Deducing the Adsorption Geometry of Rhodamine 6G from the Surface-Induced Mode Renormalization in Surface-Enhanced Raman Spectroscopy

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ABSTRACT: Surface-enhanced Raman spectroscopy probes adsorbates on a plasmonic substrate and offers high sensitivity with molecular identification capabilities. In this study, we present a refined methodology for considering the supporting substrate in the computation of the Raman spectra. The supporting substrate is taken into account by employing a periodic slab model when doing the geometry optimization and normal mode analysis, and then the Raman spectrum is calculated for the isolated molecule but with the normal modes from the surface structure. We find that the interaction with the surface induces internal distortion in the molecule, and spectral shifts in the computed Raman spectrum. By comparing a low temperature surface-enhanced Raman spectroscopy measurement of Rhodamine 6G (R6G) with the computed Raman spectra of a series of adsorption geometries, we propose that the binding state captured in the experiment tends to possess the least internal distortion. This binding state involves upward orientation of ethylamine on R6G, and our calculations indicate that this is the lowest energy adsorption structure. Following this route, it is possible to infer both a molecular orientation and an adsorption geometry of the molecule from its Raman spectrum. Importantly, we note that, if the substrate correction is established to play a role, we also discuss that this corrected approach still has several shortcomings that significantly limit its overall accuracy in comparison with experimental spectra.

INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS)†‡ is a well-established and powerful spectroscopic tool for acquiring vibrational properties of molecules adsorbed on surfaces of plasmonic nanostructures such as nanoparticles (NP), metallic films on nanosphere (MFON), and so on. It is well-known that the Raman scattering signal in SERS is significantly amplified by many orders of magnitude (compared to the traditional Raman experiment of molecules in solution) due to the huge electromagnetic enhancement offered by the plasmonic substrate.‡ When combined with the resonance enhancement of some dye molecules (due to molecular electronic excitation), SERS can detect and identify the Raman spectrum of a single molecule. Rhodamine-6G (R6G) adsorbed on a silver nanoparticle (AgNP) is such a system, regarded as the first success of single molecule SERS (SMSERS) detection.¶,† In principle, the SERS signal of an adsorbed molecule is directly correlated with adsorption geometry. Accordingly, one can imagine identifying this geometry from a careful analysis of the Raman spectrum. To do so by a comparison of theory and experiment, computation of the Raman spectrum requires consideration of the effect of the metal substrate. However, the

Recently, R6G has been used in combination with SERS to demonstrate single (few) molecule electrochemistry experiments.‡ To interpret these results, we showed‡ that R6G can adsorb in many different geometries on a silver surface. This leads to a large distribution of reduction potentials, as observed experimentally.‡ For each single molecule electrochemical event, the reduction of R6G is monitored by watching the SMSERS signal loss. Although a relationship is established between adsorption geometries and the reduction potential distribution, the association of an individual reduction event with a specific binding geometry is still lacking. Such a relationship at the single molecule level is of great interest both for understanding the electron transfer process at the nanoscale and for the design of highly efficient electrocatalytic electrodes.

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currently reported Raman spectra of R6G in the literature were only calculated for its gas phase geometry,16–18,20 and in fact it is extremely challenging to calculate Raman spectra that include more than a few atoms in the metal substrate.

In this study, we consider the effect of substrate in the computation of Raman spectra with a slab model (Figure 1). Our computational procedure considers interaction of R6G with the substrate during geometry optimization and the normal modes evaluation. This allows for investigating the effect of adsorption geometry variations on the Raman signature of R6G, as adsorbed on a Ag-(111) surface. The consideration of the interaction with such a large substrate lies at the current edge of the ab initio normal mode capabilities for adsorbed molecules, due to a high computational cost. Although the interaction with the substrate is still neglected in the computation of the molecular polarizabilities, the induced changes in the normal mode frequencies are captured. We observe that the interaction with the substrate may significantly distort the molecule and consequently induce spectral shifts in the corresponding Raman spectrum. By comparing our several results with low temperature SERS (LT-SERS) experiments for R6G done in ultrahigh vacuum,14 we show that the least distorted configuration, which also has the strongest adsorption, is the most likely one to be probed during the SERS experiment. This fact offers a pathway to infer geometrical details of the adsorbate, allowing us to exploit the information contained in the Raman signal to determine the adsorption geometry of the molecule. However, the quantitative prediction of the Raman spectrum is still limited by a few shortcomings that exist at both theoretical and experimental levels.

**METHODOLOGY AND COMPUTATIONAL DETAILS**

In the commonly reported procedure for calculating the Raman spectrum, the optimized geometry and normal modes of the molecule are obtained in a first computational step. The polarizability derivative and the Raman scattering cross section of each normal mode are then computed with a linear response time-dependent density functional theory (LR-TDDFT) method22,25 in a second step.22,24 This procedure has been applied for commonly used dye molecules in SERS, e.g., R6G and Nile Blue, and good agreement with experimental spectra has been demonstrated.2,19 In this study, we refine the first computational step by including the interaction between the metal surface and the adsorbed molecule.

To describe the substrate, either a cluster model or a periodic slab model could be considered. Intuitively, a cluster is a reasonable atomistic model for a AgNP. However, we opted for a slab model that we used in a previous study.21 This is motivated by three main reasons. First, the AgNPs used in the SERS experiment range from 20 to 100 nm in diameter.15 Nonetheless, only clusters made of a small number of metallic atoms are tractable computationally. For example, several studies of the pyridine-Ag_{50} system using ab initio methods have been reported in the literature.27–31 Although these studies provided some fruitful insights into the molecule–substrate interaction, a Ag cluster exhibits a discrete electronic spectrum. On the contrary, the nanoparticles employed experimentally are much larger than those considered previously, and possess a bulk-like electronic structure.32,33 Therefore, a cluster approach will not be able to accurately reproduce the energetic state of the adsorbate. Second, the small size of R6G (\sim 1 nm) makes the periodic slab a good approximation of the nanoparticle surface. Third, it has been demonstrated experimentally that transition metal nanoparticles exhibit well-defined crystal facets.34–36 Noteworthy, the (111)-like facet is frequently observed for silver nanoparticles.37–39

The slab model is introduced using periodic boundary conditions, with a unit cell that includes the R6G molecule and two (111) silver layers (144 atoms) and of 25.8 \times 19.9 Å^2 dimensions. These layers are frozen during the geometry optimization and the normal mode evaluation. The consideration of such a large sized silver surface might constitute a current limit in terms of computational resources. We rely on a plane-wave basis set as implemented in the Vienna Ab initio Simulation Package (VASP).40,41 The electronic structure is computed at the DFT/PBE level of theory.42 The missing dispersion effect is corrected by the Tkatchenko-Scheffler (TS) scheme.43 This dispersion correction scheme has proven its validity in our previous study,21 which overcame the failure of PBE in describing the physisorption of R6G on the Ag surface. More details on this computational procedure are given in our previous study and in the Supporting Information. All the normal mode frequencies are rescaled by a factor of 1.01 to account for the missing anharmonicity. This rescaling factor was determined at our level of theory by following an established and widely used procedure44–46 on the basis of a molecule database set compiled by Alecu et al.46 (see the Supporting Information for details). The resonant Raman scattering cross section is then computed for each normal
mode at the TDDFT/B3LYP level of theory, using a 6-311G** basis set, as implemented in the AOResponse module of the NWChem DFT package. An excitation with a laser wavelength of 532 nm is used for the consistency with the experiment.\textsuperscript{23,47,48} The scattering cross section is computed for the isolated R6G with the adsorption geometry obtained in the first computational step, after the removal of the silver surface. The silver slab is excluded here due to the extreme computational cost. However, this approximation is not expected to lead to large deviations in the overall Raman signals because the component of chemical enhancement due to charge transfer, which is usually observed upon covalent bonding, can be neglected for physisorbed molecules like R6G.\textsuperscript{27} Still, due to the lack of surface enhancement in the calculation of the polarizability derivatives, we stress that our proposed method does not intend to quantitatively reproduce the relative intensities of the characteristic Raman peaks.

Figure 2. (a) Raman spectrum of R6G taken from the chosen LT-SERS experiment (Adapted with permission from ref 14. Copyright 2014 American Chemical Society). Nine characteristic modes are labeled alphabetically. Computed Raman spectra of (b) isolated R6G, (c) adsorbed R6G on Ag slab in ethylamine down geometry, (d) adsorbed R6G on Ag slab in twisted flip geometry, and (e) adsorbed R6G on Ag slab in ethylamine up geometry. Characteristic modes are marked with their corresponding frequencies in figures from (a) to (e).
In this study, we compare our simulations with the Raman spectrum of R6G obtained in a low temperature, ultra-high-vacuum SERS (LT-SERS) experiment. By choosing LT-SERS, we aim at simplifying the investigation of the adsorbate–substrate interaction by excluding solvent and thermal effects which are present in ambient, room temperature SERS. These effects make it much more difficult to find the source of inconsistency between simulations and the experiments. In our atomistic model of R6G-AgNP, the interslab space is assumed to be vacuum. Also, the optimized geometry obtained by the conjugate gradient algorithm is expected to correspond to the ground state at absolute zero temperature. Thus, our atomistic model agrees with the experimental conditions associated with LT-SERS. Note-worthy, the chosen low temperature Raman spectrum also agrees reasonably well with room temperature ambient SERS experiments for R6G.

The experimental spectrum of the chosen LT-SERS measurement (green line) is presented in Figure 2a. Nine characteristic peaks of R6G (at 1652, 1608, 1579, 1512, 1364, 1318, 1187, 775, and 614 cm$^{-1}$) are marked by corresponding wavenumbers and labeled from A to I for convenience. These vibrational modes are chosen because they can be recognized in SERS experiments under different conditions.

We start the discussion with an analysis of the Raman spectrum of the isolated R6G in its gas phase geometry. This calculation excludes the silver surface in the first computational step. We note that this calculation assumes a starting geometry with the ethylamine groups pointing in the direction that is opposite to the tail of the phenyl group, as highlighted by a circle in Figure 5. This geometry has been commonly used in previous theoretical characterizations of R6G. As illustrated in Figure 2b, the computed Raman spectrum of isolated R6G presents a spectrum that matches well with the experiment. All of the nine characteristic peaks can be recognized from the computed Raman spectrum. The mode frequencies differ from the corresponding experimental values by less than 6 cm$^{-1}$ for 6 of the 9 modes. Only the reported frequencies for mode A and mode G are off by more than 10 cm$^{-1}$. We note that mode G may also be a combination of two modes that lie at 1173 and 1201 cm$^{-1}$, as discussed below. The computed frequency of mode C is off by 9 cm$^{-1}$, if we attribute it to the mode at 1569 cm$^{-1}$. We will further discuss these three modes in the next paragraphs.

The success of the isolated molecule model is consistent with several computed Raman spectra of R6G using similar methodologies. This suggests that the adsorbate observed in the experiment should not differ significantly from its gas phase geometry. This indication provides us a helpful guideline in selecting the most appropriate adsorption geometry for computing the Raman spectrum of R6G, as presented below.

Before proceeding to the calculation that includes the metal surface, we stress that, due to the neglect of the substrate in the computation of polarizability derivatives, our comparison between simulated Raman spectra and LT-SERS is mainly focused on the spectral positions of the chosen characteristic peaks. Despite being used as a well-established technique to detect and identify molecular adsorbates, we acknowledge that SERS experiments can suffer from reproducibility issues, including the position of characteristic peaks. This is especially true considering that different substrates or solvents are regularly used in different experimental setups. In this context, it is important to highlight here that we focus on a specific substrate, in ultra-high-vacuum conditions, which greatly increases the reproducibility of SERS experiments.

Moreover, the RT-SERS (room temperature) spectrum is compared to the LT-SERS spectrum in our experimental reference. This comparison shows a limited decrease of the peak broadening about 12% on average. As some broadening remains at low temperature, it is not of thermal nature. Importantly, this broadening is further reduced significantly, about 50% on average, when using the LT-TERS characterization technique. As this technique intrinsically reduces the number of sampled molecules ($\leq10^4$ in TERS vs $\sim10^9$ in SERS) by a very large factor, it is reasonable to assume that the broadening of the peaks in the LT-SERS experiment is given by an accumulation of signals emitted by molecules in slightly different adsorption geometries.

Since the isotropic contributions of the polarizability derivatives are dominant in SERS, the Raman scattering is not sensitive to the relative molecular orientation and we can reasonably assume that the ensemble of molecules probed during the experiment ($\sim10^9$) generates an equivalent scattering intensity. For these reasons, we assume here that the SERS experimental Raman signal is dominated by the most energetically favorable configuration and the binding state energy plays an important role to determine this configuration. Our choice of the Ag-(111) slab is thus further justified as it is the most stable exposed facet of the AgNP surface.

The crooked shape of R6G leads to several different adsorption geometries as was suggested in our previous work. Regarding the molecular orientation, our previous study revealed that the “parallel” geometry of R6G (shown in Figure 5c) is the most stable binding state on the Ag-(111) surface among a large number of tested configurations. Therefore, this binding state is chosen as the first attempt to simulate the Raman spectrum for LT-SERS. The fact that the “parallel” geometry is the least distorted geometry among all the possible binding geometries we tested on the Ag-(111) surface also makes it a reasonable choice for assessing the Raman signature of R6G captured in the experiment. In the later discussion, this “parallel geometry” will be referred to as the “ethylamine down” configuration for convenience, because its two ethylamine groups point downward onto the silver surface.

We note that the geometries in our previous study were assessed “on the fly”; i.e., we optimized the geometry of the molecule adsorbed on the surface, starting from a set of intuition-driven geometries. Then, we compared the obtained set of adsorption energies, after convergence of the optimization algorithm. A better approach would be a “thermal annealing” procedure, allowing for a direct determination of a global minimum structure, given by the possibility to overcome potential energy barriers. Unfortunately, the size of our system renders molecular dynamics approach computationally intractable. We then envision the determination of the adsorption geometry as a trial and error procedure, guided by the adsorption energy and the comparison between simulated and measured Raman spectra. This is the procedure that we follow in this paper.

From a calculation that includes the metal surface, we compute the Raman spectrum of the “ethylamine down” configuration, as represented in Figure 2c (with comparison to the isolated molecule calculation). This shows that interaction...
with the surface does not lead to obvious changes in the overall Raman spectrum concerning the spectral locations and the relative intensities of the modes (when neglecting the substrate in the computation of the polarizability derivatives). This generally indicates that the “ethylamine down” configuration is a reasonable assumption for the R6G configuration probed in SERS.

By comparing Figure 2c to the isolated molecule spectrum Figure 2b, only modes A and I show large mode frequency changes (>10 cm\(^{-1}\)), apart from mode C that is discussed below. The “ethylamine down” configuration gives these two modes at 1655 and 619 cm\(^{-1}\), respectively. The accuracy of mode A is significantly improved while mode I is still off the experiment by 4 cm\(^{-1}\) (vs 5 cm\(^{-1}\) for the isolated molecule calculation). According to the mode visualization obtained for the isolated molecule model (Figure S2), mode A corresponds to a xanthene plane deformation and mode I is associated with in-plane stretching in the xanthene plane and the phenyl ring. Our assignment is consistent with previous studies.\(^{14,17,18}\)

Therefore, the spectral shift of mode A is an indicator of the substrate—adsorbate interaction, which is dominated by the xanthene/silver van der Waals interactions, as also noted in our previous work.\(^{21}\) The spectral shift of mode I may be affected by the distortion of the molecule as this latter has contributions of both the xanthene and the phenyl planes, while the angle between these two parts is clearly distorted, as evidenced by a comparison between spectra (b) and (c) in Figure 2.

In the computed Raman spectrum of the isolated R6G, the frequencies of modes A, C, and G do not follow the experiment. The comparison between the Raman spectra of isolated R6G and the “ethylamine down” configuration reveals that the unsatisfied predictions in these modes are caused by different reasons.

First, the prediction of mode A is off the experimental value by 12 cm\(^{-1}\) due to the missing adsorbate—substrate interaction. Indeed, it is only off by 3 cm\(^{-1}\) in the “ethylamine down” configuration. Such an improvement in mode A then corroborates the necessity and validity of the surface inclusion. By considering the isolated molecule model as a weak binding state, it is reasonable to postulate that both 1655 and 1664 cm\(^{-1}\) may be observed in the experiment if the binding strength could be weakened due to an external disturbance, e.g., thermal fluctuation. This postulate is consistent with the experimental data in the seminal paper by Nie and Emory.\(^{4}\) Figure 5 in this reference, and reproduced here in Figure 3, presented nine Raman spectra taken from the same nanoparticle captured at different times. According to the assumption made in that paper, there was only one molecule on each nanoparticle. These nine Raman spectra exhibited an abrupt change in Mode A from 1653—1655 cm\(^{-1}\) to 1661—1664 cm\(^{-1}\) together with a reduction in the mode intensity. This is consistent with a partial desorption, according to our simulations.

Second, the deviation in mode C could be attributed to a failure of our methodology in evaluating its correct Raman intensity. The normal mode evaluation in fact shows a mode at 1580 cm\(^{-1}\) for the isolated molecule. This mode is more likely the origin of mode C, but is unidentifiable in the spectrum due to its limited intensity. Our mode visualization (see the Supporting Information) shows that the mode at 1570 cm\(^{-1}\) is associated with a xanthene plane deformation, while the mode at 1580 cm\(^{-1}\) is a motion of the lower phenyl ring. This specific motion has been assigned to mode C in previous studies.\(^{14,17}\)

Here, we choose to adopt the same assignment: mode C is the mode at 1580 cm\(^{-1}\). This means that we consider that the mode intensities in an approximate region in between 1555 and 1585 cm\(^{-1}\) are not qualitatively accurate. Indeed, the intense theoretical peak at 1570 cm\(^{-1}\) is not observed experimentally. The same situation occurs in the “ethylamine down” configuration. A tiny peak is given by the normal mode evaluation at 1576 cm\(^{-1}\) and an intense peak lies at 1561 cm\(^{-1}\).

We suspect that the qualitatively correct intensities in this region may only be captured by a model including the chemical enhancement effect,\(^{22}\) i.e., the interaction with the surface in the polarizability derivative calculation.

Third, we suspect that mode G originates from the addition of the two modes at 1173 and 1200 cm\(^{-1}\). Indeed, we observe that, among the nine modes we discuss here, these two are among the least affected ones by the metal/molecule interaction. However, mode G is also the mode that is the most broadened at the experimental level (26 cm\(^{-1}\) in comparison to 12 cm\(^{-1}\) for mode I for instance), which we cannot explain by fluctuation in the metal/molecule interaction. This highly suggests that mode G is a superposition of

![Figure 3. Time-resolved surface-enhanced Raman spectra from a single molecule characterization of R6G, recorded at 1 s intervals (Reproduced from Figure 5 in ref 4). These SERS signals are measured at room temperature from a single adsorbed molecule on a Ag colloidal substrate in water. For more experimental details, refer to ref 4.](Image 324x385 to 564x749)
two modes having similar wavenumbers and Raman intensities, such as the modes at 1173 and 1200 cm⁻¹.

Among the nine modes, we observe that the inclusion of the metal surface only improves the experimental agreement for mode A, in comparison with a simpler isolated molecule calculation. Strikingly, modes C, E, and F are all in better agreement for the isolated molecule calculation. A careful examination of the “ethylamine down” configuration indicates that the xanthene plane and its angle with respect to the phenyl ring are significantly distorted. The distortion is due to the van der Waals attraction between this plane and the silver surface, together with steric repulsion between the surface and ethylamine and phenyl groups; see Figures 4 and 5c. We consider that this distortion could be at the source of this inconsistency and, likely, it could prevent us from getting good agreement with the experimental data, in comparison with the isolated configuration. Such a consideration is consistent with the computed Raman spectrum of a much more severely distorted binding state which was labeled as “twisted flip” in our previous work²¹ and results from a flip of the “ethylamine down” configuration. As is shown in Figure 2d, this configuration leads to worse experimental agreement, in comparison with the “ethylamine down” configuration. It completely misses the modes B and F, broadens mode E, and does not give better predictions for the other modes. The bad performance of the “twisted flip” configuration confirms the hypothesis that reducing the internal distortion in the molecule is an important feature to determine the adsorption state. It also demonstrates that twisted flip configurations are to be excluded, in agreement with their lower adsorption energy (2.00 eV for the twisted flip configuration vs 2.18 eV for the “ethylamine down” configuration, as computed at the DFT/PBE+TS level of theory in ref 21).

Taking the distortion into account, it is worthwhile to realize that the ethylamine groups connect to the xanthene plane by a σ bond in sp³ geometry. Each ethylamine group is thus able to rotate around this bond without experiencing a significant energy barrier.⁴⁹,⁵⁰ This observation suggests a new possible configuration of adsorbed R6G in which the ethylamine groups could point in the opposite direction: “ethylamine up” (see Figure 5d). The distortion in the xanthene plane is expected to be significantly reduced for this configuration, and this motivates us to study the adsorption properties of this new configuration, following our trial and error procedure.

As expected, the computed adsorption energy of the “ethylamine up” configuration is larger than the “ethylamine down” configuration by 0.33 eV; see Figure 5. We used the same procedure as given in our previous work to compute the adsorption energy.⁶ We note that twisting the ethylamine groups up even lowered the energy of the molecule in gas phase by 0.002 eV. By decomposing the adsorption energy using the method adopted in our previous study, it is revealed that the “ethylamine up” configuration reduces the internal distortion by 0.24 eV and increases the interaction with the surface by 0.09 eV, in comparison with the “ethylamine down” configuration. The distortion in the xanthene plane is highly reduced as can be observed in Figures 4 and 5. Therefore, this new configuration is a more probable binding geometry.

Looking at the computed Raman spectrum, we observe that the “ethylamine up” configuration matches with “ethylamine down” in all the highlighted modes, except for some minor shifts (<2 cm⁻¹) that are seen for modes D, E, F, and I, with respect to the experiments. The prediction at mode I is improved from 619 to 614 cm⁻¹ which is a perfect agreement with the experimental result in Figure 2a. This change from 619 cm⁻¹ to a lower wavenumber shows the right trend in comparison with the “ethylamine up” configuration, since Mode I is observed at mode frequencies equal to or less than 615 cm⁻¹ in most experiments.³⁰,¹²,¹⁴–¹⁶ We show in the Supporting Information (Figure S1) that the twist of the ethylamine group does not lead to any shift in normal mode energies of the isolated molecule. This leads to the conclusion that both the twisted ethylamine groups and the consideration of the metal/molecule interaction are responsible for the more accurate prediction of modes D, E, F, and I. Importantly, we lose a bit of accuracy for mode A by 3 cm⁻¹, in comparison to the experimental spectrum. This is the only mode that is in poorer agreement with experiment in this structure, and we note that the metal-induced renormalization of this mode is still present for this “ethylamine up” configuration.

Considering our characterization of the simulated Raman spectrum of the “ethylamine up” configuration, together with its higher adsorption energy, our calculations suggest that the
R6G molecules are mainly adsorbed on the silver surface in a parallel configuration with the tail of the phenyl ring pointing out from the surface. In this case, there is very limited distortion, which is a configuration that cannot be achieved for "ethylamine down". This directly suggests that the molecule is adsorbed with the ethylamine group pointing up from the silver surface.

To be complete, our discussion also shows that it is a challenging problem to determine the adsorption geometry from a comparison between a simulated and measured Raman spectra. Indeed, we observe that the correction given by the inclusion of the metal surface, despite generating a much larger computational cost, remains limited. Only three peaks (A, D, and I), among the nine peaks we identified, are improved by more than 2 cm⁻¹, in comparison with the isolated molecule and the experimental SERS signal. Moreover, the agreement for modes C and E is actually better in the isolated molecule configuration.

This shows that significant inaccuracies are still present in our study, and therefore, we consider that our assigned geometry constitutes a reasonable suggestion, but with room for improvement. We believe that this limited success is due to several shortcomings of the computational methodology. First, the relative mode intensities that we compute are not in quantitative agreement, which could lead to a mode misidentification, as we suggest being the case for mode C. Second, the silver surface is kept frozen during our normal modes calculation, which cannot account for modes that delocalize on both the metal and the adsorbent. Third, semilocal exchange-correlation functionals possess notorious errors, which could be corrected using more sophisticated hybrid functionals but at greater cost. Fourth, a coupling between the modes, which goes beyond the harmonic approximation, might further modify a few peak positions. However, at the present stage of ab initio computational techniques, the correction of each of these shortcomings associates with a computational cost that is very likely to be prohibitive. This issue confers a high interest in parametrized or empirical quantum chemistry methods.

To finish this discussion, we stress that, even though there are expected quantitative shortcomings, the fact that the surface–molecule interaction leads to a significant distortion of the molecule, and that it should be observable in the Raman spectrum, constitutes a qualitative trend, which we consider is well captured by our level of DFT calculations.

**CONCLUSION**

To summarize, we propose in this paper that the R6G molecule-substrate system probed in the SERS experiment can be characterized by combining a periodic slab model with existing methodology for calculating SERS spectra. We find that inclusion of the slab does not drastically improve the predicted Raman spectra compared to the previous isolated molecular models. We interpret this as a direct demonstration that the R6G molecules probed in the SERS experiment possess very limited distortion from the gas phase structure. This observation can be further used as a guideline toward identification of the adsorption geometry.

Following this reasoning, we conclude that the R6G molecule adsorbs on the silver surface with the xanthene plane lying parallel and both the tail of the phenyl group and the ethylamine groups pointing up from the surface. This is on the basis of a better agreement between simulated and experimental Raman spectra, but is also evidenced by a higher computed adsorption energy. We believe that this reasoning can be applied to other systems of interest, which paves the way to directly probe the adsorption geometry of the reactant in SM-SERS experiments. We note, however, that it constitutes a complex challenge, which was here greatly facilitated by the fact that we based our reasoning on a low temperature and high-vacuum experimental SERS acquisition. We believe that another factor that could facilitate this comparison would be to tether the molecule to the metal substrate, with a chemical group.

While some mode energies can be improved after consideration of the substrate, our approach possesses several shortcomings, such as the lack of the interaction with the substrate when calculating the polarizability derivatives. Therefore, the relative intensities of a few peaks may be questionable, after comparison with the experimental spectrum. A possibility to overcome this weakness might be given by the replacement of our second computational step by another computational scheme that would include the interaction with the plasmonic surface.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b09441. Computational details; computed Raman spectra of isolated R6G in "ethylamine down" and "ethylamine up" configurations; modes assignments for characteristic modes of R6G; data set employed for determining rescaling factor (PDF)

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**Notes**

The authors declare no competing financial interest.

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