FT - RAMAN FT -IR SPECTROSCOPIC STUDY AND VIBRATIONAL ANALYSIS OF DITHIOOXAMIDE

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ABSTRACT

The polarized IR and Raman spectra of Dithiooxamide as a single crystal on solution and as a KBr pellet are powder and the inelastic incoherent neutron scattering spectra of the powder were measured and compared with the corresponding napthlene spectra. The previous assignment of fundamental vibration was confirmed. The medium dependent relative Intensities and frequencies of the vibrational bands are interpreted in terms of the competition between an intermolecular change transfer interacting (vibrating coupling) and hydrogen bonding.

Keyword:, FT -IR, FT-Raman, HOMO-LUMO, Density functional theorem

INTRODUCTION

Dithiooxamide, originally known as rebeanic acid is a deep red crystalline solid with a decomposition temperature of approximately 200 °C. It is a chelating agent for the detecting determining copper, cobalt, and nickel . It is also used to stabilize ascorbic acid in acidic solutions.

In early 2015, H. Firouzabdi, N, Iranpoor, and co-workers at shiraz university (Iran) discovered that dithiooxamide can be used as a thiolating agent. Because it is stable, odorless, and commercially available. It is an excellent alternative to thiol reagents, which are foul-smelling and oftn require harsh reaction conditions. It reacts with alkyl or benzyl halides in base at 35 c to form sulfides. With aryl halides, the reaction is run at 120c with a catalyst.

APPLICATION

- Synthesis of thiazolothiazole-linked porous organic polymers under solvothermal conditions.
- As modifier to prepare the modified glassy carbon electrode, used to investigate the electrochemical properties of quercetin. An important flavonoid derivative.
- Synthesis of new chelating resin of dithiooxamide (rubeanic acid)- formaldehyde (DTOF), used in separation and concentration of silver ions.
- Synthesis of N,N'- disubstituteddithiooxamide.
- Dithiooxamide is reported to form complexes with Ni.

Both ab initio and semi-empirical approaches involve approximations. These range from simplified forms of the first-principle equations that are easier or faster to solver, to approximations limiting the size of the system (for example, periodic boundary conditions), to fundamental approximations to the underlying equations that are required to achieve any solution to them underlying equations that calculations make the Born-Oppenheimer approximations, which greatly simplifies the underlying Schrodinger equation by assuming that the nuclei remain in place during solution of the underlying equations as the number of approximations, and residual error inevitably remains. The goal of computational chemistry is to minimize this residual error while keeping the calculations tractable.

METHODS IN COMPUTATIONS:

One molecular formula can represent more than one molecular isomer: a set of isomers. Each isomer is a local minimum on the energy surface (called the potential energy surface) created from the total energy(i.e., the electronic energy, plus the repulsion energy between the nuclei) as a function of the coordinates of all the nuclei. A stationary point is geometry such that the derivative of the energy with respect to all displacements of the nuclei is zero. A local (energy) minimum is a stationary point where all such displacements lead to an increase in energy. The local minimum that is lowest is called the global minimum and corresponds to the most stable isomer. If there is one particular coordinate change that leads to decrease in the total energy in both directions, the stationary point is a transition structure and the coordinate is the reaction coordinate. This process of determining stationary points is called geometry optimizing.

The determination of molecular structure by geometry optimizing became routine only after efficient methods for calculating the first derivatives of the energy with respect to all atomic coordinates became available. Evaluation of the related second derivatives allows the prediction of vibrational frequencies of harmonic motion is estimated. More importantly, it allows for the characterization of stationary points. The frequencies are related to the eigenvalues of the Hessian matrix, which contains second derivatives. If the eigenvalues are all positive, then the frequencies are all real and the stationary point is a local minimum. Of one eigenvalue is negative (i.e., an imaginary frequency), then the stationary point is a transition structure. Of more than one eigenvalue is negative, then the stationary point is a more complex one, and is usually of little interest. When one of these is found, it is necessary to move the search away from it if the experimenter is looking solely for local minima and transition structures.

The total energy is determined by approximate solutions of the time-dependent Schrodinger equation, usually with no relativistic terms included, and by making use of the Born-Oppenheimer approximation, which allows for the separation of electronic and nuclear motions, thereby simplifying the schrodinger equation. This leads to the evaluation of the total energy as a sum of the electronic energy at fixed nuclei positions and the repulsion energy of the nuclei. Notable exceptions are certain approaches called direct quantum chemistry, which treat electrons and nuclei on a common footing. Density functional methods and semi-empirical methods are variants on the major theme. For very systems, the relative total energies can ne compare using, molecular mechanics. The ways of determining the total energy to predict molecular structures are.

The hetroaromatic structure shows the presence of C–H stretching vibrations in the region 3184 - 3179 cm^{-1} which is the region for ready identification of C–H stretching vibrations. The band appeared at 3100 and 3000 cm^{-1} in the Dithiooxamide. Dithiooxamide have been assigned to C–H stretching vibrations. In the present case, C–H in-plane bending vibrations of the present compounds are identified at 1461 cm^{-1} for Dithiooxamide. The calculated frequencies of HF for C–H in-plane bending vibrations showed in Table1.The C–H out-of-plane bending vibrations are normally observed in the region 1359 cm^{-1}. The C–H out-of-plane bending vibrations are observed at 877 cm^{-1} for Dithiooxamide. These in-plane and out-of-plane vibrational frequencies are found to be well within their characteristic region.

DENSITY FUNCTIONAL THEORY FORMALISM

Derivation and formulation of density functional theory, which eliminates the formal and practical inconsistencies and limitations of previous theories and allows its extension to stationary states other than the ground state, is given. The theory presented here can also be stated as a series of three theorems that define a family of its mathematical forms, as far as the physical content of the third theorem can either be implicitly incorporated in the density functional or explicitly in the procedure to find a solution to the equations. Examples of both cases are discussed, including the statement of configuration interaction procedure in density functional form.

C–C vibrations

The aromatic carbon–carbon stretching vibrations of the title compound are observed at 1625 and 1400 cm^{-1} and 1380 – 1280 cm^{-1} in IR spectrum. C-C stretching are observed at 1617 cm^{-1} and 807 cm^{-1}. Several ring modes were affected by the substitution to the aromatic ring of the title compound Dithiooxamide

In the present study, the IR bands for compound have been assigned to ring in-plane modes and the out-of-plane deformation modes, are considered carefully by their quantitative descriptions. These assignments are shown in Table1

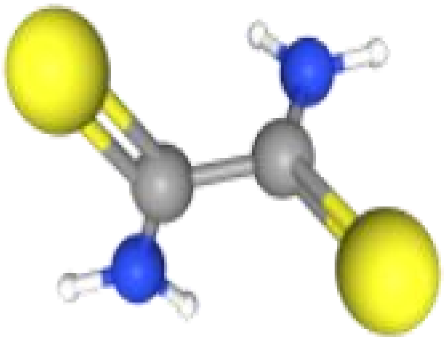
C-C-C VIBRATION

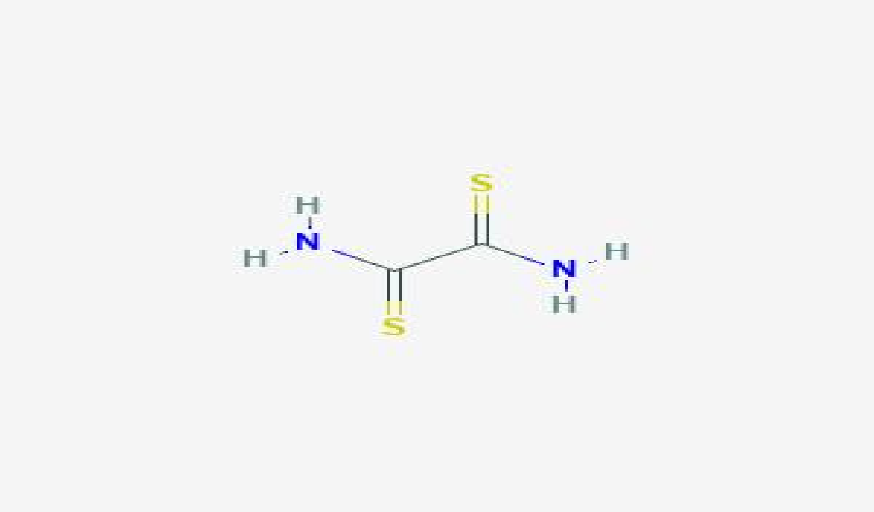
The ring C-C and CAC stretching vibrations known as scientific stretching usually occur in the region 392cm^{-1} . Hence in the present investigate the FT-IR bands identified at 392,760cm^{-1} are assigned to CAC stretching vibrations of dithiooxamide.The band ascribed at 760cm^{-1} in FT-IR and 392, 760cm^{-1} in thr FT-Raman spectra has been designated to CC in-plane and out-of-plane bending mode.

List of Figures:

MOLECULAR STRUCTURE OF DITHIOOXAMIDE

Fig;1 structure of Dithiooxamide

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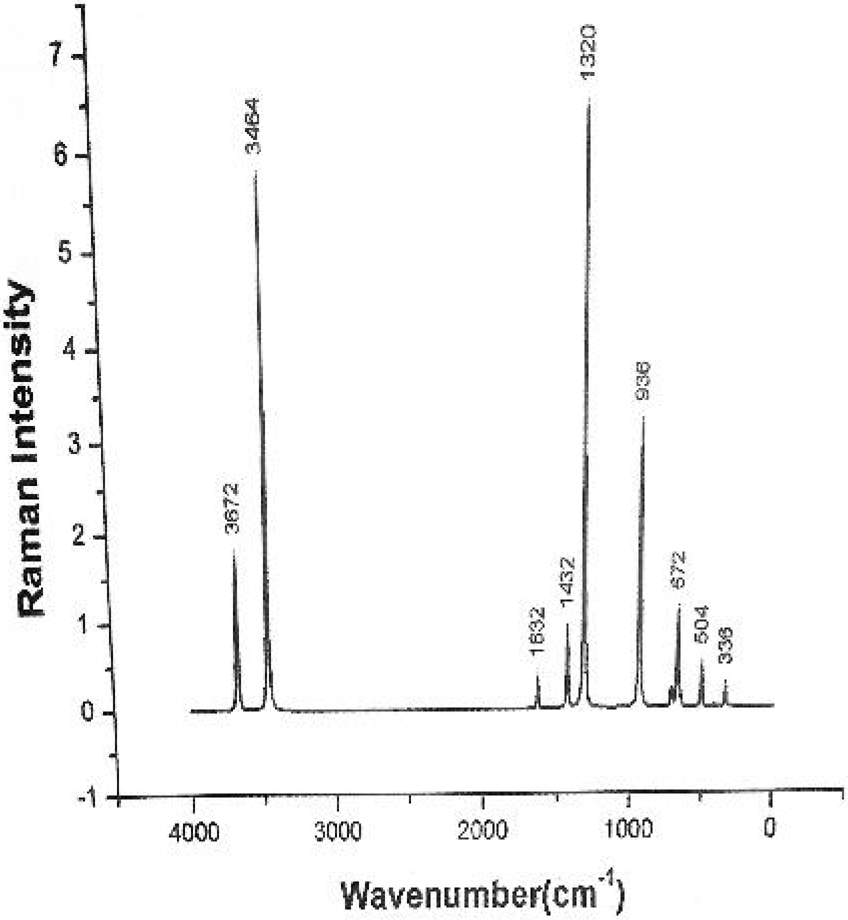

FT – Raman Graph

List of Table :

Table 1 Vibrational assignments of Dithiooxamide

DITHIOOXAMIDE

IR	RAMAN	ASSIGNMENTS
48	-	
280	-	CH wages (symmetrical)
392	336	Asymmetrical bending (CCC) (ring)
528	504	Out-of-plane bending (CC)
664	672	CC out-of Plane bending
864	936	CC In Plane bending
1240	1320	Stretching aromatic amines
1424	1432	Asymmetrical bending (CH3)
1600	1632	In Plane bending HNH
3472	3464	Stretching asymmetric
3680	3672	

CONCLUSION

The vibrational spectral analysis of Dithiooxamide was performed using DFT calculation, attempts have been made in the current for the proper frequency assignments for the compound Dithiooxamide from the FT-IR spectrum. The Raman and infrared assignment a calculated and analyzed by DFT method. Comparison between the calculated vibrational frequencies and the experimental values indicates that the methods can predict. The FT-IR spectral of the title compound well.

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