Gauge invariant theory for super high resolution Raman images

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The use of a highly localized plasmonic field has enabled us to achieve sub-nanometer resolution of Raman images for single molecules. The inhomogeneous spatial distribution of plasmonic field has become an important factor that controls the interaction between the light and the molecule. We present here a gauge invariant interaction Hamiltonian (GIIH) to take into account the non-uniformity of the electromagnetic field distribution in the non-relativistic regime. The theory has been implemented for both resonant and nonresonant Raman processes within the sum-over-state framework. It removes the gauge origin dependence in the phenomenologically modified interaction Hamiltonian (PMIH) employed in previous studies. Our calculations show that, in most resonant cases, the Raman images from GIIH are similar to those from PMIH when the origin is set to the nuclear charge center of the molecule. In the case of nonresonant Raman images, distinct differences can be found from two different approaches, while GIIH calculations provide more details and phase information of the images. Furthermore, the results from GIIH calculations are more stable with respect to the computational parameters. Our results not only help to correctly simulate the resonant and nonresonant Raman images of single molecules but also lay the foundation for developing gauge invariant theory for other linear and nonlinear optical processes under the excitation of non-uniform electromagnetic field. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983391>]

I. INTRODUCTION

Light-matter interaction governs all optical spectroscopies and is also the reason why we can see objects. Among diverse types of spectroscopies, emission spectroscopy is one of the most suitable techniques for optical imaging because it can avoid the background noise from incident sources. For example, fluorescence microscope has been used to visualize gene expression as well as protein distribution by using fluorescent proteins.¹

Because of the breakdown of the diffraction limit,² the resolution of near-field based imaging techniques is superior than that of far-field based imaging techniques, although the latter can be significantly improved with the help of “super-resolution” microscopies.^{3–5} In this context, tip-enhanced Raman spectroscopy (TERS),^{6–9} which takes the advantage of the hugely enhanced localized surface plasmon, is a promising technique to obtain high resolution images. By precisely controlling the surface plasmons, the resolution of TERS images has been significantly improved.^{10–17} For instance, under the ultra-high vacuum and low temperature conditions, the TERS images for a porphyrin derivative adsorbed on the silver surface with sub-nanometer resolution have been reported,¹⁶ which opens the door for exploring the inner molecular structures by optical means. In this case, the spatial distribution of the

plasmonic field has been considered as the decisive factor for such amazingly high resolution.^{18,19} It also brings in a great challenge to the conventional response theory, in which the light is considered to be uniformly interacted with the molecule.^{20–27} However, without position dependence, it is not possible to generate any images from the TERS measurements.

To take the non-uniformity of the spatially confined plasmon (SCP) into account, we introduced the amplitude distribution of SCP as the electromagnetic (EM) field in the interaction Hamiltonian.^{19,28,29} Specifically, the conventional interaction Hamiltonian $\hat{H}' = -\hat{\mathbf{E}}_i \cdot \hat{\boldsymbol{\mu}}$ was modified as $\hat{H}' = -Mg(\mathbf{r}, \mathbf{R}_T)\hat{\mathbf{E}}_i \cdot \hat{\boldsymbol{\mu}}$, where M is the enhancement factor, g is the normalized amplitude distribution function depending on the position of the TERS tip ($\mathbf{R}_T$), and $\hat{\boldsymbol{\mu}}$ and $\hat{\mathbf{E}}_i$ are the operators for electron position ($\mathbf{r}$) and incident electric field, respectively. Using this phenomenologically modified interaction Hamiltonian (PMIH), we could nicely reproduce the experimental observations when the size of the SCP was set to around 20 Å.¹⁹ It is worth noting that such a small size of the SCP is consistent with advanced EM field simulations^{30–33} and further confirmed by recent experiments.³⁴ We also found that, because of the dominance of Franck-Condon contributions, calculated resonant Raman images for the porphyrin derivative are not sensitive to the vibrational modes,¹⁹ which is in good agreement with the experimental observations.¹⁶ To enhance the vibrational dependent Herzberg-Teller contributions, nonresonant Raman processes were considered with

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the same Hamiltonian. The calculated nonresonant Raman images for water clusters adsorbed on the gold surface demonstrated that they are not only vibrationally resolved but also resemble the corresponding vibrational modes.²⁸ As a result, tip-enhanced nonresonant Raman images could be a practical technique for the visualization of molecular vibrational modes in real space.²⁸

So far, the theoretical frameworks for both resonant and nonresonant Raman images are based on PMIH. It is noted that, when the gauge origin moves by an arbitrary vector $\mathbf{a}$, the transition matrix element between initial state $|i\rangle$ and final state $|f\rangle$ of PMIH would have an additional term of $M\mathbf{E}_0 \cdot \mathbf{a}\langle i|g|f\rangle$, where $\mathbf{E}_0$ represents the amplitude of the electric field.³⁵ Therefore, a gauge problem in PMIH arises from nonzero value of matrix element $\langle i|g|f\rangle$, which is the characteristic feature of the non-uniform EM field. Although the gauge problem could be circumvented by the “common-origin” method if the field is approximately truncated by the field gradient,³⁶ the high-order terms always have important contributions in Raman images.³⁷ Thus, in this work, we derive a more general gauge invariant interaction Hamiltonian (GIIH) from the rigorous quantization of EM field for SCP to completely eliminate the gauge problem in the PMIH. Our numerical simulations show that, in resonant conditions, the GIIH gives similar results to those from the PMIH when the origin is set to the nuclear charge center of the adsorbates. On the other hand, for nonresonant Raman images, GIIH results highlight the pattern phases that reveal more vibrational information. We also find that the results from GIIH are more stable than those from the Coulomb’s gauge with respect to the choices of the computational parameters. Within the sum-over-state framework, a complete theory for Raman images is thus established. It should be emphasized that GIIH is general for the interaction between non-uniform EM field and matters, which could find applications in the description of other linear and nonlinear optical processes.

II. METHODOLOGY

The non-relativistic electronic Hamiltonian of a N -electron molecule in a general EM field could be expressed as^{25,38}

$$\hat{H}_e = \sum_{i=1}^N \frac{1}{2} \hat{\pi}_i^2 - \sum_{i=1}^N \sum_{A=1}^{M_A} \frac{Z_A}{r_{iA}} + \sum_{i<j}^N \frac{1}{r_{ij}}, \quad (1)$$

where i and A are the indices for electron and nucleus, respectively, $\hat{\pi} = \hat{\mathbf{p}} + \hat{\mathbf{A}}$ is the generalized momentum operator,^{25,38–40} Z_A represents the charge of nuclei, M_A is the number of nuclei, r_{iA} and r_{ij} are the distances between nucleus-electron and electron-electron, respectively. Here, $\hat{\mathbf{p}} = -i\nabla$ is the momentum operator of electrons and $\hat{\mathbf{A}}$ is the operator of vector potential. Compared with the electronic Hamiltonian without EM field (the unperturbed Hamiltonian $\hat{H}_0$), through simple algebra, we have the (time-dependent) perturbation Hamiltonian^{25,38}

$$\hat{H}' = \frac{1}{2} \sum_i (\hat{\mathbf{p}}_i \cdot \hat{\mathbf{A}} + \hat{\mathbf{A}} \cdot \hat{\mathbf{p}}_i), \quad (2)$$

where the high order $\hat{\mathbf{A}}^2$ term is neglected. We should emphasize that, in proper gauge, the scale potential is set to zero.⁴¹ It is well known that the magnitude of magnetic field is much smaller than that of the vector potential.³⁶ Moreover, in the minimal coupling Hamiltonian, magnetic fields are always associated with the spin operator.^{25,38} In our simulations, the spin of Raman processes is conserved. Thus, magnetic fields can be neglected even for Raman processes in an inhomogeneous EM field.³⁶

For a general EM field, the operator related to the vector potential can be written as^{42,43}

$$\hat{\mathbf{A}}(\mathbf{r}, t) = \sqrt{\frac{2\pi}{\omega V}} (\mathbf{f}_{\mathbf{k}}(\mathbf{r}) \hat{a} e^{-i\omega t} + \text{H.c.}), \quad (3)$$

where ω is the frequency of the light, V is the system volume, $\mathbf{f}_{\mathbf{k}}$ is the mode function that represents the spatial distribution of the field, $\mathbf{k}$ is the wave vector, $\hat{a}$ is the annihilation operator for photon, and H.c. is the Hermitian conjugate. Here the quantization of EM field is particularly necessary for spontaneous emission that is involved in Raman processes as shown in Fig. 1. Notice that, for specific nanostructures, the distribution function $\mathbf{f}_{\mathbf{k}}$ can be determined by the classical Maxwell’s equations⁴¹ if the quantum correction for tunneling is adopted.⁴⁴ According to the energy conservation law in classical electromagnetic theory for metallic nanostructures without considering losses,^{45,46} the following normalization condition should be fulfilled:

$$\int d\mathbf{r} \frac{1}{2} \left[\frac{\partial(\omega\epsilon)}{\partial\omega} + \frac{\mu_0}{\epsilon_0} \frac{\partial(\omega\mu)}{\partial\omega} \frac{|\tau|^2}{|\mu|^2} \right] |\mathbf{f}_{\mathbf{k}}(\mathbf{r})|^2 = V, \quad (4)$$

where ϵ_0 (ϵ) is the permittivity of free space (relative permittivity), μ_0 (μ) is the permeability of free space (relative permeability), and τ is the ratio of magnetic induction to electric field. Therefore, substituting Eq. (3) into Eq. (2), the general *adiabatic* interaction Hamiltonian can be rewritten as a harmonic perturbation

$$\hat{H}'(\mathbf{r}, t) = \hat{V}(\mathbf{r}) e^{(-i\omega + \gamma)t} + \text{H.c.}, \quad (5)$$

where

$$\hat{V}(\mathbf{r}) = \sqrt{\frac{2\pi}{\omega V}} \sum_i \frac{1}{2} (\hat{\mathbf{p}}_i \cdot \mathbf{f}_{\mathbf{k}} + \mathbf{f}_{\mathbf{k}} \cdot \hat{\mathbf{p}}_i) \hat{a} \quad (6)$$

FIG. 1. Diagrams of resonant (type I) and nonresonant (type II) terms. $|i\rangle$, $|r\rangle$, and $|f\rangle$ represent molecular initial, intermediate, and final states, respectively. ω and ω_s are frequencies of incident and scattering lights. The number of incident (scattering) light-quantum is also labeled.

is time independent. Here γ is a positive infinitesimal that ensures $\hat{H}'(\mathbf{r}, -\infty) = 0$.⁴⁷

Once the interaction Hamiltonian is determined, the Raman intensity could be easily calculated by the second-order time-dependent perturbation theory. It is well-known that Raman scattering has two terms as shown in Fig. 1.^{24,48,49} Specifically, the resonant term (type I) represents that the initial state $|i\rangle|n_\omega\rangle$ first excites to the intermediate state $|r\rangle|(n-1)_\omega\rangle$ by absorbing an incident light-quantum. Then, the intermediate state $|r\rangle|(n-1)_\omega\rangle$ relaxes to the final state $|f\rangle|(n-1)_\omega 1_{\omega_s}\rangle$ by emitting a scattering light-quantum. Here, $|i\rangle$, $|r\rangle$, and $|f\rangle$ represent molecular initial, intermediate, and final states, respectively, $|n_\omega\rangle$ is the state for n photon with frequency of ω , and ω_s (ω_s) is the frequency of incident (scattering) light. The nonresonant term (type II) in Fig. 1 corresponds to that the initial state first relaxes to the intermediate state $|r\rangle|n_\omega 1_{\omega_s}\rangle$ by emitting a scattering photon and then excites to $|f\rangle|(n-1)_\omega 1_{\omega_s}\rangle$ by absorbing an incident photon.

It is noted that, in both terms, the plasmonic field is only responsible for the absorption and the vacuum field is responsible for the spontaneous emission. For the plasmonic field, we assume $\mathbf{f}_\mathbf{k} = M\mathbf{g}$, while for the scattering field, $\mathbf{f}_\mathbf{k} = e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$. We focus on the scattering light that can be experimentally detected in the far field. Thus, the dipole approximation is a good approximation for scattering and can be used in our current simulations.²⁹ Again, here M is the enhancement factor and $\mathbf{g}$ is the normalized amplitude distribution function. Therefore, according to Eq. (5), for the $\rho\sigma$ -component of the polarizability, we have

$$\begin{aligned} H'_{\sigma,\omega} &= \sqrt{\frac{2\pi}{\omega V}} M \hat{V}_\sigma \hat{a}_\omega e^{(-i\omega+\gamma)t} + \text{H.c.}, \\ H'_{\rho,\omega_s} &= \sqrt{\frac{2\pi}{\omega_s V}} \hat{V}_\rho^\dagger \hat{a}_{\omega_s}^\dagger e^{(i\omega_s+\gamma)t} + \text{H.c.}, \end{aligned} \quad (7)$$

where

$$\begin{aligned} \hat{V}_\sigma &= \frac{1}{2} \sum_i (\hat{p}_{i,\sigma} g_\sigma + g_\sigma \hat{p}_{i,\sigma}), \\ \hat{V}_\rho^\dagger &= \sum_i \hat{p}_{i,\rho} \end{aligned} \quad (8)$$

are the time-independent operators and ρ (σ) represents the corresponding Cartesian coordinate. Here the annihilation ($\hat{a}$) and creation ($\hat{a}^\dagger$) operators highlight the absorption and emission processes, respectively.

Following the standard second-order time-dependent perturbation theory,^{40,48,50} the differential Raman scattering cross section could be obtained (see the Appendix for details). In brief, the total second-order perturbation coefficient for Raman is

$$c_{fi}^{(2)}(t) = \frac{2\pi M}{V} \sqrt{\frac{n}{\omega\omega_s}} \frac{e^{i(\omega_{fi}-\omega+\omega_s)t+2\gamma t}}{\omega_{fi}-\omega+\omega_s-2i\gamma} \sum (\omega_{fi}), \quad (9)$$

where n is the photon number of incident light, ω_{fi} is the frequency difference between molecular states $|f\rangle$ and $|i\rangle$,

and

$$\sum (\omega_{fi}) = \sum_r \left(\frac{\langle f | \hat{V}_\rho^\dagger | r \rangle \langle r | \hat{V}_\sigma | i \rangle}{\omega_{ri} - \omega - i\gamma} + \frac{\langle f | \hat{V}_\sigma | r \rangle \langle r | \hat{V}_\rho^\dagger | i \rangle}{\omega_{ri} + \omega_s - i\gamma} \right). \quad (10)$$

Thus, the transition rate becomes

$$\Gamma_{fi}^{(2)} = \frac{(2\pi)^3 M^2 n}{V^2 \omega \omega_s} \left| \sum (\omega_{fi}) \right|^2 \delta(\omega_{fi} - \omega + \omega_s) \quad (11)$$

because γ is a positive infinitesimal. If the density of final state is considered, we have

$$\frac{d\Gamma_{fi}^{(2)}}{d\Omega} = \frac{n\omega\omega_s^3 M^2 M_d^2 F_P}{Vc^3} \left| \frac{1}{\omega\omega_s} \sum (\omega_{fi}) \right|^2, \quad (12)$$

where Ω is the solid angle, M_d is the directional radiation pattern factor owing to the nanostructure,²⁷ F_P is the Purcell factor⁵¹ that accounts for the enhancement of spontaneous emission, and c is the speed of light. Here the Purcell factor is necessary, which leads to the well-known $|E|^4$ scaling in the surface-enhanced Raman scattering.²⁹ Finally, the differential scattering cross section for Raman processes under plasmonic field can be calculated as

$$\frac{d\sigma_{fi}}{d\Omega} = \frac{\omega\omega_s^3 M^2 M_d^2 F_P}{c^4} |\alpha_{fi}|^2, \quad (13)$$

where, comparing with the cross section of classical oscillating dipole,^{21,48} we can define the general polarizability derived from Eq. (7) as

$$\alpha_{fi,\rho\sigma} = \frac{1}{\omega\omega_s} \sum_r \left(\frac{\langle f | \hat{V}_\rho^\dagger | r \rangle \langle r | \hat{V}_\sigma | i \rangle}{\omega_{ri} - \omega - i\gamma} + \frac{\langle f | \hat{V}_\sigma | r \rangle \langle r | \hat{V}_\rho^\dagger | i \rangle}{\omega_{ri} + \omega_s - i\gamma} \right). \quad (14)$$

Here Eq. (10) is used.

It should be emphasized that, in free space, we have $\hat{V}_\sigma = \sum_i \hat{p}_{i,\sigma}$ and $\hat{V}_\rho^\dagger = \sum_i \hat{p}_{i,\rho}$. Thus, Eq. (14) becomes exactly the original Dirac's expression for polarizability shown in Ref. 48 if the small term $i\gamma$ is neglected. Notice that, from the Dirac's expression to the more popular Kramers and Heisenberg's expression,⁵² the relationship $\hat{V}_\sigma = i[\hat{H}_0, \hat{\mu}_\sigma]$ plays an essential role.⁴⁸ However, for the cases with plasmonic field, the corresponding relationship may be invalid. Thus, we have to keep the general polarizability Eq. (14) for Raman images from GIIH.

In practical calculations, the Born-Oppenheimer approximation⁵³ is adopted. As a result, analogy to the elegant Albrecht's Raman theory,^{20,26} the general polarizability for resonant Raman images from GIIH could be expressed by

$$\alpha_{fi,\rho\sigma} = A_{\rho\sigma} + B_{\rho\sigma}, \quad (15)$$

where

$$\begin{aligned}
A_{\rho\sigma} &= \frac{1}{\omega\omega_s} \left[\langle \Psi_g | \hat{V}_\rho^\dagger | \Psi_r \rangle \langle \Psi_r | \hat{V}_\sigma | \Psi_g \rangle \sum_{v^r=0}^{\infty} \frac{\langle v^f | v^r \rangle \langle v^r | v^i \rangle}{\omega_{e^r v^r; e^g v^i} - \omega - i\gamma} \right] + \text{NRT}, \\
B_{\rho\sigma} &= \frac{1}{\omega\omega_s} \sum_k \left[\frac{\partial \langle \Psi_g | \hat{V}_\rho^\dagger | \Psi_r \rangle}{\partial Q_k} \langle \Psi_r | \hat{V}_\sigma | \Psi_g \rangle \sum_{v^r=0}^{\infty} \frac{\langle v^f | Q_k | v^r \rangle \langle v^r | v^i \rangle}{\omega_{e^r v^r; e^g v^i} - \omega - i\gamma} \right. \\
&\quad \left. + \langle \Psi_g | \hat{V}_\rho^\dagger | \Psi_r \rangle \frac{\partial \langle \Psi_r | \hat{V}_\sigma | \Psi_g \rangle}{\partial Q_k} \sum_{v^r=0}^{\infty} \frac{\langle v^f | v^r \rangle \langle v^r | Q_k | v^i \rangle}{\omega_{e^r v^r; e^g v^i} - \omega - i\gamma} \right] + \text{NRT}.
\end{aligned} \tag{16}$$

Here $|\Psi_g\rangle$ and $|\Psi_r\rangle$ are the electronic ground and resonant excited states, Q_k is the vibrational normal mode, $|v^i\rangle$ and $|v^f\rangle$ are the initial and final vibrational states in $|\Psi_g\rangle$, $|v^r\rangle$ is the vibrational state in $|\Psi_r\rangle$, $\omega_{e^r v^r; e^g v^i}$ is the frequency difference between $|\Psi_r\rangle|v^r\rangle$ and $|\Psi_g\rangle|v^i\rangle$, and NRT is the non-resonant term. On the other hand, for nonresonant Raman processes, the NRT will come into play.^{20,26} Using the state-to-state mapping relationship between the Albrecht's theory and the perturbation theory,⁵⁴ the general polarizability becomes

$$\alpha_{fi,\rho\sigma}^k = \frac{\partial \alpha_{\rho\sigma}^{\text{eff}}}{\partial Q_k} \langle v^f | Q_k | v^i \rangle, \tag{17}$$

where

$$\begin{aligned}
\alpha_{\rho\sigma}^{\text{eff}} &= \frac{1}{\omega\omega_s} \sum_r \left(\frac{\langle \Psi_g | \hat{V}_\rho^\dagger | \Psi_r \rangle \langle \Psi_r | \hat{V}_\sigma | \Psi_g \rangle}{\Delta E_{rg} - \omega} \right. \\
&\quad \left. + \frac{\langle \Psi_g | \hat{V}_\sigma | \Psi_r \rangle \langle \Psi_r | \hat{V}_\rho^\dagger | \Psi_g \rangle}{\Delta E_{rg} + \omega_s} \right).
\end{aligned} \tag{18}$$

Here ΔE_{rg} represents the vertical excitation energy between $|\Psi_g\rangle$ and $|\Psi_r\rangle$ and $i\gamma$ is neglected. It should be stressed that, owing to the multimode nature of vibrations, i.e., $|v\rangle = |v_1 v_2 \cdots v_N\rangle$ (where N is the number of vibrational modes), we can calculate the required vibrational integral in Eq. (17) as $\langle v^f | Q_k | v^i \rangle = \delta_{1f,1i} \delta_{2f,2i} \cdots \langle v_k^f | Q_k | v_k^i \rangle \cdots \delta_{Nf,Ni}$. Thus, the normal mode “ k ” is naturally selected out for harmonic potential energy surfaces in nonresonant Raman cases. Substituting Eqs. (15) and (17) into Eq. (13), the cross section from GIIH could be readily calculated.

For clear comparison, the polarizability expressions from PMIH are also listed. For resonant Raman images, we have

$$\begin{aligned}
A_{\rho\sigma}^r &= \left[\langle \Psi_g | \hat{\mu}_\rho | \Psi_r \rangle \langle \Psi_r | \hat{\mu}_\sigma g_{\sigma} | \Psi_g \rangle \sum_{v^r=0}^{\infty} \frac{\langle v^f | v^r \rangle \langle v^r | v^i \rangle}{\omega_{e^r v^r; e^g v^i} - \omega - i\gamma} \right] + \text{NRT}, \\
B_{\rho\sigma}^r &= \sum_k \left[\frac{\partial \langle \Psi_g | \hat{\mu}_\rho | \Psi_r \rangle}{\partial Q_k} \langle \Psi_r | \hat{\mu}_\sigma g_{\sigma} | \Psi_g \rangle \sum_{v^r=0}^{\infty} \frac{\langle v^f | Q_k | v^r \rangle \langle v^r | v^i \rangle}{\omega_{e^r v^r; e^g v^i} - \omega - i\gamma} \right. \\
&\quad \left. + \langle \Psi_g | \hat{\mu}_\rho | \Psi_r \rangle \frac{\partial \langle \Psi_r | \hat{\mu}_\sigma g_{\sigma} | \Psi_g \rangle}{\partial Q_k} \sum_{v^r=0}^{\infty} \frac{\langle v^f | v^r \rangle \langle v^r | Q_k | v^i \rangle}{\omega_{e^r v^r; e^g v^i} - \omega - i\gamma} \right] + \text{NRT},
\end{aligned} \tag{19}$$

and for nonresonant Raman images

$$\begin{aligned}
\alpha_{\rho\sigma}^{\text{eff},r} &= \sum_r \left(\frac{\langle \Psi_g | \hat{\mu}_\rho | \Psi_r \rangle \langle \Psi_r | \hat{\mu}_\sigma g_{\sigma} | \Psi_g \rangle}{\Delta E_{rg} - \omega} \right. \\
&\quad \left. + \frac{\langle \Psi_g | \hat{\mu}_\sigma g_{\sigma} | \Psi_r \rangle \langle \Psi_r | \hat{\mu}_\rho | \Psi_g \rangle}{\Delta E_{rg} + \omega_s} \right).
\end{aligned} \tag{20}$$

III. COMPUTATIONAL DETAILS

To illustrate the algorithm for the GIIH and compare its results with those from the PMIH, we chose a single *meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (H_2TBPP) molecule adsorbed on the Ag(111) surface^{16,19} and water clusters on the Au(111) surface²⁸ for the simulations of resonant and non-resonant Raman images, respectively. All calculation details

could be found in our previous studies^{19,28} as well as the [supplementary material](#). Briefly, geometrical optimizations and vibrational calculations were performed at the periodic boundary conditions implemented as in the Vienna *ab initio* simulation package.⁵⁵ Then, the optimized geometries as well as the vibrational modes were extracted for electronic structure calculations of ground and excited states by the GAUSSIAN suite of program.⁵⁶

For vibrational integrals in Eq. (16), the linear coupling model⁵⁷ was used for the excited state potential energy surfaces. Therefore, all vibrational integrals and energy differences could be calculated by the DYNABIB program from the vertical energy derivatives extracted from time-dependent density functional theory (TDDFT) calculations.⁵⁸ In addition, all other quantities for the electronic part in Eqs. (16) and (18), including transition velocity dipole moments, vertical

excitation energies as well as their derivatives, could be directly extracted from calculations by the GAUSSIAN program except the integral

$$I = \langle \Psi_r | \hat{V}_\sigma | \Psi_g \rangle. \quad (21)$$

According to the experimental setups,¹⁶ evaluation of the zz component is adequate for Raman images. For practical simulations, we expanded the z component of the amplitude distribution of the SCP by a set of Gaussian functions, i.e.,

$$g_z = \sum_D \sum_{l,m,n} \sum_\alpha c_{\alpha,D}^{lmn} g_{\alpha,D}^{lmn}, \quad (22)$$

where $g_{\alpha,D}^{lmn}$ is a Gaussian function localized at the center $\mathbf{r}_D$ with exponent α , which can be written as

$$g_{\alpha,D}^{lmn} = (x - x_D)^l (y - y_D)^m (z - z_D)^n e^{-\alpha(\mathbf{r}-\mathbf{r}_D)^2} \quad (23)$$

and $c_{\alpha,D}^{lmn}$ is the corresponding coefficient. Thus, the integral

$$I^{lmn} = \langle \Psi_r | \hat{V}_z^{lmn} | \Psi_g \rangle \quad (24)$$

should be evaluated. It should be emphasized that the superscript “ lmn ” relates to the angular momentum of Cartesian Gaussian functions (see Eq. (23)).

In the framework of TDDFT, using the coefficients of excitation (X) and de-excitation (Y), we have⁵⁹

$$I^{lmn} = \sum_{ia} (X_{i \rightarrow a}^r \langle \phi_a | \hat{v}_z^{lmn} | \phi_i \rangle + Y_{i \leftarrow a}^r \langle \phi_i | \hat{v}_z^{lmn} | \phi_a \rangle), \quad (25)$$

where ϕ_i and ϕ_a are the occupied and unoccupied molecular orbitals (MOs), respectively, and the definition

$$\hat{v}_z^{lmn} = \frac{1}{2} (\hat{p}_z g_{\alpha,D}^{lmn} + g_{\alpha,D}^{lmn} \hat{p}_z). \quad (26)$$

Expanding MOs by atomic orbitals, the required integral between arbitrary MOs ϕ_p and ϕ_q could be

$$I_{pq}^{lmn} = \sum_{\chi\eta} c_{\chi p}^* c_{\eta q} \left(\sum_{KL} D_\chi^K D_\eta^L \langle g_\chi^K | \hat{v}_z^{lmn} | g_\eta^L \rangle \right), \quad (27)$$

where $c_{\chi p}$ and $c_{\eta q}$ are the MO coefficients, g_χ^K and g_η^L are the primitive Cartesian Gaussian functions, and D_χ^K and D_η^L are the corresponding contraction coefficients. Therefore, the integral with primitive Cartesian Gaussian functions

$$I_{KL}^{lmn} = \langle g_\chi^K | \hat{v}_z^{lmn} | g_\eta^L \rangle \quad (28)$$

has to be calculated. It is noted that if

$$I_{KL,r}^{lmn} = \langle g_\chi^K | z g_{\alpha,D}^{lmn} | g_\eta^L \rangle \quad (29)$$

is evaluated instead, results from the PMIH are obtained.

Owing to the relationship⁶⁰

$$\frac{\partial}{\partial z} g_\alpha^{lmn} = -2\alpha z g_\alpha^{lm(n+1)} + n g_\alpha^{lm(n-1)}, \quad (30)$$

I_{KL}^{lmn} could be converted to a linear combination of the three-center overlap integrals. Here g_α^{lmn} is the general expression of both the $g_{\alpha,D}^{lmn}$ in amplitude distribution function and primitive Cartesian Gaussian functions, meanwhile, α_z is the z component of the exponent. Practically, the integral Eq. (28) could be factored as

$$\begin{aligned} I_{KL}^{lmn} &= I_{KL,x}^l I_{KL,y}^m I_{KL,z}^n \\ &= \langle l_a | l_D | l_b \rangle \langle m_a | m_D | m_b \rangle \langle n_a | \hat{v}(n_D) | n_b \rangle, \end{aligned} \quad (31)$$

where subscripts a , b , and D represent the different centers of Gaussian functions, and $\hat{v}(n_D)$ is the n related component of $\hat{v}_z^{lmn}$. To calculate Eq. (31), both direct and recursive methods could be used.⁶⁰ Here we only present the efficient recursive method. Specifically, for $I_{KL,x}^l$ and $I_{KL,y}^m$ (here only taking $I_{KL,x}^l$, for example), we have⁶⁰

$$\begin{aligned} \langle l_a + 1 | l_D | l_b \rangle &= (G_x - \mathbf{r}_{\chi,x}) \langle l_a | l_D | l_b \rangle + \frac{l_a}{2\alpha_x^{\text{Tot}}} \langle l_a - 1 | l_D | l_b \rangle \\ &+ \frac{l_b}{2\alpha_x^{\text{Tot}}} \langle l_a | l_D | l_b - 1 \rangle + \frac{l_D}{2\alpha_x^{\text{Tot}}} \langle l_a | l_D - 1 | l_b \rangle \end{aligned} \quad (32)$$

with

$$\begin{aligned} \langle 0_{a,x} | 0_{D,x} | 0_{b,x} \rangle &= \exp \left(\alpha_x^{\text{Tot}} G_x^2 - \alpha_\chi^K \mathbf{r}_{\chi,x}^2 - \alpha_\eta^L \mathbf{r}_{\eta,x}^2 - \alpha_x^L \mathbf{r}_{D,x}^2 \right) \\ &\times \sqrt{\frac{\pi}{\alpha_x^{\text{Tot}}}}, \end{aligned} \quad (33)$$

where $\mathbf{r}_\chi$ ($\mathbf{r}_\eta$) is the center of atomic basis set χ (η), and

$$\begin{aligned} \alpha_x^{\text{Tot}} &= \alpha_\chi^K + \alpha_\eta^L + \alpha_x, \\ G_x &= \frac{\alpha_\chi^K \mathbf{r}_{\chi,x} + \alpha_\eta^L \mathbf{r}_{\eta,x} + \alpha_x \mathbf{r}_{D,x}}{\alpha_x^{\text{Tot}}}. \end{aligned} \quad (34)$$

It is noted that the l and m components in $I_{KL,r}^{lmn}$ could also be calculated by Eq. (32) and both are gauge origin independent. For $I_{KL,z}^n$, the recurrence formula reads

$$\begin{aligned} \langle n_a + 1 | \hat{v}(n_D) | n_b \rangle &= (G_z - \mathbf{r}_{\chi,z}) \langle n_a | \hat{v}(n_D) | n_b \rangle \\ &+ \frac{n_a}{2\alpha_z^{\text{Tot}}} \langle n_a - 1 | \hat{v}(n_D) | n_b \rangle \\ &+ \frac{n_b}{2\alpha_z^{\text{Tot}}} \langle n_a | \hat{v}(n_D) | n_b - 1 \rangle \\ &+ \frac{n_D}{2\alpha_z^{\text{Tot}}} \langle n_a | \hat{v}(n_D - 1) | n_b \rangle \\ &+ \iota \frac{2\alpha_\eta^L + \alpha_z}{2\alpha_z^{\text{Tot}}} \langle n_a | n_D | n_b \rangle \end{aligned} \quad (35)$$

with

$$\begin{aligned} \langle 0_{a,z} | \hat{v}(n_D + 1) | 0_{b,z} \rangle &= (G_z - \mathbf{r}_{D,z}) \langle 0_{a,z} | \hat{v}(n_D) | 0_{b,z} \rangle \\ &+ \frac{n_D}{2\alpha_z^{\text{Tot}}} \langle 0_{a,z} | \hat{v}(n_D - 1) | 0_{b,z} \rangle \\ &- \iota \left(0.5 - \frac{2\alpha_\eta^L + \alpha_z}{2\alpha_z^{\text{Tot}}} \right) \langle 0_{a,z} | n_{D,z} | 0_{b,z} \rangle \end{aligned} \quad (36)$$

and

$$\begin{aligned} \langle 0_{a,z} | \hat{v}(0_{D,z}) | 0_{b,z} \rangle &= \iota \left[2\alpha_\eta^L (G_z - \mathbf{r}_{\eta,z}) + \alpha_z (G_z - \mathbf{r}_{D,z}) \right] \\ &\times \langle 0_{a,z} | 0_{D,z} | 0_{b,z} \rangle, \end{aligned} \quad (37)$$

where $\langle 0_{a,z} | 0_{D,z} | 0_{b,z} \rangle$ as well as α_z^{Tot} and G_z could be calculated from Eqs. (33) and (34) by replacing the subscript x with z . It should be emphasized that all distances in the evaluation of Eq. (35) are relative values, which manifests that the integral I_{KL}^{lmn} is gauge origin independent. On the other hand, for n

related component of $I_{KL,r}^{lmn}$, we have the recurrence formula²⁹

$$\begin{aligned} \langle n_a + 1 | z n_D | n_b \rangle = & (G_z - \mathbf{r}_{\chi,z}) \langle n_a | z n_D | n_b \rangle \\ & + \frac{n_a}{2\alpha_z^{\text{Tot}}} \langle n_a - 1 | z n_D | n_b \rangle \\ & + \frac{n_b}{2\alpha_z^{\text{Tot}}} \langle n_a | z n_D | n_b - 1 \rangle \\ & + \frac{n_D}{2\alpha_z^{\text{Tot}}} \langle n_a | z (n_D - 1) | n_b \rangle \\ & + \frac{1}{2\alpha_z^{\text{Tot}}} \langle n_a | n_D | n_b \rangle, \end{aligned} \quad (38)$$

with

$$\langle 0_{a,z} | z 0_{D,z} | 0_{b,z} \rangle = G_z \langle 0_{a,z} | 0_{D,z} | 0_{b,z} \rangle. \quad (39)$$

Because of the gauge origin dependence of G_z and the nonzero value of $\langle \phi_p | g_{\alpha,D}^{lmn} | \phi_q \rangle$, $I_{KL,r}^{lmn}$ as well as the results from the PMIH are thus also gauge origin dependent.

In practical simulations, as the same in our previous studies, we use one s -type Gaussian function for g_z .^{19,28} Specifically, we set the full width at half maximum for the x

and y components to 20 Å and its theoretical limit^{18,45} of 1 Å for resonant¹⁹ and nonresonant²⁸ Raman image calculations, respectively. Meanwhile, the full width at half maximum for the z component was set to 5 Å.⁶¹ For resonant Raman images, the two near degenerate excited states around the experimental excitation energy for each isomer are accounted equally in the current simulations. For nonresonant cases, the wavelength of the incident light was set to 632.8 nm. All Raman images were calculated by the “FIRST-PRINCIPLES APPROACHES FOR SURFACE AND TIP ENHANCED RAMAN SCATTERING (FASTERS)” program.⁶²

IV. RESULTS AND DISCUSSIONS

We first consider the resonant Raman images for H₂TBPP adsorbed on the Ag(111) surface¹⁶ from three different adsorption configurations,¹⁹ namely, concave, plane, and convex, respectively. All calculated results from both GIIH and PMIH are depicted in Fig. 2. It should be emphasized that, for different interaction Hamiltonians, the near field around the

FIG. 2. Calculated resonant Raman images for concave, plane, and convex configurations (from left to right) of H₂TBPP adsorbed on the Ag(111) surface from (a) gauge invariant interaction Hamiltonian (GIIH) and (b) phenomenologically modified interaction Hamiltonian (PMIH). In (a) the optimized structures extracted from Ref. 19 are shown in the top panel; the experimentally observed Raman images from Ref. 16 are shown as insert to the top left panel. In (b) the origins were set to the plasmonic center (PC), nuclear charge center of adsorbates (NC), and the topmost layer of the Ag(111) surface (SL) from top to bottom, respectively. The solid lines represent the skeleton of H₂TBPP.

molecule is the same. The only difference is that we artificially chose different origins in our simulations.

We could immediately notice that the calculated images from GIIH are similar to those from PMIH with the origin set to the nuclear charge center of adsorbates (labeled as NC hereafter) for concave and plane configurations. Specifically, four bright corner lobes with less contrast for the bottom-left corner lobe and two (top and bottom) bright ribbons are predicted by both GIIH and PMIH. On the other hand, for the convex configuration, the image from GIIH shows three bright lobes, which are significantly different from the oval-shaped pattern predicted by the PMIH with the origin set to NC but similar to that with the origin set to the plasmonic center (labeled as PC hereafter). It is noted that only the concave configuration can nicely reproduce the experimental observations, which is consistent with the results from PMIH with origin at NC.¹⁹ It is also noted that the concave configuration is the most stable one on the Ag(111) surface.¹⁹ For instance, its energy is around 2.9 eV lower than that of the convex configuration.

From Fig. 2, we could find that the results from the PMIH are indeed origin dependent, especially for the convex

configuration. Specifically, when the origin is set to the PC, three bright lobes are highlighted, which is similar to the result from GIIH as mentioned before. When the origin is set to the topmost metallic surface layer (labeled as SL hereafter), a slight deformation of the oval-shaped pattern is observed. Meanwhile, for the concave and plane configurations, the origin dependence of Raman images is relatively weak with minor contrast changes of bottom-left and top patterns for concave and plane configurations, respectively.

Then we move on to the nonresonant cases. All calculated nonresonant images for water monomer adsorbed on the Au(111) surface²⁸ from both GIIH and PMIH are depicted in Fig. 3. In contrast to the resonant case, all nonresonant Raman images including bending mode (ν_2) as well as symmetric (ν_1) and asymmetric (ν_3) O–H stretching modes from GIIH are significantly different from their counterparts from PMIH when the origin is set to NC. Specifically, the patterns associated with hydrogen atoms in the ν_1 and ν_3 images become obscure, while, the patterns near to the oxygen atom are highlighted. It should be emphasized that the phases (sign of $\partial\alpha^{\text{eff}}/\partial Q_k$ in Eq. (17)) of each pattern are important. In the ν_1 image, the

FIG. 3. Calculated nonresonant Raman images for bending (ν_2), symmetric stretching (ν_1), and asymmetric stretching (ν_3) modes (from left to right) of water monomer adsorbed on the Au(111) surface from (a) gauge invariant interaction Hamiltonian (GIIH) and (b) phenomenologically modified interaction Hamiltonian (PMIH). In (a) the vibrational modes extracted from Ref. 28 are shown as top panel; the values are calculated frequencies in cm⁻¹. In (b) the origins were set to the plasmonic center (PC), nuclear charge center of adsorbates (NC), and the topmost layer of the Au(111) surface (SL) from top to bottom, respectively. The solid lines represent the skeleton of water monomer.

phase of pattern associated with oxygen is different from that with hydrogens. In addition, in the ν_3 image, the phases of four patterns are the same as that of the d_{xy} atomic orbital. The phases suggest the constructive and destructive coherence of O–H stretching in the ν_1 and ν_3 images, which is consistent with the normal modes. The images for bending mode (ν_2) from GIIH and PMIH with origin at NC both give a bright ribbon pattern associated with two hydrogen atoms. However, the ball-shaped pattern from PMIH splits into two weak patterns along the outside area of O–H bonds. Comparing the results from PMIH and GIIH, we find that the simulation results from PMIH, for example, with origin at NC shown in Fig. 3(b), may lead to the missing of vibrational phase information. The phase information could exist in experiments and would be the important characteristic feature of different vibrational modes.

Figure 3(b) shows that, for PMIH results, ν_3 images are not sensitive to the origin position. However, ν_1 and ν_2 images exhibit significant origin dependence. For instance, when the origin is set to PC, the two patterns associated with O–H bonds in ν_1 image are obscure and a new bright pattern associated with the oxygen atom emerges. For the ν_2 image, the contrast of ribbon associated with the two hydrogen atoms becomes lower and the size of the bell-shaped pattern associated with

the oxygen is reduced when the origin is set to either PC or SL.

For larger water clusters adsorbed on the Au(111) surface, because the images of O–H stretching modes are simple and highly localized (see Figs. S1-S3 in the [supplementary material](#) for details), only the stretching modes for hydrogen bonds as well as the bending modes are shown in Fig. 4. Calculated results show that GIIH and PMIH can give similar patterns for the O–H stretching modes (see Figs. S1-S3 in the [supplementary material](#) for details).

For water dimer, the image calculated from GIIH for the hydrogen bond stretching mode (ν_H) displays a bright pattern between the two water molecules. The image for anti-symmetric mixing of ν_2 modes (ν_2^a) has three bright patterns associated with the top water molecule, while, the image for symmetric mixing (ν_2^s) has one bright pattern associated with the bottom water molecule. All these images are similar to those from PMIH with origin at NC, except that the patterns of the top water molecule are obscure in the image of ν_2^s . When the origin is set to PC or SL, the images from PMIH again show some differences. For instance, the moderate pattern between the two water molecules in ν_H image becomes obscure. In addition, for the ν_2^s image, the contrast of three patterns associated with the top water is lower, meanwhile,

FIG. 4. Calculated nonresonant Raman images for hydrogen bonding stretching modes (ν_H for dimer; ν_H^E and ν_H^A for trimer) and bending modes (ν_2^s and ν_2^a for dimer; ν_2^E and ν_2^A for trimer) of water dimer (left) and trimer (right) adsorbed on the Au(111) surface from ((a) and (b)) gauge invariant interaction Hamiltonian (GIIH) and ((c) and (d)) phenomenologically modified interaction Hamiltonian (PMIH). In ((a) and (b)) the vibrational modes extracted from Ref. 28 are shown as top panel; the values are calculated frequencies in cm^{-1} . In ((c) and (d)) the origins were set to the plasmonic center (PC), nuclear charge center of adsorbates (NC), and the topmost layer of the Au(111) surface (SL) from top to bottom, respectively. The solid lines represent the skeleton of water dimer and trimer.

the pattern associated with oxygen in the bottom water is highlighted.

We now turn our attention to the case of water trimer. The calculated pattern for the degenerate asymmetric modes of hydrogen bonds stretching (v_H^E) from GIIH is similar to that from PMIH with origin at NC. It is noted that the calculated image for symmetric stretching of hydrogen bonds (v_H^A) from GIIH exhibits the constructive coherence, which leads to the bright center of the trimer ring. This constructive coherence is also observed in the PMIH result with origin at NC.²⁸ However, the contrast of the bright center is higher in the PMIH result. For the bending modes, the GIIH images for the degenerate asymmetric modes (v_2^E) and the symmetric modes (v_2^A) both show bright ribbon patterns associated with each water monomer. However, the phases of the patterns reveal the destructive coherence between v_2 images for water monomer in the v_2^E image, while the constructive coherence in the v_2^A image. This is opposite to the results from PMIH with origin at NC, where the v_2^E and v_2^A images exhibit the constructive and destructive coherence, respectively.²⁸ It is noted that, when the

origin is set to PC or SL, the coherence would be significantly reduced in PMIH results.

In some cases, the Coulomb's gauge^{25,39,41,46}

$$\text{div} \mathbf{A}(\mathbf{r}, t) = 0 \quad (40)$$

is usually adopted. Using the mathematic relationship⁴¹ $\nabla \cdot (\mathbf{a}f) = \mathbf{a} \cdot \nabla f + f \nabla \cdot \mathbf{a}$, where $\mathbf{a}$ and f are the arbitrary vector and scale functions, we can rewrite Eq. (26) as

$$\hat{v}_z^{lmn} = g_{\alpha,D}^{lmn} \hat{p}_z + \hat{w}_z^{lmn}. \quad (41)$$

Here we have the operator definition for gradient contribution

$$\hat{w}_z^{lmn} = -\frac{i}{2} \frac{\partial g_{\alpha,D}^{lmn}}{\partial z}. \quad (42)$$

In the current simulations, the gradient contribution in general is not zero. Therefore, in the Coulomb's gauge, we should subtract the gradient contribution from the whole GIIH.

To evaluate the gradient contribution, the integral

$$I_{KL,w}^{lmn} = \langle l_a | l_D | l_b \rangle \langle m_a | m_D | m_b \rangle \langle n_a | \hat{w}(n_D) | n_b \rangle \quad (43)$$

FIG. 5. Calculated (a) resonant Raman images for concave, plane, and convex configurations (from left to right) of H₂TBPP adsorbed on the Ag(111) surface and (b) nonresonant Raman images for bending (ν_2), symmetric stretching (ν_1), and asymmetric stretching (ν_3) modes (from left to right) of water monomer adsorbed on the Au(111) surface from the Coulomb's gauge (CG, top) and the gradient contribution (GC, bottom). The values represent the corresponding scale factor and the scale of the contrast is the same as that in Figs. 2 and 3.

FIG. 6. Calculated (a) resonant Raman images for concave, plane, and convex configurations (from left to right) of H_2TBPP adsorbed on the $\text{Ag}(111)$ surface and (b) nonresonant Raman images for bending (ν_2), symmetric stretching (ν_1), and asymmetric stretching (ν_3) modes (from left to right) of water monomer adsorbed on the $\text{Au}(111)$ surface from gauge invariant interaction Hamiltonian with α_z set to zero.

has to be calculated. The recurrence formula for the only unknown integral in Eq. (43) reads

$$\begin{aligned} \langle n_a + 1 | \hat{w}(n_D) | n_b \rangle = & (G_z - \mathbf{r}_{\chi,z}) \langle n_a | \hat{w}(n_D) | n_b \rangle \\ & + \frac{n_a}{2\alpha_z^{\text{Tot}}} \langle n_a - 1 | \hat{w}(n_D) | n_b \rangle \\ & + \frac{n_b}{2\alpha_z^{\text{Tot}}} \langle n_a | \hat{w}(n_D) | n_b - 1 \rangle \\ & + \frac{n_D}{2\alpha_z^{\text{Tot}}} \langle n_a | \hat{w}(n_D - 1) | n_b \rangle \\ & + i \frac{\alpha_z}{2\alpha_z^{\text{Tot}}} \langle n_a | n_D | n_b \rangle \end{aligned} \quad (44)$$

with

$$\begin{aligned} \langle 0_{a,z} | \hat{w}(n_D + 1) | 0_{b,z} \rangle = & (G_z - \mathbf{r}_{D,z}) \langle 0_{a,z} | \hat{w}(n_D) | 0_{b,z} \rangle \\ & + \frac{n_D}{2\alpha_z^{\text{Tot}}} \langle 0_{a,z} | \hat{w}(n_D - 1) | 0_{b,z} \rangle \\ & - i \left(0.5 - \frac{\alpha_z}{2\alpha_z^{\text{Tot}}} \right) \langle 0_{a,z} | n_{D,z} | 0_{b,z} \rangle \end{aligned} \quad (45)$$

and

$$\langle 0_{a,z} | \hat{w}(0_{D,z}) | 0_{b,z} \rangle = i\alpha_z (G_z - \mathbf{r}_{D,z}) \langle 0_{a,z} | 0_{D,z} | 0_{b,z} \rangle. \quad (46)$$

It is noteworthy that $I_{KL,w}^{lmn}$ is again gauge origin independent.

The calculated resonant Raman images for H_2TBPP adsorbed on the $\text{Ag}(111)$ surface and nonresonant Raman images for water monomer adsorbed on the $\text{Au}(111)$ surface from the Coulomb's gauge as well as the gradient contribution have been depicted in Fig. 5 as examples. For concave and convex configurations, the results from the Coulomb's gauge are similar to their counterparts from the GIIH as well as the gradient contributions. On the other hand, the image for plane configuration from the Coulomb's gauge shows a bright bottom-right corner lobe, which is of significant difference from the result from GIIH, whereas, the gradient

contribution for the plane configuration displays two bright patterns that are similar to the result from GIIH. For the nonresonant cases, the results from the Coulomb's gauge nicely reproduce their GIIH counterparts for all vibrational modes.

It is noted that, in Fig. 5, the gradient contribution is important in resonant images, while, it is negligible in nonresonant images. This should be attributed to the different confinement parameters used for resonant and nonresonant images. Specifically, for resonant images, $\alpha_{x,y}$ is smaller than α_z , while for nonresonant images, $\alpha_{x,y}$ is larger. It is anticipated that smaller α_z will reduce the importance of the gradient contribution. Therefore, it is beneficial to consider the case of $\alpha_z = 0$. In this case, the gradient contribution is zero and the Coulomb's gauge is automatically fulfilled. Now, the distribution of plasmon becomes a Gaussian cylinder and the tip position is no longer important.

All calculated Raman images with $\alpha_z = 0$ are shown in Fig. 6. The calculated resonant images for concave and convex are similar with those from finite α_z . However, for the plane configuration, the significant shape changes of two patterns are observed. For nonresonant cases, the images with $\alpha_z = 0$ are the same as those from finite α_z . By comparing all results with different α_z , we find that the images from the whole GIIH are more stable with respect to the choice of α_z than those from the Coulomb's gauge.

V. CONCLUSIONS

We have derived and implemented the gauge invariant algorithm from the GIIH for both resonant and nonresonant Raman images, where the gauge origin dependence in PMIH is eliminated. The similarity and difference between the results of GIIH and PMIH have been carefully examined. The GIIH based theory is ready for simulating Raman images of different

molecular systems and can also be further extended to describe other linear and nonlinear optical processes under the electromagnetic field with inhomogeneous spatial distribution in general.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the detailed computational parameters and other nonresonant Raman images for water dimer and trimer adsorbed on the Au(111) surface.

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APPENDIX: DERIVATION OF GENERAL RAMAN POLARIZABILITY

In time-dependent perturbation theory, the time-dependent coefficients for state $|m\rangle$ with different orders could be calculated by the Dyson series, i.e.,^{40,50}

$$\begin{aligned} c_{mi}^{(0)}(t) &= \delta_{mi}, \\ c_{mi}^{(1)}(t) &= -i \int_{-\infty}^t \langle m | H'(t') | i \rangle e^{i\omega_{mi}t'} dt', \\ c_{mi}^{(2)}(t) &= -i \sum_r \int_{-\infty}^t \langle m | H'(t') | r \rangle e^{i\omega_{mr}t'} c_{ri}^{(1)}(t') dt', \end{aligned} \quad (\text{A1})$$

where $|i\rangle$ and $|r\rangle$ are the initial and intermediate states, respectively. Using Eq. (7) and according to Fig. 1, we can find the first-order time-dependent coefficient for type I as

$$\begin{aligned} c_{I,ri}^{(1)}(t') &= -i \sqrt{\frac{2\pi}{\omega V}} M \int_{-\infty}^{t'} \langle (n-1)_{\omega} | \langle r | \hat{V}_{\sigma} \hat{a}_{\omega} | i \rangle | n_{\omega} \rangle \\ &\quad \times e^{i(\omega_{ri}-\omega)t''+i\gamma t''} dt'' \\ &= -i \sqrt{\frac{2\pi n}{\omega V}} M \langle r | \hat{V}_{\sigma} | i \rangle \frac{e^{i(\omega_{ri}-\omega)t'+i\gamma t'}}{i(\omega_{ri}-\omega)+\gamma}, \end{aligned} \quad (\text{A2})$$

and for type II

$$\begin{aligned} c_{II,ri}^{(1)}(t') &= -i \sqrt{\frac{2\pi}{\omega_s V}} \int_{-\infty}^{t'} \langle n_{\omega} 1_{\omega_s} | \langle r | \hat{V}_{\rho}^{\dagger} \hat{a}_{\omega_s}^{\dagger} | i \rangle | n_{\omega} 0_{\omega_s} \rangle \\ &\quad \times e^{i(\omega_{ri}+\omega_s)t''+i\gamma t''} dt'' \\ &= -i \sqrt{\frac{2\pi}{\omega_s V}} \langle r | \hat{V}_{\rho}^{\dagger} | i \rangle \frac{e^{i(\omega_{ri}+\omega_s)t'+i\gamma t'}}{i(\omega_{ri}+\omega_s)+\gamma}. \end{aligned} \quad (\text{A3})$$

Therefore, the desired second-order coefficient for type I is

$$\begin{aligned} c_{I,fi}^{(2)}(t) &= -\frac{2\pi M}{V} \sqrt{\frac{n}{\omega \omega_s}} \sum_r \frac{\langle r | \hat{V}_{\sigma} | i \rangle}{i(\omega_{ri}-\omega)+\gamma} \int_{-\infty}^t e^{i(\omega_{fi}+\omega_{ri}-\omega+\omega_s)t'+2i\gamma t'} \\ &\quad \times \langle (n-1)_{\omega} 1_{\omega_s} | \langle f | \hat{V}_{\rho}^{\dagger} \hat{a}_{\omega_s}^{\dagger} | r \rangle | (n-1)_{\omega} 0_{\omega_s} \rangle dt' \\ &= \frac{2\pi M}{V} \sqrt{\frac{n}{\omega \omega_s}} \sum_r \frac{\langle f | \hat{V}_{\rho}^{\dagger} | r \rangle \langle r | \hat{V}_{\sigma} | i \rangle}{\omega_{ri}-\omega-i\gamma} \frac{e^{i(\omega_{fi}-\omega+\omega_s)t+2i\gamma t}}{\omega_{fi}-\omega+\omega_s-2i\gamma}, \end{aligned} \quad (\text{A4})$$

and for type II

$$\begin{aligned} c_{II,fi}^{(2)}(t) &= -\frac{2\pi M}{V} \sqrt{\frac{n}{\omega \omega_s}} \sum_r \frac{\langle r | \hat{V}_{\rho}^{\dagger} | i \rangle}{i(\omega_{ri}+\omega_s)+\gamma} \int_{-\infty}^t e^{i(\omega_{fi}+\omega_{ri}+\omega_s-\omega)t'+2i\gamma t'} \\ &\quad \times \langle (n-1)_{\omega} 1_{\omega_s} | \langle f | \hat{V}_{\sigma} \hat{a}_{\omega} | r \rangle | n_{\omega} 1_{\omega_s} \rangle dt' \\ &= \frac{2\pi M}{V} \sqrt{\frac{n}{\omega \omega_s}} \sum_r \frac{\langle f | \hat{V}_{\sigma} | r \rangle \langle r | \hat{V}_{\rho}^{\dagger} | i \rangle}{\omega_{ri}+\omega_s-i\gamma} \frac{e^{i(\omega_{fi}-\omega+\omega_s)t+2i\gamma t}}{\omega_{fi}-\omega+\omega_s-2i\gamma}, \end{aligned} \quad (\text{A5})$$

where the relationship $\omega_{fi} = \omega_{fr} + \omega_{ri}$ is used. Therefore, adding $c_{I,fi}^{(2)}$ and $c_{II,fi}^{(2)}$, the total second-order coefficient can be obtained as shown in Eq. (9).

By definition, the second-order transition rate from initial state to final state is^{39,40}

$$\begin{aligned} \Gamma_{fi}^{(2)} &= \frac{d}{dt} |c_{fi}^{(2)}(t)|^2 \\ &= \frac{(2\pi)^2 M^2 n}{V^2 \omega \omega_s} \left| \sum_r (\omega_{fi}) \right|^2 \frac{4\gamma e^{4\gamma t}}{(\omega_{fi}-\omega+\omega_s)^2 + (2\gamma)^2}. \end{aligned} \quad (\text{A6})$$

Here the definition of Eq. (10) is used. Furthermore, using the relationship

$$\lim_{\gamma \rightarrow 0} \frac{4\gamma e^{4\gamma t}}{(\omega_{fi}-\omega+\omega_s)^2 + (2\gamma)^2} = 2\pi \delta(\omega_{fi}-\omega+\omega_s), \quad (\text{A7})$$

Eq. (A6) could be rewritten as Eq. (11). It is noted that the density state of spontaneous emission is continuum and can be expressed as^{27,40,51}

$$d^3k = \frac{V \omega_s^2 M_d^2 F_P}{(2\pi c)^3} d\Omega d\omega_s. \quad (\text{A8})$$

As a result, we have

$$\Gamma_{fi}^{(2)} = \int d\Omega d\omega_s \frac{V\omega_s^2 M_d^2 F_P (2\pi)^3 M^2 n}{(2\pi c)^3 V^2 \omega \omega_s} \times \left| \sum (\omega_{fi}) \right|^2 \delta(\omega_{fi} - \omega + \omega_s), \quad (\text{A9})$$

which leads to Eq. (12). Because the flux of incident light is

$$J = \frac{nc}{V}, \quad (\text{A10})$$

according to the definition of cross section

$$\frac{d\sigma_{fi}}{d\Omega} = \frac{\frac{d\Gamma_{fi}^{(2)}}{d\Omega}}{J}, \quad (\text{A11})$$

the general differential scattering cross section for Raman processes Eq. (13) is obtained.

- ¹M. Chalfie, Y. Tu, G. Euskirchen, W. W. Ward, and D. C. Prasher, *Science* **263**, 802 (1994).
- ²E. Betzig and J. K. Trautman, *Science* **257**, 189 (1992).
- ³S. W. Hell and J. Wichmann, *Opt. Lett.* **19**, 780 (1994).
- ⁴E. Betzig, G. H. Patterson, R. Sougrat, O. W. Lindwasser, S. Olenych, J. S. Bonifacino, M. W. Davidson, J. Lippincott-Schwartz, and H. F. Hess, *Science* **313**, 1642 (2006).
- ⁵M. J. Rust, M. Bates, and X. Zhuang, *Nat. Methods* **3**, 793 (2006).
- ⁶R. M. Stöckle, Y. D. Suh, V. Deckert, and R. Zenobi, *Chem. Phys. Lett.* **318**, 131 (2000).
- ⁷M. S. Anderson, *App. Phys. Lett.* **76**, 3130 (2000).
- ⁸N. Hayazawa, Y. Inouye, Z. Sekkat, and S. Kawata, *Opt. Commun.* **183**, 333 (2000).
- ⁹B. Pettinger, G. Picardi, R. Schuster, and G. Ertl, *Electrochem. Jpn.* **68**, 942 (2000).
- ¹⁰A. Hartschuh, E. J. Sánchez, X. S. Xie, and L. Novotny, *Phys. Rev. Lett.* **90**, 095503 (2003).
- ¹¹N. Anderson, A. Hartschuh, S. Cronin, and L. Novotny, *J. Am. Chem. Soc.* **127**, 2533 (2005).
- ¹²J. Steidtner and B. Pettinger, *Phys. Rev. Lett.* **100**, 236101 (2008).
- ¹³T. Ichimura, S. Fujii, P. Verma, T. Yano, Y. Inouye, and S. Kawata, *Phys. Rev. Lett.* **102**, 186101 (2009).
- ¹⁴T.-A. Yano, P. Verma, Y. Saito, T. Ichimura, and S. Kawata, *Nat. Photonics* **3**, 473 (2009).
- ¹⁵J. Stadler, T. Schmid, and R. Zenobi, *Nano Lett.* **10**, 4514 (2010).
- ¹⁶R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang, and J. G. Hou, *Nature* **498**, 82 (2013).
- ¹⁷C. Chen, N. Hayazawa, and S. Kawata, *Nat. Commun.* **5**, 3312 (2014).
- ¹⁸J. M. Atkin and M. B. Raschke, *Nature* **498**, 44 (2013).
- ¹⁹S. Duan, G. Tian, Y. Ji, J. Shao, Z. C. Dong, and Y. Luo, *J. Am. Chem. Soc.* **137**, 9515 (2015).
- ²⁰A. C. Albrecht, *J. Chem. Phys.* **34**, 1476 (1961).
- ²¹J. Neugebauer, M. Reiher, C. Kind, and B. A. Hess, *J. Comput. Chem.* **23**, 895 (2002).
- ²²D. J. Masiello and G. C. Schatz, *Phys. Rev. A* **78**, 042505 (2008).
- ²³S.-Y. Lee, D. Zhang, D. W. McCamant, P. Kukura, and R. A. Mathies, *J. Chem. Phys.* **121**, 3632 (2004).
- ²⁴J. J. Sakurai, *Advanced Quantum Mechanics* (Addison-Wesley Publishing Company, Reading, MA, 1967).
- ²⁵M. O. Scully and M. S. Zubairy, *Quantum Optics*, 1st ed. (Cambridge University Press, Cambridge, New York, 1997).
- ²⁶D. A. Long, *The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules* (Wiley, Chichester, New York, 2002).
- ²⁷E. Le Ru and P. Etchegoin, *Principles of Surface-Enhanced Raman Spectroscopy: And Related Plasmonic Effects*, 1st ed. (Elsevier, Amsterdam, Boston, 2009).
- ²⁸S. Duan, G. Tian, and Y. Luo, *Angew. Chem., Int. Ed.* **55**, 1041 (2016).
- ²⁹S. Duan, G. Tian, and Y. Luo, *J. Chem. Theory Comput.* **12**, 4986 (2016).
- ³⁰M. Sun, Z. Zhang, L. Chen, S. Sheng, and H. Xu, *Adv. Opt. Mater.* **2**, 74 (2014).
- ³¹L. Meng, Z. Yang, J. Chen, and M. Sun, *Sci. Rep.* **5**, 9240 (2015).
- ³²C. Zhang, B.-Q. Chen, and Z.-Y. Li, *J. Phys. Chem. C* **119**, 11858 (2015).
- ³³M. Barbry, P. Koval, F. Marchesin, R. Esteban, A. G. Borisov, J. Aizpurua, and D. Sánchez-Portal, *Nano Lett.* **15**, 3410 (2015).
- ³⁴S. Jiang, Y. Zhang, R. Zhang, C. Hu, M. Liao, Y. Luo, J. Yang, Z. Dong, and J. G. Hou, *Nat. Nanotech.* **10**, 865 (2015).
- ³⁵S. Luber and M. Reiher, *Chem. Phys.* **346**, 212 (2008).
- ³⁶D. V. Chulhai and L. Jensen, *J. Phys. Chem. C* **117**, 19622 (2013).
- ³⁷W. Hu, S. Duan, and Y. Luo, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **7**, e1293 (2017).
- ³⁸F. Jensen, *Introduction to Computational Chemistry* (John Wiley & Sons, Chichester, England, Hoboken, NJ, 2007).
- ³⁹R. Shankar, *Principles of Quantum Mechanics*, 2nd ed. (Plenum Press, New York, 1994).
- ⁴⁰N. Zettili, *Quantum Mechanics: Concepts and Applications*, 1st ed. (Wiley, Chichester, New York, 2001).
- ⁴¹J. D. Jackson, *Classical Electrodynamics*, 3rd ed. (Wiley, New York, 1998).
- ⁴²M. S. Tame, K. R. McEnery, Ş. K. Özdemir, J. Lee, S. A. Maier, and M. S. Kim, *Nat. Phys.* **9**, 329 (2013).
- ⁴³A. Parkins, "Single-atom transistors for light" in *Fundamentals of Pico-science* (CRC Press, 2013), pp. 635–654.
- ⁴⁴W. Zhu, R. Esteban, A. G. Borisov, J. J. Baumberg, P. Nordlander, H. J. Lezec, J. Aizpurua, and K. B. Crozier, *Nat. Commun.* **7**, 11495 (2016).
- ⁴⁵J. A. Kong, *Electromagnetic Wave Theory*, 2nd ed. (Wiley, New York, 1990).
- ⁴⁶A. Archambault, F. Marquier, J.-J. Greffet, and C. Arnold, *Phys. Rev. B* **82**, 035411 (2010).
- ⁴⁷J. Olsen and P. Jørgensen, *J. Chem. Phys.* **82**, 3235 (1985).
- ⁴⁸P. A. M. Dirac, *Proc. R. Soc. London, Ser. A* **114**, 710 (1927).
- ⁴⁹S.-Y. Lee and E. J. Heller, *J. Chem. Phys.* **71**, 4777 (1979).
- ⁵⁰F. J. Dyson, *Phys. Rev.* **75**, 1736 (1949).
- ⁵¹E. M. Purcell, *Phys. Rev.* **69**, 681 (1946).
- ⁵²H. A. Kramers and W. Heisenberg, *Z. Phys.* **31**, 681 (1925).
- ⁵³M. Born and R. Oppenheimer, *Ann. Phys.* **389**, 457 (1927).
- ⁵⁴Z.-Y. Gong, G. Tian, S. Duan, and Y. Luo, *J. Chem. Theory Comput.* **11**, 5385 (2015).
- ⁵⁵G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ⁵⁶M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *GAUSSIAN 09*, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.
- ⁵⁷P. Macak, Y. Luo, and H. Ågren, *Chem. Phys. Lett.* **330**, 447 (2000).
- ⁵⁸G. Tian, S. Duan, G.-P. Zhang, W. Hu, and Y. Luo, *Phys. Chem. Chem. Phys.* **17**, 23007 (2015).
- ⁵⁹T. B. Pedersen and A. E. Hansen, *Chem. Phys. Lett.* **246**, 1 (1995).
- ⁶⁰S. Obara and A. Saika, *J. Chem. Phys.* **84**, 3963 (1986).
- ⁶¹X. H. Qiu, G. V. Nazin, and W. Ho, *Science* **299**, 542 (2003).
- ⁶²S. Duan, G. Tian, and Y. Luo, First-principles Approaches for Surface and Tip Enhanced Raman Scattering (FASTERS), version 1.0, Royal Institute of Technology, Sweden, 2016.