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Vibrational spectroscopy and density functional theory study of 4-mercaptobenzoic acid

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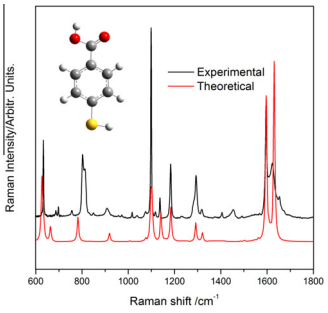
HIGHLIGHTS

- Most of the fundamentals vibrations agree well with the predicted frequencies.
- Hydrogen bond donors and acceptors are predicted.
- The vibrational spectra of 4-MBA are studied experimentally and theoretically.

GRAPHICAL ABSTRACT

4-Mercaptobenzoic acid was designed as a model molecule for theoretical and experimental studies of the molecule structure. Fourier transform infrared (FTIR) and Raman spectra of the compound have been obtained experimentally. Most of the fundamentals vibrations agree well with the predicted frequencies.



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ABSTRACT

In this paper, 4-mercaptobenzoic acid (4-MBA/pMBA) was designed as a model molecule for theoretical and experimental studies of the molecule structure. Density functional theory (DFT) calculations have been performed to predict the IR and Raman spectra for the molecule. In addition, Fourier transform infrared (FTIR) and Raman spectra of the compound have been obtained experimentally. Based on the modeling results obtained at the B3LYP/6-311++G** level, all FTIR and Raman bands of the compound obtained experimentally were assigned. Our calculated vibrational frequencies are in good agreement with the experimental vales. The molecular electrostatic potential surface calculation was performed and the result suggested that the 4-MBA had two hydrogen bond donors and three hydrogen bond acceptors. HOMO–LUMO gap was also obtained theoretically at B3LYP/6-311++G** level.

Introduction

Recently, a benzene derivative containing a sulfhydryl (-SH) and a carboxyl (-COOH) function group, 4-mercaptobenzoic acid (4-MBA, p-MBA) was widely used in surface enhanced Raman scattering (SERS) [1] since it was found [2,3]. Self-assembled monolayers (SAMs) of 4-MBA; also known as thiosalicylic acid, on gold are quite stable and efficiently provide surface carboxyl groups for conjugation with enzymes, antibodies, or antigens [4]. Therefore, 4-MBA presented as a good SERS probe in DNA detections [5]. The SERS signals of 4-MBA molecules are sensitive to the pH value,

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thus the 4-MBA was used as chemical pH sensors based on SERS [6]. Xia et al. reported a microwave-assisted synthesis of sensitive silver substrate and evaluated it by calculating the enhance factor of 4-MBA [27]. Part of the IR and Raman bands have been assigned in previous works and only some selected Raman bands have been theoretically assigned especially for the title molecule [7]. The developed detection methods are highly relying on the accurate and detailed assignments. On the other hand, the symmetric assignments are very important for discussions on the chemical enhancement mechanism of SERS [8] and to our best knowledge there is no directly symmetrical assignments.

Surface-enhanced Raman scattering (SERS) has been widely used as a powerful tool for ultrasensitive chemical analysis, which allows this technique sensitive enough to detect single-molecules [9,10]. Applications of SERS range from nanostructure characterization to chemical-biochemical analysis [11–13]. For the selected enhancement in SERS-based study of molecules, the orientation of the studied molecule on the substrate can be identified. Therefore, the molecular structure information, the vibration mode assignment, and the frontier molecular orbital information of a probe molecular are important for analyzing the complex structure of molecule and the mechanism of the enhancement.

Although molecular conformation and the frontier molecular orbital data are very significant for many applications, they were extremely hard to attain by employing experiment method. Fortunately, such information can be calculated theoretically by using the density functional theory (DFT) which describes the electronic states of atoms, molecules, and materials in terms of the three-dimensional electronic density of the system. DFT is generally accepted as a reliable means for predicting the spectrum information and molecular conformation. Wu et al. [14] successfully assigned their corresponding vibrational modes of aflatoxins (AFs) and AFs-Ag complexes by using DFT method at the B3LYP/6-311G** level. Our previous works [15,16] also showed the advantage of DFT method in application of obtaining the vibrational information.

We report the conformational, IR, and Raman study of 4-MBA based on DFT calculations at the B3LYP/6-311++G** level. FT-IR and confocal Raman spectra of the compound have also been obtained experimentally and accurately assigned using the results of the theoretical calculations. For further application, the energy difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the HOMO/LUMO gap, has also been calculated, which were valuable for explaining the enhancement mechanism of SERS. In addition, the hydrogen bond donors and receptors are predicted based on the theoretical calculations.

Experimental

Materials

4-Mercaptobenzoic acid (4-MBA, 99%) was obtained from Sigma. All other chemicals were of analytical grade and were purchased from Beijing Chemical Reagent Factory and were used without further purification.

Instruments

Raman spectra of 4-MBA were recorded on a LabRam Aramis Raman Microscope system (Horiba-Jobin Yvon) equipped with a multichannel air cooled charge-coupled device (CCD) detector. Spectra were excited using the 633 nm line of a HeNe narrow bandwidth laser (Melles Griot). The Raman spectra were collected at room temperature with the laser power at the sample position typically at 400 μW with an average spot size diameter of 1 μm. The typical acquisition time used in this work was 30 s. The FT-IR spectra of 4-MBA were recorded as KBr disks at room temperature by a Bruker IFS-66V FT-IR spectrometer, equipped with a DTGS detector at a resolution of 4 cm^{-1}.

Theoretical method

All the geometries we got in this work were optimized by DFT method of B3LYP which is the hybrid of Becke's three-parameter exchange functional [17,18] with the Lee–Yang–Parr correlation functional [19].The triple split valence basis set of 6-311+G** was adapted. The frequency calculation was performed at the same level. All calculations were carried out with the aid of the Gaussian 09 program [20]. The molecular electrostatic potential (MEP) were obtained by the WFA [21] software package. Potential energy distribution (PED) calculation was carried out by the VEDA 4 (Vibrational Energy Distribution Analysis) [22]. The method for calculating scaling factors was same as that proposed by Scott and Radom [23].

Results and discussion

The title compound, 4-MBA, is a benzene derivative containing a carboxyl and a sulfhydryl group. The optimized geometry of 4-MBA was characterized as potential energy minima at the same level by verifying that all vibrational frequencies are real.

Molecular geometry

The optimized geometry of 4-MBA is shown in Fig. 1, and the corresponding structural parameter of bond lengths, bond angles, and dihedral angles are shown in Table 1. The atom numerical labels in the following discussion refer to Fig. 1.

A similar molecule we studied very recently [16], 4-mercaptophenol (4-MPH), the sulfhydryl was off the benzene ring plane whereas all the atoms of 4-MBA was in the same plane as the Fig. 1 and Table 1 described. In contrast to 4-MPH, the C–S bond length (1.7819 Å) of 4-MBA was shorter, even shorter than that of thiophenol (1.7875 Å). Furthermore, the angles of C–C–S and C–S–H were both less than that of 4-MPH.

Vibrational assignment

The 4-MBA consists of 16 atoms, which undergoes 42 normal modes of vibrations. The optimized 4-MBA is non-axe-symmetrical because of the carboxylic group, by remove the hydrogens of the

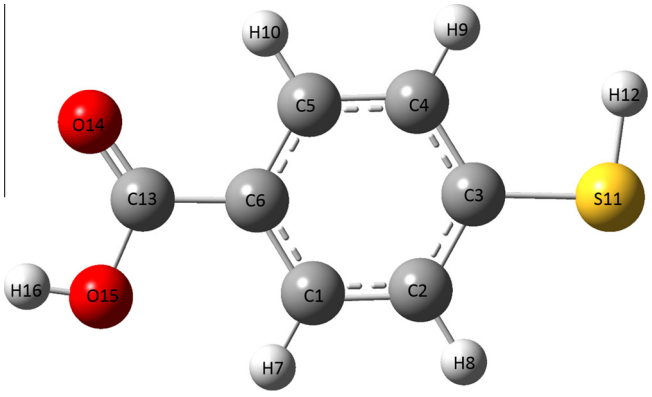

Fig. 1. Sketch map for 4-mercaptobenzoic acid structure calculated at the B3LYP/6-311++G** level.