CLASSICAL DECAY RATES FOR MOLECULES IN THE PRESENCE OF A SPHERICAL SURFACE. (U) STATE UNIV OF NEW YORK AT BUFFALO DEPT OF CHEMISTRY Y S KIM ET AL. OCT 87
Classical Decay Rates for Molecules in the Presence of a Spherical Surface:

A Complete Treatment

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ABSTRACT

A comprehensive treatment of the classical decay rates for a molecule in the vicinity of a spherical surface is presented through the application of the work of van del Pol and Bremmer and that of Fock. This theory takes full advantage of the Hertz vector formalism, which is mathematically simpler than the widely-adapted Lorenz-Mie approach which uses the complicated vector harmonic expansions. Results are obtained for both radiative and nonradiative transfer when the molecule is located outside or inside the surface. Numerical results are given for the cases of a surface, cavity and aerosol, and comparison with other works are made.

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I. INTRODUCTION

Ever since the role of surface roughness was recognized as prominent in leading to such dramatic surface phenomena as surface-enhanced Raman scattering and other photochemical processes,\textsuperscript{1} the problem of the decay rates for molecules in the vicinity of a spherical particle has been investigated intensively.\textsuperscript{2-5} While the classical electromagnetic approach has been followed to establish the results for the reduced (normalized) decay rates in both the electrostatic limit\textsuperscript{2} and the more exact electrodynamical treatment,\textsuperscript{3-5} we feel that a complete analysis of such a problem has not yet been available in the literature. Given two possible orthogonal orientations of the molecule (radial/tangential), the two possible locations of the molecule (outside/inside the sphere) and the two different kinds of energy transfers during the decay process (radiative/nonradiative), there are altogether eight problems to be solved. In a paper following the analogous treatment of Chance, Prock and Silbey for a flat surface,\textsuperscript{6} Ruppin solved the complete problem for a molecule located outside the sphere.\textsuperscript{3} Very recently, Chew\textsuperscript{4} published results using the energy flux method\textsuperscript{3,6} for both the cases where the molecule is located outside and inside the sphere, and the equivalence with the results obtained from Green's dyadic method\textsuperscript{6} is proven in the limit where all the dielectric constants are real. Hence, all the nonradiative transfers are ignored in Chew's treatment.\textsuperscript{4} As a matter of fact, Eqs. (6) and (7) in Ref. 4 are identical to the results for radiative transfer for a molecule located outside the sphere as given in Eqs. (27) and (28) in Ruppin's work.\textsuperscript{3} Hence, combining the work of Ruppin\textsuperscript{3} and Chew,\textsuperscript{4} we conclude that six of the eight problems are solved, leaving the two problems of nonradiative rates for a molecule inside the sphere to be solved. Moreover, all these past treatments have been based on the Lorenz-Mie theory\textsuperscript{7} established by the expansion of the field quantities using vector spherical harmonics.
A comprehensive treatment of the classical decay rates for a molecule in the vicinity of a spherical surface is presented through the application of the work of van del Pol and Bremmer and that of Fock. This theory takes full advantage of the Hertz vector formalism, which is mathematically simpler than the widely-adapted Lorenz-Mie approach which uses the complicated vector harmonic expansions. Results are obtained for both radiative and nonradiative transfer when the molecule is located outside or inside the surface. Numerical results are given for the cases of a surface, cavity and "aerosol", and comparisons with other works are made.
Classical Decay Rates for Molecules in the Presence of a Spherical Surface: A Complete Treatment

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In this present work, we present a complete solution of the eight problems via a different approach, namely, the Hertz vector formalism. This formalism has a mathematically simpler feature, since the expansions of the Hertz functions are more of a scalar type, and one can see easily from the Green's function property that there exists a simple transformation which relates the fields for the outside-molecule case to those where the molecule is located inside the sphere. Hence it is not necessary to solve again the boundary value problem for the inside-molecule case as is done in Chew's work. We elaborate the theory in Sec. II, where we shall see that for the case where the molecule is inside a sphere with a complex dielectric constant, a straightforward application of the methods of Ruppin and Chew is not appropriate, such that one must resort to more microscopic models for the treatment of the bulk decay rates (i.e., in the absence of the surface). Numerical examples are given in Sec. III, where we shall illustrate that the neglect of the nonradiative rates as in Chew's formalism can lead to serious errors in some cases. Discussion and conclusion of the present work are given in Sec. IV.

II. Theory

It is well known that the electromagnetic scattering problem in the presence of a dielectric sphere can in general be formulated in two different ways. While the scattering of a plane wave from a sphere has been well treated in both the Lorenz-Mie approach and the Hertz vector (Debye potential) approach, it seems that the problem of dipole-sphere interactions (hence the problem of molecular lifetimes) has always been treated by the former approach using the vector harmonics expansion. Here we want to solve the lifetime problem in the Hertz vector formalism using expansions in ordinary spherical functions. For those mathematical results which have been obtained already by
the former approach, we shall only indicate briefly how the same results may be obtained in our present approach, with possible simplifications being emphasized.

For a dipole located outside the sphere, the problem has been solved for both the vertical (radial) and the horizontal (tangential) dipoles. Assuming nonmagnetic media and the region outside (inside) the sphere (of radius $a$) to be characterized by the local dielectric function $\varepsilon_1 (\varepsilon_2)$, the Hertz vectors (along the radial direction) can then be expressed in the following series expansions in terms of the various "Mie coefficients":

For a vertical dipole located at $(d,0,0)$ with $y_1 = k_1d$, $\rho_1 = k_1a$ and $k_1 = \sqrt{\varepsilon_1 - \omega/\omega}$,

$$\Pi_1 = \left\{ \begin{array}{l} ik_1 \sum_{n=0}^{\infty} \left( (2n+1) j_n(k_1r) + B_n h_n^{(1)}(k_1r) \right) \frac{1}{r} \int_0^\infty j_n(r') \frac{1}{r'} P_n(\cos \theta) d\theta, \quad a < r < d \\ ik_1 \sum_{n=0}^{\infty} \left( (2n+1) \frac{h_n^{(1)}(y_1)}{j_n(\rho_1)} \right) \frac{1}{\rho_1} \int_0^\infty j_n(r') \frac{1}{r'} P_n(\cos \theta) d\theta, \quad d < r < a \end{array} \right. \quad (1)$$

where $j_n$ and $h_n^{(1)}$ are the ordinary spherical Bessel and Hankel functions. The nonvanishing field components are then given by

$$E_r = \frac{1}{rd \sin \theta} \left( \sin \theta \frac{d}{d\theta} \frac{\partial}{\partial \theta} \right) \left( \frac{1}{r} \times \Pi_1 \right), \quad (3a)$$

$$E_\theta = \frac{1}{rd} \frac{d^2}{dr^2} (r\Pi) \quad (3b)$$
For a horizontal dipole located at \( (d,0,0) \), we need two Hertz vectors with one along \( \hat{r} \) and one along \( \hat{\theta} \), given by \( (i=1,2) \):

\[
\begin{align*}
\vec{H}_i^E &= -\cos \phi \frac{\partial \vec{P}_i}{\partial \theta}, \\
\vec{H}_i^M &= -\sin \phi \frac{\partial \vec{Q}_i}{\partial \theta},
\end{align*}
\]

where \( P, Q \) are expressed in series for: as (with \( \psi_n(x) \equiv x j_n(x) \) and \( \zeta_n(x) \equiv x h_n^{(1)}(x) \))

\[
P_1 = \frac{1}{rd} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \zeta_n'(y_1) \left[ \psi_n(k_1 r) + B_n \zeta_n(k_1 r) \right] P_n(\cos \theta), \quad a < r < d
\]

\[
P_2 = \frac{k_1^2}{ad} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} D_n^{-1} \zeta_n'(y_1) j_n(k_2 r) P_n(\cos \theta), \quad 0 < r < a
\]

\[
Q_1 = \left\{ \begin{array}{ll}
\frac{k_1^2}{n(n+1)} \sum_{n=1}^{\infty} h_n^{(1)}(y_1) \left[ j_n(k_1 r) + A_n h_n^{(1)}(k_1 r) \right] P_n(\cos \theta), \quad a < r < d \\
\frac{k_1^2}{n(n+1)} \sum_{n=1}^{\infty} \left[ j_n(y_1) + A_n h_n^{(1)}(y_1) \right] h_n^{(1)}(k_1 r) P_n(\cos \theta), \quad d < r
\end{array} \right.
\]

\[
\begin{align*}
\vec{H}_\phi &= -\frac{ic}{\omega} k^2 \frac{\partial \vec{H}_\phi}{\partial \theta}.
\end{align*}
\]
The nonvanishing field components are then given by

\[ E_r = \frac{1}{r} L^2 r E \]  
\[ E_\theta = -\frac{1}{r} \frac{\partial}{\partial r} (r P^E) + \frac{i \omega}{\cos \theta} \frac{\partial P^M}{\partial \theta} \]  
\[ E_\phi = -\frac{1}{r \sin \theta} \frac{\partial}{\partial r} (r P^E) - \frac{i \omega}{\cos \theta} \frac{\partial P^M}{\partial \phi} \]  
\[ H_r = -\frac{1}{r} L^2 r M \]  
\[ H_\theta = \frac{i \omega}{\sin \theta} \frac{\partial P^E}{\partial \phi} + \frac{1}{r} \frac{\partial}{\partial r} (r P^M) \]  
\[ H_\phi = -i \frac{\omega}{\sin \theta} \frac{\partial P^E}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} (r P^M) \]  

with

\[ L^2 = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \]

The "Mie coefficients" in the above equations are defined as

\[ A_n = \frac{j_n(r_1)j'_n(r_2) - j_n(r_2)j'_n(r_1)}{j_n(r_2)c_n(r_1) - b_n^{(1)}(r_1)c_n(r_2)} \]
From this formulation and by making use of the well-known properties of Green's functions, we can easily obtain via a simple transformation $T$ the solution for the reflected and transmitted fields for the case where the dipole is located inside the sphere without having to solve again the boundary value problem. If we define $T$ by

\[ T\left( \begin{array}{c}
\epsilon_n \\
\epsilon_n^{(1)} \\
k_1, \epsilon_1, \ldots \\
k_2, \epsilon_2, \ldots
\end{array} \right) = \left( \begin{array}{c}
h_n \\
h_n^{(1)} \\
k_2, \epsilon_2, \ldots \\
k_1, \epsilon_1, \ldots
\end{array} \right), \]

then it is not difficult to check that the "inside solutions" are easily obtained from the outside solutions through the operation with $T$.

Now let us apply the above results for our decay rate problem. According to the classical approach, there are two different methods for calculating the decay rate of the molecule as induced by the presence of the surface. In the Green's dyadic approach, the dipole is modeled as a damped harmonic oscillator being driven by the surface field. The induced decay rate is then given by

\[ \gamma = \gamma_0 + \frac{a}{c} \text{ Im } G, \]
where $\gamma_0$ is the decay rate in the absence of the boundary surface (i.e., with the whole space filled with the dielectric medium in which the dipole is located), $\alpha = e^2/m$, $\omega$ being the emission frequency (which is assumed to change negligibly), and $\text{Im } G$ is the imaginary part of the dyadic function defined as the surface field $(E_R)$ reflected at the dipole site per unit dipole moment $(\mathbf{n})$. The other approach would be to calculate the rate of the energy carried away from the molecule, which can further be divided into that radiated to infinity [radiative (R) transfer] and that lost in the form of Joule heat into any dissipative medium present [nonradiative (NR) transfer]. Hence, combining these two approaches, the total rate given by Eq. (13) can be written as

$$\gamma = \gamma^R + \gamma^\text{NR}$$

(14)

with

$$\gamma^R = \frac{1}{W} \int \frac{d\Omega}{r^2} \mathbf{\mathbf{\hat{r}}} \cdot \mathbf{\hat{n}} ,$$

(15)

and

$$\gamma^\text{NR} = \frac{1}{2W} \int_V d\tau \sigma |\mathbf{\mathbf{E}}|^2 .$$

(16)

Here $\mathbf{E}$ is $\frac{C}{\Omega} \text{Re}(\mathbf{\hat{r}} \times \mathbf{\hat{n}})$ is the Poynting vector, $\sigma = \frac{\omega}{4\pi} \text{Im } \varepsilon$ is the conductivity of the dissipative medium, and $W = \omega^2 \mu^2 / 2\alpha$ is the average energy of the dipole. The integral in Eq. (15) is over a surface at infinity, and that in Eq. (16) is over the volume of the dissipative medium. Very often, the Joule heat integral is quite complicated, and one can obtain it indirectly through Eqs. (13)-(15). We
shall apply the fields obtained from Eqs. (1)-(10) to calculate the \( \gamma \)'s given in Eqs. (13)-(15) for the following three cases:

Case (i): The surface problem

Here \( \hat{\mu} \) is located in vacuum \( (\varepsilon_1 = 1) \) outside a sphere of dielectric constant \( \varepsilon_2 = \varepsilon' + i\varepsilon'' \), and \( \gamma_0 \) is then given by \( \frac{1}{3} \varepsilon_1 c k_1^4 \mu^2 / \omega = 2ak_1^3 / 3\omega \). Using Eqs. (1), (3a) and (13), we obtain for a vertical dipole

\[
\frac{\gamma_1}{\gamma_0} = 1 + \frac{3}{2} \text{Re} \sum_{n=1}^{\infty} \frac{(2n+1)n(n+1)B_n[n^{-1}h_n'(y_1)]^2}{y_1} .
\]  

(17)

Furthermore, using Eqs. (1)-(3), the Poynting vector can readily be calculated, and from Eq. (15) we obtain

\[
\frac{\gamma_1^R}{\gamma_0} = \frac{3}{2} \sum_{n=1}^{\infty} \frac{n(n+1)(2n+1)}{y_1^2} \left| j_n(y_1) + B_n h_n'(y_1) \right|^2 .
\]  

(18)

Similarly, using Eqs. (4)-(10), (13) and (15), we obtain the corresponding results for a horizontal dipole

\[
\frac{\gamma_1}{\gamma_0} = 1 + \frac{3}{2} \text{Re} \sum_{n=1}^{\infty} \frac{(n+1/2)B_n[n^{-1}h_n'(y_1)]^2 + A_n h_n'(y_1)]^2}{y_1} .
\]  

(19)

\[
\frac{\gamma_1^R}{\gamma_0} = \frac{3}{4} \sum_{n=1}^{\infty} (2n+1) \left( |j_n(y_1)| + A_n h_n'(y_1)|y_1|^2 + \frac{v_n(y_1) + B_n \zeta_n'(y_1)}{y_1} \right)^2 .
\]  

(20)
The nonradiative rates can then be obtained from the difference between the total and radiative rates.

Case (ii): The cavity problem

Here \( \vec{\mu} \) is located inside a spherical vacuum \((\epsilon_2 = 1)\) with a dielectric \((\epsilon_1 = \epsilon' + i\epsilon'')\) occupying the whole space outside the vacuum. The total decay rates can readily be obtained from the outside solutions (Eqs. (17) and (19)) through the transformation \( T \) (Eq. (12)) as discussed above, whereby we obtain

\[
\frac{\gamma_1}{\gamma_0} = 1 + \frac{3}{2} \text{Re} \sum_{n=1}^{\infty} (2n+1)n(n+1)E_n \left( \frac{j_n(y_2)}{y_2} \right)^2 ,
\]

\[
\frac{\gamma_2}{\gamma_0} = 1 + \frac{3}{2} \text{Re} \sum_{n=1}^{\infty} (n + \frac{1}{2})\left( \frac{\psi'(y_2)}{y_2} \right)^2 + P_n j_n^2(y_2) ,
\]

with \( E_n \) and \( P_n \) given by

\[
E_n = T(B_n) ,
\]

\[
P_n = T(A_n) .
\]

We want to remark that in this configuration the decay rates can only be purely radiative or purely nonradiative, depending on whether the outside medium is transparent \((\epsilon'' = 0)\) or dissipative \((\epsilon'' = 0)\) with respect to the molecular emission frequency. Furthermore, it is interesting to note that in the perfectly-conducting limit \((|\epsilon_2| >> |\epsilon_1|)\) where we have
both Eqs. (21) and (22) vanish. Thus, in the present classical treatment, the molecular lifetime becomes infinite in a perfectly-conducting cavity. This is understandable since in this approach only two mechanisms can "cause" the molecule to decay, i.e., either for energy being brought to infinity (radiative transfer) or dissipated into a host medium (nonradiative transfer). Since no field can penetrate into the perfect conducting environment and hence both these transfers cannot occur, it is not surprising to see that both decay rates vanish in Eqs. (21) and (22). In the more exact quantum treatment, however, the vanishing of the decay rates in a perfectly-conducting cavity can only restrictively occur.\(^{12}\)

Case (iii): The "aerosol" problem\(^{13}\)

Here \(\hat{\mu}\) is located inside a dielectric sphere \((\varepsilon_2 = \varepsilon' + i\varepsilon'')\) with the outside being vacuum \((\varepsilon_1 = 1)\). We shall further divide this into the following two cases for discussion:

(a) **Transparent dielectric**

This case has already been treated by Chew.\(^4\) In the present approach, the total decay rate can again be obtained directly from Eqs. (17) and (19) through T. With \(\gamma_0\) being given by \(\frac{1}{3}\varepsilon_2^4\varepsilon_2^{3/2}m^2/\mu = 2\varepsilon_2^3/3\omega_2\),\(^4\) we obtain the same expressions as given in Eqs. (21)-(24). The radiative transfers in this case can similarly be obtained as in Eqs. (18) and (20) via the transformation \(\hat{\mathbf{E}}_{\text{in}} = T(\hat{\mathbf{E}}_{\text{out}})\) to give\(^4\)
In this case, since \( \varepsilon_2 \) is real (transparent, \( \varepsilon'' = 0 \)), there is no dissipative (nonradiative) effects, and it has been shown explicitly by Chew that the radiative rates in Eqs. (26) and (27) are identical to the total rates as given in Eqs. (21) and (22).

(b) **Dissipative dielectric**

This is the case which has not been discussed before in the context of "surface problems". Nevertheless, the same problem for a molecule in the bulk of an adsorptive medium has received considerable attention in the literature.\(^{14}\) The difficulty lies in the evaluation of \( \gamma_0 \) in Eq. (13). Obviously, the decay in a dissipative medium of infinite extent can only be nonradiative. However, if one applies Eq. (16) directly to calculate \( \gamma_0 \) in this case, one will get divergences in the integral due to the predominance of the near field in this case, unless one adopts a cutoff volume (forbidden volume\(^{14}\)) in the lower bound of the integral.\(^{15}\) Moreover, this approach has been criticized by Agranovich and Dubovskii (AD),\(^{16}\) who proposed a more exact microscopic treatment which shows that the result from such macroscopic theory\(^{15}\) can be correct only under certain restrictive conditions. In the following, we shall make use of the results of AD to investigate the surface effects in Eq. (13).
According to AD, under the condition that the "Mössbauer-type" effect (in the optical region) can be neglected, $\gamma_0$ can be expressed in a form which is very similar to that obtained from Feinberg's theory.

$$\frac{\gamma_0}{\gamma_{sp}} = \frac{32}{64\pi^4} \varepsilon'' N_0 \lambda^3 ,$$

where $\gamma_{sp}$ is the spontaneous decay of the free molecule, $N_0$ is the molecular number density of the dielectric medium, $\lambda$ is the emission wavelength, and $Z$ is a numerical factor depending on the lattice structure of the medium. A rough estimate gives $Z \approx 10$. Eq. (28) holds as long as $\lambda$ is much greater than the lattice constant of the medium and the spatial dispersion of the dielectric constant $\varepsilon''$ can be neglected. Using Eqs. (13), (21), (22) and (28), we finally obtain the total decay rates for $\Phi$ in a dissipative dielectric sphere as

$$\frac{\gamma_1}{\gamma_0} = 1 + \frac{3}{2} f(\omega) \text{Re}(\sqrt{\varepsilon_2}) \sum_{n=1}^\infty (2n+1)n(n+1) E_n \left[ \frac{j_n(y_2)}{y_2} \right]^2 ,$$

$$\frac{\gamma_2}{\gamma_0} = 1 + \frac{3}{2} f(\omega) \text{Re}(\sqrt{\varepsilon_2}) \sum_{n=1}^\infty (n+\frac{1}{2})[E_n \left( \frac{j_n(y_2)}{y_2} \right)^2 + F_n j_n(y_2)] ,$$

where $f(\omega) \equiv \gamma_{sp}/\gamma_0$ is the reciprocal ratio as given in Eq. (28). The radiative rates can analogously be obtained from Eqs. (26) and (27) by multiplying each of them by $f(\omega)$. The nonradiative rates can then be obtained again from the difference between the total and the radiative rates. Furthermore, for $\Phi$ located at the center of the sphere, we have results analogous to those for the case of a transparent sphere obtained by Chew where for a dissipative sphere are given by
\[
\frac{\gamma_\perp}{\gamma_0} = \frac{\gamma_\parallel}{\gamma_0} = 1 + f(\omega)\ \text{Re}(\sqrt{\varepsilon_2} E_1), \quad (31)
\]
\[
\frac{\gamma_\perp}{\gamma_0} = \frac{\gamma_\parallel}{\gamma_0} = f(\omega) \left| \frac{\varepsilon_2}{\rho_2 D_1} \right|^2 . \quad (32)
\]

III. Numerical Results

We have performed numerical studies for each of the above three classes of problems. For simplicity, we treat one of the two media as a vacuum (\(\varepsilon = 1\)). The other medium, if it is transparent to the molecular emission, is taken to be glycerol with \(\varepsilon = 2.16,^4,^{13}\) and if it is dissipative, it is taken to be silver at \(\lambda = 413\) nm with \(\varepsilon = -4.42 + 0.73 i.\) \(^{18}\) Figure 1 shows the results for a dipole above a Ag spherical surface of radius \(a = 100\ \AA\). We see that while the neglect of the nonradiative transfer (as in Chew's formulation) leads to somewhat lower values for \(\gamma\) for the radial dipole case, it leads to tremendous differences for the tangential dipole case as \(r \rightarrow a\). This phenomenon also occurs in the flat-surface case, with its origin due to the parallel (antiparallel) orientation of the "image dipole" with respect to the normal (tangential) orientation of the source dipole.\(^6\) Of course, the extremely large values of the rates at \(r = a\) are not physical either, and it is known that more reasonable values for \(\gamma\) at \(r = a\) can be obtained by considering the spatial dispersion of the dielectric function of the substrate at close distances.\(^{19}\) Nevertheless, we should add that in all the numerical calculations of Ref. 4, the substrate sphere is taken either as transparent (\(\varepsilon'' = 0\)) or as perfectly conducting (hence no penetration of fields and \(\gamma^{NR} = 0\)), so that the neglect of the nonradiative rates does not lead to any error in these cases.\(^4\)
Figure 2 shows the results for a dipole in a cavity of radius $a = 4000 \, \text{Å}$. The outside medium is taken to have a real $\varepsilon_1 = 2.16$. We observe that both radial and tangential dipoles decay at the same rate ($= 1 + \text{Re}K_1$ (see Eq. (23)) at the center, with the tangential dipole showing appreciable oscillating behavior as the dipole is moving towards the cavity wall. We also note that both enhanced and diminished values (with respect to the free molecule case) for $\gamma$ can occur in this case. Figure 3 shows the results for the same cavity problem with the outside medium being absorptive ($\text{Ag at } \lambda = 413 \, \text{nm}$). We notice that there is no oscillating behavior, and the decay for this case is very small (unless the dipole is far away from the center) and purely dissipative in nature (we recall that in the extreme limit where the outside medium becomes perfectly conducting, the decay is zero as discussed in Sec. II).

Figures 4 and 5 show results for a dipole inside an "aerosol" of transparent and dissipative media, respectively. For the transparent case (radius $a = 4000 \, \text{Å}$), we again observe similar oscillatory behavior as for the flat-surface case and a possible "diminution effect" for the decay rate. For the dissipative case (radius $a = 1000 \, \text{Å}$), it is interesting to note that (for both orientations) most of the decays are nonradiative in nature, and the surface effect is hardly noticeable except when the molecule is very close to the surface. This means that most of the molecular deexcitation energy is dissipated within a very small region of the medium around the molecule, which can be understood from Eq. (28) showing that $\gamma_0$ is very large for molecular emission wavelengths. To have appreciable surface effects, one must look for much higher emission frequencies, which can occur, for example, in nuclear spectroscopy in the $\gamma$-ray range. Thus for our interest here which focuses on molecular lifetimes, the surface effect is hardly manifested.
IV. Conclusion

We have in this paper presented a complete treatment of the classical decay rates of a molecule in the vicinity of a spherical surface. We have adopted a different formulation of the dipole-sphere interaction problem via the Hertz vector formalism, which is distinct from the more common approach via the Lorenz-Mie expansions of the field quantities in terms of complicated vector spherical harmonics. We have explored all the eight problems as stated in the Introduction within this classical approach. Since this approach is limited to only two kinds of mechanisms (radiative and dissipative transfers) through which the molecular decay rates can be examined, some interesting features (e.g., possible enhanced decays for a perfectly-conducting cavity) cannot be obtained in the present formalism. Recently, a quantum electrodynamical formalism (QED) of the spherical cavity problem was published, although the electrostatic image concept was adopted and hence the dynamical nature of the dipole field was omitted. It would therefore be interesting to incorporate the dynamical dipole fields, as treated in our present paper, into the QED formalism to see if it would give rise to new interesting phenomena for the decay rate.

Acknowledgments

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5. P. T. Leung and T. F. George, J. Chem. Phys. (in press). This article compares the static and the dynamic theories and gives an assessment of the accuracy of the former theory.


11. The solutions obtained here are essentially the dynamical version for the reaction fields in the Onsager model (cf. L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936)).


14. See the classic monograph by V. M. Agranovich and M. D. Galanin, Electronic Excitation Energy Transfer in Condensed Matter (North Holland, Amsterdam, 1982), and references therein.


Figure Captions

1. Transition rates for the two polarizations of an oscillator molecule outside a dielectric sphere of radius \( r = 100 \text{ Å} \) for \( \lambda = 4133 \text{ Å} \) and \( \epsilon_2 = -4.42 + 0.73i \). The molecule is located at a distance \( d \) from the center, and \( T \) and \( R \) stand for the total and radiative transition rates, respectively. The solid curve is for the radial dipole, while the dashed curve is for the tangential dipole.

2. Transition rates for the two polarizations for an oscillator molecule in a vacuum cavity \((\epsilon_2 = 1)\) of radius \( r = 4000 \text{ Å} \) for \( \lambda = 4133 \text{ Å} \) and \( \epsilon_1 = 2.16 \). The molecule is located at \( d \) from the center. The solid curve is for the radial dipole while the dashed curve is for the tangential dipole.

3. Same as Fig. 2, except that \( \epsilon_1 = -4.42 + 0.73i \).

4. Transition rates for the two polarizations for an oscillator molecule inside a dielectric sphere of radius \( r = 4000 \text{ Å} \) for \( \lambda = 4133 \text{ Å} \) and \( \epsilon_2 = 2.16 \). The molecule is located at \( d \) from center. The solid curve is for the radial dipole while the dashed curve is for the tangential dipole.

5. Same as Fig. 4 except that \( \epsilon_2 = -4.42 + 0.73i \) and \( r = 1000 \text{ Å} \).
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