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Experimental (FT-IR and FT-Raman) and theoretical (HF and DFT) investigation, IR intensity, Raman activity and frequency estimation analyses on 1-bromo-4-chlorobenzene

V. Udayakumar [a], S. Periandy [b], S. Ramalingam [c,*]

[a] Department of Physics, Thiru A. Govindaswamy Arts college, Tindivanam, Tamilnadu, India
[b] Department of Physics, Tagore Arts college, Puducherry, India
[c] Department of Physics, A.V.C. College, Mayiladuthurai, Tamilnadu, India

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ABSTRACT

The FT-IR and FT-Raman spectra of 1-bromo-4-chlorobenzene (1-Br-4-CB) have been recorded using Bruker IFS 66V spectrometer in the region of 4000-100 cm^{-1}. Ab-initio-HF (HF/6–311+G (d, p)) and DFT (B3LYP/6–31++G (d, p)/6–311++G (d, p)) calculations have been performed giving energies, optimized structures, harmonic vibrational frequencies, depolarization ratios, IR intensities, Raman activities. The vibrational frequencies are calculated and scaled values are compared with FT-IR and FT-Raman experimental values. Comparison of simulated spectra with the experimental spectra provides important information, the computational method have the ability to describe the vibrational methods. The frequency estimation analysis on HF and DFT is made. The impact of di-substituted halogens on the benzene molecule has also been discussed.

1. Introduction

Aromatic compounds such as Benzene derivative compounds are commonly used for chronic inflammation treatment products in pharmaceutical products. Benzene is frequently used as an industrial solvent, especially for degreasing metal. Chlorobenzene is an important industrial solvent and a widely used intermediate in production of commodities such as herbicides, dyestuffs, and rubber [1]. The major use of chlorobenzene is as an intermediate in the production of commodities such as herbicides, dyestuffs, and rubber. Chlorobenzene is also used as a high-boiling solvent in many industrial applications as well as in the laboratory. Bromobenzene can be used to prepare the corresponding Grignard reagent, phenylmagnesium bromide [2]. Bromobenzene can also be used to prepare the corresponding Grignard reagent, phenylmagnesium bromide. The combined chlorobromobenzene is also used for manufacture some biological and industrial solvents. In recent years, chlorobromobenzene have been the frequent subjects of experimental and theoretical work because of their significance in industry and environment. Literature survey reveals that to the best of our knowledge no ab-initio-HF/DFT with 6–31++G (d, p) and 6–311++G (d, p) basis sets calculations of 1-Br-4-CB have been reported so far. It is, therefore thought worthwhile to make a comprehensive vibrational analysis using both experimentally observed IR and Raman wave numbers and theoretically calculated vibrational spectra.

In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for ab initio (HF), hybrid density functional methods B3LYP at 6–31++G (d, p) and 6–311++G (d, p) 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. In DFT methods, Becke's three parameter exact exchange-functional (B3) [3] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [4,5] are the best predicting results for molecular geometry and vibrational wave numbers for moderately larger molecule [6–8].

2. Experimental details

The spectroscopic grade 1-Br-4-CB was purchased from Sigma–Aldrich Chemicals, U.S.A. and used as such for record-

* Corresponding author. Tel.: +91 9003398477.
E-mail address: ramalingam.physics@gmail.com (S. Ramalingam).

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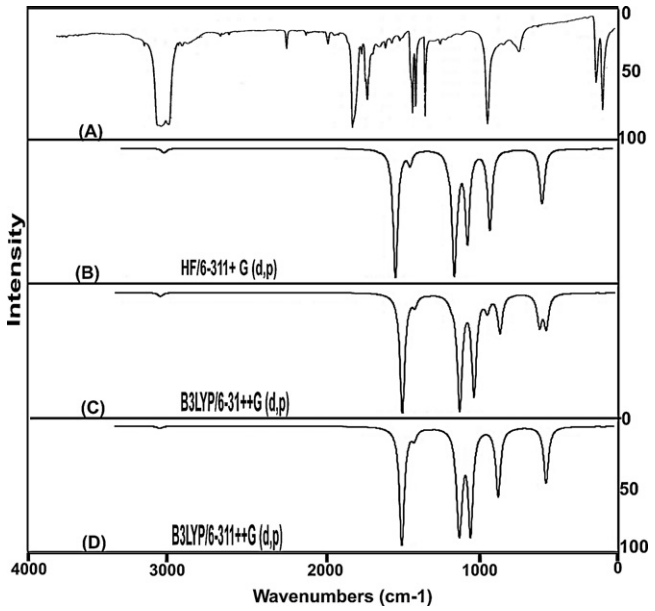

Fig. 1. Experimental (A), calculated (B), (C and D) FTIR spectra of 1-bromo-4-chlorobenzene.

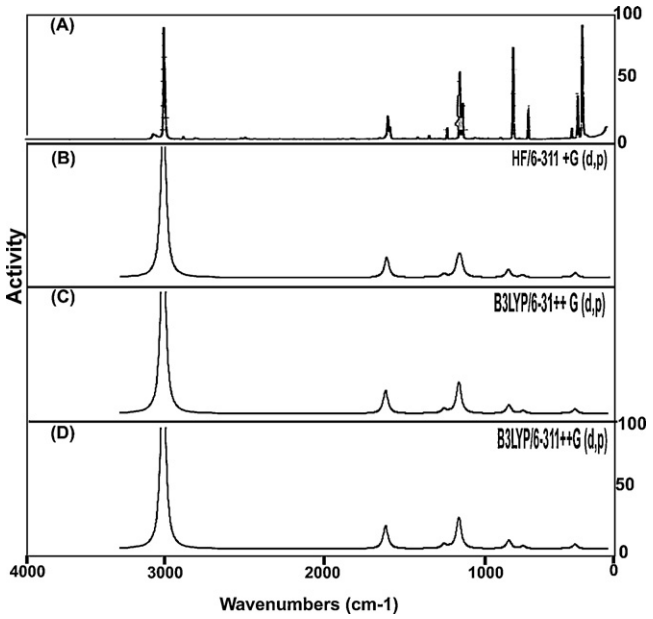

Fig. 2. Experimental (A), calculated (B), (C and D) FTIRaman spectra of 1-bromo-4-chlorobenzene.

ing spectra without further purification. The FT-IR spectrum of the 1-Br-4-CB was recorded in Bruker IFS 66V spectrometer in the range of 4000–100 cm^{-1}. The spectral resolution is $\pm 2\,cm^{-1}$. The FT-Raman spectrum of 1-Br-4-CB was also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm with 200 MW power. Both the spectra were 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 $\pm 1\,cm^{-1}$.

3. Computational methods

HF/DFT calculations for 1-bromo-4-chlorobenzene are performed using GAUSSIAN 03W program package on Pentium IV processor personal computer without any constraint on the geometry. The molecular structure of the title compound in the ground state is computed both ab-initio-HF with 6–311+G (d, p) and DFT (B3LYP) with 6–311++G (d, p) and 6–31++G (d, p) basis sets. The comparative IR and Raman spectra of experimental and calculated (HF/B3LYP) are given in the Figs. 1 and 2, respectively. 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 same basis sets of HF and DFT methods those which are previously mentioned. All the computations have been done by adding polarization function d and diffuse function on heavy atoms and polarization function p and diffuse function on hydrogen atoms, in addition to triple split valence basis set (6–311++G (d, p)), for better treatment of polar bonds. The calculated frequencies are scaled by 0.902 and 0.884 for HF/6–311+G (d, p) [9,10]. For B3LYP/6–31++G (d, p) is scaled by 0.923, 0.977, 0.872 and 0.945 and for B3LYP/6–311++G (d, p) basis set is scaled with 0.927, 0.976, 0.987, 0.885 and 1.008 [11]. HF/DFT calculations for 1-Br-4-CB are performed using GAUSSIAN 03W program package on Pentium IV processor personal computer without any constraint on the geometry [12,13]. The comparative values of IR intensities and Raman activities are presented in the Table 3 and their corresponding graphs are given in the Figs. 3 and 4, respectively.

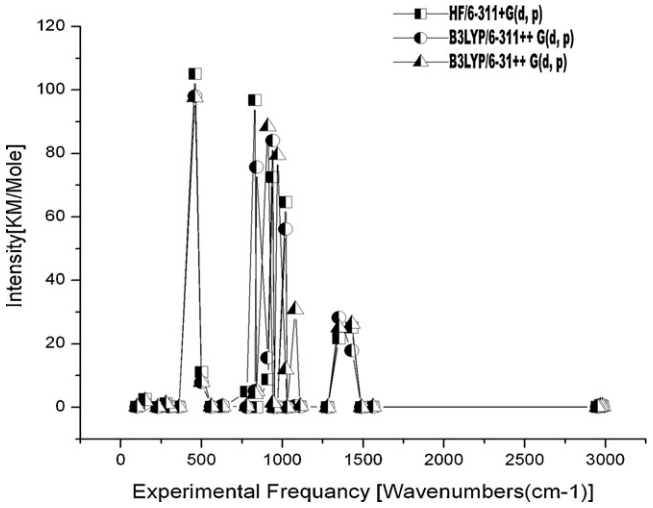

Fig. 3. Comparative graph of IR intensities by HF and DFT(B3LYP).

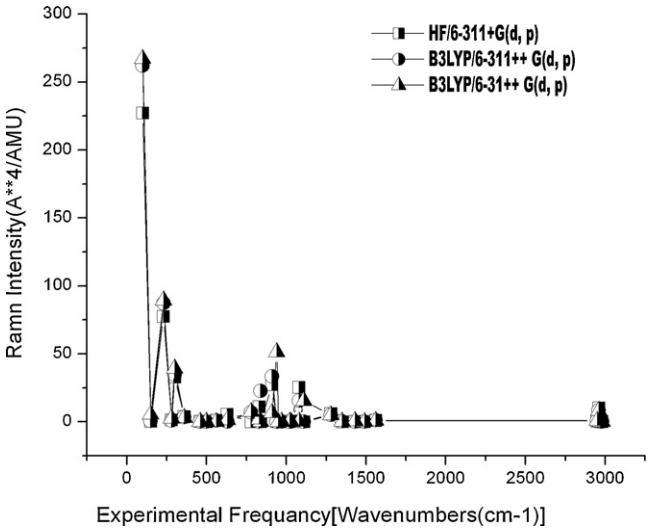

Fig. 4. Comparative graph of Raman activities by HF and DFT(B3LYP).