipoles are of the same sign as the molecular dipole and constructively add to it.

(b) The reduction or enhancement of the relative decay rate  $\delta\Gamma = (\Gamma_R/\Gamma_R^{(f)} - 1)$  is approximately given by a sum of contributions from the individual perturbing atoms. This results from Eq. (14) together with the observation [based on Eqs. (16) and (17)] that  $\mu^{\text{tot}} = \mu + \sum_{k=1}^N \mu_k$  and with our expectation that  $|\mu_k| \ll |\mu|$ . When this holds, we have  $\delta\Gamma \approx \sum_k \delta\Gamma_k$  with  $\delta\Gamma_k > 0$  for the parallel geometry and

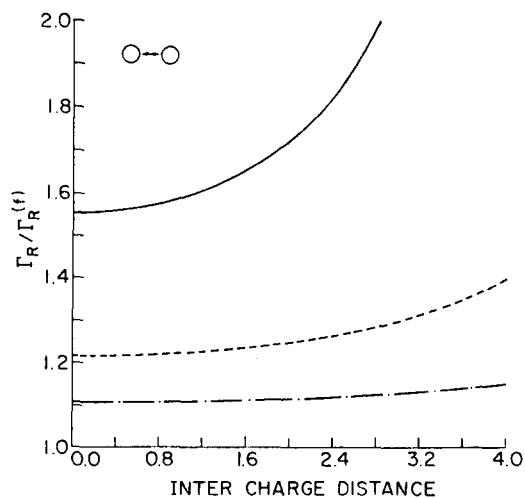


FIG. 6. Same as Fig. 5, with the configuration of Fig. 2.

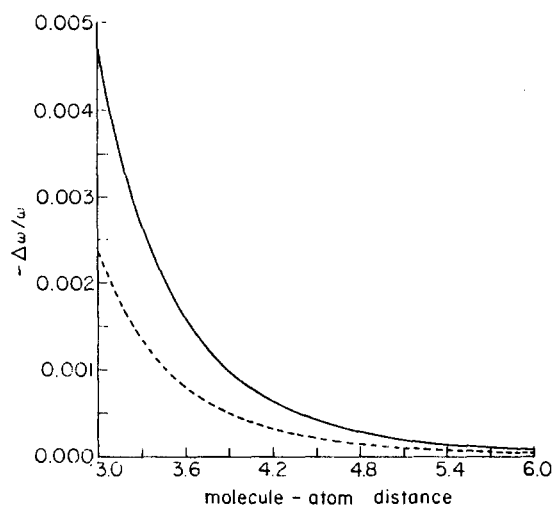


FIG. 7. Relative frequency red shift  $-\Delta\omega/\omega$  as a function of molecule-atom distance (in units of the atomic radius) for a molecule clustered with one (dashed line) and two (full line) atoms, in the configuration of Fig. 1.

$\delta\Gamma_k < 0$  for the perpendicular geometry. This conclusion is indeed borne out by our numerical calculations. It should be kept in mind, however, that deviations from this behavior may appear for highly polarizable atoms when the inequality  $|\mu_k| \ll |\mu|$  is not satisfied.

(c) The behavior pattern just discussed implies that the effect of a second attached atom is approximately equal to that of the first atom when the two atoms are attached to geometrically equivalent configurations (Figs. 1 and 2). For more complicated structures (Figs. 3 and 4), the balance between the constructive and destructive contributions from the induced dipoles determine the overall behavior.

(d) The difference between the results for the molecular decay rates, which are based on the point molecular dipole model and those for a finite-size molecular charge distribution, can be considerable. The trends shown in Figs. 5 and 6 can easily be understood by considering the strength of the

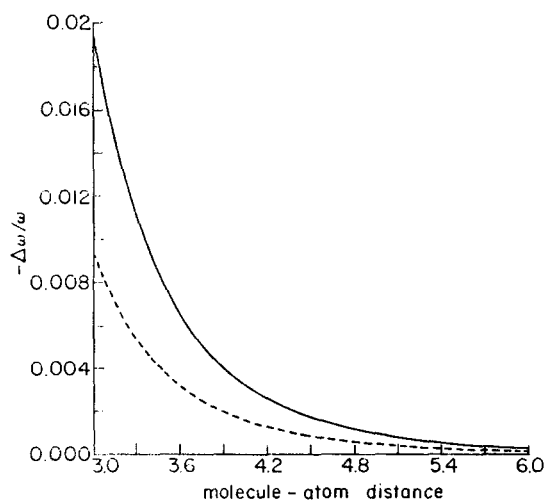


FIG. 8. Same as Fig. 7, for the configuration of Fig. 2.

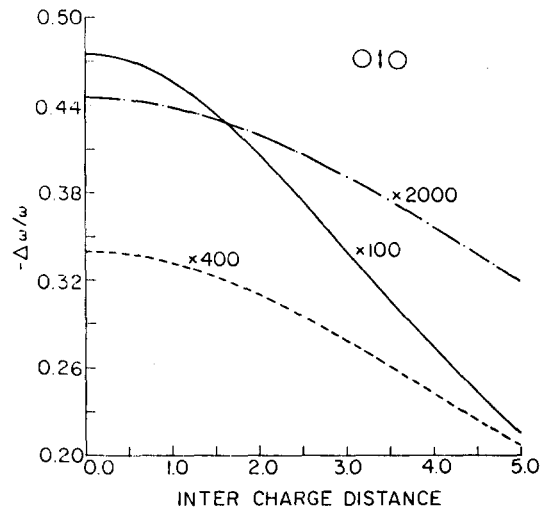


FIG. 9. Relative frequency red shift  $-\Delta\omega/\omega$  as a function of dipole size for a molecule between two Ar atoms in the configuration of Fig. 1. Full dashed and dashed-dotted lines correspond to distances 3, 4, and 5 (in units of atomic radius), respectively, between the centers of the molecule and each atom.

electrostatic interactions. Increasing the spatial size of the molecular dipole for the perpendicular configuration (Fig. 5) makes these interactions weaker, resulting in the reduction of the medium effect on the radiative relaxation rate, which in this case brings  $\Gamma_R$  closer to  $\Gamma_R^{(0)}$ . In the case of the parallel geometry (Fig. 6), the increase of the spatial size of the molecular dipole enhances the interaction, which results in further increase of the molecular decay rate in this geometry. Unfortunately, we have no estimate of the molecular property corresponding to the spatial length of the charge distribution which represents the molecular transition dipole, apart from the fact that this length should be some fraction of the molecular size in the corresponding polarization direction. This quantity should therefore be considered (at present) as a parameter of the theory.

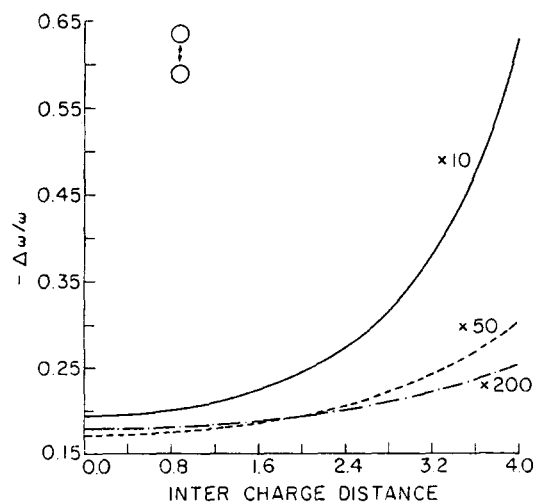


FIG. 10. Same as Fig. 9, for the configuration of Fig. 2.

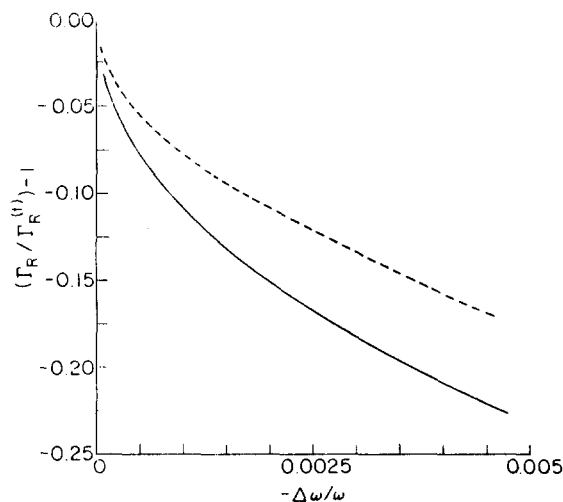


FIG. 11.  $\Gamma_R - \Gamma_R^{(l)}/\Gamma_R^{(l)}$  vs  $-\Delta\omega/\omega$  in perpendicular configuration (as in Fig. 1).  $\omega$  and  $\Gamma_R$  are changed by changing the molecule atom distance. Full and dashed lines are for two atom and one atom clusters, respectively. This plot is for a point dipole but is almost insensitive to the dipole size  $l$ .

(e) The frequency shifts  $\Delta\omega/\omega_0$  (Figs. 7 and 8) are all to the red, i.e.,  $\Delta\omega < 0$ , as appropriate for dispersive interactions.

(f) The magnitude of the frequency shift is different for distinct cluster geometries, being considerably higher for the parallel configuration (Fig. 8) than for the perpendicular one (Fig. 7). This result is in accord with the electrostatic considerations of the strength of the molecular dipole-induced atomic dipole interaction in the two configurations.

(g) The spectral shift approximately consists of a sum of contributions of the individual perturbing atoms, i.e.,  $\Delta\omega = \sum_{\alpha} \Delta\omega_{\alpha}$ , where  $\Delta\omega_{\alpha}$  is the spectral shift induced by the  $\alpha$ th atom, as expected. Additivity of spectral shifts prevails only for geometrically equivalent atoms.

(h) The finite size of the molecular charge distribution exerts a considerable effect on the frequency shift. In the

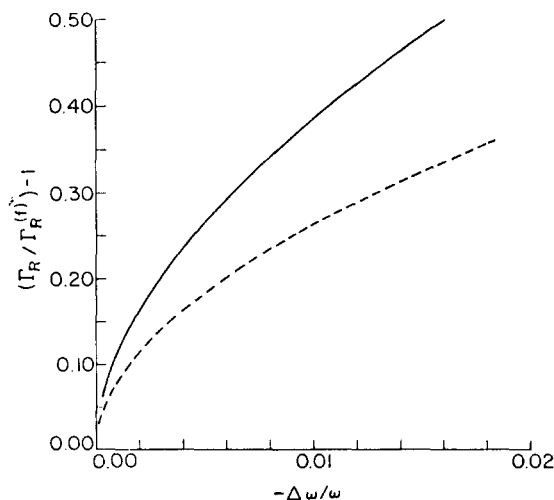


FIG. 12. Same as Fig. 11, for the parallel configuration.

perpendicular configuration (Fig. 9), the increase of the intersize distance results in the decrease of the induced dipole and of the spectral shift, while the reverse behavior is exhibited for the parallel configuration (Fig. 10).

(i) The plots of the dependence of the relative change of the radiative decay  $\delta\Gamma = (\Gamma_R/\Gamma_R^{(l)} - 1)$  vs the relative spectral shift at various molecule-atom distances are not linear (Figs. 11 and 12). It is instructive to note that these plots exhibit only a weak dependence on the finite size of the molecular charge distribution. The marked effects of the finite charge distribution on the individual observables  $\Gamma_R/\Gamma_R^{(l)}$  (Figs. 5 and 6) and  $\Delta\omega/\omega_0$  (Figs. 9 and 10) are washed out in the reduced plots. Furthermore, as both  $\delta\Gamma$  and  $\Delta\omega/\omega_0$  are proportional to the polarizability  $\alpha$  of the perturbing atoms, one expects that the plots of  $\alpha^{-1}(\Delta\omega/\omega_0)$  vs  $\alpha^{-1}\delta\Gamma$  will be universal for all perturbing atoms at a given geometrical configuration.

#### IV. CONCLUSIONS

The structure of large MR complexes, which consists of an aromatic molecule (M) bound to a rare-gas (R) atom is characterized by some universal features, with R being located at a distance  $Z_0$  above the central ring(s) of M ( $Z_0 = 3.45 \pm 0.05 \text{ \AA}$  for Ar and  $Z_0 = 3.85 \pm 0.05 \text{ \AA}$  for Xe).<sup>13</sup> The  $\pi\pi^*$  transitions of M are polarized within the molecular plane. Accordingly, the microscopic solvent effect of R on the radiative decay of the  $\pi\pi^*$  excitation of M corresponds to the perpendicular case. On the basis of our calculations, we expect that the radiative decay rate will be reduced for MR relative to that of M. The experimental observation of the lengthening of  $\tau_r$  in some aromatic rare-gas complexes (Table I) is in accord with these theoretical predictions. Obviously, theoretical estimates of  $\delta\Gamma$  cannot be performed at present. However, the universal  $\delta\Gamma$  vs  $\Delta\omega/\omega_0$  relation established in Sec. III can be utilized for prediction of general trends. This relation is not sensitive to the nature of the molecular transition dipole moment and can be used to infer the change in the radiative decay rate from the experimental value of the spectral shift. From Fig. 11 and the experimental  $\Delta\omega/\omega_0$  data of Table I, we infer that the reduction of the radiative decay rates  $\delta\Gamma = \tau_r^{(l)}/\tau_r - 1$  should be  $\delta\Gamma = -0.10$  for tetracene Ar,  $\delta\Gamma = -0.10$  for 9-cyanoanthracene Ar, and  $\delta\Gamma = -0.15$  for 9-cyanoanthracene Xe. These results are consistent with the experimental data of Table I. Further accurate information on pure radiative lifetimes  $\pi\pi^*$  excitation of MR complexes will be of considerable interest.

Finally, it may be pointed out that for a Rydberg excitation of an aromatic molecule the transition moment is perpendicular to the molecular plane, so that the configuration of the transition moment in the MR complex is parallel and the oscillator strength and the radiative decay rate will be enhanced by the R atom. It will be extremely difficult to confirm this prediction in view of the dissociative nature<sup>14</sup> of Rydberg states of large van der Waals complexes.

#### ACKNOWLEDGMENT

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