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Determination of the optical constants of 2-amino-5-phenyl-1,3,4-thiadiazole by Hartree–Fock and density functional method (B3LYP)

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Abstract

The optical constants (real and imaginary refractive index) and complex dielectric constants of 2-amino-5-phenyl-1,3,4-thiadiazole between 4000 and 400 cm^{-1} at 25 °C were calculated using the Hartree–Fock and density functional method (B3LYP) and are reported for the first time. The Cauchy parameters obtained from the refractive index spectrum were found to be $A=9.870$, $B=2.85\times10^{-5}$ cm^2 and $C=8.86\times10^{-12}$ cm^4 for experimental results and $A=15.369$, $B=3.19\times10^{-5}$ cm^2 and $C=1.49\times10^{-12}$ cm^4 for HF model and $A=9.871$, $B=1.73\times10^{-5}$ cm^2 and $C=9.24\times10^{-13}$ cm^4 for B3LYP model. The real and imaginary parts of the complex dielectric constant of the compound were calculated. The real part of the dielectric constant is higher than the imaginary part. The variation of the dielectric constant with photon energy indicates that some interactions between photons and electrons in the film are produced in the investigated energy range. These interactions are observed on the shapes of the real and imaginary parts of the dielectric constant and they cause formation of peaks in dielectric spectra. As a result, the optical constants obtained by using HF and DFT (B3LYP) methods show the best agreement with the experimental data.

Keywords: Thin film; Refractive index dispersion; Complex dielectric constant

1. Introduction

The 2-amino-5-phenyl-1,3,4-thiadiazole ring is associated with diverse biological activities, which can be explained by the presence of the toxiphocic –N=C–S– linkage, the importance of which in many pesticides has been reported [1–3]. Various 2-amino-substituted 1,3,4-thiadiazolles and their Schiff bases also exhibit diverse biological and pharmacological activities [4–9]. The new optical materials can be produced with these compounds. These compounds, containing Schiff bases, seem to be suitable candidates for further chemical modifications and may be optical communication and optical devices [10,11]. The optical constants, such as refractive index, extinction coefficient and dielectric constant are important parameters to design the optical materials and they include the valuable information for technological applications of studied materials. Furthermore, the changes in refractive index are an important for controlling optical properties of organic compounds. Optical properties of any organic compound and metal complex are important for optical applications, because optical properties are directly related with the structural and electronic properties of their. The optical constants, such as refractive index, absorption index and dielectric constant can be analyzed by transmittance and reflectance spectra [12–14] and these constants are calculated using Kramers–Kronig (KK) transformations. Infrared spectra (IR) properties of the organic compounds and metal complexes can provide an insight into the high-frequency dielectric properties and optical constants of materials studied. The theoretical IR spectrums of the organic compounds can be calculated by various methods such as Hartree–Fock and density functional method (B3LYP) to determine optical constants of the materials. Density functional theory calculations are reported to

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provide excellent vibrational frequencies of organic compounds, if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [15,16]. Rauhut and Pulay calculated the vibrational spectra of thirty-one molecules by using B3LYP method with 6-31G(d) basis set [17–19]. In their work, they calculated vibrational frequencies of 20 smaller molecules whose experimental vibrational frequencies are well assigned, and derived transferable scaling factors by using least-square method. The scaling factors are successfully applied to other 11 larger molecules. Thus, vibrational frequencies calculated by using the B3LYP functional with 6-31G(d) basis could be utilized to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra [20].

In present study, we report theoretical studies of the optical constants of 2-amino-5-phenyl-1,3,4-thiadiazole by Hartree–Fock and density functional method (B3LYP).

2. Experimental

2.1. The preparation of the thin film

In previous publication; the crystal structure and vibrational spectra of the title compound had been studied [9]. The experimental chemical structure of the compound is shown in Fig. 1a. The film of the compound was prepared by evaporating the solvent from a solution of the compound with subsequent drying of the film deposited on quartz substrate. The solution of the compound was homogenized for 3 h and was rotated for homogeneous mixing. The film thickness was calculated from the transmittance spectrum of the film and was obtained as ~5.5 μm [21]. IR spectrum of the thin film was recorded by FT-IR spectrophotometer at room temperature.

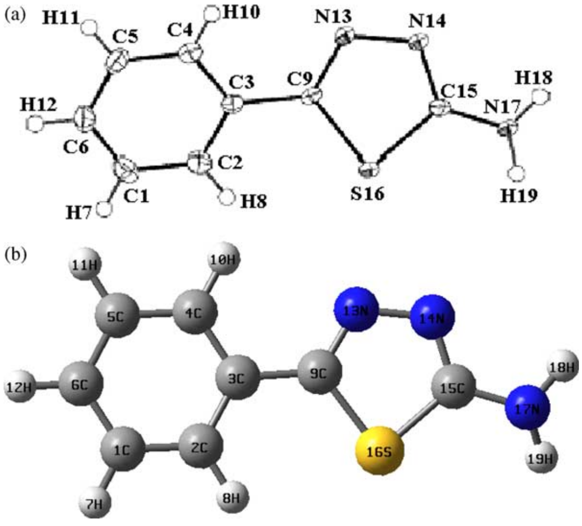

Fig. 1. (a) The experimental geometric structure of the title compound (displacement ellipsoids for non-H atoms are drawn at the 50% probability level) taken from Ref. [14]. (b) The theoretical geometric structure of the title compound.

2.2. Theoretical calculations

The molecular structure of the title compound ($C_8H_7N_3S$) in the ground state (in vacuo) are optimized by HF and B3LYP with the 6-31G(d) basis set. Two sets of vibrational frequencies for these species are calculated with these methods and then scaled by 0.8929 and 0.9613 [22], respectively. The theoretical geometric structure of the title compound is given in Fig. 1b. The title compound has been drawing by using Gauss-View molecular visualisation program [23] and GAUSSIAN 98 program package on personal computer [24]. In our calculations, we have used 6-31G(d) basis set for the heavy atoms. Even though the double plus version 6-31++G(d) adds diffuse functions to the hydrogen atom, we have not used that edition as these kind of diffuse functions on hydrogen atom seldom make significant change in accuracy [25]. The optimized parameters of IR spectrum by HF and B3LYP with 6-31G(d) as the basic set are calculated and compared with the experimental crystal geometry for the title compound ($C_8H_7N_3S$).

2.3. Determination of the optical constants

The spectral curves including refractive index, transmittance, reflectance, dielectric constant parameters are obtained by Kramers–Kroning (KK) relations [26]. The KK relations linking ε_1 and ε_2 can be derived and these are

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\int_0^{\infty} \frac{\omega'\varepsilon_2(\omega')}{(\omega')^2 - \omega^2}\,d\omega' \tag{1}$$

$$\varepsilon_2(\omega) = -\frac{2\omega}{\pi}\int_0^{\infty} \frac{\varepsilon_1(\omega')}{(\omega')^2 - \omega^2}\,d\omega' \tag{2}$$

These equations are of fundamental importance.

The complex refractive index for the compound can be expressed as

$$\hat{n}(E) = n(E) + ik(E) \tag{3}$$

where $n(E)$ is the ordinary (real) refractive index and $k(E)$ is the extinction coefficient, also called the attenuation index. The $n(E)$ and $k(E)$ constants can be determined from the optical measurements. From Eq. (3), it follows that

$$\varepsilon_1 = n^2 - k^2 \tag{4}$$

and

$$\varepsilon_2 = 2nk \tag{5}$$