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Vibrational spectra and first-order molecular hyperpolarizabilities of p-hydroxybenzaldehyde dimer

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ABSTRACT

Single crystals of p-hydroxybenzaldehyde (PHBA) were grown by the slow evaporation technique and vibrational spectral analysis was carried out using near-IR Fourier transform Raman and Fourier transform IR spectroscopy. The density functional theoretical (DFT) computations were also performed at the B3LYP/6-311++G(d,p) level to derive the equilibrium geometry, vibrational wavenumbers and intensities. The detailed interpretation of the vibrational spectra has been carried out with the aid of normal coordinate analysis (NCA) following the scaled quantum mechanical force field methodology. The various intramolecular interactions that is responsible for the stabilization of the molecule was revealed by natural bond orbital analysis. Vibrational analysis based on the NIR-FT-Raman, FT-IR and computed spectrum reveals that the CH in-plane bending of the aldehyde group interacts with its stretching mode via Fermi Resonance and evidence for intermolecular interaction can be well identified as two CH bands in IR spectra at 2740 and 2804 cm^{-1} aldehyde group of the p-hydroxybenzaldehyde dimer. The red shift of the O–H stretching wavenumber is due to the formation of strong O–H···O hydrogen bonds by hyperconjugation between the carbonyl oxygen lone electron pairs and the O–H σ^* anti-bonding orbitals.

1. Introduction

The search for new materials with non-linear optical (NLO) properties has been the subject of intense research due to their application in a wide range of technologies such as optical computing and optical communication [1,2]. In the past years much attention has been paid to organic NLO materials due to their promising applications in optoelectronics technology [3,4], their large nonlinear response, extremely fast switching time and convenient optimization routes through molecular engineering compared to the currently studied inorganic materials [5]. It has been generally understood that for a material to have useful and highly efficient NLO properties, the constituting molecules need first to exhibit large molecular hyperpolarizabilities, which are generally characterized by a highly extended π-conjugated chain with strong electron donor–acceptor pairs at the ends (D–π–A) [6]. Since a large molecular hyperpolarizability β is the basis of a strong second harmonic generation (SHG) response; organic molecules with long conjugation systems that usually exhibit large β values are certainly candidate molecules for NLO materials.

The benzaldehyde and substituted benzaldehydes have been subjected to various spectroscopic studies [7–24]. Mono-, halo-, methoxy and ethoxy-substituted benzaldehydes, among others, have attracted the attention of the spectroscopists. *o*- and *m*-Chlorobenzaldehydes have been shown to have *trans* and *cis* conformers by Matrix Isolation IR spectroscopy [25]. Vibrational spectral studies of the molecules can provide deeper knowledge about the relationships between molecular architecture, non-linear response, and hyperpolarizability and support the efforts towards discovery of new efficient materials for technological applications. NIR-FT-Raman spectroscopy combined with quantum chemical computations have recently been used as effective tools in the vibrational analysis of drug molecules, biological compounds natural products and NLO active compounds [26–30], since fluorescence free Raman spectra and computed results can help unambiguous identification of vibrational modes as well as the bonding and structural features of complex organic molecular systems. The present work deals with detailed vibrational spectral investigation of p-hydroxybenzaldehyde (PHBA) dimer (Fig. 1) molecules using NIR-FT-Raman and FT-IR spectra, along with density functional theoretical computations to study the structural and bonding features, nature of hydrogen bonding and vibrational

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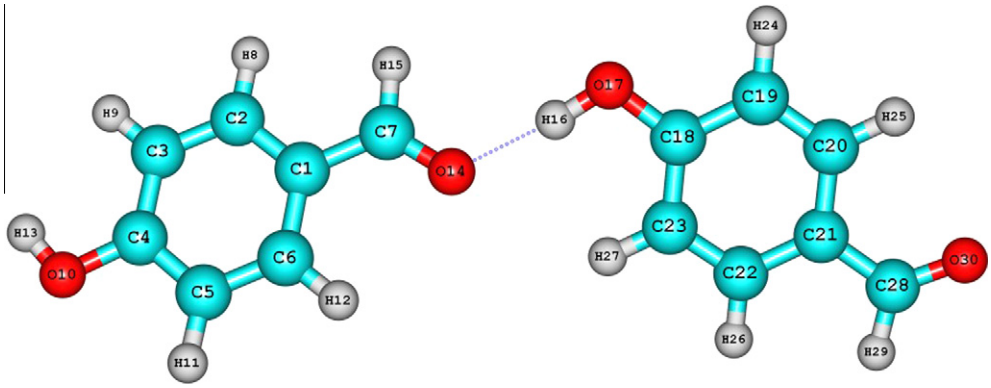

Fig. 1. Optimized structure of PHBA dimer calculated at B3LYP/6-31++G(d,p).

interactions of the molecule supported by scaled quantum mechanical (SQM) force field calculations.

2. Materials and methods

2.1. Sample preparation

The title compound 4-hydroxybenzaldehyde (98% Aldrich) was obtained from Sigma–Aldrich and was recrystallized from ethylacetate by slow evaporation [31] to obtain good quality crystals.

2.2. IR and Raman measurements

The FT-IR spectrum of PHBA was recorded using Perkin Elmer RXI spectrometer in the region 4000–500 cm^{-1}, with samples in the KBr. The resolution of the spectrum is 2 cm^{-1}. The NIR-FT-Raman spectrum of PHBA crystal was obtained in the range 3500–10 cm^{-1} using Bruker RFS 100/S FT-Raman spectrophotometer with a 1064 nm Nd: YAG laser source of 100 mW power. Liquid nitrogen cooled Ge-diode was used as a detector. Spectra were collected for samples with 1000 scan accumulated for over 30 min duration. The spectral resolution after apodization was 2 cm^{-1}.

3. Computational methods

The DFT computations has been used to calculate the equilibrium structures of PHBA in the form of Becke's three-parameter exchange functional in combination with the Lee, Yang and Parr (LYP) correlation functional (B3LYP) combined with split valence basis sets 6-311++G(d,p). Equilibrium molecular geometry was fully optimized and harmonic vibrational wavenumber analysis was then performed to confirm the minima on the potential energy surface. All calculations were performed using the Gaussian'09 program package [32]. In order to assist assignments of vibrational modes, the theoretical infrared and Raman spectra were calculated. The calculated vibrational wavenumbers were scaled [33] with the scale factors in order to figure out how the calculated data were in agreement with those of the experimental ones. The vibrational modes were assigned on the basis of PED analysis using Scaled Quantum Mechanics (SQM) program [34]. The infrared intensities were calculated on the basis of the dipole moment derivatives with respect to the Cartesian coordinates. The Raman activities (S_i) calculated by the Gaussian-09 program have been converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [35,36].

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

where ν_o is the exciting frequency (in cm^{-1} units), ν_i is the vibrational wavenumber of the ith normal mode, hc and k are universal constants, and f is the suitably chosen common scaling factor for all the peak intensities. The simulated IR and Raman spectra have been plotted using pure Lorentzian band shapes with full width at half maximum (FWHM) of 10 cm^{-1}.

4. Results and discussion

4.1. Crystal structure

PHBA crystallizes in space group $P2_{1/C}$. From the single crystal XRD data [31] it is observed that the crystal belongs to monoclinic system with the following cell dimensions: a = 6.6992 Å, b = 13.5550 Å, c = 7.1441 Å, $\alpha = \gamma = 90°$, β = 112.871°. Crystal packing is stabilized by intermolecular O–H···O interactions between the hydroxyl and aldehyde groups which link the molecules into chains in a zigzag pattern along the [1 1 0] plane of the unit cell.

4.2. Optimized geometry

The optimized geometrical parameters are given in Table 1 with the comparison of the XRD data. The global minimum energy of PHBA monomer and dimer calculated by DFT structure optimization method is −420.9188 Hartrees and −841.8522 Hartrees, respectively. The molecules in PHBA dimer (Fig. 1) are bound together via O_{17}–H_{16}···O_{14} hydrogen-bonded interaction. This interaction arises largely through the one equivalent stable hydrogen bonded O_{17}–H_{16}···O_{14} and contacts that result in increased stabilization. By examining Table 1 it becomes evident that O17–H_{16} (0.016 Å) and C_7=O_{14} (0.01 Å) bonds are significantly elongated while C_{18}–O_{17} bonds are shortened. The shortening of the C_{18}–O_{17} bond (single) upon dimerization is due to the redistribution of partial charges on the O atoms as the unpaired electron is significantly delocalized and thereby the C_{18}–O_{17} bond shows considerable double bond character typical of a carbonyl group. The intermolecular hydrogen bond O_{17}–H_{16}···O_{14} is 1.793 Å which is slightly lower as compared to that reported values [31]. The optimized geometry shows that OH and CHO groups substituted in para position of phenyl ring which predicts maximum conjugation of molecule with donor and acceptor groups. The C_{18}–O_{17} [1.348 Å] and C_1–C_7 [1.460 Å] bond lengths are only slightly shorter than normal C–O and C–C single bonds, indicating conjugation between the two aromatic ring systems.