Computational study of SERS effects in some aliphatic and cyclic carboxylic acids with silver nanomaterials

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Abstract. Quantum chemical calculations have been shown to provide convenient means in estimating surface-enhanced Raman scattering (SERS) spectral shifts and the adsorption possibilities associated with such shifts. In a recent work, the computed Raman spectra provided very good agreement with the experimental results for valeric acid. To attain a conclusive picture of the Raman shifts in related molecules, namely, butyric acid, caproic acid, γ-butyrolactone, γ-valerolactone and γ-caprolactone, full optimizations and frequency calculations have been carried out. The vibrational frequency shifts caused by the interaction of these molecules with the Ag₄ cluster simulate the experimental shifts with silver nanoparticles (AgNPs). The most prominent shift noticed is in the case of γ-caprolactone through its ether C-O-C group interacting with the silver cluster. Such a shift may be due to the +I effect of the alkyl side chains and corresponds to a theoretical interaction energy and distance of -12.92 kcal/mol and 2.45Å, respectively.

1. Introduction

The implementation of advanced computational techniques, and in particular the use of Density Functional Theory (DFT) approach, to better interpret vibrational spectra of small organic molecules is well-established [1, 2]. When properly adopted, computational methods along with suitable scaling factors would provide great help in identifying the most probable conformations, carrying out conclusive vibrational mode assignments and predicting the spectral features [3, 4]. For the cases where coordinated covalent bonding in inorganic complexes or interactions of organic systems with metal-containing nanomaterials are of interest, density functionals coupled with basis sets capable of describing the relativistic effects in heavy elements can also provide reliable results [5, 6]. Vibrational mode assignments assisted with the calculated spectral details brought good basis to assess metal-olefin [7] and functional group-nanomaterial [8] interactions.

One area which has increasingly attracted the attention is the prediction of surface-enhanced Raman scattering (SERS) spectra that result from the interaction of organic analytes with active substrates normally composed of silver or gold nanoparticles. SERS approach has been known to be attractive for chemists and materials scientists in the trace-level molecular detection as well as useful in various fields of applied material sciences, including biomedical, food and water. Since the driving factor for SERS effect is the interaction at the atomisic level, first-principle calculations are currently employed to shed light on the nature and
spectral properties emanated from such interactions [9, 10]. For instance, T. You et al. through a comprehensive DFT evaluation demonstrated the effect of changing the graphene type and doping it with boron and nitrogen atoms on the properties of interaction of 1,3-benzenedithiol with the modeled substrate [10].

Recently, we reported SERS investigations of a number of important organic-based compounds [11-13] including valeric acid (pentanoic acid) [11] which is mostly used as a food flavor. A very low detection limit competing with those achieved by conventional analytical techniques was successfully established. What is important here is that in all of these studies DFT assessments of the SERS spectra have been reliably performed and deemed to be extremely useful in predicting the most dominant modes of interaction [11-13]. Hence, we have extended similar theoretical evaluations to explore aliphatic and cyclic analogues of valeric acid (Fig. 1). Preliminary results on comparative basis addressing the influence of the functional groups, adsorption energy, molecular orientation, and aliphatic and cyclic properties exhibited by these molecules have been presented.

![Figure 1: Aliphatic and cyclic carboxylic acids investigated in this work.](image)

2. Methodology

The GAUSSIAN 09 [14] suit was utilized to carry out all theoretical calculations adopting the hybrid B3LYP functional introduced by Becke [15, 16] and Lee et al. [17]. While the basis set 6-311++G(d,p) basis set is used for non-metals, the Stuttgart/Dresden (SDD) basis set was included to describe the silver atoms. These basis sets were selected due to their cost-effective protocol and ability to assent to experimental results of valeric acid interacting with silver atoms being modeled as an Ag₄ complex [11]. The aqueous solution was simulated by implementing the Polarizable Continuum Model (PCM) [18]. Full optimization of the six carboxylic acids (Fig. 2) to identify their global minima were carefully performed.

Further, harmonic frequency and infrared/Raman intensity calculations were conducted at the same basis sets to ascertain the nature of convergence of the molecule-silver complex and to provide rational assignments of the associated vibrational modes. Molecular-level interaction studies of the acid molecules and the metal nanoparticles through the hydroxyl, carboxyl and ether functional groups were conducted. For successfully converged interactions, the magnitudes of interaction energies were quantified using the following equations:
where $E_{\text{binding}}$, $E_{\text{complex}}$, $E_{\text{Ag}_4}$, and $E_{\text{molecule}}$ denote the free energies of silver-molecule complex, silver cluster, and isolated molecule, respectively.

3. Results and Discussion

Optimized geometries of the studied compounds are depicted in Fig. 2. Notably, all compounds adopt $C_1$ symmetry, since they lack higher symmetry aspects other than the identity element ($E$). As reported in a previous work [11] where we carried out comprehensive quantum chemical molecular interaction studies in order to investigate possible scenarios giving rise to the SERS effects of silver nanoparticles on valeric acid (VA), interaction of silver atoms with the carboxylic moiety of VA led to a significant enhancement in Raman signals. Ultimately such an interaction allows to attain a lower detection limit for the quantification of VA in aqueous media. Wondering about the influence of the molecular size and functional groups on the nature of such an interaction, in the present study a theoretical SERS evaluation was extended to cover aliphatic and cyclic derivatives of VA with the aim of gaining more insights into the role played by the side chains and functionalities on the plasmonic properties of silver nanoparticles and how this affects the wavenumber shifts.

Three feasible interaction modes were optimized, namely with the hydroxyl (Ag---HO), the ether (Ag---COC) and the carboxylic (together Ag---HO and Ag---CO) groups. The computed binding energies (Table 1) revealed that CLC exhibited the highest interaction with an energy of -12.90 kcal/mol via the ether oxygen. Other molecules showed comparable energies. Interestingly however, the cyclic compounds gave higher energies when the interaction via the ether oxygen compared to the aliphatic analogues is considered. This could be attributed to the positive inductive effect (+I) of the alkyl groups on the ether linkage. The inductive effect shall furnish the oxygen atom with a relatively high electron density thereby strengthening the interaction with Ag atoms. To demonstrate that further, the computed molecular electrostatic potential (MEP) map (Fig. 3) depicts a wider electron density area in the cyclic acids indicating that the interface of these systems with silver nanomaterials could be more feasible and hence SERS interaction would be more viable compared to aliphatic analogues.
Fig. 2 Optimized geometries of the studied Aliphatic and cyclic carboxylic acids.

Table 1 Interaction energies and bond lengths of Ag interactions with carboxylic acids

| Compound          | $E_{\text{interaction}}$ (kcal/mol) | Bond length (Å) |
|-------------------|-------------------------------------|-----------------|
|                   | Alcohol | Ether | Carboxylic | Alcohol | Ether | Carboxylic |
| Butyric acid (BA) | -9.534  | -     | -8.337     | 2.478   | -     | 4.139     |
| Valeric acid (VA) | -10.04  | -     | -10.21     | 2.473   | -     | 4.374     |
| Caproic acid (CA) | -9.441  | -     | -9.140     | 2.481   | -     | 4.038     |
| $\gamma$-Butyrolactone (BLC) | - | -9.709 | -9.217 | - | 2.438 | 5.016 |
| $\gamma$-Valerolactone (VLC) | - | -11.63 | -9.492 | - | 2.442 | 4.609 |
| $\gamma$-Caprolactone (CLC) | - | -12.90 | -10.05 | - | 2.449 | 4.807 |

Inductive effect refers to an electronic phenomenon which occurs due to unequal sharing of electrons involved in a sigma bond leading to the polarization of such bonds. When this happens, neighboring carbon atoms tend to release partial charges towards the polarized center in an attempt to stabilize the electropositive atom. This effect however diminishes after the 3rd carbon atom and is usually not felt beyond. It is apparent in the present study that the proximity of the alkyl substituents on the cyclic compounds to the ether oxygen is the driving force for the enhancement in interactions of the compounds with Ag atoms and this even became obvious as the energy increases with an increase in chain length. Furthermore, the predicted bonding distances between the Ag and oxygen atoms signified a strong Lewis acid-base interaction as the distances were shorter than the Van der Waals radii of both atoms (3.14 Å) [19], except for the carboxylic interactions where there is no proper overlap of the atoms, in agreement with the calculated interaction energies (Table 1).
Fig. 3 Total electron density map on the surface of (a) BA, (b) VA, (c) CA, (d) BLC, (e) VLC and (f) CLC.

Fig. 3 (a) Raman spectrum of CLC and (b) SERS spectrum of Ag-CLC ether interaction. Asterisk (*) bands represents the highly shifted bands.
Similarly, BLC, VLC and CLC all exhibited –C=O vibrational stretching modes at 1687 cm\(^{-1}\), while the -C-C=O bending mode appeared at 1216 cm\(^{-1}\) in BLC, 1238 cm\(^{-1}\) in VLC and 1249 cm\(^{-1}\) in CLC, accordingly. Furthermore, the C-O-C asymmetric stretching, the -C-O stretching and the O=C-O bending modes appeared at 1125, 1002 623 cm\(^{-1}\) in BLC, 1125, 1005 and 638 cm\(^{-1}\) in VLC and 1125, 1007 and 646 cm\(^{-1}\) in CLC, respectively. Upon interactions at the hydroxyl, ether and carboxyl groups, noticeable shifts in Raman bands were observed as shown in Tables 2 and 3. However, the most prominent shifts are expected to occur in CLC when interacting via the ether oxygen at the band corresponding to -C-O stretching due to the +I effect of the alkyl side chains.

Overall, the present DFT-based evaluation of SERS effects on carboxylic acid derivatives provided a rationale behind the underlying processes leading to Raman signal shift and indicated the significance of positive inductive effects of alkyl side chains which could be helpful in the design of SERS-based experiments for the quantification of organic compounds.

| S/N | Vibrations                  | BA  | VA  | CA  |
|-----|-----------------------------|-----|-----|-----|
|     | Isolated | Alcohol | Carboxylic | Isolated | Alcohol | Carboxylic | Isolated | Alcohol | Carboxylic |
| 1.  | O-H stretching              | 3556 | 3545 | 3540 |
| 2.  | C=O stretching              | 1680 | 1683 | 1660 |
| 3.  | C-C=O bending               | 1227 | 1273 | 1280 |
| 4.  | C-O-C asym. stretching      |     |     |     |
| 5.  | C-O stretching              | 1049 | 1029 | 1052 |
| 6.  | O-H out-of-plane bending    | 820  | 817  | 824  |
| 7.  | O=C-O bending               | 600  | 612  | 611  |
Table 3 Assignment of vibrational modes from Raman and SERS spectra of BLC, VLC and CLC (cyclic acids)

| S/N | Vibrations                  | BLC          | VLC          | CLC          |
|-----|-----------------------------|--------------|--------------|--------------|
|     | Isolated | Ether | Carboxylic | Isolated | Ether | Carboxylic | Isolated | Ether | Carboxylic |
| 1.  | O-H stretching              | -           | -           | -           | -       | -         | -       | -       | -         |
| 2.  | C=O stretching              | 1687        | 1699        | 1706        | 1687    | 1706      | 1706    | -       | -         |
| 3.  | C-C=O bending               | 1216        | 1257        | 1250        | 1238    | 1265      | 1252    | 1249    | 1174      | 1143     |
| 4.  | C-O-C asym. stretching      | 1125        | 1151        | 1159        | 1125    | 1105      | 1113    | 1125    | 1143      | 1121     |
| 5.  | C-O stretching              | 1002        | 1052        | 1055        | 1005    | 1067      | 1068    | 1007    | 1121      | 1075     |
| 6.  | O-H out-of-plane bending    | -           | -           | -           | -       | -         | -       | -       | -         |
| 7.  | O=C-O bending               | 623         | 650         | 649         | 638     | 619       | 619     | 646     | 649       | 649      |

4. Conclusion

Comparative quantum chemical DFT evaluation of SERS effects on six aliphatic (butyric acid, valeric acid and caproic acid) and cyclic (γ-butyrolactone, γ-valerolactone and γ-caprolactone) acids were successfully conducted at the B3LYP/6-311++G(d,p) level of theory, with the aim of gaining more insights into the role played by alkyl side chains on the plasmonic effects of silver substrates. The vibrational frequency shifts caused by the interactions of these compounds with Ag atoms were studied. It was noticed that the most prominent shift occurred in the Raman of γ-caprolactone when interacting with Ag atoms through its C-O-C moiety. Such a shift was attributed to the positive inductive effect (+I) contribution by the alkyl side chains and corresponds to a theoretical interaction energy of -12.92 kcal/mol and a bonding distance if 2.45 Å. The present study hereby demonstrates the significance of positive inductive effects of alkyl side chains which could be helpful in rationalizing relevant SERS experiments for the quantification of organic compounds.
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