



Vibrational and electronic investigations, thermodynamic parameters, HOMO and LUMO analysis on crotonaldehyde by *ab initio* and DFT methods

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ABSTRACT

The energy, geometrical parameters and vibrational wavenumbers of crotonaldehyde were calculated by using *ab initio* and B3LYP with 6-31G(d,p) and 6-311G(d,p) basis sets. The FT-IR and FT-Raman spectra for liquid state crotonaldehyde have been recorded in the region 3400–400 cm⁻¹ and 3400–100 cm⁻¹, respectively and compared with the theoretical spectrographs constructed from the scaled harmonic vibrational frequencies calculated at HF and DFT levels. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. Detailed interpretations on vibrational modes have been made on the observed and theoretical spectra and PED for each mode was also reported more precisely. HOMO and LUMO energy levels are constructed and the corresponding theoretical frontier energy gaps are calculated to realise the charge transfer occurring in the molecule. The thermodynamic properties of the title compound have been calculated at different temperatures and the results reveals the standard heat capacities (C_p^0), standard entropies (S^0) and standard enthalpy changes (ΔH^0) increases with rise in temperature.

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1. Introduction

The study of the vibrational spectra of crotonaldehyde (C₄H₆O) attracts the attention of many spectroscopists due to its wide industrial applications in particular, in the manufacture of sorbic acid, which is used as a food preservative, yeast and mold inhibitor. Crotonaldehyde is clear, highly flammable, lachrymatory liquid, moderately soluble in water and miscible in organic solvents. It is used as a warning agent in gas fuels to detect small leakages, in the preparation of rubber accelerators, in leather tanning, as an alcohol denaturant and as a stabilizer for tetraethyl lead. It is a raw material for trimethylhydroquinone—a precursor to the vitamin E, crotonic acid—crotonylidene ureas, thiophenes, pyridines, pharmaceuticals, dyes and pesticides [1–3]. Crotonaldehyde is versatile intermediate in the synthesis of butanol, butanal and quinaldine too [4,5]. The vapours of crotonaldehyde are extremely irritating to eyes, skin, and mucous membranes.

The combination of DFT calculations and vibrational spectroscopy leads to a good understanding of the molecular characteristics and bonding in compounds [6–10]. In particular, for polyatomic molecules the HF and DFT methods lead to the predic-

tion of more accurate molecular structure, vibrational frequencies of the fundamental modes, thermodynamic and electronic properties. Several investigations like optical transmission, refractive index, electro-optic effect and dielectric constant were reported by Tao et al. [11]. Vibrational spectroscopic study on crotonaldehyde oxime was carried out using microwave spectra and its excited vibrational states were studied [12]. Recently a complementary experimental and theoretical study of crotonaldehyde was carried out by Haubrich et al. [13] using high resolution electron energy loss spectroscopy. Though few vibrational studies on the title molecule and its derivatives are available in the literature in recent years [6–14], a detailed quantum chemical study on the observed FT-IR and FT-Raman spectra of crotonaldehyde has not been ornately reported so far. Also it is observed that the electronic data and thermodynamic parameters at various temperatures, which are vital to elucidate the relations among energetic, structural and reactivity of the title molecule, are insufficient in the literature. Thus, an attempt has been made in the present work to compute and compare the ground state optimised molecular geometrical parameters, harmonic frequencies, thermodynamic and electronic properties using the Hartee–Fock (HF) and Becke's three parameter exact exchange functional (B3) combined with gradient corrected correlation functional of Lee, Yang and Parr (LYP) methods with 6-31G(d,p) and 6-311G(d,p) basis sets. These methods predict substantial optimised molecular structure and wavenumbers for the vibrational

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modes with moderate computational effect. The present vibrational spectroscopic studies of crotonaldehyde not only help for the proper assignments of the observed and computed frequencies but also offer a comprehensive picture on the molecular dynamics and electronic properties.

2. Experimental details

The compound crotonaldehyde of spectroscopic grade was purchased from Aldrich chemicals, U.S.A. and used as such for recording the spectra without any further purification. The FT-IR spectrum of the compound was recorded as neat liquid in Bruker IFS 66V spectrometer in the range of 3400–400 cm^{-1} . The FT-Raman spectrum of the compound was also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm excitation wavelengths, with 200 mW powers. The FT-Raman spectrum is recorded in the range of 3400–100 cm^{-1} with scanning speed of 30 $\text{cm}^{-1} \text{min}^{-1}$ of spectral width 2 cm^{-1} . The frequencies of all sharp bands are accurate to 1 cm^{-1} .

3. Computational details

The geometry of crotonaldehyde was optimised at HF [15–17] and DFT level Becke's three parameter exchange functional (B3) [18,19] combined with gradient corrected correlation functional of Lee, Yang and Parr (LYP) [20] on a Pentium core-i3 processor using Gaussian 03W program [21] with 6-31G(d,p) and 6-311G(d,p) basis sets. The optimised structural parameters, vibrational frequency of the fundamental modes and ground state energy of optimised structure were also computed. The absence of imaginary frequency modes for the optimised structure of crotonaldehyde at HF and DFT levels confirm a true minimum on the potential energy surface. GaussView 5.0.8 program has been used to construct optimised molecular geometry, HOMO, LUMO energy distributions, and HOMO–LUMO energy gap [22,23]. As the HF and hybrid B3LYP functional tend to overestimate the fundamental normal modes of vibration, the computed frequencies were scaled with appropriate values to bring harmonisation between theoretical and experimental wavenumbers [24,25]. The theoretical results have enabled us to make the appropriate assignments of the experimental FT-IR and FT-Raman spectra of the molecule. The force constants calculated using B3LYP method with basis set 6-311G(d,p) have been employed in the normal coordinate analysis to carry out potential energy distribution (PED) calculation using Wilson's FG matrix method [26–28] with the perturbation program provided by Fuhrer et al. [29]. High level of accuracy was adopted for vibrational frequency assignments with symmetry considerations. Subsequent potential energy distribution (PED) to each observed frequencies, predicts well the purity of the fundamental modes and shows the reliability and accuracy of the spectral analysis. The HF and B3LYP methods have also been used to calculate the thermodynamic and electronic parameters like self-consistent field (SCF) energy (Hartree), zero point vibrational energy (ZPVE) (kcal mol^{-1}), rotational constants (GHz), heat capacity at constant volume (C_V) ($\text{cal mol}^{-1} \text{K}^{-1}$), heat capacity at constant pressure (C_p) ($\text{cal mol}^{-1} \text{K}^{-1}$), entropy (S) ($\text{cal mol}^{-1} \text{K}^{-1}$), enthalpy change ($\Delta H_{0 \rightarrow T}$) (kcal mol^{-1}), dipole moment μ (Debye), HOMO and LUMO energies (eV), frontier molecular orbital energy gaps (eV) and atomic charges (eV) by natural bond orbital analysis.

3.1. Prediction of Raman intensities

The Raman intensities (I_i) were calculated from the Raman activities (S_i) obtained with Gaussian 03 program, using the following

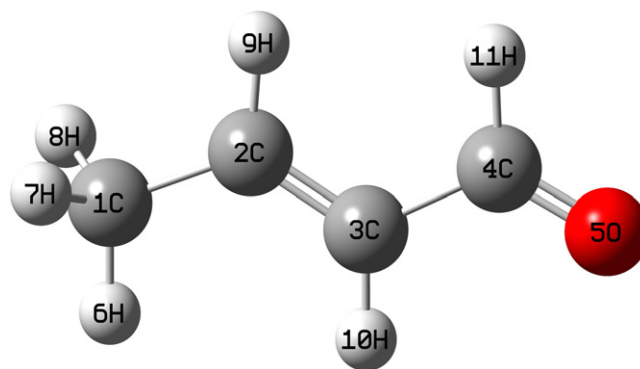


Fig. 1. Molecular structure of crotonaldehyde.

relationship derived from the intensity theory of Raman scattering [30,31]

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i/kT)]} \quad (1)$$

where ν_0 is the laser exciting wavenumber in cm^{-1} , ν_i the vibrational wavenumber of the i th normal mode (cm^{-1}), S_i is the Raman scattering activity of the normal mode ν_i , f is a suitably chosen common normalisation factor (a constant equal to 10^{-12}) for all peak intensities. While h , k , c and T are Planck constant and Boltzmann constants, speed of light and temperature in Kelvin, respectively. In the present work, the excitation wavenumber $\nu_0 = 9398.5 \text{ cm}^{-1}$, which corresponds to the wavelength of 1064 nm Nd:YAG laser has been used. The calculated Raman and IR spectra have been plotted using the pure Lorentian band shape with a band width of FWHM of 2 cm^{-1} .

4. Results and discussion

4.1. Molecular geometry

The optimised molecular structure of crotonaldehyde with the numbering scheme of the atoms obtained from GaussView 5.0.8 program [32] is shown in Fig. 1.

The optimised structural parameters such as bond lengths, bond angles and dihedral angles determined by theoretical HF and B3LYP methods with 6-31G(d,p) and 6-311G(d,p) basis sets were compared with experimental parameters obtained from the electron diffraction studies [33,34] in Table 1. The differences of the calculated geometrical parameters from the experimental parameters were found to be about 0.034 Å (C=O), 0.037 Å (C=C), 0.051 Å (C–C) and 0.01 Å (C–H) bond lengths while for bond angles 3.07° (C–C–H, H–C–H), 2.7° (C=C–C) and 0.92° (C–C=O). The deviation of theoretical parameters of optimised geometry from the experimental values is due to fact that the theoretical calculations belong to molecule in the gaseous phase while the experimental results belong to the molecule in liquid state. The calculated geometrical parameters represent a good approximation and they are the basis for calculating vibrational frequencies and thermodynamic parameters. The calculated bond lengths by HF method are slightly shorter, while the values of B3LYP method are closer with experimental values. This indicates that B3LYP method estimate the electron correlation effect well than the HF method.

In order to portray the conformational flexibility of the title molecule, the relative energy profile as a function of C2–C3–C4–O5 torsion angle was obtained using B3LYP/6-311G(d,p) method by varying the dihedral angle from 0° to 360° with a grid size of 10°. From Fig. 2 it is observed the conformational energy profile shows a local minimum observed at 180° and the respective energies is

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