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Molecular polarization bridging physical and chemical enhancements in surface enhanced Raman scattering†

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We present a practical method which demonstrates how the physical and chemical enhancements in SERS for a molecule adsorbed on metal junctions are conceptually coupled through the polarization of the molecule and its surroundings. Calculations with the state-of-the-art density functional reveal that the coupling factor considered in the present work can be as large as 10^6, such that it is indeed important for certain vibrational modes.

Surface-enhanced Raman scattering (SERS) is a powerful diagnostic technique that has been widely applied to various fields.[1–4] It takes advantages of two enhancing mechanisms, allowing significant amplication of the Raman signals of molecules. The first one is the so-called physical enhancement (G^{Phys}), originated from plasmonic excitation of the metal surface induced by the external electromagnetic field.[3,5,6] This is the driving force behind the observed SERS effects. In comparison with the free molecule, chemical bonding and light-induced charge transfer between the adsorbed molecule and the substrate can also lead to certain enhancement, which is the origin of the so-called chemical enhancement (G^{Chem}).[7–9]

These two enhancements are usually considered separately for simplicity,[6,8] whereas recent experimental studies revealed that the plasmonic excitation can be significantly affected by the adsorbed molecules,[10] hence they have to be considered as a whole. Attempts have already been made to simultaneously calculate these two enhancement factors. For instance, by using the density matrix formalism, Xu and co-workers recently developed a unified theory of fluorescence and Raman scattering processes near metal surfaces.[11,12] They found that the response behaviors of the molecules can be changed by the physical enhancement.[11,12] On the other hand, simulations of Persson *et al.* showed that the vibrational motion of the adsorbed molecules could modulate the substrate polarizability,[13] resulting in the change of the plasmonic field. Hence, physical and chemical enhancements are indeed inter-correlated. At the moment, it is, however, not very obvious how to extend their model systems, for example, based on two electronic levels,[11,12] to more realistic molecular systems, for which sophisticated electronic structure theory needs to be applied.

Jensen and co-workers have investigated the SERS mechanism by employing time dependent density functional theory for molecules on metal clusters.[7,14] They took the plasmonic incident electromagnetic filed as a constant with no feedback of the molecular polarizabilities. Along this line, Lombardi and Birke proposed a unified model that can treat normal Raman and SERS on the equal footing through the parameterizations of the chemical interactions between molecules and the substrates.[9] The first application of the electronic structure theory for simulating SERS of realistic molecular systems surrounded by metal particles would be that of Corni and Tomasi,[15] where the effects of metal surrounding on the Raman spectra of molecules have been taken into account. Although only physisorption was considered, the actual connection between the physical and chemical enhancements is already hidden in the simulated results. Hence their proposed approach provides a good platform for further development.

Let F^{P} be the field from the surface plasmon, which is induced by the electromagnetic filed (F^{0}) from the incident light of frequency ω, the physical enhancement is then generally defined as $G_0^{\mathrm{Phys}} = |F^{\mathrm{P}}/F^{0}|^2$. However, according to the classical theory of dielectrics, it is well known that the actual electric field, F^{i}, acting on the adsorbed molecule shall be expressed as:[16,17]

$$F^{\mathrm{i}}(r,\omega) = F^{\mathrm{P}}(r,\omega) + F^{\mathrm{R}}(r,\omega), \qquad (1)$$

where F^{R} is the reaction field generated by the polarization of the molecule. It is then clear that, from the viewpoint of the molecule, the physical enhancement G^{Phys} should be obtained from the ratio $|F^{\mathrm{i}}/F^{0}|^2$ instead of G_0^{Phys}. Therefore, there is an extra factor, $G_{\mathrm{Coup}}^{\mathrm{Phys}} = |F^{\mathrm{i}}/F^{\mathrm{P}}|^2$, that couples the electromagnetic field and the molecule. Simplification of $G_{\mathrm{Coup}}^{\mathrm{Phys}}$ to be unity is not always a valid assumption, if the plasmonic excitation is significantly affected due to the excistence of the adsorbed molecules.[7,13]

It is well known that the Raman scattering factor S is calculated *via* the gradient of the polarizability with respect to the normal mode Q of interest, which is defined as:[18,19]

$$S \leftarrow \frac{\partial \alpha_{\mathrm{ab}}}{\partial Q} = \frac{\partial^3 E(\mathrm{tot})}{\partial F_{\mathrm{a}} \partial F_{\mathrm{b}} \partial Q}, \qquad (2)$$

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where $E(\text{tot})$ is the total energy of the whole system. Hence the chemical enhancement fact is defined as $G^{\text{Chem}} = S^{\text{i}}/S^{0}$, where the superscripts i and 0 stand for the situations where the molecule is interacting with the substrate and it is a free molecule, respectively. A cluster made of a few metals is a convenient model for the substrate and has been widely used.[14,20] Such a local approximation is more appropriate to treat the short range chemical bond interaction, the long range effect of the substrate is actually missing. Assuming the calculated chemical enhancement fact with such a local cluster model is $G_0^{\text{Chem}} = S^{\text{Loc}}/S^{0}$, it has to be corrected by an extra factor $G_{\text{Coup}}^{\text{Chem}} = S^{\text{i}}/S^{\text{Loc}}$ to take into account the long rang effect of the substrate properly.

The total enhancement factor G is formally defined by G^{Phys} multiplied by G^{Chem}. It is, however, commonly approximated by $G_0 = G_0^{\text{Phys}}{\cdot}G_0^{\text{Chem}}$ for simplicity:

$$G(r, \omega) = G_0(r, \omega)G_{\text{Coup}}(r, \omega) \approx G_0(r, \omega). \qquad (3)$$

We argue here that the coupling factor $G_{\text{Coup}} = G_{\text{Coup}}^{\text{Chem}}{\cdot}G_{\text{Coup}}^{\text{Phys}}$ can be as large as 10^6 in some specific conditions, and therefore has to be taken into account properly.

The calculation of the coupling factor is not a trivial task since it strongly depends on the dielectric structure around the molecule, the specific bonding between the molecule and the metal surface. However, to demonstrate the importance of this extra coupling factor, we have adopted a simple Onsager model[16] to take into account the long range effects of the environment, whose relevance to the real experimental conditions is clearly illustrated in Fig. 1. The hot spot can be simplified as a molecule sitting in an elliptic/spherical cavity whose size is controlled by the distance between two nanoparticles.[21,22] Since SERS enhancements are highly localized,[22–25] we only considered the molecule in the hot spot. Here the polarizability of the adsorbed molecule with and without considering the reaction field are related by eqn (4):[16,26]

$$\alpha^{\text{i}} = (I - f^{\text{R}}\alpha^{\text{Loc}})^{-1}\alpha^{\text{Loc}}, \qquad (4)$$

where f^{R} denotes the reaction field factor matrix in the Onsager model.[16] The corresponding relationship between F^{i} and F^{P} is given by eqn (5):[16,26]

$$F^{\text{i}} = (I - f^{\text{R}}\alpha^{\text{i}})^{-1}F^{\text{P}}. \qquad (5)$$

Therefore, with the help of the reaction field theory, the physical and chemical enhancements are correlated by molecular polarizability (see ESI† for more details).

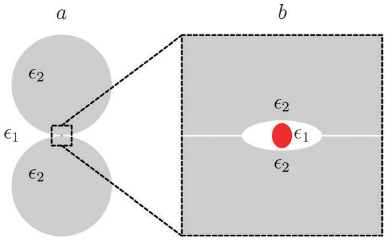

Fig. 1 A schematic model for a molecule (shown in red) in the normal surface-enhanced Raman scattering conditions. (a) A 'hot-spot' in SERS. (b) An Onsager model. ε_1 and ε_2 are dielectric constants corresponding to the solution and the metal substrates, respectively.

There are some earlier SERS models based on the reaction field theory, with which our present model shares some common concepts.[17,27–30] However, these earlier models focused on the effects of a non-local metal dielectric constant on SERS and the molecules were generally simplified as polarizable dipoles. Our present model, on the other hand, can be conveniently combined with modern electronic theory for practical calculations. Here we report the calculated results for two molecules, benzene and pyridine, which represent typical adsorbates for physi- and chemisorption on gold, silver and copper surfaces (see ESI† for more computational details).

Fig. 2 plots the calculated Raman spectra with different models. The last column displays the spectra for a typical physisorption case, benzene adsorbed on gold. As is expected, there is little spectral feature's change from free (shown in black) to adsorbed molecules (shown in blue and red). Generally, bare molecule/metal cluster models give spectral features (blue) that compare well with those (red) from the embedded molecule/metal cluster models with the reaction field. This demonstrates the usefulness of the conventional cluster model calculations.[14,20] The pyridine/Ag system (the second column) presents a typical case where the reaction field plays an important role. Not only the peak features around 1000 cm^{-1} change as the red lines are compared with those in blue, but also the relative intensity for peak around 1200 cm^{-1} is dramatically decreased. Indeed, after considering the effects of the reaction field, the calculated spectra are in better agreement with experimental observations.[20,31]

Calculations have clearly shown that different vibration modes can have quite different coupling factors. We have here selected the strongest Raman modes of pyridine (ν_1) and benzene (ν_{12}), respectively,[32] to discuss the general behavior and the order of magnitudes of the coupling factors. They are both breathing modes involving six membered rings. Logarithmic representations of G_{Coup} as functions of the excitation energy of the light and the distance between two nanoparticles for

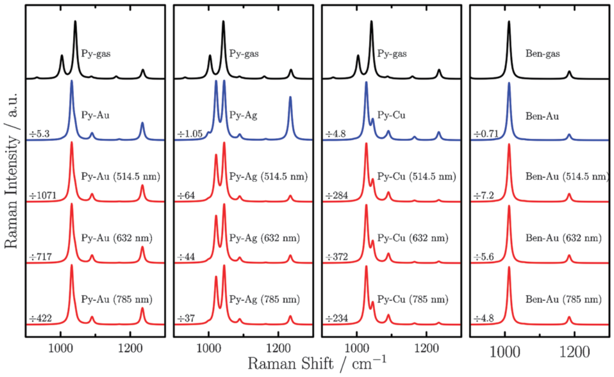

Fig. 2 Calculated Raman scattering factors of pyridine/benzene in vacuum using α^0 (black line), pyridine/benzene metal complex systems in vacuum using α^{Loc} (blue line), and pyridine/benzene metal complex systems in reaction field using α^i (red lines). Diameters in the Onsager model were set to be 6 Å. Three excitation light wavelengths, *i.e.* 514.5, 632, and 785 nm, typically used in experiments, were used here in calculating the chemical enhancement factors. These numbers were labelled along with the spectra as the scaling factors with respect to the corresponding gas phase numbers.

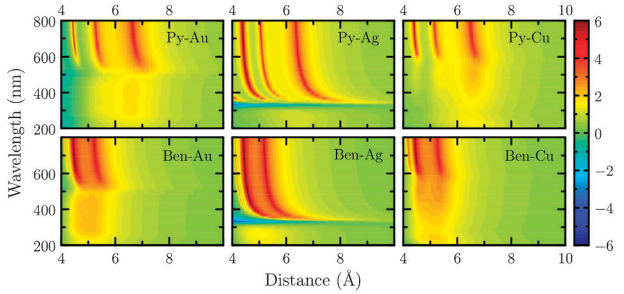

Fig. 3 Logarithm G_{Coup} of ring breathing mode for pyridine (top) and benzene (bottom) adsorbed on gold, silver, and copper substrates from left to right. Excitation wavelength from 200 to 800 nm and distance between two nanoparticles from 4 to 10 Å are considered.

pyridine and benzene adsorbed on gold, silver, and copper are given in Fig. 3, in which the excitation energy from ultraviolet to visible (200 to 800 nm) and the distance from 0.4 to 1 nm are included. The separate $G_{\mathrm{Coup}}^{\mathrm{Phys}}$ and $G_{\mathrm{Coup}}^{\mathrm{Chem}}$ contributions can be found in ESI.†

It is noted that for very large distance between nanoparticles G_{Coup} approaches unity, *i.e.* the coupling between physical and chemical enhancements does not play a role. For the systems under investigation, it can be seen that the coupling factor G_{Coup} can be as large as 10^6, which is comparable with the physical enhancement that has been obtained for many systems from conventional finite-difference time-domain (FDTD) calculations. It might explain why the actual measurements would often result in a much larger enhancement factor than what the physical enhancement alone could provide.[3] However, as shown in Fig. 3 the coupling factor is very sensitive to the excitation energy and the distance between the nanoparticles. For benzene on metal surfaces, the coupling factor has large values in the distance range of 0.4 to 0.6 nm with two maxima at two different distances. Similar situations can be found for pyridine on three metal surfaces. It is noted that for different metal surfaces, the "cut-off" of the excitation energy is also quite different. For gold, the coupling factor is drastically reduced when the wavelength of the light is shorter than 550 nm, and this value becomes 350 nm for silver. This should be attributed to the interband transition of metal.[33] For benzene on copper, the coupling factor shows much less dependence on the excitation energy. One can notice that when the excitation energy falls into the ultraviolet region, the coupling factor can be even less than 1 with silver substrates. This seems to confirm the early observations that in the ultraviolet region silver is not a good choice for SERS[34] although Raman intensity is proportional to the fourth power of scattering wave number.

To conclude, we have demonstrated how the physical and chemical enhancements in SERS for a molecule adsorbed on metal junctions are conceptually coupled through the polarization of the molecule and its surroundings. Calculations with the state-of-the-art density functional have revealed that the coupling factor considered in the present work can be as large as 10^6. Such a factor is sensitive to the excitation energy, the structure of molecular surrounding and the property of the metal surface. The present work shows examples for a non-resonant situation. By calculating polarizabilities under different incident light, the present model can be easily extended to resonant situation by employing, for instance, Lombardi's model[9] or the complex propagator approach.[35]

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