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FT-IR and FT-Raman spectral analysis of 3-(trifluromethyl) phenyl isothiocyanate

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ABSTRACT

The molecular geometry, vibrational frequencies of 3-(trifluromethyl) phenyl isothiocyanate in the ground state have been analyzed using density functional theory calculation (B3LYP) with 6-311++G (d,p) and 6-311++G (2d,2p) basis sets. The optimized geometrical parameters obtained by DFT calculations are in good agreement with experimental values. Comparison of the observed fundamental vibrational frequencies of the 3-(trifluromethyl) phenyl isothiocyanate and calculated result by DFT/B3LYP/6-311++G(d,p)/6-311++G (2d,2p) is superior for molecular vibrational problems. A detailed interpretation of the FTIR and FT-Raman spectra of 3-(trifluromethyl) phenyl isothiocyanate are reported on the basis of the calculated potential energy distribution (PED).

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Introduction

The derivatives of phenyl isothiocyanate are of spectroscopic interest due to the role of NCS and substituents play in the vibrational structures and spectra. It seems that there have been a fewer studies on the vibrational spectroscopy of the derivatives. 3-(trifluromethyl) phenyl isothiocyanate is a colourless liquid with molecular formula CF3 C6H5NCS. It is of irritating odor and is readily volatilized with steam. It is soluble in alcohol and ether, insoluble in water. In the infrared assignments of five mono substituted benzenes, namely nitrobenzenes, phenyl isocyanate, phenyl isothiocyanate, thionylaniline and anisole, Stephenson et al.[1] treated them all, following Whiffelrn [2] as belonging to C2v symmetry. Literature survey reveals that to the best of our knowledge, the results based on quantum chemical calculation, FT-IR and FT-Raman spectral studies on 3-(trifluromethyl) phenyl isothiocyanate have not been reported so far. Hence in the present study, we reported detailed interpretations of the infrared and Raman spectra based on the experimental and theoretical results, which are acceptable and supportable to each other.

Experimental Details

The fine sample of 3-(trifluromethyl) phenyl isothiocyanate was obtained from Lancaster Chemical Company, UK, with a stated purity of 99% and it was used as such without further purification. The FT-Raman spectrum of 3-(trifluromethyl) phenyl isothiocyanate was recorded using 1064nm line of Nd:YAG laser for excitation wavelength in the region 3500-100 cm-1 on thermo electron corporation model Nexus spectrometer equipped with FT-Raman module accessory. The FT-IR spectrum of the title compound was recorded in the region 4000-400 cm-1 on Perkin Elmer spectrophotometer in KBr pellet.

Computational details

The combination of vibrational spectra with quantum chemical calculation is effective for understanding the fundamental mode of vibration of the compound. The structural characteristic, stability and energy of the compound under investigation are determined by density functional theory (DFT) with the three-parameter hybrid functional (B3)[3] for the exchange part and the Lee-Yang Parr (LYP)[4] correlation functional, using 6-311++G(d,p) and 6-311++G (2d,2p) basis sets with Gaussian 09 program package[5]. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming the molecule belongs to Cs point group symmetry. The transformation of force field from Cartesian to internal local symmetry coordinates, the scaling, the subsequent normal coordinate analysis(NCA) calculation of potential energy distribution (PED) were done on a PC with the version V7.0-G77 of the MOLVIB program written by Sundius[6]

Results and Discussion

Molecular geometry

The molecular structure of 3-(trifluromethyl) phenyl isothiocyanate having Cs symmetry is shown in Fig.1. The global minimum energy obtained by DFT/ B3LYP/6-311++G (d,p) and 6-311++G(2d,2p) structure optimization for 3-(trifluromethyl) phenyl isothiocyanate are -559.5122 and -559.5056 Hartrees, respectively. The calculated optimized geometrical parameters obtained in this study for the title compound are compared with the experimental [7,8] values are presented in Table1.

Fig.1 Optimized molecular structure of 3-(trifluromethyl) phenyl isothiocyanate

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Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 58 standard internal coordinates (containing 13 redundancies) for the title compound is presented in Table 2. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combination of internal coordinates following the recommendations of Pulay[9] and Fogarasi [10] are presented in Table 3.

Vibrational assignments

The title compound belongs to Cs symmetry consists of 17 atoms have its 45 normal modes are distributed amongst the symmetry species as √3N-6 = 31 A' (in-plane) + 14 A" (out-of-plane). The detailed vibrational assignments of fundamental modes of 3-(trifluromethyl) phenyl isothiocyanate along with observed and calculated frequencies, Raman activities, infrared intensities, and normal mode descriptions are reported in Table 4. The observed experimental FT-IR, FT-Raman spectra are shown in Figs. 2 and 3, respectively.

C-H vibration — The 3-(trifluromethyl) phenyl isothiocyanate gives rise to the four C-H stretching, four C-H in-plane-bending and four out-of-plane bending vibration corresponding to C2-H10, C6-H17, C5-H16, C4-H15, since 3-(trifluromethyl) phenyl isothiocyanate is di-substituted aromatic system therefore the four C-H moieties are adjacent to one another. The C-H stretching frequency in phenyl[11] is normally lies between 3000 cm-1 and 3100 cm-1. In this region, the bands are not affected appreciably by the nature of substituents. Hence in our present work, the FT-IR bands observed at 3142, 3081, 2950 and 2812 cm-1 are assigned to C-H stretching vibrations, the counter part of the FT-Raman observed at 3085 cm-1. The C-H in-plane bending vibrations which occur in the 1400-1200 cm-1 are very useful characterization purpose and made be very strong indeed[12].

Hence in our present study, the FT-IR bands observed at 1388, 1338 and 1016 cm-1 are assigned in C-H in-plane-bending vibration, the same vibration in FT-Raman spectra at 1109 cm-1 are assigned to C-H in-plane-bending vibrations. The frequencies of the C-H out-of-plane bending vibrations are mainly determined by the number of adjacent hydrogen atoms on the ring and not very much affected by the nature of substitutions[13] normally these vibrations occur in the region 1000-700 cm-1.

The experimentally observed wave numbers for C-H out-plane-bending mode in FT-IR spectrum at 894 cm-1, while the counter part of the Raman spectrum at 1000, 932, and 923 cm-1 are assigned to C-H out-plane bending vibrations. The stretching, in-plane and out-of-plane bending vibration of CH group were found within the characteristic region [14] and literature [15,16]. The theoretically computed frequencies are presented in Table 4.

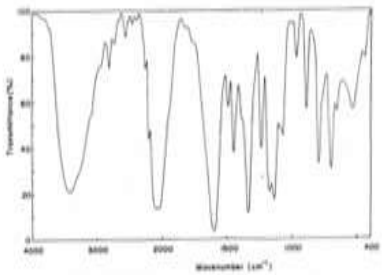
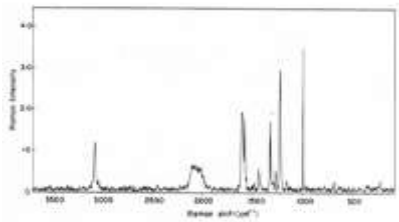


Fig.2 FT-IR spectrum of 3-(trifluromethyl) phenyl isothiocyanate



C-N Vibration — The C-N stretching frequency is a rather difficult task since there are problem in identifying these frequencies from other vibrations. Silverstein *et al*[17] assigned C-N stretching absorption in the region 1382-1266cm^{-1}. In benzotrizole, the C-N stretching bands are found to be present at 1307 and 1382 cm^{-1}. Shanmugam *et al*[18] reported the C-N stretching frequency observed at 1368 cm^{-1}. The same stretching vibration has predicated at 1335 cm^{-1} in 2,4-dinitrophenyl hydrogen[19]. Mani *et al*.[7] assigned C-N stretching absorption at 1169 cm^{-1} in FT-IR and 1120 cm^{-1} in FT-Raman. Hence, in the present work, the band observed at 1245 cm^{-1} both in FT-IR and FT-Raman has been assigned to C-N stretching vibrations. The C-N in-plane bending vibrations are found to be at 695, and 697 cm^{-1} during computation while the experimentally assigned value is 698 cm^{-1}. The band observed at 498 cm^{-1} in Raman spectrum is assigned to the C-N out-of-plane bending mode of the title compound which is good agreement with the computed values by B3LYP/6-311++G(d,p) and 6-311++G(2d,2p) basis sets.

CF_3 vibration — Usually asymmetric and symmetric CF_3 stretching vibrations are in the ranges 1270-1235 cm^{-1} and 1226-1200 cm,$^{-1}$ respectively [20,21]. Therefore, the bands located at 1136, 1104 cm^{-1} and 1071 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations, respectively. They were also supported by the literature[14] . CF_3 deformation [22] vibrations usually occur in the regions 690-630 cm^{-1}, 640-580 cm^{-1} and 590-490 cm^{-1}. Accordingly CF_3sb, CF_3ipb and CF_3opb are identified at 575, 506 and 655 cm^{-1}, respectively. CF_3 rocking vibrational frequency ranges are 450-350 cm^{-1} and 350-260 cm^{-1}. The bands located at 333 and 286 cm^{-1} in infrared spectra are assigned to rocking modes of the CF_3. This is purify because at the low wave number of the CF_3 torsion absorption and the strong intensities rotational spectrometer hosting is not a vacuum instrument also due at fundamental group which is much heavier than the methyl group.

C-C vibrations — The ring carbon-carbon stretching vibrations occur in the region 1625-1430 cm^{-1}. For aromatic six member rings, e.g., benzene and pyridines, there are two or three bands in this region due to skeletal vibrations, the strongest usually being at about 1500 cm^{-1}. In the case where the ring is conjugated further band at about 1580 cm^{-1} is also observed. In general, the bands are of variable intensity and are observed at 1625-1590, 1590-1575, 1525-1470 and 1465-1430 cm^{-1}. For the substituted benzenes with identical atoms or groups on all para-pair of ring carbon atoms, the vibrations causing the bands at 1625-1590 cm^{-1} are infrared-inactive due to symmetry considerations the compound having a centre of symmetry at the ring centre. If the groups on a para-pair of carbon atoms are different them there is no centre of symmetry and vibrations are infrared active[14]. Based on the above literature data, in our present study the medium and strong bands observed at 1593, 1504, 1449, 1171 cm^{-1} in FT-IR spectrum and 1640, 1315 cm^{-1} in Raman are assigned to C-C stretching vibrations. The

theoretical values by B3LYP/6-311++G (d,p)/6-311++G (2d,2p) show satisfactory agreement with recorded spectral data.

NCS vibrations — There are six vibrations for NCS moiety; in phenyl isothiocyanate molecule asymmetric, symmetric stretching, in-plane-bend, in plane wag, out-of-plane bend and out-of-plane wag vibrations[7]. Similarly in our title molecule also for NCS moiety in one can expect the above said vibrations. Hence in our present work, the FT-IR bands are observed at 2100 cm^{-1} and 965 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations. The scaled vibration by B3LYP/6-311++G (d,p)/6-311++G (2d,2p) predict at 2104, 2101, and 965, 965 cm^{-1} are good agreement with the experimentally recorded spectra. The FT-Raman bands observed at 721 and 234 cm^{-1} are assigned to in-plane bend and in-plane wagging vibrations. The theoretically computed values at 720, 235 cm^{-1} and 721, 235 cm^{-1} B3LYP/6-311++G (d,p)/6-311++G(2d,2p) show good agreement with experimental observation. The FT-IR band is observed at 531 cm^{-1} is assigned to out-plan bending vibration. The theoretically computed values are 530 and 531 cm^{-1} by B3LYP level good agreement with experimental observation.

Conclusion

The normal mode frequencies and corresponding vibrational assignments of the title compound are examined theoretically using the Gaussian 09 package. The optimized geometry parameters calculated at B3LYP/6-311++G(d,p)/6-311++G (2d,2p) are slightly shorter as well as longer than experimental data on the whole. The harmonic vibrational frequencies, infrared intensities, Raman scattering activities and IR and Raman spectra of 3-(trifluromethyl) phenyl isothiocyanate were determined and analyzed at DFT/B3LYP/6-311++G(d,p)/6-311++G (2d,2p) level of theory. The close agreement obtained between the observed and calculated frequencies and the PED calculations are also supporting the assignments made for various functional groups present in the molecule. Therefore, the results presented in this work for 3-(trifluromethyl) phenyl isothiocyanate indicate that this level of theory is reliable for prediction of both infrared and Raman spectra.

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