



Vibrational spectroscopy (FT-IR and FT-Raman) investigation, and hybrid computational (HF and DFT) analysis on the structure of 2,3-naphthalenediol

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ABSTRACT

The FT-IR and FT-Raman vibrational spectra of 2,3-naphthalenediol ($C_{10}H_8O_2$) have been recorded using Bruker IFS 66V spectrometer in the range of 4000–100 cm^{-1} in solid phase. A detailed vibrational spectral analysis has been carried out and the assignments of the observed fundamental bands have been proposed on the basis of peak positions and relative intensities. The optimized molecular geometry and vibrational frequencies in the ground state are calculated by using the ab initio Hartree–Fock (HF) and DFT (LSDA and B3LYP) methods with 6-31+G(d,p) and 6-311+G(d,p) basis sets. There are three conformers, C1, C2 and C3 for this molecule. The computational results diagnose the most stable conformer of title molecule as the C1 form. The isotropic computational analysis showed good agreement with the experimental observations. Comparison of the fundamental vibrational frequencies with calculated results by HF and DFT methods. Comparison of the simulated spectra provides important information about the capability of computational method to describe the vibrational modes. A study on the electronic properties, such as absorption wavelengths, excitation energy, dipole moment and Frontier molecular orbital energies, are performed by time dependent DFT approach. The electronic structure and the assignment of the absorption bands in the electronic spectra of steady compounds are discussed. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. On the basis of the thermodynamic properties of the title compound at different temperatures have been calculated. The statistical thermodynamic properties (standard heat capacities, standard entropies, and standard enthalpy changes) and their correlations with temperature have been obtained from the theoretical vibrations.

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1. Introduction

The naphthalene and its derivatives are the most important class of organic compounds. Because of their spectroscopic properties and chemical significance, naphthalene and its derivatives were studied extensively by spectroscopic and theoretical methods. The structure of naphthalene is benzene like, having two six membered rings fused together. They are biologically, pharmaceutically and industrially useful compounds. Vibrational spectra carry significant information about structure, potential energy surfaces and interaction with environment. Molecular vibrations have attracted much attention from both experimental and theoretical communities. Modern vibrational spectrometry has proven to be an exceptionally powerful technique for solving many chemical problems. It has been extensively employed both in the study of chemical kinetics

and chemical analysis. However for a proper understanding of IR and Raman, a reliable assignment of all vibrational bands is essential. Recently computational methods based on density functional theory (DFT) become widely used. This method predicts relatively accurate molecular structure and vibrational spectra with moderate computational effort [1–5].

Dihydroxynaphthalene are compounds having two hydroxyl groups are substituted to naphthalene ring system. There are positional isomers differing by the location of the hydroxyl group. The different positions provide various chemical structures which offer important roles to each characteristic. They are used directly in making several dyes and are converted into numerous corresponding amines, esters, ethers and carboxylic derivatives as well as into numerous sulfo- and nitro-group substituted (mono-, di- and tri) compounds. They find extensive applications in making dyes, pigments, fluorescent whiteners, tanning agents, antioxidants, and antiseptics. Dihydroxynaphthalene structure is found as a fable in transition-metal catalysts particularly in the form of binaphthalenediol which is composed of two naphthalenediol rings

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connected at one carbon site on each ring. 2,3-Naphthalenediol (abbreviated as 2,3-ND) is used as an intermediate for organic synthesis especially for crown ether and naphthalene sulfonic acid series used to make colorant compounds [6].

Since naphthalene and its derivatives have wide applications in the biological, pharmaceutical and industrial processes. Srivastava and Singh [7] investigated naphthalene and its cation are infrared and Raman spectrum of the condensed and liquid phase. Methoxynaphthalene was investigated the MNAP by using Wilson's F-G matrix method by Xavier et al. [8]. Nagabalasubramanian and Periandy [9] studied the FT-IR and FT-Raman vibrational spectra of 1,5-methylnaphthalene molecule. FT-IR and FT-Raman spectra of 1-methoxynaphthalene were reported by Govindarajan et al. [10]. Because of less number of works in the 2,3-ND molecules, has been taken for the present study. The complete vibrational analysis of 2,3-ND was performed by combining the experimental and theoretical information using Pulay's DFT based on scaled quantum chemical approach [11] and ab initio HF. It is expected that both ab initio HF and DFT level of theories are reliable for predicting the vibrational spectra of the title compound.

In this study, molecular geometry, optimized parameters, vibrational frequencies, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies, Frontier orbital energy gap, dipole moment and thermodynamic properties at various temperatures are computed and the performance of the computational methods for ab initio HF and DFT (LSDA and B3LYP) methods at 6-31+G(d,p) and 6-311+G(d,p) basis sets are compared. These methods expected relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the conventional ab initio HF calculations. In DFT methods, Becke's three parameter exact exchange-functional (B3) [12] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [13,14] are the best predicting results for molecular geometry and vibrational wave numbers for moderately larger molecule [15–17]. Present vibrational and electronic studies, not only helps for the proper assignments of the observed and computed frequencies but also offers a comprehensive picture about the molecular dynamics and electronic properties of 2,3-ND molecule.

2. Experimental details

The compound under investigation namely 2,3-ND is purchased from Sigma-Aldrich chemicals, USA, which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FT-IR spectrum of the compound is recorded in Bruker IFS 66V spectrometer in the range of 4000–100 cm^{-1} . The spectral resolution is $\pm 2 \text{ cm}^{-1}$. The FT-Raman spectrum of same compound is also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm line widths with 200 mW power. The spectra are recorded in the range of 4000–100 $\text{cm}^{-1} \text{ min}^{-1}$ of spectral width 2 cm^{-1} . The frequencies of all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$.

3. Computational methods

The first task for the computational work was to determine the optimized geometry of 2,3-ND molecule. The molecular structure of the title compound in the ground state is computed by performing both ab initio HF and DFT with 6-31+G(d,p) and 6-311+G(d,p) basis sets. The optimized structural parameters are used in the vibrational frequency calculations at HF and DFT levels. The minimum energy of geometrical structure is obtained by using level 6-31+G(d,p) and 6-311+G(d,p) basis sets. At the optimized

Table 1

Calculated energies and energy difference for three conformers of 2,3-ND by DFT.

Conformers	B3LYP6-311G(d,p)		
	Energy (hartree)	Energy (kcal/mol)	Energy differences ^a (kcal/mol)
C1	–536.47337217	–336642.13753	0.00000
C2	–536.46703799	–336638.16278	3.97476
C3	–536.46042192	–336634.01113	8.12640

^a Energies of the other three conformers relative to the most stable C1 conformer.

geometry for the title molecule no imaginary frequency modes were obtained, so there is a true minimum on the potential energy surface was found. All the computations have been done by adding polarization function d and diffuse function on heavy atoms [18] and polarization function p and diffuse function on hydrogen atoms [19], in addition to triple split valence basis set 6-311+G(d,p) for better treatment of hydroxyl group. Therefore, we had a discussion on calculated values using these sets. The calculated frequencies are scaled by 0.886, 0.897 and 0.905 for HF/6-31+G(d,p). For LSDA/6-31+G(d,p) set is scaled with 0.887, 0.910, 0.974, 0.960, 0.940, 1.05 and 1.130. And for LSDA/6-311+G(d,p) basis set is scaled with 0.896, 0.918, 1.08, 1.03 and 1.12. For B3LYP/6-31+G(d,p) basis set is 0.895, 0.913, 0.947, 1.001, 1.02, 1.25 and 3.04. For B3LYP/6-311+G(d,p) basis set is scaled with 0.904, 0.925, 0.992, 0.975, 1.035 and 1.15. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of the title molecule [20]. HF and DFT calculations for 2,3-ND are performed using GAUSSIAN 09 W program package on Pentium IV processor personal computer without any constraint on the geometry [21,22]. The electronic properties, such as HOMO–LUMO energies, absorption wavelengths and oscillator strengths were calculated using B3LYP method of the time-dependent TD-DFT, basing on the optimized structure in solvent (DMSO and chloroform) and gas phase. The changes in the thermodynamic functions the heat capacity, entropy, and enthalpy were investigated for the different temperatures from the vibrational frequencies calculations of title molecule.

4. Results and discussion

4.1. Molecular geometry

The molecular structure of the 2,3-ND belongs to Cs point group symmetry. The dihedral angle between the aromatic ring and OH group for 2,3-ND is computed ca. 0° (or ca. 180°). 2,3-ND may have three possible structures in connection with the hydrogen atom orientations of the oxygen atom of naphthalene molecule. Calculated energies and energy difference [the relative energy of the other conformers was as: $\Delta E = E(\text{C}_n) - E(\text{C}_1)$, the conformer C1 is the lowest energy as reference point] for all conformers of 2,3-ND are presented in Table 1. The conformer C1 is predicted to be from 3.97476 to 8.12640 kcal/mol more stable than the other conformers. Additionally, because of the imaginary frequency, the calculations showed the conformer C3 to be unstable conformer. Therefore, in this section, we tabulated only C1 conformer calculations data. Fig. 1 shows the optimized structure and demonstration of three possible conformations of compound along with numbering of the atoms. The optimized most stable molecular structure of title molecule is obtained from GAUSSIAN 09 W and GAUSSVIEW05 programs are shown in Fig. 2. The title molecule contains two hydroxylic group connected with naphthalene ring at 2nd and 3rd position. The structure optimization zero point vibrational energy of the title compound in HF/6-31+G(d,p), HF/6-311+G(d,p), LSDA/6-31+G(d,p), LSDA/6-311+G(d,p), B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p)

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