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Density functional theory investigation of p-aminothiophenol molecules adsorbed on gold nanoparticles

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The current investigation is focused on quantum-chemical calculation and modelling of the SERS spectra for p-aminothiophenol molecules on gold nanoparticles. The DFT calculations are undertaken for p-aminothiophenol with S-H groups replaced by an S-Au bond. This model allows for more appropriate vibrational modes, electronic levels and transition moments description of the adsorbed p-aminothiophenol. Strong S-Au covalent bonding is indicated by the large concentration of electron density between S and bonded Au atoms and by distinctly directional Au-S-C bond whose bond angle is 105º.

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1. Introduction

The assembly of the nanosized metal nanoparticles with functionalized molecules has received considerable attention and shown extensive applications in various fields as molecular and biomolecular recognition, nanolithography and sensing. It is well known that thiols are irreversibly adsorbed on gold surfaces and form compact molecular monolayers. The understanding of such self-assembled monolayer (SAM) thin films is necessary to enable successful and reliable devices such as label-free biosensors to be constructed. A variety of experimental methods have been used to probe the quality and chemical nature of SAM on metal surface. Among them, surface-enhanced Raman scattering (SERS) plays an important role due to its richness of molecular structure information and high sensitivity. Nowadays, nanoparticles and nanoarrays design has become more sophisticated and new platforms for SERS are being made available [1-2].

We have recently reported self-assembled small polystyrene spheres coated with gold shells as ideal substrate for SERS studies [2]. These metal nanoshells are of high interest since the SERS effect is mediated by the nanoshell surface-plasmon resonances and these are tunable throughout the visible and near-infrared regions of the spectrum via appropriate choice of inner and outer radii. Furthermore, SERS spectra of the p-aminothiophenol (p-ATP) molecule adsorbed on the immobilized gold nanoparticles have been successfully recorded by using the 532, 633, 830 and 1064 nm laser lines [3].

Recent *ab-initio* density functional theory (DFT) calculations of thiolate molecules on the Au surface show that S head groups prefer to bond at bridge with a strong chemical bonding [4]. The DFT calculations for the binding between thiolate molecules and gold clusters also find that sulphur forms strong chemical bonds with only one or two gold atoms [4].

In this work we address similar issues by comparing the experimental measurements with quantum-chemical calculation and modelling of SERS spectra. We find good agreement between our simulated spectrum and the experimental SERS spectrum. High concentration of electron density between S and bonded Au atom confirm strong S-Au covalent bonding.

2. Experimental

Aminopropyltriethoxysilane (APS),
p-Aminothiophenol (p-ATP), and $HAuCl_4{\cdot}3H_2O$ were purchased from commercial sources (Aldrich) and used as received. Ultra pure water was used throughout the experiments. All other reagents employed for substrate and solutions preparation were of analytical grade.

The gold colloidal suspension was prepared by the following procedure [5]: 500 ml of 10^{-3} M $HAuCl_4$ was brought to a boil with vigorous stirring on a magnetic stirring hot plate. Ten millilitres of 38.8 mM Na citrate was added to the solution all at once with vigorous stirring. The yellow solution turned clear, dark blue and then a deep red-burgundy colour within a few minutes. Stirring and boiling has been continued for 10-15 minutes after the burgundy colour was observed. The solution has been removed from heat and kept stirring until is getting cold and then the volume was adjusted to 500 ml with water. Colloidal solutions were stored in clean brown glass bottles until used. The assembling protocol of the gold nanoparticles was reported in a previously work [3].

The Raman spectrum was recorded using a Bruker Equinox 55 spectrometer with integrated FRA 106 module and resolution of 4 cm^{-1}. Radiation of 1064 nm from a Nd-YAG laser with a power of 400 mW was employed for Raman excitation. The 180° geometry was used to collect the scattered light.

The SERS spectrum was recorded with a DILOR Labram system equipped with a 100x/0.75 microscope objective and a 300 lines/mm grating. For excitation the 633 nm laser line with 4.3 mW power on the sample was employed. The spectral resolution was of 5 cm^{-1}.

The molecular geometry optimizations and vibrational frequencies calculations for p-APT and p-APT-Au were performed with the Gaussian G03 software package [6] by using the B3LYP DFT method in conjunction with the split valence-shell 6-31G(d) basis set [7]. For gold atom the LANL2DZ basis set [8], available in Gaussian G03, was used. All the calculations have been carried out with the restricted close shell formalism. The geometry of the p-ATP-Au was fully optimized with the help of analytical gradient procedure implemented within Gaussian G03 program.

3. Results and discussion

Raman spectrum of p-ATP, SERS spectrum of p-ATP molecule adsorbed on the self-assembled gold colloidal nanoparticles and theoretical spectra of p-aminothiophenol attach to one gold atom are presented in Fig. 1.

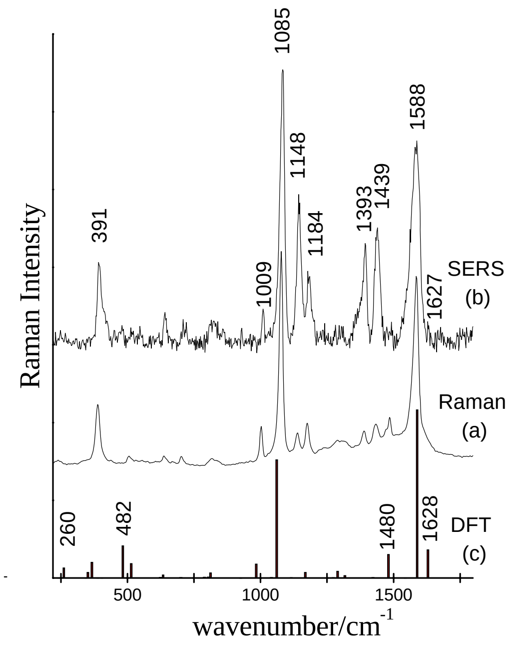


Fig. 1. Raman spectrum of p-ATP molecules (a), SERS spectrum of p-ATP molecules adsorbed on gold nanoparticles (b) and theoretical spectrum of p-ATP-Au model complex (c).

As revealed by Fig. 1 few differences occur between Raman and SERS spectra. One can see that SERS and Raman spectra are dominated by the bands around 1085 and 1588 cm^{-1} attributed to S-C and C-C stretching vibrations, respectively. In the SERS spectrum one can observe the enhancement of the bands around 1148, 1393 and 1439 cm^{-1} assigned to the thiol group vibrations. The apparent enhancement of the bands related to the phenyl group vibrations has been ascribed to the charge-transfer between the metal (gold nanoparticles) and the adsorbed molecules [3]. The absence of a S-H stretching mode (2580 cm^{-1}) in the SERS spectrum, confirms that the Au-S chemical bond is formed. Thus, the spectral characteristics of the SERS spectrum demonstrate that the p-ATP molecules are adsorbed onto the gold nanoparticles through their sulphur atoms.

Table 1 shows the main experimental vibrational modes from Raman and SERS spectra of p-ATP and the calculated modes of p-APT-Au model complex, together with their possible assignment accomplished with the help of theoretical calculations.

Table 1. Selected Raman and SERS bands of p-ATP with their vibrational assignment.

Raman	SERS	DFT	Vibrational assignment
-	245 vw	260 m	SAu str + Ph ring out of plane def + NH_2 wag
389 m	391 m	366 m	SC str + NH_2 wag + Ph ring in plane def
508 vw	512 vw	482 m	NH_2 wag + CH out of plane def
1002 m	1009 m	984 m	CC bend in Ph ring + SC str
1077 s	1085 s	1060 s	SC str
1140 m	1148 m	1115 vw	CH bend + NH_2 rock
1178 m	1184 m	1168 w	CH bend (from Ph ring)
1386w	1393m	1422 vw	Ph ring def + NH_2 rock
1436 m	1439 m	1480 m	Ph ring def + CN str
1484 m	1491 m	1544vw	Ph ring def + NH_2 rock
1585 s	1588 s	1588 s	CC str in Ph ring + NH_2 bend
-	1627 w	1628 m	NH_2 bend

Abbreviations: str=stretching, bend=bending, rock=rocking, def=deformation, wag=wagging, Ph=Phenyl, s=strong, m=medium, w=weak, vw=very weak

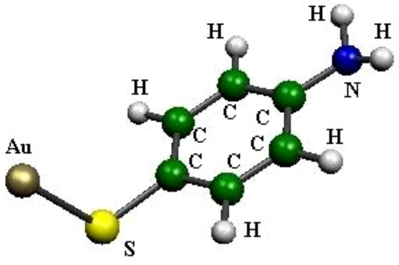
In order to be more definite about vibrational modes involved in Raman and SERS experiments, a series of *ab initio* calculations were undertaken for p-ATP covalently linked to Au through the S atom.

The geometry of p-ATP with S-H replaced by S-Au was fully optimized. This replacement allows a more appropriate description of the vibrational modes, electronic levels and transition moments of the adsorbed p-ATP on gold nanoparticles. Prior to compare the calculated vibrational frequencies with the experimental values, the former have been scaled by appropriate scaling factors recommended by Scott and Random [9]. For DFT method at B3LYP/6-G(d) level, the recommended frequency scaling factor for high and low frequencies are 0.96414 and 1.0013, respectively. To aid in mode assignments, we based on the direct comparison between experimental and calculated spectra by considering both the frequency sequence and the intensity pattern. Also, we based on the visual inspection of normal modes animated by using Molekel program [10].

Fig. 2 shows the optimized geometry of p-ATP-Au and the features of its principal vibrations. It can be seen that only low frequency mode has a significant S-Au bond stretching component, while all the other modes are dominantly ring or NH_2 vibrations.

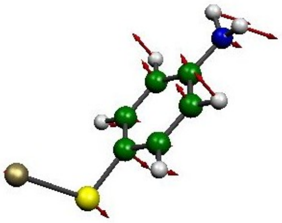
Geometry optimization of the free p-ATP molecule results in a S-C distance of 1.80 Å and C-C bonds from the phenyl ring of almost identical lengths (around 1.40 Å). The optimization of the p-ATP-Au results in a small change of the S-C bond length to 1.76 Å. The ring structure is modified as follow: four of the C-C bond lengths are 1.40 Å, whereas the other two C-C bond lengths are 1.387 Å. The Au-S bond length is 2.327 Å being very close to the value obtained by Johansson and Strafstrom [11] for phenyl molecule attached to 10-atoms gold cluster. The angle between Au-S-C atoms is 105.1°, while the angle between H-S-C in free p-ATP molecule is 98°.

In Fig. 3 are plotted the frontier highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the p-ATP-Au model complex. As easily can be seen, the HOMO-LUMO transition is clearly accompanied by significant charge transfer between the metal and molecule.

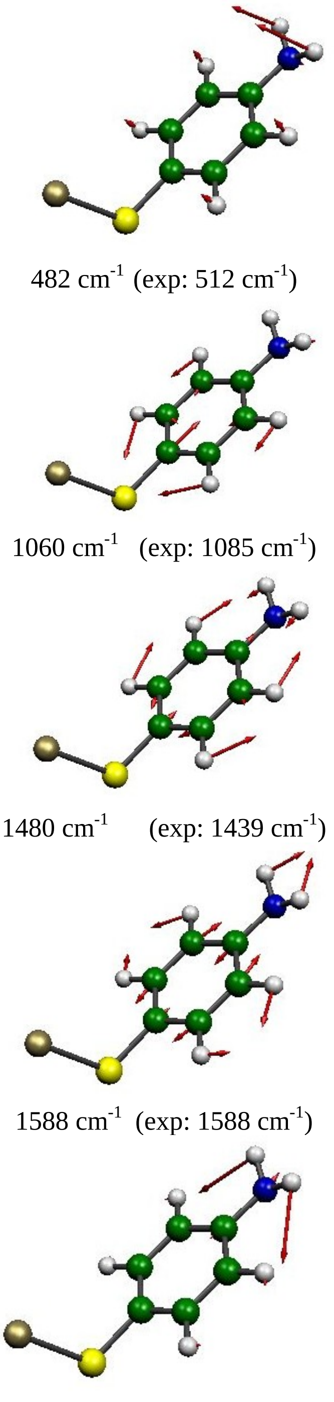


a

Fig 2. a) Optimized geometry of p-APT-Au at the B3LYP/6-31G(d) theoretical level.



260 cm^{-1} (exp: 245 cm^{-1})



482 cm^{-1} (exp: 512 cm^{-1})

1060 cm^{-1} (exp: 1085 cm^{-1})

1480 cm^{-1} (exp: 1439 cm^{-1})

1588 cm^{-1} (exp: 1588 cm^{-1})

1628 cm^{-1} (exp: 1627 cm^{-1})

b)

Fig. 2. b) Motions of principal vibrational modes in SERS spectrum.

The hybridization of orbitals located on the gold atom with orbitals of the thiol unit shows that the gold-sulphur bond has a substantial covalent character, and this fact suggest a charge transfer at the molecule-metal interface. Very important is the observation that the charge transfer is more related to the S-C group than the p-ATP molecule as a whole [11].

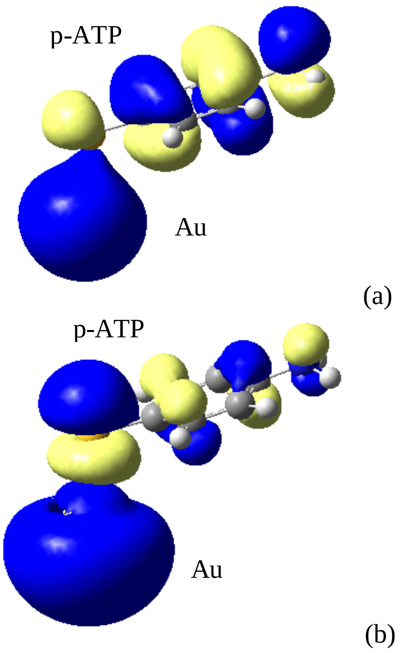


Fig. 3. HOMO (-5.63eV) (a) and LUMO (-3.03 eV) (b) orbitals of p-APT-Au model complex.

The energy gap between HOMO and LUMO is 2.63 eV, lower than ~ 4 eV for free p-ATP [1]. From the model complex calculations do yield weak transitions at significantly lower energies than in the free molecule, suggesting the possibility that closer approach to resonance with the laser frequency overshadows the weaker transition moments.

Experimentally it is known that the preferred position of the sulphur atom is in the hollow site, on top of a gold atom in the second layer of the (111) gold substrate [11]. Therefore, future work will be performed with the sulphur atom connected to more stable gold clusters. Studies appropriate for p-ATP fully coating Au nanoparticles would require more Au atoms and more p-ATP molecules, beyond the scope of the present work.

5. Conclusions

The SERS spectra for p-ATP molecules adsorbed on gold nanoparticles were theoretically investigated. The DFT calculations were made for p-ATP with S-H replaced by S-Au. This replacement brings the vibrational modes, electronic levels and transition moments significantly closer to experimental values obtained for absorbed p-ATP on gold nanoparticles. Strong S-Au covalent bonding is indicated by the large concentration of electron density between S and bonded Au atoms and by distinctly directional Au-S-C bond whose bond angle is close to 105°. Therefore, the interaction between p-ATP molecule and gold nanoparticles can be described in terms of chemisorption, in which the molecule forms a chemical bond to the metal surface.

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