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Vibrational spectroscopy and density functional theory study of ninhydrin

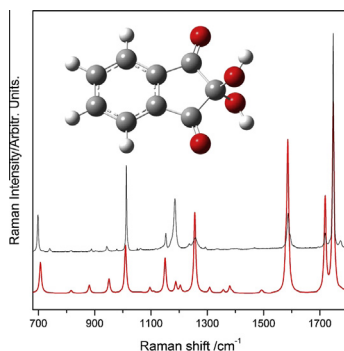
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HIGHLIGHTS

- Most of the fundamentals vibrations agree well with the predicted frequencies.
- Hydrogen bond donors and acceptors are predicted.
- The vibrational spectra of ninhydrin SERS are investigated experimentally and theoretically.

GRAPHICAL ABSTRACT

Ninhydrin 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, ninhydrin 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 values. The molecular electrostatic potential surface calculation was performed and the result suggested that the ninhydrin had two potential hydrogen bond donors and four potential hydrogen bond acceptors. HOMO–LUMO gap was also obtained theoretically at B3LYP/6-311++G** level.

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Introduction

Ninhydrin is usually considered as a tricarbonyl compound since it stable in equilibrium of indane-1,2,3-trione [1]. Ninhydrin

was first synthesized by Ruhemann in 1910 [2], and then, well known as a common coloration reagent for amino acid. In 1954, Oden and von Hofsten recognized that it was a useful reagent for developing fingerprints [3]. Fingerprints are still one of the most useful forms of physical evidence in identification. Latent prints are normally invisible without development. The techniques used for fingerprint identification vary according to the surface where

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the fingerprints are applied. The particular interest to ninhydrin-based development is the concentration of amino acids, which has been reported to be between 0.3 and 2.59 mg L⁻¹ of sweat. This value corresponds to an average amino acid content of about 250 ng per print. Small concentrations of amino acids in sweat are sufficient for development on paper [4]. Latent prints have highly potential applications, however the low amino acid content limit the detection probability.

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 [5,6]. Applications of SERS range from nanostructure characterization to chemical–biochemical analysis [7–9]. Ninhydrin is an important analytical tool in various fields, however the concentration of the ninhydrin are usually rather low, which limit its application. The limit of the low concentration could be broke though by taking the advantage of SERS analysis. For the selected enhancement in SERS-based study of molecules, the orientation of the studied molecule on the substrate can be identified and the vibrational information is the basis of SERS analysis. 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 predict the spectrum information and molecular conformation. Our previous works [10,11] also showed the advantage of DFT method in application of obtaining the vibrational information. Arivazhagan et al. [19] and Sajan et al. [20] proposed the ninhydrin monomer and dimer, respectively. However the SERS information is lack.

Herein, we report the conformational, IR, Raman, and SERS study of ninhydrin 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 by 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 is 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

Ninhydrin (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 ninhydrin 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 ninhydrin 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 [12,13] with the Lee–Yang–Parr correlation functional [14]. The triple split valence basis set of 6-311+G** for the H, C, and O atoms and lan12dz for Ag atom was adapted. The frequency calculation was performed at the same level. All calculations were carried out with the aid of the Gaussian 09 program [15]. The molecular electrostatic potential (MEP) were obtained by the WFA [16] software package. Potential energy distribution (PED) calculation was carried out by the VEDA 4 (Vibrational Energy Distribution Analysis) [17]. The method for calculating scaling factors was same as that proposed by Scott and Radom [18].

Results and discussion

The title compound, ninhydrin, is an indene derivative containing two ketose and two hydroxyls groups. The optimized geometry of ninhydrin was characterized as potential energy minima at the same level by verifying that all vibrational frequencies are real.

Molecular geometry

The optimized geometry of ninhydrin 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. All atoms lay in the same plane except the O16, H17, O18, and H19, thus the two-fold symmetry axis survived whereas the mirror planes no longer exist. Therefore, the theoretically obtained title molecule is a C₂ symmetric molecule. The C₂ symmetry equates the two rotation-free hydroxyls, thus the DFT calculated potential energy curve which is shown in Fig. 2 is obtained by twisting one of the hydroxyls. The horizontal and axes refer to torsion angles and the potential energy difference, respectively. The torsional potential energy curve shows two rotation barriers with different barrier heights of 23.5 and 15.8 kJ/mol; the saddle implied another structure in particular condition.

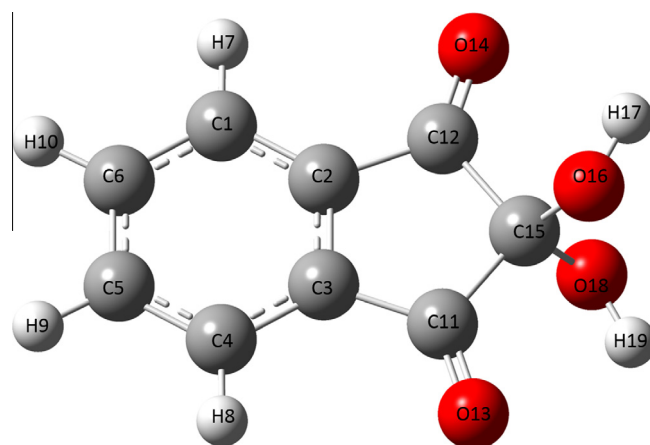


Fig. 1. Sketch map for ninhydrin structure calculated at the B3LYP/6-311+G** level.

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