FTIR and FTRaman spectra, assignments, ab initio HF and DFT analysis of 4-nitrotoluene

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ABSTRACT

In this work, the experimental and theoretical study on molecular structure and vibrational spectra of 4-nitrotoluene are studied. The FTIR and FTRaman experimental spectra of the molecule have been recorded in the range of 4000–100 cm^{-1}. Making use of the recorded data, the complete vibrational assignments are made and analysis of the observed fundamental bands of molecule is carried out. The experimental determinations of vibrational frequencies are compared with those obtained theoretically from ab initio HF and DFT quantum mechanical calculations using HF/6-31G (d, p), B3LYP/6-31++G* (d, p) and B3LYP/6-311++G* (d, p) methods. The differences between the observed and scaled wave number values of most of the fundamentals are very small in B3LYP than HF. The geometries and normal modes of vibrations obtained from ab initio HF and B3LYP calculations are in good agreement with the experimentally observed data. Comparison of the simulated spectra provides important information about the ability of the computational method (B3LYP) to describe the vibrational modes. The vibrations of NO_2 and CH_3 groups coupled with skeletal vibrations are also investigated.

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1. Introduction

Toluene is a common solvent, able to dissolve paints, paint thinners, many chemical reactants, rubber, painting ink, glues, lacquers, leather tanners, many disinfectants. It can also be used as fullerene indicator and is also a raw material for certain important products such as polyurethane foam, phenol and TNT. Industrial uses of toluene include de-alkylation to benzene and disproportionation to a mixture of benzene and xylene. Toluene can be used to break open red blood cells in order to extract hemoglobin in biochemistry tests. It is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent. Toluene reacts as a normal aromatic hydrocarbon towards electrophilic aromatic substitution [1,2]. Toluene is also known as methylbenzene or phenylmethane. It is a clear, water insoluble liquid with a typical smell of paint thinners, redolent of the sweet smell of the related compound benzene. It is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent.

4-Nitrotoluene is used as a basic chemical in the chemical industry for the manufacturing of intermediates. 4-Nitrotoluene is an important commercial chemical used to synthesize agricultural and rubber chemicals, azo and sulfur dyes, and dyes for cotton, wool, silk, leather, paper and explosives. 4-Nitrotoluene is used as an intermediate for plastic foams, dyestuffs, paints and pharmaceuticals [3,4]. The 4-nitrotoluene is further used in the production of optical brighteners, coloring agents, pharmaceuticals, and agrochemicals [5]. 4-Nitrotoluene occurs as an intermediate in the production of di- and tri-nitrotoluene but in general isolated 4-nitrotoluene is not used for the synthesis of these products [6,7].

Various spectroscopic studies of halogen and methyl substituted compounds have been reported in the literature [8–19] from time to time. Green and Harrison [8] and Dwivedi and Sharma [18] have studied the vibrational spectra of few dihalogeno toluenes of TXY type toluene halogens. Assuming C_S point group symmetry to the molecules, they carried out the theoretical analysis of the vibrations and assigned the frequencies to various modes of vibrations. Mohan and Feridoun [16] have reported the Raman spectral analysis of 2-fluoro-5-chlorotoluene and 3-fluoro-6-chlorotoluene.

More recently [20], FTIR and FTRaman spectra of ortho, meta and para nitrotoluene have been reported together with the vibrational assignments of the vibrational modes. However, the detailed HF/B3LYP comparative studies on the complete FTIR and FTRaman spectra of 4-nitrotoluene have not been reported so far. In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for HF and B3LYP at 6/31++G* and 6/311++G* (d, p)

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basis sets are compared. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional ab initio Hartree–Fock calculations. Among DFT calculation, Becke's three parameter hybrids functional combined with the Lee–Yang–Parr correlation functional (B3LYP) is the best predicting results for molecular geometry and vibrational wave numbers for moderately larger molecule [21,22].

2. Experimental details

The compound under investigation namely 4-nitrotoluene is purchased from Sigma–Aldrich Chemicals, USA, which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FTIR spectra of the compounds are recorded in Bruker IFS 66V spectrometer in the range of 4000–100 cm^{-1}. The spectral resolution is ± 2 cm^{-1}. The FTRaman spectra of these compounds are also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm line widths with 200 mW power. The spectra are recorded in the range of 4000–100 cm^{-1} with scanning speed of 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}. The frequencies of all sharp bands are accurate to ± 1 cm^{-1}.

3. Computational methods

The molecular structure of the title compound in the ground state is computed by performing both ab initio HF and DFT/B3LYP with 6-31+G (d, p), 6-31++G* (d, p) and 6-311++G* basis sets. The optimized structural parameters are used in the vibrational frequency calculations at HF and DFT levels. The minimum energy of geometrical structure is obtained by using level 6-31++G* (d, p) and 6-311++G* basis sets. Therefore, we had a discussion on calculated values using these sets. The calculated frequencies are scaled by 0.903 and 0.904 for HF [23]. For B3LYP with 6-31++G (d, p) set is scaled with 0.957, 0.904, 0.960 and 0.970 and 6-311++G (d, p) basis set is scaled with 0.967, 0.959, 1.016, 0.912, 0.960, 0.975, 1.10 and 0.967 [24].

The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of the title molecule [25]. HF calculations for 4-nitrotoluene are performed using GAUSSIAN 03W program package on Pentium IV processor personal computer without any constraint on the geometry [26,27].

4. Results and discussion

4.1. Molecular geometry

The molecular structure of the 4-nitrotoluene belongs to C$_S$ point group symmetry. The optimized molecular structure of title molecule is obtained from GAUSSIAN 98W and GAUSSVIEW programs and is shown in Fig. 1. The molecule contains nitro group and methyl group connected with benzene ring. The structure optimization zero point vibrational energy of the title compound in HF, B3LYP/6-31++G* (d, p) and B3LYP/6-311++G* (d, p) are −356, 402.3, −340, 698.4 and −339, 367.7 J/mol and 82.78, 81.42 and 81.11 kcal/mol, respectively. The comparative optimized structural parameters such as bond lengths, bond angles and dihedral angles are presented in Table 1. From the theoretical values, it is found that most of the optimized bond lengths are slightly larger than the experimental values, due to that the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state [28]. Comparing
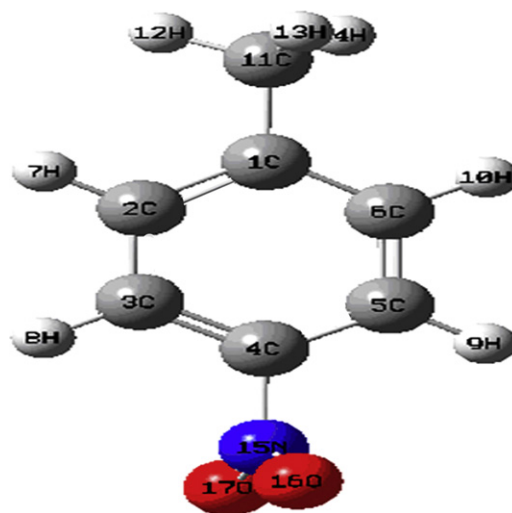

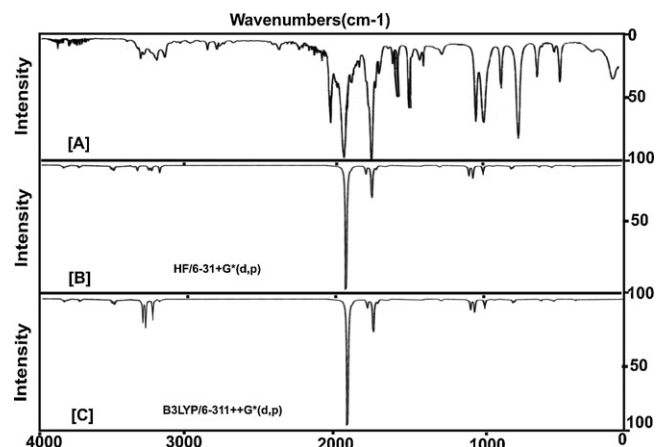Fig. 1. Molecular structure of 4-nitrotoluene.

Fig. 2. Experimental [A], calculated [B] and [C] FTIR spectra of 4-nitrotoluene.

bond angles and lengths of B3LYP with those of HF, as a whole the formers are bigger than later and the B3LYP calculated values correlates well compared with the experimental data. Although the differences, calculated geometrical parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and thermodynamics properties (Figs. 2 and 3).
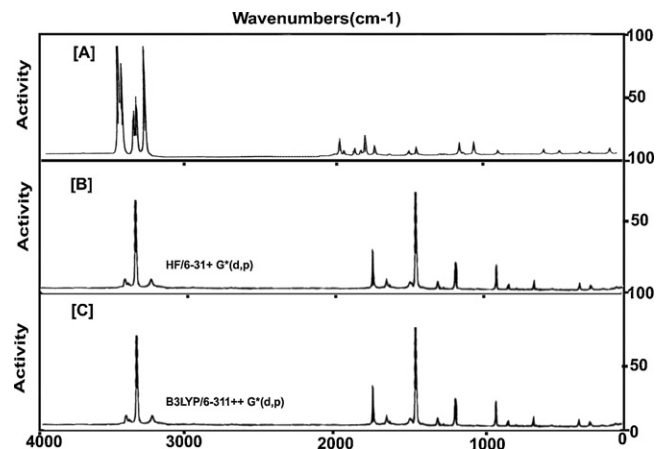

Fig. 3. Experimental [A], calculated [B] and [C] FTRaman spectra of 4-nitrotoluene.