Interpretation of the Surface-Enhanced Raman Spectroscopy Spectrum of 2,4,6-Trinitrotoluene Using Simple Chemistry Models

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Abstract

In this work we report the SERS spectrum of TNT in gold colloidal nano particles recorded at 785 nm excitation line. We have carried out an interpretation of the SERS spectrum in the 700-1650 cm-1 region using ab initio quantum mechanical calculations of Au-TNT model complexes. The model complexes [Au + 4-TNT]+ and [Au + 6-TNT]+ were optimized using the B3LYP method and Lanl2DZ/6-311+G** basis sets. The optimization produced two unidentate isoenergetic structures I and III connected by a symmetric bidentate structure II, the transition state. The SERS spectrum was interpreted using the the global minimum structures I and III, which are 2 Kcal/mol below the transition state, structure II. Frequencies were calculated for the optimized structures I and III, and comparisons with the SERS frequencies show an average absolute deviation of 19 cm-1. Our calculated results indicate a good agreement with the experimentally observed blue and red-shifts of the SERS spectrum.

Introduction

Surface-enhanced Raman spectroscopy (SERS) is a powerful vibrational spectroscopic technique to study chemical species absorbed on metal surfaces.(1-3) The very large enhancement of some of the intensities in the Raman spectrum of the absorbed molecule, not only provides high sensitivity to detect small quantities of the adsorbate, but also vibrational information to establish the chemical identity and the structural characteristics of the absorbed molecules. The enhancement of the Raman intensities in the Raman spectrum of molecules at rough metallic surfaces has been attributed to two main mechanisms: the electromagnetic effect and the chemical effect.(1,4,5) The chemical effect has been attributed to a metal-molecule charge transfer effect of molecules chemically adsorbed on metallic surfaces. Absorption of molecules on metal surfaces causes the formation of surface complexes due to chemical bonding of the molecule to the metal surface.(1)

Recently, SERS studies of the spectra of 2,4,6-trinitrotoluene (TNT) and its derivatives are being focused not only on the most prominent band around 1360 cm-1.(2,3,6,7), but also on less intense bands such as the bending modes at 820 and 850 cm-1, and the aromatic breathing mode near to 1000 cm-1. These regions appear to be very sensitive to SERS, this is clearly manifested by the enhancement of the intensities of the bands found in these regions. These changes in the spectrum suggest that there is a real interaction between the TNT molecule and the colloidal nano particle surface.(2,3,6)

In order to provide some light on the effects of the Au-TNT interaction on the SERS spectrum of TNT, we will use simple chemistry models, where the TNT molecule interacts with Au+ ion through the 2,4-NO2 groups. It is very well documented that the the NO2 group interacts with metal ions forming unidentate and bidentate complexes. Our objective is to carry out density functional theory (DFT) calculations of geometries, frequencies and intensities on these models and also to compare the experimentally measured SERS spectrum with the calculated one.

Materials and Methods

Experimental Considerations

Gold nano particles were prepared following the standard citrate procedure.
-modified by adding 1M NaCl aqueous solution in a volume ratio of 1:10.

To achieve maximum enhancement, the colloidal solution was diluted with water in a 50:50 volume ratio. Then a 1.0x10-3 M TNT methanol solution was mixed with the colloidal solution in a 1:10 volume ratio.

SERS spectra were recorded using a Renishaw Raman microspectrometer RM2000 system with an excitation line of 785 nm from a Renishaw diode laser, power of 66 mW.

The Raman spectra were obtained in the region of 100-3200 cm-1 with a resolution of 1 cm-1, an integration time of 10 seconds and 3 acquisitions.

Computational Methods

Normal modes of the complexes were assigned by visual inspection of the atomic motions of each normal mode.

Relative Raman intensities were calculated using the Raman scattering activities obtained from frequency calculations

Geometrical Parameters

The geometrical changes in the structures I,II,III and IV occur localized in the coordination site.

Results

With the exception of the red-shift of the symmetric NO2 stretch from 1364 to 1356 cm-1, our SERS spectrum is in a good agreement with similar experimentswhich suggest similar modes of interaction between TNT and the gold substrate.

Enhancement:
- asymmetric NO2 stretch at 1538 cm-1
- symmetric NO2 stretch at 1353, 1356 cm-1
- forbidden ring breathing mode at 1000 cm

Unenhancement:
- region of the CH rocking mode below 900 cm-1
- peaks at 793 and 822 cm-1 are very weak.

Red Shifts:
- 1356 and 1364 cm-1 become 1353 and 1356 cm-1
- 1619 cm-1 become 1538, 1591 cm-1
- not visible becomes 1267 cm-1
- 1178 and 1022 cm-1 become 1164 and 1016 cm-1

Table 2. Geometry changes[a] on the TNT geometry after coordination with gold ion (Au^+), geometries were calculated using B3LYP method and Lanl2DZ/6-311+G** basis sets.[b]

Parameter[c]	TNT	Au-TNT[d]	Diff.[a,d]
N8-O20	1.221	1.207	-0.015
N8-O21	1.221	1.280	+0.059
C-N	1.482	1.438	-0.045
O20-Au		2.982	
O21-Au		2.153	
C3C4	1.385	1.395	+0.010
C4C5	1.385	1.395	+0.010
C2C3	1.387	1.380	-0.007
C6C5	1.387	1.380	-0.007
C2C1	1.406	1.412	+0.006
C1C6	1.406	1.412	+0.006
C3C4N8	119.2	118.2	-1.0
C5C4N8	119.2	120.0	+0.8
C4N8O20	117.2	121.9	+4.8
C4N8O21	117.2	115.9	-1.3
C3C4N8O20	-0.2	-1.5	-1.3
C5C4N8O21	0.2	-1.3	-1.5

[a]Diff. stands for the difference between the calculated geometric parameters of TNT and those calculated of Au-TNT complexes using B3LYP method and Lanl2DZ/6-311+G** basis sets. [b]Calculations were carried out in the unidentate lower energy structure, structure I shown in Figure 1. [c]Bond lengths are are expressed in Å and angles in degrees. [d]Comparisons were made with the global minimum structures I and III.

Geometries of Au-TNT

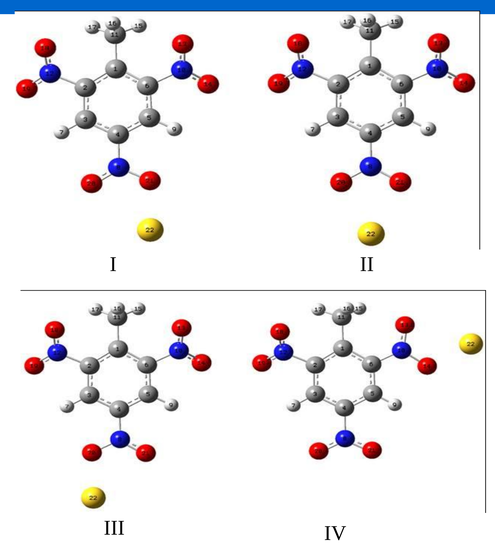

Figure 1. Geometries of Au-TNT complexes calculated using DFT (B3LYP) method and Lanl2DZ/6-311+G** basis sets. Structures I and III are the 4-NO2 unidentate asymmetrically coordinated complexes, structure II is the 4-NO2 bidentate symmetrically coordinated and structure IV the 2-NO2 unidentate asymmetrically coordinated complex.

Raman Spectrum

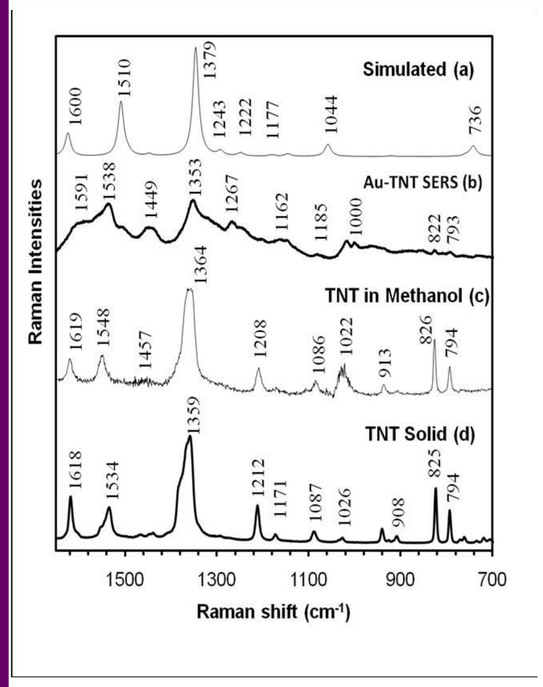

Figure 2. a) Calculated Raman spectrum of TNT at 785 nm excitation line using DFT (B3LYP) method and Lanl2DZ/6-311+G** basis sets. b) SERS experimental spectrum of TNT methanol solution on gold colloids and recorded at 785 nm excitation line. c) Raman spectrum of TNT methanol solution at 785 nm excitation line. d) Raman spectrum of TNT crystals recorded with excitation line of 785 nm.

Interpretation of SERS

To carry out an interpretation of the SERS spectrum of TNT, we have compared the theoretical calculated modes for structures I, III and IV with the experimental SERS spectrum. These comparisons have been focused on the symmetric NO2 stretching modes 1267, 1353 and 1356 cm-1; the asymmetric NO2 stretching modes 1538 and 1591 cm-1; the ring breathing modes at 1001 and 1218 cm-1; the CH out of plane bending mode at 763 cm-1 and the NO2 bending modes at 827 and 793 cm-1.

Comparisons were used to calculate the average absolute deviation of 19 cm-1, suggesting a good agreement considering the size of the TNT molecule.

Our computational model reproduces, not only the main features of the SERS spectrum in the gold colloidal surfaces, but also the main features of the SERS of TNT adsorbed onto gold metal foils .These facts suggest that the interaction of the TNT with the gold surface occurs in both types of experiments through the NO2 group.

Calculations are consistent with the TNT molecule oriented perpendicular to the gold surface interacting through the oxygens of the 4-NO2 group.

Conclusions

The most stable structures were the unidentate Au-TNT complexes, structures I and III.

The TNT SERS spectrum significantly affects the region of the NO2 symmetric and asymmetric stretches.

The main effect in the TNT NO2 stretching region after complexation with the gold surface is the red-shift of both the symmetric and asymmetric stretches.

Comparisons of the calculated Raman spectrum of Au-TNT complex with the experimental SERS spectrum showed a very good agreement.

The calculated spectrum reproduces not only the main frequencies peaks in the finger print region (700-1650 cm-1), but also the relative intensity pattern of the experimental SERS spectrum.

The red-shift of the NO2 symmetric and asymmetric stretches, and the presence of a new NO2 stretching frequency at 1267 cm-1 indicate a change of the local symmetry of the 4-NO2 group after complexation, as indicated by the calculated geometry changes.

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