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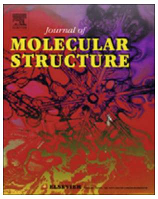

Vibrational spectroscopic studies and computational study of 4-fluoro-N-(2′-hydroxy-4′-nitrophenyl)phenylacetamide

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ABSTRACT

Fourier-transform infrared (FT-IR) and FT-Raman spectra of 4-fluoro-N-(2′-hydroxy-4′-nitrophenyl)phenylacetamide were recorded and analyzed. A surface-enhanced Raman scattering (SERS) spectrum was recorded in silver colloid. The vibrational wavenumbers and corresponding vibrational assignments were examined theoretically using quantum mechanical calculations. The red shift of the NH stretching wavenumber in the IR spectrum from the calculated wavenumber indicates the weakening of NH bond resulting in proton transfer to the neighboring oxygen atom. The presence of CH_2 and NO_2 modes in the SERS spectrum indicates the nearness of these groups to the metal surface, which affects the orientation and metal molecule interaction. The presence of phenyl ring deformation bands, show a tilted orientation of the molecule with respect to the silver surface. The first hyperpolarizability and predicted infrared intensities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar structures and is an attractive object for further studies of nonlinear optics.

1. Introduction

N-Phenyl benzamides are important and biologically active compounds [1]. Some N-(o-hydroxypheny)benzamides and phenylacetamides have been reported as possible metabolites of antimicrobial active benzoxazoles. Synthesis and microbiological activity of some N-(2-hydroxy-4-substitutedphenyl)benzamides, phenylacetamides and furamides as possible metabolites of antimicrobial active benzoxazoles are reported by Aki-Sener et al. [2]. Benzamide derivatives which are the possible metabolites of benzoxazoles show various type of biological properties such as antihelmenthic, antihistaminic, antifungal and antibacterial [1]. Vibrational spectroscopic studies and DFT calculations of 4-fluoro-N-(2′-hydroxy-4′-nitrophenyl) benzamide was reported by Ushakumari et al. [3]. The intra molecular hydrogen bond in 2-hydroxy-benzamides are reported by Kawski et al. [4]. Arslan et al. [5] reported the molecular structure and vibrational spectra of 2-chloro-N-(diethylcarbamothioyl)benzamide by Hartree–Fock and density functional methods. Gas phase structures of fundamental amides, formamide [6] and acetamide [7] were determined by electron diffraction and their crystal structures were studied by X-ray and neutron diffraction [8–12]. The crystal structures of benzamide were determined by X-ray [13] and neutron diffraction [14]. Near infrared spectroscopic studies of the hydrogen bonding between thioacetamide and N,N-disubstituted benzamide derivatives in CCl_4 is reported by Choi et al. [15]. Molecular structure benzamide was studied by gas phase electron diffraction [16]. Biagi et al. [17] reported the synthesis and biological activity of novel substituted benzanilides as potassium channel activators. Rho et al. [18] reported the studies on depigmenting activities of dihydroxyl benzamide derivatives containing adamantane moiety. DFT and ab initio study of structure of dyes derived from 2-hydroxy and 2,4-hydroxy benzoic acids are reported by Dabbagh et al. [19] Nishikawa et al. [20] reported the internal rotations of aromatic polyamides theoretically. In the present work, the IR, Raman, SERS and theoretical calculations of the wavenumbers for the title compound are reported. Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties [21]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic

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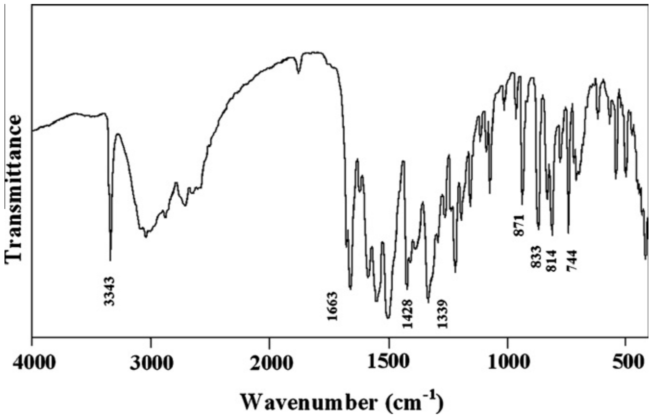

Fig. 1. FTIR spectrum of 4-fluoro-N-(2-hydroxy-4-nitrophenyl)phenylacetamide.

image processing [22,23]. Phenyl substituents can increase molecular hyperpolarizability [24,25] a result described as surprising. Many organic molecules, containing conjugated π electrons and characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy [26]. In this context, the hyperpolarizability of the title compound is calculated in the present study.

2. Experimental

The chemicals were purchased from the commercial venders and were used without purification. The reactions were monitored and the purity of the product was checked by thin layer chromatography (TLC). Silica gel 60 F_{254} chromatoplates were used for TLC. The solvent systems were chloroform/methanol (15:1). Thionyl chloride (1.5 ml) and 4-fluorophenyl acetic acid (0.5 mmol) were refluxed in benzene (5 ml) at 80° for 3 h, and then excess thionyl chloride was removed in vacuo [27]. The residue was dissolved in ether (10 ml) and the solution added during 1 h to a stirred, ice–cold mixture of 2-amino-5-nitrophenol (0.5 mmol), sodiumbicarbonate (0.5 mmol), diethyl ether (10 ml), and water (10 ml). The mixture was stirred overnight at room temperature and filtered. After the precipitate was washed with water, 2 N HCl and water, respectively, and finally with ether, compound was obtained. The crude product was purified by recrystallization from ethanol.

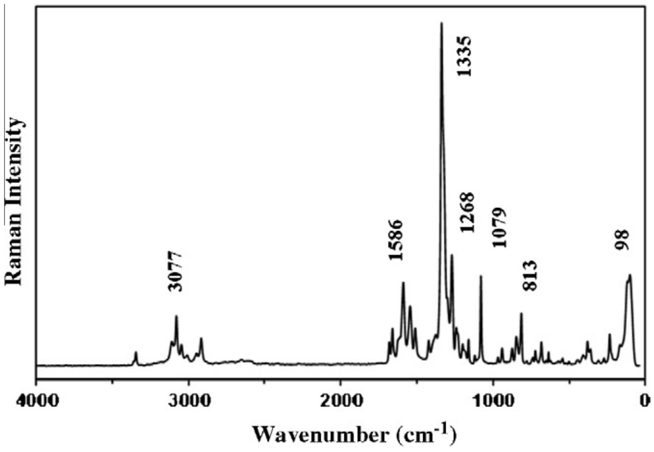

Fig. 2. FT-Raman spectrum of 4-fluoro-N-(2-hydroxy-4-nitrophenyl) phenylacetamide.

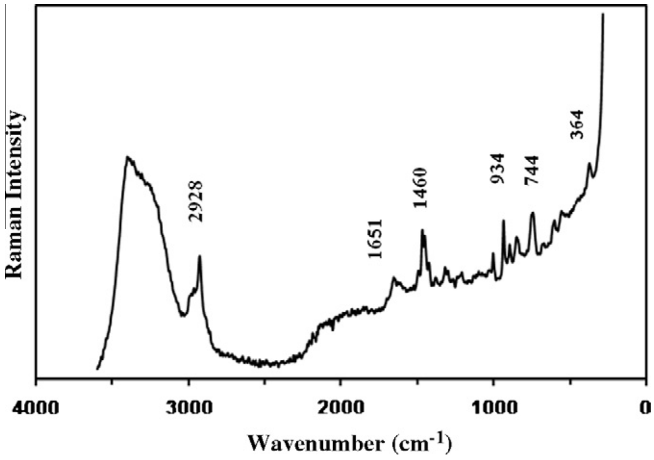

Fig. 3. SERS spectrum of 4-fluoro-N-(2-hydroxy-4-nitrophenyl)phenylacetamide.

The purity of the compound was checked by TLC (Merck TLC plates Silica gel 60 F_{254}) using solvents S1 ($CHCl_3$/MeOH 15:1). The plates were visualized using UV light. Melting points (uncorrected) was determined using a capillary melting point apparatus (Buchi SMP 20 and Electrothermal 9100): 226–228 °C. Yield was calculated after recrystallization. Yield 33%. The IR spectrum (Fig. 1) was recorded on a Jasco FT-IR-420 spectrometer with KBr disks. The FT-Raman spectra (Figs. 2 and 3) was obtained on a Bruker RFS 100/S, Germany. For excitation of the spectrum, the emission of a Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, measurement on solid sample. The aqueous silver colloid used in the SERS experiments was prepared by reduction of silver nitrate by sodium citrate, using the Lee-Meisel method [28]. Solutions of the title compound were made up in ethanol (0.1 mmol in 1 cm^3 of solvent) and transferred by a microsyringe into the silver colloid (10 μL in 1 cm^3 of colloid) such that the overall concentration was 10^{-3} mol dm^{-3}. Colloid aggregation was induced by addition of an aqueous solution of $MgCl_2$ (1 drop of a 2 mol dm^{-3} solution). Polyvinylpyrrolidone was then used to stabilize the colloid (1 drop of 0.1 g/10 cm^3 aqueous solution). The final colloid mixture was placed in a glass tube and the Raman spectrum registered.

The ^1H NMR spectra was recorded employing a VARIAN Mercury 400 MHz FT spectrometer, chemical shifts (δ) are in

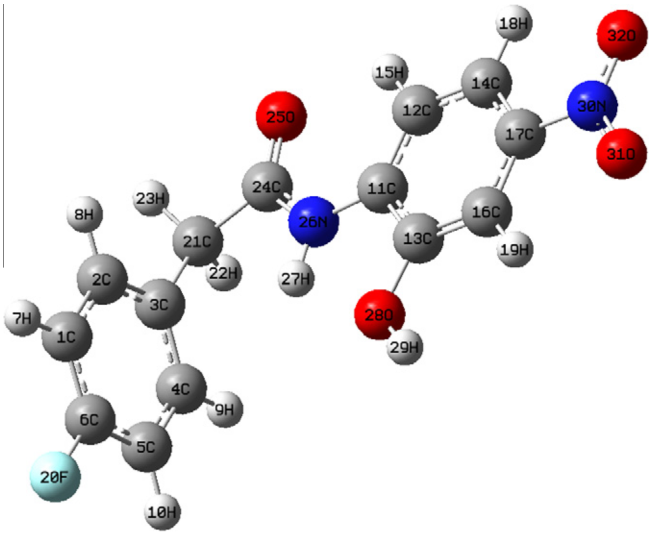

Fig. 4. Optimized geometry of 4-fluoro-N-(2-hydroxy-4-nitrophenyl) phenylacetamide.