Dynamical Analysis of Molecular Decay at Spherical Surfaces
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Dynamical Analysis of Molecular Decay at Spherical Surfaces

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A dynamical approach to the classical decay rates for molecules near a dielectric sphere is presented through the application of the diffraction theory for a dipole antenna established by Van der Pol and Bremmer. This theory is somewhat simpler than but formally equivalent to that established by Ruppin and preserves a feature which is closer to the method of the theory established by Chance, Prock and Silbey for a flat surface. The results, when compared to those obtained from the static image theory, show that this latter theory can be very inaccurate for large molecule-sphere distances or highly-conducting spheres, consistent with previous findings for surfaces with perfect flatness or small roughness.
DYNAMICAL ANALYSIS OF MOLECULAR DECAY AT SPHERICAL SURFACES

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ABSTRACT

A dynamical approach to the classical decay rates for molecules near a dielectric sphere is presented through the application of the diffraction theory for a dipole antenna established by Van del Pol and Bremmer. This theory is somewhat simpler than but formally equivalent to that established by Ruppin and preserves a feature which is closer to the method of the theory established by Chance, Prock and Silbey for a flat surface. The results, when compared to those obtained from the static image theory, show that this latter theory can be very inaccurate for large molecule-sphere distances or highly-conducting spheres, consistent with previous findings for surfaces with perfect flatness or small roughness.
I. INTRODUCTION

The theoretical aspect of the problem of molecular lifetimes in the vicinity of a flat or rough dielectric (often metallic) surface has recently received considerable attention (see, for example, Refs. 1-3). It is known that for molecules a few Angstroms away from the surface so that the "quantum spreads" of both the surface electrons and molecule can be neglected, the classical phenomenological (CP) approach works adequately.\(^4\) Within the CP approach, there are the exact dynamical (energy transfer) theory (ET) and the approximate but simpler static image theory (IT). In spite of the fact that the exact theories (ET) have been available for some time now for both the cases of flat\(^1\) and spherical\(^5\) surfaces, the simpler theories (IT) have still been applied many times to cases of flat\(^6\), spherical\(^7\) and other kinds of rough\(^2,3\) surfaces. Justification has then been given based on the argument that provided the molecule-surface distance (d) is much shorter than the emission wavelength (\(\lambda\)), IT should be as accurate as ET.\(^1,7,8\) In a recent paper,\(^9\) however, we clarified (with reference to a flat surface) that the condition d \(\ll\) \(\lambda\) is not sufficient and that IT can be very inaccurate for highly-conducting substrates, even though such a condition is realized as in most experimental situations. In a subsequent paper,\(^10\) we also established a dynamical theory (ET) for rough surfaces. Moreover, the theory established in this latter paper is a perturbative theory which is restricted to be practical only for very shallow roughness.\(^10\)

There remains, therefore, the problem of a dynamical theory for molecules decay on a surface of large roughness. For this case, however, it has been found that a tractable model is obtained by replacing the rough surface by a collection of spheres (or spheroids) and allowing the radii of the spheres to be arbitrarily large. Usually, in this approach, the exact solution for an isolated sphere is worked out and then a cluster of neighboring spheres is considered to model the
actual surface. Nevertheless, in most of this previous work except that by Ruppin, IT has been applied with again the erroneous justification for conditions satisfying \( d \ll \lambda \).

In this paper, we shall reformulate the problem for the dynamical decay rates of an admolecule near a dielectric sphere in a different but simpler approach. Our main goal here is to compare the dynamical treatment with the static one (IT) and to point out that this latter theory can be very inaccurate for highly-conducting spheres in spite of \( d \ll \lambda \). Since the formal theory (in a different approach) has already been available, here we shall present the detail of only the simplest case, namely, a perpendicular dipole, for the sake of illustrating the points we have addressed above.

II. VAN DEL POL-BREMMER THEORY

In spite of the theory worked out by Ruppin who applied the dipole scattering theory of Kerker et al which is in turn based on the Lorenz-Mie theory, one always wonders whether such a problem can be formulated in a fashion which is closer to the original dynamical theory established by Chance, Prock and Silbey (CPS) for flat surfaces through the application of the Sommerfeld theory for radiating dipoles above a "flat earth". Indeed, some time after Sommerfeld published his work, Van del Pol and Bremmer had generalized Sommerfeld's problem to the case of a spherical earth and had shown that the Sommerfeld theory is recovered in the limit where the radius of the earth becomes infinitely large. To apply their theory to our problem, we recall that the Hertz vector for the region outside the sphere is given (in spherical coordinates) by
\[ \hat{n} = \pi(r, \theta) \hat{r} \]

\[ \hat{r} \frac{-ikR}{R} + \hat{r} i\mu k \sum_{n=0}^{\infty} (2n+1)R_n \frac{j_n(ka)}{h_n^{(1)}(ka)} h_n^{(1)}(kd) h_n^{(1)}(kr) P_n(\cos \theta) , \quad (1) \]

where we have assumed a molecular dipole \( \vec{\mu} \) located at \( (d_0, 0, 0) \) and oriented radially above a sphere of radius \( a \). \( k \) is the emission wave number, \( R \) is the distance measured from \( \vec{\mu} \), and \( j_n, h_n^{(1)} \) and \( P_n \) are the usual spherical Bessel functions and Legendre polynomials, respectively. The spherical reflectance \( R_n \) in Eq. (1) is given by \(^{16} \)

\[ R_n = \frac{(1+n)(1-\varepsilon) + cka[j_{n+1}(\varepsilon ka)/j_n(\varepsilon ka) - j_{n+1}(\sqrt{\varepsilon} ka)/\sqrt{\varepsilon} j_n(\sqrt{\varepsilon} ka)]}{(1+n)(\varepsilon-1) + cka[j_{n+1}(\sqrt{\varepsilon} ka)/\sqrt{\varepsilon} j_n(\sqrt{\varepsilon} ka) - h_{n+1}^{(1)}(ka)/h_n^{(1)}(ka)]} , \quad (2) \]

where \( \varepsilon(\omega) \) is the complex dielectric constant of the substrate sphere. By considering only the reflected field and using the expression for the radial electric field \(^{16} \)

\[ E_r(r, \theta) = (k^2 + \frac{\partial^2}{\partial r^2})(\frac{\varepsilon}{d} \cdot \text{n}) , \quad (3) \]

we obtain finally the reflected field at the dipole site in the form

\[ E_r(d, 0) = i\mu k \sum_{n=0}^{\infty} R_n \frac{j_n(ka)}{h_n^{(1)}(ka)} [h_n^{(1)}(kd)]^2 \frac{n(n+1)(2n+1)}{d^2} , \quad (4) \]
and the G-function in this dynamical theory as

\[ G_{ET}(\omega) = \frac{E_x(d,0)}{\mu} . \]

(5)

The total (i.e., both nonradiative and radiative transfer) molecular decay rate in the presence of the sphere is then given by\textsuperscript{1-3}

\[ \gamma_{ET} = \gamma_0 \left( 1 + \frac{3}{2} \frac{q}{k^3} \operatorname{Im} G_{ET} \right), \]

(6)

with \( \gamma_0 \) being the rate for a free molecule and \( q \) the quantum yield of the emitting state, respectively. The results obtained in Eqs. (4)-(6) are mathematically equivalent to those obtained by summing Eqs. (27) and (33) in Ruppin's paper, except that Eq. (4) here is derived and expressed in a somewhat simpler manner, since it does not contain any integrals involving the Bessel functions and there is only one complex reflectance coefficient appearing in the final expression. We have checked numerically that our results have reproduced identically the results in Fig. 1 of Ruppin's paper. For the case of parallel dipoles, the results can be obtained similarly by introducing two Hertz vectors\textsuperscript{17} and again, one expects somewhat simpler results obtained as compared to Ruppin's Eqs. (28) and (34). In the following, we shall compare Eqs. (4)-(6) with the static image theory and assess better the limiting case provided by this latter theory.

III. LIMIT OF THE IMAGE THEORY

It has been widely argued that for \( d \ll \lambda, E_x \) in Eq. (4) can be replaced by the static image field given by\textsuperscript{18}
\[ E_r^i(d,0) = \mu \sum_{n=1}^{\infty} \alpha_n(\omega) \frac{(n+1)^2}{d^{2(n+2)}} \]  

(7)

where the n-pole polarizability \( \alpha_n(\omega) \) is given by\(^{12} \)

\[ \alpha_n(\omega) = \frac{n(\varepsilon-1)}{n(\varepsilon+1) + 1} a^{2n+1} \]  

(8)

The G-function may then be defined accordingly \( (G_{IT} = E_r^i/\mu) \), and \( \gamma_{IT} \) will be just as in Eq. (6) with \( G_{ET} \) replaced by \( G_{IT} \). We have carried out numerical calculations for both the distance dependence and the frequency spectrum of both \( \text{Im} G_{ET} \) and \( \text{Im} G_{IT} \) for a sphere of radius \( a = 100 \) Å. Figure 1 shows the distance variation of \( \text{Im} G \) according to both \( ET \) and \( IT \) at \( \omega = 2.5\text{eV} \) \((\lambda \approx 5000 \) Å\) for both a silver and a nickel sphere.\(^{19} \) It is not difficult to see that under these conditions where \( d \) and \( a \) are much smaller than \( \lambda \), \( IT \) can be very inaccurate for a highly-conducting sphere such as Ag, though for the case of a Ni sphere, \( IT \) and \( ET \) are fairly close to each other for this range of distances. This is consistent with the previous observations for a flat\(^9 \) and a shallow grating\(^{10} \) surface, and the physical origin for such a phenomenon has been well explained in the previous papers.\(^9,10 \) Figure 2 shows the frequency spectrum of \( \text{Im} G \) for \( d = 500 \) Å for a Ag sphere, for which \( IT \) is expected to break down appreciably. Nevertheless, for the small region close to the surface plasmon resonance (\(-3.5 \) eV), the relative agreement between \( ET \) and \( IT \) is the best. This is in contrast to the previous comparison for the shallow grating case\(^{10} \) and may be due to the fact that for \( ka \ll 1 \), both \( ET \) and \( IT \) have a very similar resonance structure.\(^{20} \)
IV. CONCLUSION

In this paper, we have presented an alternative formulation of the dynamical decay rates of molecules near a spherical surface following an approach which differs from that of Ruppin\textsuperscript{5} and stays closer to the framework of the original CPS theory for a flat surface.\textsuperscript{1} In fact, it is straightforward to show that Eqs. (4)-(6) lead back to the results for a perpendicular dipole in the CPS theory by taking the limit $a \to \infty$, $d \to \infty$, but with the difference $d-a$ kept as a finite constant.\textsuperscript{16} Furthermore, in spite of the availability of the Van del Pol-Bremmer theory which takes the advantage of the concept of the Hertz vector,\textsuperscript{16} it is interesting to note that most of the previous dynamical theories\textsuperscript{5,13,20,21} for molecule-sphere interactions are based on the Lorenz-Mie theory\textsuperscript{14} whose mathematical structure is in general more complicated. In the light of the present investigation, it seems that an alternative approach to all these previous problems based on the Van del Pol-Bremmer theory is worthwhile because of its comparatively simpler structure, as illustrated by the sample calculation in this paper. In addition, due to the fact that the present approach is more of a scalar-type expansion (in contrast to the use of the vector harmonics in the other theories), one may find it easier to generalize the theory to the case of a cluster of spheres.

We have further compared this theory with the static theory and have shown once again\textsuperscript{9,10} that, in contrast to many previous expectations,\textsuperscript{7,8,11,12} the static theory can be very inaccurate for highly-conducting (e.g., Ag) spheres, in spite of the fact that $d \ll \lambda$. Hence, all the previous work on SERS, fluorescence and other resonant absorption processes\textsuperscript{7} which has utilized image fields in their formalisms becomes inaccurate subject to the present observations, and therefore must be reformulated by introducing a dynamical description for the decay rates of the admolecules.
ACKNOWLEDGMENTS

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REFERENCES

17. See the discussion in Chapter VI of Sommerfeld's book as quoted at the end of Ref. 15.
FIGURE CAPTIONS

1. Comparison between the energy transfer theory (ET, solid curves) and the image theory (IT, dotted curves) for a (a) Ag and (b) Ni sphere at $\omega = 2.5$ eV for a range of molecule-sphere distances. The unit of $G$ is $\text{Å}^{-3}$.

2. Comparison between ET and IT for the frequency spectrum $\text{Im}G(\omega)$ at $d = 500$ Å for a Ag sphere.
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