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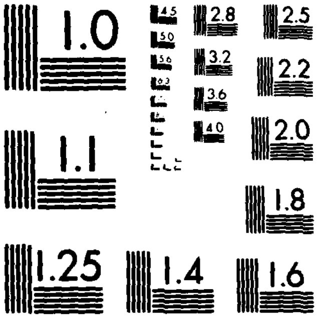

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A099606	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Image Field Effect: How Important Is It?		5. TYPE OF REPORT & PERIOD COVERED Technical Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) George C. Schatz		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0794
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Northwestern University Evanston, Illinois 60201		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE May 1981 13. NUMBER OF PAGES 16
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) LEVEL II		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

12 (6) (9) (10) (15) (11)

16. DISTRIBUTION STATEMENT (of this Report)

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

(12) 18

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DTIC
JUN 2 1981
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18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Surface Enhanced Raman Spectroscopy, SERS, Image Field Effect.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This paper reviews the current status of the image field effect model of Surface Enhanced Raman Spectroscopy (SERS), including the comparison between theoretical predications and experimental results, and attempts to improve the image model through the use of wavevector dependent dielectric constants, finite size dipoles and a continuous variation of the electron density at the interface.

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OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0794

TECHNICAL REPORT NO. 6

The Image Field Effect: How Important Is It?

by

George C. Schatz

Prepared for Publication

in

<u>Surface Enhanced Raman Scattering</u>

Edited by R. K. Chang and T. E. Furtak

Plenum, New York

1981

Northwestern University
Department of Chemistry
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May, 1981

THE IMAGE FIELD EFFECT: HOW IMPORTANT IS IT?

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INTRODUCTION

Shortly after the discovery of Surface Enhanced Raman Spectroscopy (SERS),[1] several mechanisms were proposed to explain the observed factor of 10^6 enhancement in Raman intensity seen for molecules adsorbed on Ag surfaces. (Reference 2 contains a review.) One of these mechanisms,[3,4] now known as the image field effect (IFE) mechanism, considered the interaction between the oscillating dipole moment induced in the adsorbed molecule and its image in the metal. Under the appropriate circumstances and assumptions, the interaction between adsorbed molecule and its image was found to be large enough to cause a substantial enhancement in Raman intensity, and from this it was concluded that the IFE might at least partially be responsible for the SERS enhancement. Since these first studies, a number of papers have appeared in which the various approximations and assumptions of the IFE model have been studied and tested.[5-15] At present, the conclusions of these studies are the subject of significant disagreement, and because of this, the IFE model has been both praised and condemned. In this paper I review these efforts to test the IFE model of SERS and I will summarize the current status of the comparison between IFE model predictions and experiment. With this review, I will attempt to assess just where the image model sits at this point in its application to SERS, and I will point out some approaches to the further testing of the validity of the IFE model.

Surface Enhanced Raman Spectroscopy is certainly not the first phenomenon where the application of image theory has been the subject of controversy. The current debate about the role of image effects in producing the coverage dependent frequency shifts observed in the infrared spectroscopy of CO on metals is very active.[17] Image and related theories have, however, been very successful in applications to a number of other surface phenomena, thus giving at least some support to their use in certain physical situations. The image theory of fluorescence lifetimes of molecules as a function of distance from metal surfaces is quite successful (with some improvements and modifications).[18] Recent spacer experiments indicate that the R^3 dependence of lifetime on molecule-surface separation remains valid at separations as small as 7Å.[19] Image models have also been used in theories of chemisorption[20] and adsorption induced work function changes[21] where more accurate density functional calculations indicate the usefulness of these models for distances as close as 2Å. Image theories have also seen application in studies of photoemission,[22] of electron and ion scattering from surfaces,[23] and other phemonena, often with quantitative results if carefully applied.

Of course the application of image theories to surface phenomena becomes increasingly suspect as the separation between molecule and surface becomes small. This is perhaps at the heart of the controversy with respect to the IFE interpretation of SERS. Density functional calculations[21] indicate that at small molecule-surface separations, the point charge image formula can be accurate provided that distances are measured relative to an appropriately defined image plane. The location of this plane relative to the "true surface" (usually taken as the positive background edge in jellium calculations) is roughly independent of molecule-surface separation for distances down to 2Å, but thereafter varies rapidly with distance.[20] The incorporation of an effective distance into image model calculations provides one method of accounting for the effects of screening and the absence of a sharp discontinuity in the electron density at the surface.

Still another complication in the use of image models at short range is the problem of finite molecular size. For adsorbed atoms or symmetrical molecules, it is common to locate the point charge or dipole representing the atom or molecule at its center of symmetry.[3,21] Other prescriptions have been used,[22] but only a few studies have attempted to model finite size effects through the use of distributions of charges.[24]

For studies of frequency dependent properties such as Raman intensities, an additional difficulty in the use of image models concerns the proper modelling of the metal dielectric response in determining the magnitude of image charges and dipoles. Most of the simple image models use bulk metal optical dielectric constants to model this frequency dependence. This ignores the fact that the surface dielectric constants differ from bulk constants, and that they exhibit independent frequency and wavevector dependence. Only very recently have studies of the wavevector dependence of image models been made,[10,12,13] but these show that such effects are quite important.

Still another problem with the use of image models at short molecule-surface distances arises from chemisorption effects. Since the image model treats the Coulomb interactions between the adsorbed molecule and surface, it is important that the molecular charge distribution is not strongly altered by adsorption, otherwise the "bare" molecule properties will not be representative of admolecule interactions. To date the only studies of chemisorption effects are the density functional calculations mentioned above,[21] and most of these refer to H atom adsorption (where the bare molecule is assumed to be a proton).

In spite of these numerous problems associated with image model applications to molecules close to metal surfaces, the simplest point dipole IFE Model of SERS has been surprisingly successful as a phenomenological theory. The current status of comparisons between IFE predictions and experiment will be reviewed in Section II, and there we will find that such features of SERS intensities as their dependence on frequency, on metal, and on adsorbate are properly described qualitatively by the IFE model. Indeed, several of the IFE model predictions concerning the magnitude of enhancements on Cu, Au and Hg were made well in advance of observations on these metals, and were at least partially responsible for motivating the observations. Thus, in discussing the IFE Model we are faced by an apparent contradiction in that the model's predictions are qualitatively correct, yet the assumptions underlying the model are suspect and certainly cannot be *quantitative*.

As mentioned previously, there have now been several papers published in which certain of the approximations of the simple IFE model have been tested. These studies, which will be reviewed in Section III, include for the wavevector dependent dielectric response of the metal,[8-10,12-13] for the smooth variation of the electron density across the interface[8-10,12] and for finite molecular size.[11,16] It should be emphasized that none of these calculations represents a quantitative microscopic treatment of the complete SERS problem, but they do provide insight concerning the importance of certain assumptions made in the IFE model. In the conclusion (Section IV) will be described some very recent ab initio calculations which apparently do contain the necessary elements of a truly microscopic theory of SERS.

CURRENT STATUS OF PREDICTIONS OF THE SIMPLE POINT DIPOLE IFE MODEL

The point dipole IFE model was first introduced by King, et al.,[13,15] and has been greatly expanded upon by Metiu and coworkers.[4-6] A closely related model has also been presented by Easley and Smith[7] and a less closely related model by Morawitz and Koehler.[14] In all of these studies, a point dipole is used to represent the oscillating dipole moment induced by the applied electromagnetic field in the molecule. In calculating the image field associated with this induced dipole, all difficulties associated with dispersion and chemisorption described above are neglected. The overall expression for the SERS enhancement factor ε arising from this model is given by[15]

$$\varepsilon = G \left| 1 - \frac{\gamma\alpha_o}{4R^3} \right|^{-4} \qquad (1)$$

where

$$\gamma = (\varepsilon_M - \varepsilon_A) / (\varepsilon_M + \varepsilon_A) \varepsilon_A \, . \qquad (2)$$

In this expression, ε_M is the metal dielectric constant, ε_A the adsorbate dielectric constant, α_o the unperturbed molecular polarizability (the component associated with the axis perpendicular to the surface) and R is the molecule to image plane separation. G is a geometrical factor which has been discussed previously for the case of smooth surfaces[4-6,15] where its value is roughly 10. For scattering from rough surfaces G incorporates the effect of roughness induced surface electromagnetic field enhancements and its value is correspondingly larger.

Recently, the electrodynamics of random distributions of hemispheroidal metal bosses on flat perfectly conducting metal surfaces has been studied for several metals.[25] These distributions were chosen to simulate the types of rough surfaces that are prepared by anodization in electrochemical cells. For Ag and other strong SERS enhancing metals (Cu, Au, Hg), maximum roughness induced enhancements of 10^2 were found, along with relatively flat dependences of enhancement on excitation frequency below the flat surface plasmon frequency. This estimate of roughness induced enhancement is in good agreement with recent experimental estimates for electrochemical systems.[26] Combining the factor of 10^2 with the factor of 10 which arises from flat surface contributions to local field en-hancements[15] leads to an estimate of $G = 10^3$ for SERS scattering from rough Ag surfaces.

The factor $| 1- \gamma\alpha_o/4R^3 |^{-4}$ in Eq.(1) arises from image field induced enhancement of the molecular polarizability derivative. The parameters γ and α_o are not difficult to estimate in evaluating this enhancement for any given system, but the choice of R is not at all straightforward. This is because neither the location of the image plane relative to the surface nor the position of the point dipole which represents the ad-molecule is well defined. While previous estimates do indicate that "reasonable" prescriptions for choosing R lead to large image enhancements, it is also true that $| 1- \gamma\alpha_o/4R^3 |^{-4}$ varies rapidly with R for small molecule-surface separations. This makes any simple prescription which happens to give large enhance-ments suspect. To circumvent this problem, R can be chosen by requiring ε to have approximately the correct value for some metal (such as Ag) at some frequency (say 500nm). In addition, it is desirable to pre-average the factor $\left| 1-\gamma\alpha_0/4R^3 \right|^{-4}$ over a Gaussian distribution of R's with standard deviation σ (typically 0.1Å) to simulate the possibility of a distribution of distances from the surface. Thus if G = 10 (for smooth Ag surfaces), R is chosen so that $\left| 1-\gamma\alpha_0/4R^3 \right|^{-4}$ averages to 10^5 at 500nm in order to make $\varepsilon = 10^6$.

While it is clear that the assumptions used to evaluate Eq.(1) are somewhat ad hoc, it is interesting to see what predictions come from this phenomenological model for different metals and frequencies. Fig.1 summarizes the results for pyridine adsorbed on Ag, Au, Cu, Hg and Li using pyridine polarizabilities discussed previously,[15] and literature values of the metal dielectric constants.[27-29] This graph

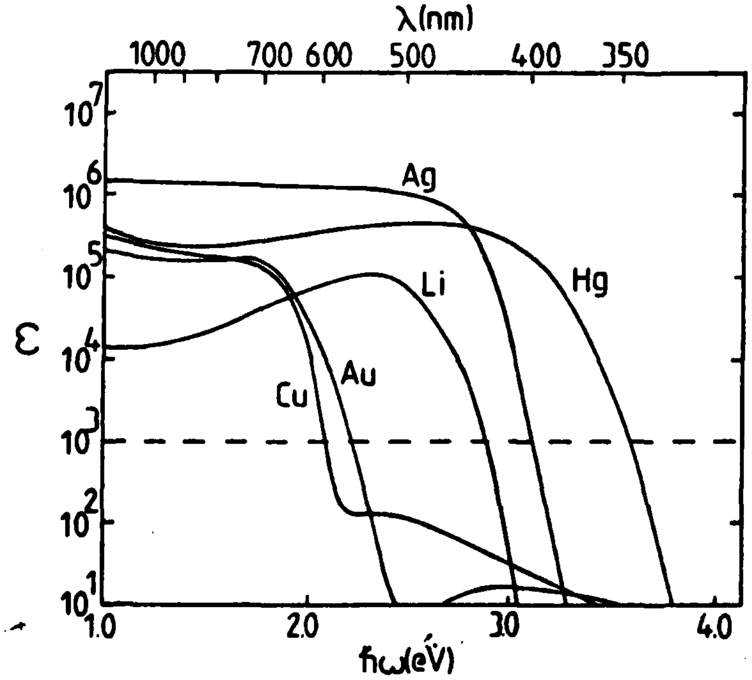

Figure 1. Smooth surface IFE-SERS enhancement factor ε versus photon energy $\hbar\omega$ (in eV) and wavelength λ (in nm) for Ag, Hg, Li, Cu and Au. The parameters in this calculation apply to adsorbed pyridine and are taken from Ref.15 with the exception of R. R is chosen to make $\varepsilon = 10^6$ at 500nm for Ag, and is shifted in value for other metals as discussed in the text. The dashed line at $\varepsilon = 10^3$ indicates the approximate value of ε required for experimental observation to be possible in electrochemical systems.

incorporates the smooth surface enhancement factor of Ref.15 in determining G, and uses an R value for Ag of 1.55Å. For metals other than Ag, a small shift in R is made in order to describe shifts in image plane location with changing metal properties (screening and surface electron density profiles). Using shifts obtained from jellium calculations,[20] the R values are 1.51 for Cu, 1.55 for Au, 1.51 for Hg and 1.58Å for Li.

Fig.2 compares the IFE results from Fig.1 with experimental ε values for Ag from Refs.26 and 30, Cu from Ref.26 and Au from Refs.31 and 32. The two experimental reports of enhancements for

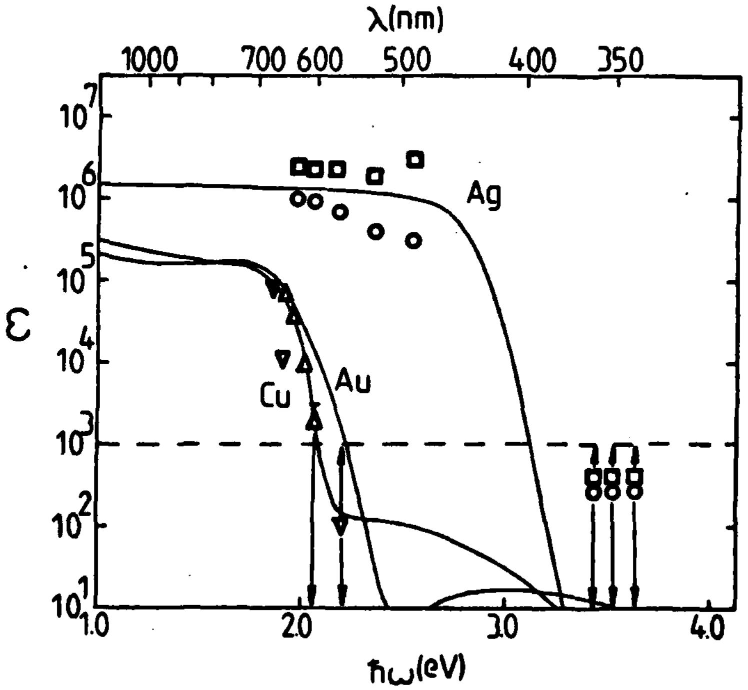

Figure 2: IFE and experimental SERS enhancement factor for pyridine adsorbed on Ag, Au, Cu. The IFE curves are identical to those plotted in Fig.1. The experimental results are from Ref.26 and 30 for Ag (the ε's for Raman enhancements at 1008 (circles) and 1215 cm^{-1} (squares) are plotted), Ref.26 for Cu (1015 cm^{-1} is plotted (triangles Δ)) and Refs.31 and 32 for Au (1015 cm^{-1} is plotted, with open triangles ∇ for Ref.31 and filled triangles ▼ for Ref. 32). All measured ε values at or below 10^3 are upper bounds due to instrument limitations.

Hg[32,33] are not very quantitative, but they appear to indicate that ε is roughly $10^4 - 10^6$ at 515nm. Neither the frequency dependence of ε on Hg, nor the experimental enhancements on Li has been reported.

Comparison of the simple point dipole IFE model results with experiment in Figs.1 and 2 indicates the following:

1. Both IFE and experimental enhancements on Ag are relatively flat up to $\hbar\omega = 2.6$ eV, then drop to below detection threshold ($\varepsilon = 10^3$) at higher ω.

2. Enhancements on Cu and Au are large below $\hbar\omega = 2$ eV, and drop off at higher ω. The experimental and theoretical enhancements for Cu and Au at 1.9 eV are quite similiar in magnitude, with values lower than the analogous Ag enhancements by factors of 10-100.

3. The IFE enhancements on Hg are quite large throughout the visible though not as large as on Ag except in the near UV. IFE enhancements on Li are one to two orders of magnitude smaller than on Ag.

It is especially noteworthy that the IFE enhancements for Au and Cu drop suddenly by over two orders of magnitude near 2 eV. This indicates a strong sensitivity to metal dielectric properties which is in good agreement with experiment. Although the rough surface electrodynamic models[25] also predict a drop in enhancement near 2 eV, the magnitude of the predicted drop is over an order of magnitude smaller than is seen experimentally.

The overall agreement between theory and experiment in Fig.2 amazingly good in view of the crudeness of the theory and the fact that the one adjustable parameter R is fixed for only one metal at one frequency. For this reason, the IFE model has been useful as a predictive tool in guiding experiments on new metals. (Indeed, curves similar to those in Figs.1 and 2 were originally calculated well before experiments on Cu, Au, and Hg were first done.) At the same time, the calculations described in the next section indicate that more sophisticated image models often give poorer agreement between theory and experiment for many properties.

The simple IFE model can also be used to predict other optical properties (depolarization ratios, second harmonic generation enhancements, etc.) some of which have been discussed previously in Ref.15. Because the IFE and roughness enhancement mechanisms work in parallel, many properties seem to reflect that mechanism which has the most rapidly varying dependence on measurable parameters. For example, the angular dependence of scattering on weakly roughened surfaces is dominated by the geometrically defined conditions which optimize surface plasmon excitation.[34] Since the IFE mechanism shows a weak variation of scattered intensity with incident or outgoing angle,[15] measurements of angular distributions are primarily sensitive to the enhancement which arises from surface plasmon excitation. Related statements can be made concerning depolarization ratios, relative mode intensities and other geometrically based information. In addition, both the roughness and IFE mechanisms predict enhancements in second harmonic generation (SHG) cross sections. Existing SHG experiments[35] have demonstrated the importance of the roughness mechanism, but estimates of adsorbate induced smooth surface SHG enhancements have not yet been made.

From the above comments, it is clear that the process of differentiating the contributions of different enhancement mechanisms to SERS will be difficult without more quantitative intensity calculations. This makes the improved IFE models to be discussed below especially important.

REVIEW OF MORE SOPHISTICATED IFE MODELS

Table I summarizes those studies of SERS which have used or tested the image field model. Refs.3-8 and 14-15 can all be categorized as *simple point dipole models* in which the wavevector dependence of the dielectric constant has been ignored and a sharp surface boundary is assumed. The remaining papers[9-13,16] represent attempts at removing one or more of these assumptions, as will now be described.

Table 1. Summary of Image Model Calculations

Reference	Point Dipole Approximation?	Include Wavevector Dependence of Dielectric Constants?	Include for Continuous Variation of Electron Density?	Estimated SERS Enhancement (Ag, R~1.6Å)
3-8, 14-15	Yes	No	No	10^3-10^6
11	No	No[a]	No[a]	~1
13	Yes	Yes	No	10^3
16	No	Yes	No	10^3
9, 10	Yes	Yes	Yes	~10^4
12	Yes	Yes	Yes	~1

[a] Perfect mirror approximation used.

The study of Hilton and Oxtoby[11] determined the static polarizability of a hydrogen atom which is next to a flat perfect metal surface. In this model, the image of the hydrogen atom is simply an antihydrogen atom, and the wavefunction describing this system of hydrogen-antihydrogen is determined by a Hartree SCF procedure. This model thus relaxes the point dipole approximation, though it oversimplifies the metal response, and ignores any chemical bonding effects. The calculated polarizability as a function of the proton-antiproton separation distance d ($d=2R$) shows very little change from the infinite separation distance result for d as small as 1Å. This is followed by a rapid increase with decreasing d for $d < 1$Å. The analogous image model polarizability exhibits a similar dependence of polarizability on d, but the rapid increase begins at $d =$ 1.6Å. Hilton and Oxtoby used their calculated total energies to estimate that the minimum allowed d at room temperature was 2.4Å. This rather large value is a consequence of the neglect of chemisorption, since this causes the hydrogen-antihydrogen interaction to be repulsive at longer distances than would normally be the case. Since the polarizability enhancement was negligible at 2.4Å, they concluded that the IFE mechanism is not important in SERS. An analogous calculation of image induced infrared frequency shifts by Palke[36] lead to a similar conclusion concerning the importance of image effects, though with some reservations because of difficulties with overlap between molecular and image charge clouds.

Perhaps the two main problems with Hilton and Oxtoby's conclusion concerning SERS are: (1) that their calculation actually refers to the static polarizability, and not to the frequency dependent polarizability derivative which is relevant to Raman scattering, and (2) that because of omission of chemisorption, the 2.4Å distance d at which they located their H atom is much larger than that which characterizes true H atom adsorption on metals. An illustration of the importance of the first problem is found in the recent ab initio calculations of frequency dependent polarizability derivatives for H_2 adsorbed onto Li clusters by Pandey and Schatz[37] (to be described in Section IV). They find that the frequency dependent polarizability derivative enhancements at optical frequencies can be quite large (several orders of magnitude) even when the static polarizability enhancements are close to unity. To understand the significance of the second problem, it is important to realize that molecule to surface distances are not constrained to be larger than the cube root of the molecular polarizability. As an example, consider the case of atomic iodine adsorbed onto Ag in UHV. The SERS spectrum of this has recently been observed, with the AgI stretch mode clearly resolved[38] in submonolayer converages. This system has also been studied by SEXAFS[39] and the AgI bond distance is found to be 2.87Å, corresponding to a distance to the surface of 0.92Å. This distance is certainly smaller than the cube root of the iodine static polarizability, and is much smaller than the cube root of the frequency dependent polarizability in the visible region (where I has resonant transitions). All of this indicates that $\alpha_o/4R^3$ can be unity or greater for I on Ag, and thus one cannot rule out the importance of image effects on geometrical grounds alone for this and many other systems.

Perhaps the more useful conclusion to be drawn from Hilton and Oxtoby's calculation is that the calculated dependence of polarizability on d is qualitatively similar though quantitatively different from that obtained from the simple image model. This is presumably one manifestation of finite molecular size effects, and illustrates a major difficulty in choosing appropriate values of d (or R) in image theory applications.

A rather different approach to improving the image model has been used by Weber and Ford.[13,16] Using the Kliewer-Fuchs model of metal dielectric response,[40] they have studied the influence of spatial dispersion (wavevector dependent dielectric constants) on the IFE mechanism. Their first paper[13] used the point dipole approximation, and found that spatial dispersion reduced the maximum image enhancement by about 10^2 (down to roughly 10^6 if no average over R is included). The dependence of ε on R remains as strong as for the simple image model, however. In a more recent paper,[16] Weber and Ford have included for the effects of finite molecular size in their model by replacing the molecule by a sphere of finite radius. By using multipole polarizabilities to describe the response of the adsorbed molecule to the image field (also including for spatial dispersion), Weber and Ford find that the maximum Raman enhancement is reduced by 10^3 from the point dipole result to an overall value of $\varepsilon = 10^3$. Combining this with a factor of 10^3 which they estimate as due to roughness effects[13] (see also Ref.41), gives an overall enhancement factor of 10^6. While this result agrees with the estimates we presented in Section II, the Weber-Ford model still contains several approximations which require further study before these conclusions can be considered reliable. These include: (1) the use of a free electron model to describe the metal dielectric response, (2) assumption of a sharp boundary at the metal interface and for the sphere which describes the molecule, (3) omission of chemisorption effects.

A closely related series of papers by Korzeniewski, Maniv, and Metiu[9,10] and by Feibelman[12] have recently tackled the very difficult problem of incorporating the continuous variation of electron density across the interface into the SERS enhancement factor calculations. These papers also include for the wavevector dependent dielectric response, but to date all numerical evaluations have treated the adsorbed molecule as a point dipole. The Korzeniewski et al. and Feibelman models are physically identical, but each group has focused attention on somewhat different pieces of information. Particularly, Feibelman has determined the asymptotic corrections to the classical image dipole enhancement factor while Korzeniewski et al. have directly evaluated the short distance image field enhancement. In these models, the response of the metal electrons to the oscillating induced molecular dipole is treated using linear response theory, with a polarization propagator which is obtained for an infinite barrier jellium model using the random phase approximation (RPA).

Using a radius parameter $r_s = 5.0$, Korzeniewski et al.[9] found that at R ~ 1.6Å the polarizability derivative enhancement factor was reduced by roughly 10^2 in their model compared to the simple image model result. They attributed the origin of this reduction as due to screening, and if so then their reduction factor is consistent with that of Weber and Ford.[13] It was also found that the position averaged enhancement factor exhibited a more resonant frequency dependence than is exhibited in Fig.1 for the simple image model.

Feibelman[12] analyzed his results in terms of the leading asymptotic correction to the image plane location. This is analogous to the corrections found by Lang and Kohn for the static image model,[20] but generalizes these to the frequency dependent case. An important feature of this generalization is that the image plane location (and hence R in Eq.(1)) is complex. This causes a reduction in the maximum image enhancement which is inversely proportional to the imaginary part of R. Estimates of this reduction for $r_s = 2$ jellium lead Feibelman to conclude that the image enhancement was quite small, perhaps on the order of unity. Just why this enhancement factor is so much smaller than that estimated by Korzeniewski et al. for the same model is not entirely clear at this time. The Korzeniewski calculation did find that the imaginary part of the image field was substantially larger than in the simple image model, but the influence of this on image enhancement was not as large as was concluded by Feibelman. Somewhat different r_s parameters were used in the respective calculations though both groups argued that this was not important. It is also possible that the asymptotic corrections of Feibelman underestimated the magnitude of image fields at the small distances considered by Korzeniewski et al.

Although the calculations of Korzeniewski et al. and of Feibelman provide a significant improvement in the sophistication of admolecule electrodynamics, they are still far from being truly realistic for several reasons. The use of a point dipole is an obvious approximation, as is the use of a jellium model to describe the metal response. To remove either of these limitations without simultaneously including for chemisorption effects can lead to inconsistencies (such as the problem of overlapping charge clouds described earlier), but to incorporate chemisorption into this treatment seems extremely difficult at present.

CONCLUSION

We can succinctly summarize the current status of the image field effect mechanism of SERS by the following four statements:

1. The simple point dipole phenomenological image model (whose enhancement factor is given by Eq.(1) and which is plotted in Figs.1 and 2 for several metals) shows remarkably good correspondence with experiment.

2. The attempts to improve this model discussed in Section III all conclude that the simple image model is quantitatively and perhaps even qualitatively inaccurate, and that the correct IFE enhancements should be several orders of magnitude lower than is predicted by the simple models.

3. There is currently substantial disagreement concerning how large the image effect is for real admolecule-metal systems. Estimates of the enhancement vary from 1 to 10^4.

4. None of the models in Table 1 have relaxed all of the approximations indicated in the Table simultaneously. Even if they did, they would still be unrealistic unless chemisorption effects are also included, and unless both the molecule and metal electronic properties are described accurately.

All of this indicates that the current status of the IFE mechanism is uncertain, and that it may remain so unless a truly microscopic description of SERS is obtained. Fortunately it appears that such a description may soon be available. Recently, Pandey and Schatz[37] have calculated ab initio time dependent Hartree-Fock frequency dependent polarizability derivatives for H_2 adsorbed onto Li clusters. Considering the H_2Li_2 system, they found that for frequencies close to the lowest excitation frequency of Li_2 and at geometries close to equilibrium, the polarizability derivative with respect to H_2 stretch was enhanced by 10-10^2 compared to that in isolated H_2. This corresponds to a Raman enhancement of 10^2-10^4 not including local field effects. This enhancement factor was found to be a strong function of the molecule-metal distance, dropping to a small value at just a few Å separation. Although the precise magnitude of this enhancement factor depends somewhat on how the widths of the resonant metal states are modelled, this calculation does indicate that strong enhancements are obtained from truly microscopic calculations. A major advantage of this approach is that all of the problems associated with finite molecular size, choice of molecule to metal separation, proper metal dielectric response and chemisorption are simultaneously taken care of in the Hartree-Fock description.

What is not clear at this point is what is the coupling responsible for the enhancement effect. It should be possible to disentangle the calculation, however, to assess how much of this enhancement is due to image effects, and how much to chemical effects. Presumably, at that point a fairly concrete assessment of the IFE mechanism will (at last!) be possible.

ACKNOWLEDGEMENTS

Helpful discussions with U. Laor, P.K.K. Pandey and R.P. Van Duyne are gratefully acknowledged. This research was supported by the Office of Naval Research (Contract N00014-79-C-0794).

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