

On the anomalous vibration spectra and O–H···N bond dictated structure of 3-fluoroisonicotinic acid

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ABSTRACT

The vibrational structure of solid 3-fluoroisonicotinic acid, as measured by IR absorption and Raman spectra in the 4000–50 cm⁻¹ region and aided by B3LYP/6-311++G(d,p) and NBO calculations has been analyzed. While anomalous spectral behavior similar to that in pyridine-carboxylic acids has been observed as two broad medium absorptions 2436 and 1870 cm⁻¹, the inverted bands observed in isonicotinic acid, are present as ‘normal’ bands near 1488, 1308, 1132, 1062, and 823 cm⁻¹. It has been shown by dimer modeling that the absorptions at 2436 and 1308 cm⁻¹ correspond to O–H stretching and in-plane vibrations originating from inter-molecular O–H···N bonding. Formation of a network of dimer chains has been shown to be a result of C–H···O bond links, giving rise to a local center of inversion between monomer species in the network. This has been validated by observing one broad low intensity Raman band at 1708 cm⁻¹ and one strong broad IR band at 1727 cm⁻¹ assigned as symmetric and anti-symmetric carbonyl modes respectively. In the proposed dimer model, the O–H···N bond length is calculated to be 2.742 Å, shorter than the van der Waals approach, 2.750 Å, placing it in the category of a strong hydrogen bond. The C–H···O bond length for the dimer is calculated to be ~3.282 Å. It has been found that the dimer model is only suggestive of the complex nature of O–H···N bonding but the results generally are in agreement with experiment.

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1. Introduction

The vibrational structures of heterocyclic-carboxylic acids are distinctly ‘anomalous’ when compared with those of common carboxylic acids as characterized by the two broad absorptions near 2450 and 1900 cm⁻¹ [1–3]. In the same manner as the pyridine-carboxylic acids, the three derivatives – isonicotinic acid, nicotinic acid and picolinic acid – show characteristic anomalous features: the anomalously low wavenumber absorptions near 2408 and 1960–1850 cm⁻¹ in isonicotinic acid; 2450 and 1930 cm⁻¹ in nicotinic acid; and 2152 and 2062–1850 cm⁻¹ in picolinic acid. Characteristics entailing these absorptions are that, while the absorption near 2450 cm⁻¹ downshifts to 1900 cm⁻¹ upon deuteration, the 1900 cm⁻¹ band does not show similar behavior; as a result, there appears a rather very broad band or a doublet near 1900 cm⁻¹. These two are assigned to O–H stretching modes. The in-plane O–H bending mode appears at lower region, 1340–1300 cm⁻¹ and shifts to slightly higher wave number values on deuteration [4]. The absorption due to C–O stretching mode ~1360 cm⁻¹ shows similar behavior. The out-of-plane O–H deformation mode does not appear in absorption. Isonicotinic

acid in the crystalline phase has been reported to show strongly anomalous IR absorption and Raman “type ii” spectra: lower broad absorption near 2395 and 1900 cm⁻¹ with a series of inverted bands forming “transmission windows” when the sample is undeuterated, deuterated and under high pressure. Further studies involving X-ray diffraction measurements have determined crystalline structure showing the existence of O–H···N bonding leading to sheets of network linked by C–H···O with simple electrostatic forces, with total O_H···N bond length ~2.582 Å [4,5]. What is of interest is “type ii” spectral behavior showing inverted absorption bands near 1488, 1308, 1132, 1062, and 823 cm⁻¹ attributed to coupling of vibrations, among others, to O–H stretching modes within the molecule or across inter-molecular O–H···N bonding. Even the Raman spectrum shows one inverted band near 1320 cm⁻¹. Theoretical considerations involving perturbation between discrete vibration levels lying above a continuum and the continuum has been invoked to account for the inverted bands [4].

In the present work being reported on the molecular solid 3-fluoroisonicotinic acid, we have sought to investigate whether or not the inverted bands in the vibrational structure of isonicotinic acid survive if the ring is perturbed by, say, a more electronegative halogen fluorine as substituent, since some studies reported on bromine-substituted nicotinic acids apparently have not shown “type ii” spectra [6]. It has been observed that the strongly ‘anomalous behavior’ becomes ‘partially normal’ with no inverted

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bands observed both in IR and Raman spectra but showing lower broad absorptions near 2436 and 1868 cm^{-1} , caused by 'uncommon' O–H...N bonding-assisted crystalline structure as in isonicotinic acid and a modified vibronic structure caused by the presence of fluorine. The band at 2436 cm^{-1} will be shown to arise from O–H...N bonding in a dimer species at 2971 cm^{-1} , modeled at the B3LYP/6-311++G(d,p) level and NBO calculations by assuming a similar inter-molecular network as for isonicotinic acid. Further, it will be shown that O–H...N bond chains are, as in isonicotinic acid, linked by weak electrostatic C–H...O bonds. Two rather broad bands, one as IR at 1727 cm^{-1} and another as Raman at 1708 cm^{-1} , strongly suggest that the network of molecules has a center of inversion causing the two modes to appear mutually exclusively: the 1727 cm^{-1} band does not appear in Raman and the 1708 cm^{-1} band does not appear in IR. We have not observed any inverted bands either as IR or Raman bands near 1496 , 1317 , 1136 , 1062 , and 823 cm^{-1} as in isonicotinic acid; however, some bands observed near these regions have occurred as 'normal' bands. Both IR and Raman spectral features show deviations from characteristic carbonyl and ring vibrations near 1700 – 1500 cm^{-1} . Modes involving the O–H...N and C–H...O bonds have all been shown as identifiable bands by their shapes, broadening and vibration coupling. Vibrational structure has been interpreted on the basis of dimer species formed by O–H...N bonding and is in fair agreement with experiment.

2. Experimental details

The solid sample of 3-fluoroisonicotinic acid was obtained from Aldrich Chemical Co., Bangalore and used as received. The Fourier-transform mid infrared (FT-MIR) spectral measurements (4000 – 400 cm^{-1}) were made on the Bruker IFS66 spectrometer. The spectrometer was equipped with the Globar mid IR source, a KBr beam splitter and air cooled deuterium triglycine sulfate (DTGS) detector. The sample was prepared using KBr pellet technique. The signals were collected for 128 scans at the interval of 4 cm^{-1} . The Raman spectrum was recorded in the region (4000 – 50 cm^{-1}) on Bruker's Multi-Ram FT-Raman. The spectrometer was coupled to Nd-YAG laser source providing 1064 nm as exciting line. It consisted of CaF_2 beam splitter and liquid nitrogen cooled Ge detector. The sample was excited with power ca 100 mW . Co-addition of 500 scans at the interval of 4 cm^{-1} produced high quality interferograms.

3. Computational

Optimization, conformational, vibrational wavenumber analysis, dimer modeling and NBO calculations were carried out at B3LYP/6-311++G(d,p) level using Gaussian 09W and GaussView 5 (GV5) suite of programs [7,8]. Energies, equilibrium geometries, harmonic vibration spectra, molecular constants, orbitals, and hydrogen bonding parameters have been calculated. As for the dimer modeling, appropriate choice of basis set was made from BSSE energy calculations for 6-31G(d,p), 6-311G(d,p) and 6-311++G(d,p). Further, force constants and potential energy distributions (PED) have been deduced from a normal mode analysis for monomer species [9].

4. Results and discussion

4.1. Conformational analysis

Molecular structure with numbering for 3-fluoroisonicotinic acid (3FINA) is presented in Fig. 1. As remarked in Section 1 that the isonicotinic acid (INA) crystal structure is strongly

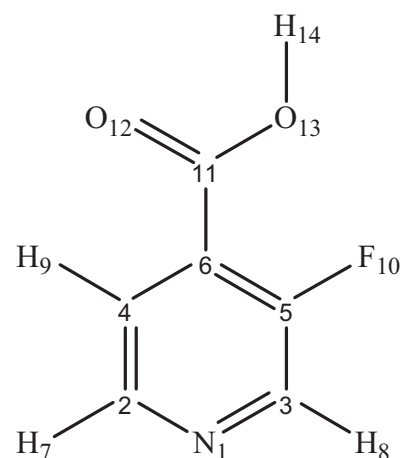


Fig. 1. Molecular structure of 3FINA.

hydrogen-bonded molecular solid, we assumed a similar network for computing dimer species. Initially, to search for monomer conformers, potential energy surface (PES) scanning was carried out for torsional angles O12–C11–C6–C4 and H14–O13–C11–C6 simultaneously from 0° to 360° at the interval of 10° and the results are shown in Fig. 2. We found four distinct conformers, called C-I, C-II, C-III and C-IV as shown in Fig. 3 and their equilibrium energies, relative energies, dipole moments, Boltzmann populations and orientations of carboxylic and OH groups are presented in Table 1. Harmonic vibrational frequencies were calculated for all the located minima in order to ascertain that each structure corresponds to a minimum (stationary point) on the PES. The C-I structure corresponds to the global minimum on the PES with a Boltzmann population $\sim 74.5\%$ and the same conformer as monomer species has been used in the analysis. The next logical step was dictated by the fact that the observed large down-shifted absorption at 2436 cm^{-1} in 3FINA and crystal structure of INA as strongly hydrogen-bonded molecular solid, we needed to model using the C-I conformer, inter-molecular O–H...N hydrogen bonding between the –O–H in carboxylic acid and the nitrogen N in pyridine producing a planar network parallel to *b*-axis (this *b*-axis is the same as established in the XRD studies [5]), linked by C–H...O with simple electrostatic forces. The results of basis set superposition error (BSSE) energy calculations for different basis sets for the dimer species are given in Table 2. The BSSE energy for 6-311++G(d,p) is 0.6795 kcal/mol for dimer which is low and hence this basis set was used for the dimer modeling. This also explains as to why 6-311++G(d,p) basis set has been preferred to

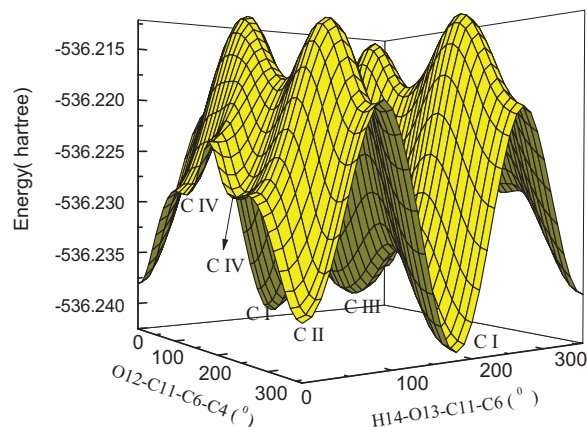


Fig. 2. Potential energy surface of 3FINA.

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