



Vibrational Spectroscopy

Elixir Vib. Spec. 92 (2016) 38706-38717

Elixir
ISSN: 2229-712X

FT-IR and FT-Raman Spectra Molecular Geometry Vibrational Assignments, First Order Hyper Polarizability HOMO-LUMO Analysis of Benzyl Fluoride

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ARTICLE INFO

Article history:

Received: 30 June 2016;

Received in revised form:

1 August 2016;

Accepted: 8 August 2016;

Keywords

FT-IR,

FT-Raman vibrational spectra,

NBO,

HOMO-LUMO,

Benzyl fluoride.

ABSTRACT

The FT-IR and FT-Raman spectra of benzyl fluoride were recorded and analyzed. The vibrational wavenumbers were examined theoretically with the aid of the GAUSSIAN 09 package of programs using the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands obtained in IR and Raman spectroscopy of the studied molecule. The first hyperpolarizability, NBO, HOMO-LUMO, infrared intensities and Raman intensities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non-linear optics. The geometrical parameters of the title compound are in good agreement with the values of similar structures.

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1. Introduction

Benzyl halides derivatives are of great interest in biological activity and widely used as a parent compound to make drugs. The sample benzyl Fluoride (BF) is a clear liquid with aromatic odour[1]. benzyl fluoride is also known as trifluoromethyl benzene. It is a raw material for the synthesis of some pharmaceuticals and used as a therapeutic agent [2,3]. It is also used as an intermediate in the preparation of important chemical products [4]. It is used as an intermediate for dyes, vulcanizing agent and insecticide and other organic compounds such as transformers oils. Similarly, fluorinated compounds are widely used in industries and heat transfer fluids, chemical intermediates and polymers etc, Therefore the study of fluorinated compounds is of considerable importance due to highest electron negativity of fluorine atom, fluorinated compounds show entirely different physical and chemical properties compared to the other halogenated compounds. As the vibrational modes of molecules are closely related to its geometrical and electronic structures, the vibrational spectra provide considerable information regarding the physical and chemical properties of the molecules [5].

In the present investigation the complete vibrational spectral properties of Benzyl fluoride (BF) at ab-initio Hartree-fock (HF) and density functional theory (DFT) levels B3LYP using 6-311++G(d,p) basis set and to identify the various normal modes with greater accuracy has been under taken the p-polarization function on hydrogen atoms, which are known to be very important for reproducing the out-of-plane vibrations involving hydrogen atoms. Is included it is anticipated that both HF and DFT (B3LYP) level of theories are reliable for predicting the vibrational spectra of BF. The density functional theory calculation are reported to provide accurate vibrational frequencies of organic compounds. If the calculated frequencies are scaled to compensate for the

approximate treatment of electron correlation for basis set deficiencies and for the anharmonicity.

2. Experimental Details

The pure benzyl fluoride (BF) sample obtained from Lancaster Chemical Company, UK that is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FT-IR spectrum of BF is measured in the BRUKER IFS 66V spectrometer in the range 4000-400 cm^{-1} . The FT-Raman spectrum of BF is also recorded in FT-Raman BRUKER RFS 100/S instrument equipped with Nd:YAG laser source operating at 1064 nm wavelength in the range 3500-50 cm^{-1} .

3. Computational Methodology

Hartree-Fock (HF) and DFT calculations are carried out for BF using GAUSSIAN 09W program package [6]. The geometry optimization was carried out using the initial geometry at Hartree-Fock level adopting the standard 6-311++G(d,p) basis set. This geometry is then re-optimized again at DFT level employing the B3LYP keyword, which invokes Becke's three-parameter hybrid method [7] using the correlation function of Lee *et al.* [8]. All the parameters are allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wave number calculations. The multiple scaling of the force constants are performed according to SQM procedure [9], the subsequent normal coordinate analysis including the least square refinement of the scale factors and calculation of the total energy distribution (TED) are done on a PC with the MOLVIB program (version V7.0 - G77) written by Sundius [10,11]. The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wave numbers.

The Normal coordinate analyses were carried out for BF to provide a complete assignment of fundamental frequencies. The theoretically calculated force fields are transformed to this set of vibrational coordinates and used in all subsequent calculations.

3.1. Prediction of Raman intensities

The Raman activities (S_i) calculated with the GAUSSIAN 09W program are subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [12-14].

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left[1 - \exp\left(-\frac{hc v_i}{kT}\right) \right]} \quad \dots (1)$$

where v_0 is the exciting frequency in cm^{-1} , v_i the vibrational wave number of the i^{th} normal mode, h , c and k are the fundamental constants and f is a suitably chosen common normalization factor for all the peak intensities.

4. Results And Discussion

4.1 Molecular geometry

The optimized molecular structure of BF along with numbering of atoms is shown in Fig.1. The optimized geometrical parameters of BF obtained by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels are listed in Table 1. From the structural data given it is observed that the various bond lengths are found to be almost same at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. However, the B3LYP/6-311++G(d,p) level of theory, in general slightly overestimates bond lengths but it yields bond angles in excellent agreement with the HF and B3LYP method. The calculated geometric parameters can be used as foundation to calculate the other parameters of BF.

Table 1. Optimized geometrical parameters of benzyl fluoride computed at HF/6-311++G(d,p) and B3LYP/6-31++G(d,p) level calculations.

| Bond Length | Value (Å) | | Bond Angle | Value (°) | | Dihedral Angle | Value (°) | |
|-------------|-----------|--------|------------|-----------|-----------|----------------|-----------|-----------|
| | HF | B3LYP | | HF | B3LYP | | HF | B3LYP |
| C1-C2 | 1.392 | 1.4063 | C2-C1-C6 | 119.1016 | -119.9106 | C6-C1-C2-H8 | 0.0054 | 0.0558 |
| C1-C6 | 1.3922 | 1.4063 | C2-C1-C7 | 120.4548 | 120.4364 | C6-C1-C2-H8 | -179.6691 | -179.674 |
| C1-F7 | 1.4956 | 1.495 | C6-C1-C7 | 120.4311 | 120.4365 | C7-C1-C2-C3 | 178.7243 | 178.587 |
| C2-C3 | 1.3883 | 1.3996 | C1-C2-C3 | 120.5514 | 120.5004 | C7-C1-C2-H8 | -0.9501 | -1.1429 |
| C2-H8 | 1.0743 | 1.0867 | C1-C2-H8 | 119.6929 | 119.5275 | C2-C1-C6-C5 | 0.0218 | -0.0558 |
| C3-C4 | 1.3891 | 1.402 | C3-C2-H8 | 119.7549 | 119.9715 | C2-C1-C6-H12 | 179.7243 | 179.674 |
| C3-H9 | 1.0732 | 1.0856 | C2-C3-C5 | 119.9461 | 119.9754 | C7-C1-C6-C5 | -178.6975 | -178.587 |
| C4-C5 | 1.3893 | 1.402 | C2-C3-H9 | 119.9336 | 119.9376 | C7-C1-C6-H12 | 0.9543 | 1.1429 |
| C4-H10 | 1.0733 | 1.0857 | C4-C3-H9 | 120.1203 | 120.0869 | C2-C1-C7-H13 | 26.638 | 27.4581 |
| C5-C6 | 1.3881 | 1.3996 | C3-C4-C5 | 119.9023 | 119.9376 | C2-C1-C7-H14 | 152.1778 | 150.0319 |
| C5-H11 | 1.0732 | 1.0856 | C3-C4-H10 | 120.0509 | 120.0312 | C2-C1-C7-H15 | -90.6138 | -89.255 |
| C6-H12 | 1.0743 | 1.0867 | C5-C4-H10 | 120.0468 | 120.0312 | C6-C1-C7-H13 | -154.6601 | -154.0303 |
| C7-H13 | 1.0771 | 1.0915 | C4-C5-C6 | 119.9516 | 119.9754 | C6-C1-C7-H14 | -29.1204 | -27.4565 |
| C7-H14 | 1.0772 | 1.0915 | C4-C5-H11 | 120.1123 | 120.0869 | C6-C1-C7-F15 | 88.088 | 89.2566 |
| C7-F15 | 1.4422 | 1.4844 | C6-C5-H11 | 119.9361 | 119.9376 | C1-C2-C3-C4 | -0.0027 | -0.014 |
| N12-O14 | 1.1825 | 1.2618 | C1-C6-C5 | 120.5468 | 120.5004 | C1-C2-C3-H9 | -179.969 | 179.9643 |
| | | | C1-C6-H12 | 119.6804 | 119.5275 | H8-C2-C3-C4 | 179.6715 | 179.7147 |
| | | | C5-C6-H12 | 119.7718 | 119.9715 | H8-C2-C3-H9 | -0.2948 | -0.307 |
| | | | C1-C7-H13 | 112.5105 | 112.8873 | C2-C3-C4-C5 | -0.027 | -0.0285 |
| | | | C1-C7-H14 | 112.5461 | 112.8873 | C2-C3-C4-H10 | 179.9562 | 179.9124 |
| | | | C1-C7-F15 | 110.1017 | 110.0816 | H9-C3-C4-C5 | 179.9362 | 179.8832 |
| | | | H13-C7-H14 | 110.435 | 110.0161 | H9-C3-C4-H10 | -0.0776 | -0.0659 |
| | | | H13-C7-F15 | 105.4065 | 104.7983 | C3-C4-C5-C6 | 0.054 | 0.0285 |
| | | | H14-C7-F15 | 105.3539 | 104.7983 | C3-C4-C5-H11 | -179.9363 | -179.9932 |
| | | | | | | H10-C4-C5-C6 | -179.9292 | -179.9125 |
| | | | | | | H10-C4-C5-H11 | 0.0805 | 0.0659 |
| | | | | | | C4-C5-C6-C1 | -0.0516 | 0.014 |
| | | | | | | C4-C5-C6-H12 | -179.7031 | -179.7146 |
| | | | | | | H11-C5-C6-C1 | 179.9387 | -179.9643 |
| | | | | | | H11-C5-C6-H12 | 0.2873 | 0.307 |

For numbering of atoms Ref. Fig. 1

Vibrational Assignments

From the structural point of view BF is assumed to have C_s point group symmetry. The 39 fundamental modes of vibrations arising for BF are classified into 27A' and 12A'' species. The A' and A'' species represent the in-plane and out-of plane vibrations, respectively. The FTIR and FT-Raman spectra of BF are shown in Figs. 2 and 3, respectively. The detailed vibrational assignment of fundamental modes of BF along with the calculated IR and Raman intensities and normal mode descriptions (characterized by TED) are reported in Table 2. The vibrational analysis obtained for BF with the unscaled HF and B3LYP/6-311++G(d,p) force field are

generally somewhat greater than the experimental values due to neglect of anharmonicity in real system. These discrepancies can be corrected either by computing anharmonic corrections explicitly or by introducing a scaled field or directly scaling the calculated wavenumbers with proper scale factor [15,16]. A tentative assignment is often made on the basis of the unscaled frequencies by assuming the observed frequencies so that they are in the same order as the calculated ones. Then, for an easier comparison to the observed values, the calculated frequencies are scaled by the scale to less than 1, to minimize the overall deviation.

Table 2. Vibrational assignments of fundamental modes of benzyl fluoride along with calculated IR intensity (km mole⁻¹); Raman intensity (normalised to 100) reduced mass (amu); force constant (mdyne A⁻¹), and normal mode description characterized by TED) based on quantum mechanical force field calculations using HF/B3LYP method with 6-311++G(d,p) basis set.

| Sl. No. | Symmetry Species C _s | Observed fundamentals (cm ⁻¹) | | Calculated frequencies (cm ⁻¹) | | | | | | | | | | Assignments with TED% among type of internal coordinates |
|---------|---------------------------------|---|-----------|--|--------|--------------|-----------------|----------------|----------------------|--------|--------------|-----------------|----------------|--|
| | | FT-IR | FT- Raman | HF/6-311++G(d,p) | | | | | B3LYP /6-311++G(d,p) | | | | | |
| | | | | Unscaled | Scaled | IR intensity | Raman intensity | Force constant | Unscaled | Scaled | IR intensity | Raman intensity | Force constant | |
| 1. | A' | 3093 | - | 3422 | 3106 | 9.8794 | 135.3194 | 7.5812 | 3372 | 3092 | 10.5777 | 144.0109 | 7.3575 | γCH (98) |
| 2. | A' | - | 3080 | 3412 | 3100 | 47.0884 | 0.3041 | 7.5144 | 3362 | 3075 | 48.1157 | 0.593099 | 7.2893 | γCH (96) |
| 3. | A' | 3068 | - | 3403 | 3086 | 19.0743 | 33.5028 | 7.4547 | 3354 | 3062 | 17.9795 | 35.20615 | 7.2330 | γCH (98) |
| 4. | A' | 3037 | - | 3398 | 3044 | 12.9527 | 54.6586 | 7.5201 | 3352 | 3028 | 15.6131 | 45.0315 | 7.3252 | γCH (96) |
| 5. | A' | - | 2980 | 3391 | 2997 | 3.9514 | 118.3006 | 7.4085 | 3345 | 2976 | 1.3812 | 182.7187 | 7.1773 | γCH (94) |
| 6. | A' | 2962 | - | 3386 | 2972 | 1.2646 | 11.5364 | 7.3469 | 3339 | 2960 | 1.1451 | 11.8142 | 7.1332 | CH ₂ ass(95) |
| 7. | A' | 2910 | - | 3337 | 2922 | 39.2286 | 46.2026 | 6.9285 | 3288 | 2987 | 42.5631 | 51.3975 | 6.7212 | CH ₂ ss(91) |
| 8. | A' | 1680 | - | 1751 | 1692 | 0.0430 | 10.8858 | 8.5776 | 1643 | 1677 | 0.1909 | 11.1071 | 9.5892 | γCC (83) |
| 9. | A' | - | 1650 | 1736 | 1656 | 0.4022 | 7.8744 | 8.7168 | 1640 | 1647 | 0.1300 | 5.4755 | 10.0035 | γ CC (80) |
| 10. | A' | 1606 | - | 1674 | 1614 | 4.0644 | 4.9062 | 1.8328 | 1534 | 1604 | 0.0300 | 1.9423 | 2.3487 | γ CC(89) |
| 11. | A' | - | 1580 | 1642 | 1590 | 10.8286 | 0.9566 | 3.0262 | 1517 | 1575 | 14.3444 | 3.6417 | 1.7456 | γCC(84) |
| 12. | A' | 1550 | - | 1603 | 1560 | 10.4580 | 0.04968 | 2.8894 | 1492 | 1545 | 7.2202 | 0.2160 | 2.9005 | γCC(81) |
| 13. | A' | 1489 | - | 1532 | 1497 | 39.2869 | 3.8641 | 1.8090 | 1382 | 1485 | 31.0874 | 7.6848 | 31.0874 | γCC(83) |
| 14. | A' | - | 1480 | 1492 | 1490 | 0.7462 | 0.4250 | 1.7233 | 1372 | 1478 | 0.0049 | 0.6738 | 0.0049 | γCC(89) |
| 15. | A' | 1466 | - | 1376 | 1473 | 2.7879 | 9.2453 | 1.3137 | 1357 | 1465 | 0.7885 | 1.1179 | 0.7885 | CH ₂ sciss (86) |
| 16. | A' | - | 1390 | 1328 | 1410 | 0.0704 | 4.6631 | 1.4449 | 1267 | 1389 | 108.5853 | 28.5765 | 4.9870 | CH ₂ rock(71) |
| 17. | A' | 1379 | - | 1315 | 1388 | 96.8512 | 23.9901 | 4.1439 | 1241 | 1375 | 0.9102 | 12.1895 | 1.0254 | b CH(73) |
| 18. | A' | 1329 | - | 1300 | 1337 | 1.6909 | 8.2883 | 1.1800 | 1205 | 1327 | 1.5536 | 8.0040 | 1.1016 | b CH(74) |
| 19. | A' | 1312 | - | 1266 | 1326 | 29.9145 | 9.4883 | 4.3105 | 1198 | 1310 | 8.5056 | 31.2081 | 2.2553 | b CH(72) |
| 20. | A' | - | 1250 | 1242 | 1262 | 0.2510 | 4.5674 | 1.9968 | 1188 | 1247 | 0.0028 | 7.2089 | 0.8783 | b CH(76) |
| 21. | A' | 1217 | 1215 | 1185 | 1225 | 0.3650 | 0.1516 | 1.2511 | 1107 | 1213 | 4.7504 | 1.7381 | 1.0707 | b CH(73) |
| 22. | A' | - | 1180 | 1176 | 1190 | 1.8428 | 0.5376 | 1.4641 | 1054 | 1175 | 4.8717 | 1.3794 | 1.6034 | trigd(61) |
| 23. | A' | - | 1160 | 1140 | 1170 | 0.0018 | 0.06783 | 1.1112 | 1034 | 1155 | 0.0247 | 133.0542 | 2.9795 | Rsymd(64) |
| 24. | A' | 1150 | - | 1127 | 1160 | 4.2033 | 1.2996 | 2.2336 | 981 | 1147 | 0.0688 | 0.3656 | 0.8141 | Rasynd(63) |
| 25. | A' | 1082 | - | 1082 | 1092 | 0.3973 | 139.7032 | 2.5308 | 952 | 1080 | 0.0044 | 0.0729 | 0.7996 | γCF(75) |
| 26. | A' | - | 1060 | 1069 | 1072 | 6.7840 | 21.5827 | 1.0990 | 939 | 1057 | 3.9863 | 1.5759 | 0.8727 | bCC(75) |
| 27. | A' | - | 996 | 1045 | 1011 | 5.0536 | 1.1204 | 1.0836 | 897 | 997 | 5.5968 | 3.7150 | 0.8423 | ωCH(64) |
| 28. | A'' | 980 | - | 968 | 997 | 0.0002 | 2.3851 | 0.6882 | 809 | 980 | 9.7502 | 35.1236 | 1.2743 | ωCH (60) |
| 29. | A'' | 914 | - | 901 | 927 | 31.5166 | 19.2136 | 1.1549 | 800 | 910 | 0.003 | 1.6614 | 0.4731 | ωCH (62) |
| 30. | A'' | - | 850 | 832 | 865 | 29.1656 | 57.2102 | 1.3188 | 755 | 845 | 5.3717 | 13.9440 | 1.0252 | ωCH (61) |
| 31. | A'' | 820 | - | 791 | 829 | 86.5600 | 0.1849 | 86.5600 | 666 | 815 | 61.1979 | 1.5024 | 0.4163 | ωCH (59) |
| 32. | A'' | 745 | - | 697 | 754 | 0.1030 | 19.7615 | 0.1030 | 647 | 740 | 0.1206 | 16.7650 | 1.5306 | CH ₂ wag(72) |
| 33. | A'' | 698 | - | 665 | 703 | 36.9796 | 2.3776 | 36.9796 | 585 | 696 | 54.2791 | 3.6209 | 0.4785 | trigd(53) |
| 34. | A'' | - | 640 | 536 | 647 | 7.9509 | 25.9933 | 0.6490 | 477 | 637 | 10.6580 | 18.8412 | 0.4598 | bCF(67) |
| 35. | A'' | 593 | - | 477 | 599 | 0.0043 | 0.084849 | 0.3474 | 402 | 590 | 0.0082 | 0.0965 | 0.2332 | tRsymd (56) |
| 36. | A'' | - | 490 | 360 | 497 | 3.4476 | 7.1002 | 0.3656 | 313 | 487 | 3.0056 | 3.8338 | 0.2420 | tRsymd (54) |
| 37. | A'' | 481 | - | 336 | 489 | 0.6239 | 0.1544 | 0.1625 | 278 | 480 | 0.0505 | 0.5433 | 0.0976 | ωCC(60) |
| 38. | A'' | - | 402 | 264 | 407 | 5.7231 | 15.7511 | 0.0342 | 256 | 399 | 4.9115 | 16.7572 | 0.0377 | ωCF(57) |
| 39. | A'' | - | 153 | 93 | 157 | 5.70491 | 5.7762 | 0.0862 | 101 | 151 | 4.0839 | 6.2675 | 0.1264 | CH ₂ twist(58) |

Abbreviations:

ν - stretching; as - asymmetric stretching; ss - symmetric stretching; b - in-plane-bending; ω - out-of-plane bending;

t - torsion.

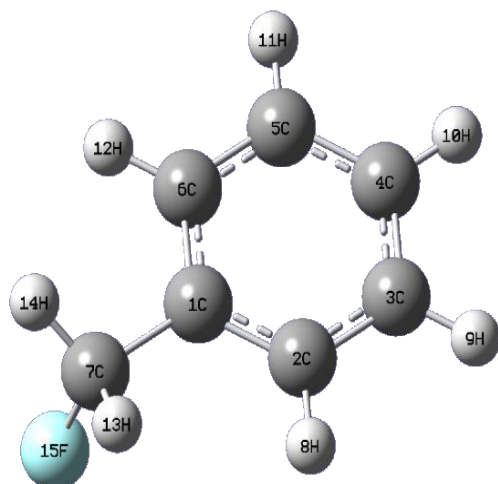


Fig 1. Molecular model of benzyl fluoride along with numbering of atoms.

A better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different regions of vibrations. For that purpose, the different scaling factors for all fundamental modes have been utilized the scaled frequencies of the compound. The resultant scaled frequencies are also listed in Table 2.

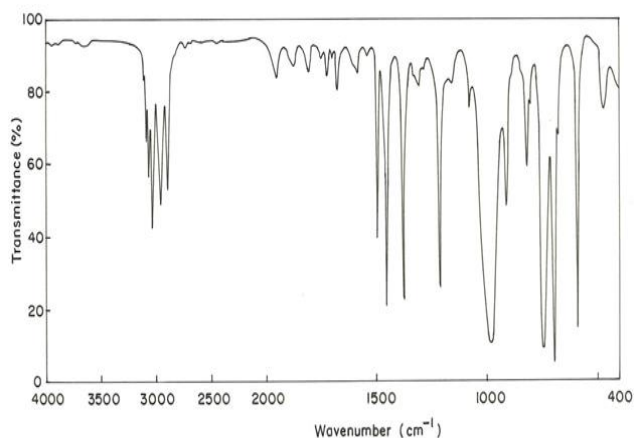


Fig 2. FTIR Spectrum of benzyl fluoride.

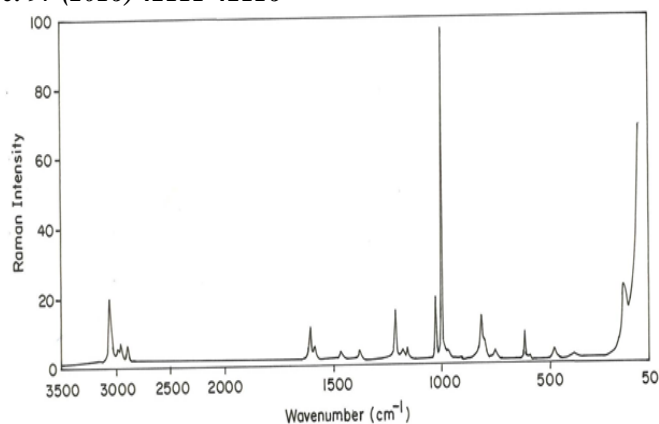


Fig 3. FT-Raman Spectrum of benzyl fluoride.

C–H Vibrations

The Aromatic group does not appear to affect the position of characteristic C–H bands and these bands occur in the range 3100–3000 cm^{-1} . The C–H in-plane bending vibrations appear in the range 1300–1000 cm^{-1} in the substituted benzenes and the out-of-plane bending vibrations in the range 1000–750 cm^{-1} [17]. The FTIR and FT-Raman peaks are obtained at 3093, 3068, 3037 cm^{-1} and 3080, 2980 cm^{-1} are assigned to C–H stretching vibrations of BF respectively. The FT-IR bands at 1379, 1329, 1312, 1217 cm^{-1} and Raman bands at 1250 cm^{-1} are assigned to C–H in-plane bending vibrations of BF. The observed C–H out-of-plane bending modes show consistent agreement with the computed B3LYP results and also listed in Table 2.

C–C vibrations

The bands observed at 1430–1670 cm^{-1} are assigned to C–C stretching modes [18]. The six ring carbon atoms undergo coupled vibrations called skeletal vibrations and give a maximum of four bands in the region 1660–1420 cm^{-1} [19]. In the title compound BF also there are six prominent peaks at 1680, 1606, 1550 and 1489 cm^{-1} in FT-IR spectrum and peaks observed at 1650, 1580 cm^{-1} in FT-Raman spectrum are assigned to C–C stretching vibrations. The C–C in-plane out-of bending vibrations are listed in Table 2. These assignments are in good agreement with the literature [20].

Table 3. Second order perturbation theory analysis of Fock matrix in NBO basis for benzyl fluoride using B3LYP/6-311++G(d,p) level calculation.

| Donor | ED/e | Acceptor | ED/e | $E^{(2)a}$ (kJ mol^{-1}) | $\epsilon_i - \epsilon_j^b$ (a.u.) | $F(i,j)^c$ (a.u.) |
|-----------------|---------|-------------------|---------|--|---------------------------------------|----------------------|
| σ C1-C2 | 1.97825 | σ^* C1-C6 | 0.02234 | 3.20 | 1.26 | 0.057 |
| π C1-C2 | 1.65530 | π^* C5-C6 | 0.32478 | 20.47 | 0.27 | 0.067 |
| σ C1-C6 | 1.97825 | σ^* C1-C2 | 0.02235 | 3.20 | 1.26 | 0.057 |
| σ C1-C7 | 1.98453 | σ^* C5-C6 | 0.01543 | 2.50 | 1.18 | 0.034 |
| σ C2-C3 | 1.98030 | σ^* C1-C7 | 0.03299 | 3.34 | 1.06 | 0.053 |
| σ C2-H8 | 1.98113 | σ^* C1-C6 | 0.02234 | 4.50 | 1.09 | 0.063 |
| σ C3-C4 | 1.98176 | σ^* C2-H8 | 0.01198 | 2.11 | 1.18 | 0.045 |
| σ C3-H9 | 1.98244 | σ^* C4-C5 | 0.01609 | 3.64 | 1.09 | 0.056 |
| σ C4-C5 | 1.98176 | σ^* C5-C6 | 0.01543 | 1.99 | 1.19 | 0.043 |
| σ C5-C6 | 1.98030 | σ^* C1-C7 | 0.03299 | 3.34 | 1.06 | 0.053 |
| σ C5-H11 | 1.9824 | σ^* C3-C4 | 0.01609 | 3.64 | 1.09 | 0.056 |
| σ C6-H12 | 1.9811 | σ^* C1-C2 | 0.02235 | 4.50 | 1.09 | 0.063 |
| σ C7-H13 | 1.98983 | σ^* C1-C6 | 0.02234 | 3.18 | 1.10 | 0.021 |
| σ C7-H14 | 1.98983 | σ^* C7-F15 | 0.02813 | 3.18 | 1.10 | 0.053 |
| σ C7-F15 | 1.99546 | π C1-C2 | 0.34900 | 1.00 | 1.02 | 0.031 |

^a $E^{(2)}$ means Energy of hyper conjugative interaction.

^b $\epsilon_i - \epsilon_j$ means Energy difference between donor and acceptor i and j NBO orbitals.

^c $F(i,j)$ is the Fock matrix element between i and j NBO orbitals.

C–F Vibrations

The vibrations belongs to the bond between the ring and halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the presence of heavy atoms on the periphery of molecule [21]. The C-F bond shows lower absorption frequencies as compared to C-H bond.

In BF, the C-F stretching and in-plane bending vibrations are appeared at 1082 and 640 cm^{-1} in IR and Raman spectra, respectively. The FT-Raman band observed at 402 cm^{-1} is assigned to C-F out-of-plane bending vibration and it is also supported by their TED value.

CH₂ group vibrations

The ethyl group of the title compound gives rise to four stretching modes and the couple of scissoring, wagging, rocking and twisting modes. The band observed at 2962 cm^{-1} and 2910 cm^{-1} in FT-IR are assigned to asymmetric and symmetric stretching modes of the ethyl group of BF respectively. One of the CH₂ deformation modes called CH₂ scissoring generates band at 1466 in FT-IR spectrum, The band at 1390 cm^{-1} in FT-Raman is attributed to CH₂ rocking vibration. The peak at 153 cm^{-1} in FT Raman is ascribed to ethyl twisting vibration. The title compound display the peak at 745 cm^{-1} in FT-IR spectrum due to ethyl wagging vibration. All these ethyl vibrations are agreed well with the literature [22].

5. HOMO-LUMO Analysis

The most important orbitals in molecule are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way of molecule interacts with other species. The frontier molecular energy gap characterizes the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [23]. The 3D plot of the frontier orbital's HOMO and LUMO of BF molecule is shown in Fig.4. The positive phase is red and negative phase one is green.

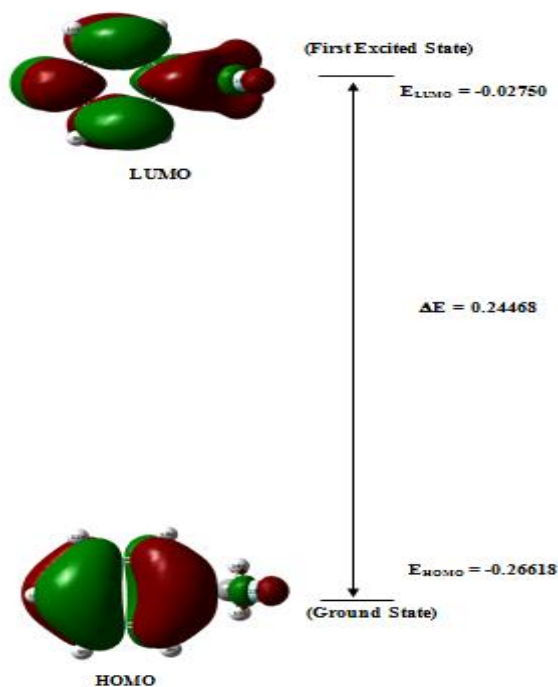


Fig 4. The atomic orbital composition of the molecular orbital for benzyl fluoride.

The electronic transition absorption corresponds to the transition from the ground to the first excited state is mainly described by an electron excitation from the HOMO to LUMO. Generally, if the energy gap between the HOMO and LUMO decreases, it is easier for the electrons of the HOMO to be excited. The higher energy of HOMO, it is easier for HOMO to donate electrons whereas it is easier for LUMO to accept electrons when the energy of LUMO is low.

HOMO energy = -0.26618

LUMO energy = -0.02750

Energy gap = 0.24468

6. NBO Analysis

The second-order Fock matrix was carried out to evaluate donor (i)–acceptor (j), i.e., donor level bonds to acceptor level bonds interaction in the NBO analysis. A filled bonding or lone pair orbital can act as a donor and an empty or filled bonding, antibonding or lone pair orbital can act as an acceptor. These interactions strengthen and weaken bonds. For example, a lone pair donor– antibonding acceptor orbital interaction will weaken the bond associated with antibonding orbital. Conversely, an interaction with a bonding pair as the acceptor will strengthen the bond. Strong electron delocalization in Lewis structure will also show up as donor–acceptor interaction. For each donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ associates with the delocalization $i \rightarrow j$ is estimated as

$$E^{(2)} = \Delta E_{ij} = \frac{q_i F(i,j)^2}{\epsilon_j - \epsilon_i} \quad (2)$$

where q_i is the donor orbital occupancy ϵ_i and ϵ_j are diagonal elements orbital energies and $F(i, j)$ is the off diagonal NBO Fock matrix element. The larger $E^{(2)}$ value the more intensive is the interaction between electron donors and acceptors, i.e., the more donation tendency from electron donors to electron acceptor and the greater the extent of conjugation of the whole system [24]. Delocalization of electron density between occupied Lewis type (bond or lone pair) NBO orbital and formally unoccupied (antibond or Rydberg) non- Lewis NBO orbital corresponds to a stabilizing donor–acceptor Interaction. NBO analysis has been performed on the title compound at the DFT/B3LYP/6-311++G(d,p) level in order to elucidate charge transfer or conjugative interaction, the intracomound rehybridization and delocalization of electron density within the compound. The second-order perturbation theory analysis of Fock matrix in the NBO basis of the compound shows the strong intramolecular hyperconjugative interactions that are presented in Table 3.

The intra molecular interaction is formed by orbital overlap between π (C1-C2) and π^* (C5-C6) bond orbital which result intermolecular charge transfer causing stabilization of the system. The interaction (C1-C2) \rightarrow π (C5-C6) is given the high stabilization energy 20.47 kJ mol^{-1} .

7. NLO Property

The energy of an uncharged linear molecule in a weak, homogenous electric field can be written as,

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \dots \quad (2)$$

where E_0 is the energy of the unperturbed molecule; F^i is the field at the origin; and μ_i , α_{ij} , β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyper polarizabilities and second hyperpolarizabilities, respectively.

The number of independent components for these tensors is regulated by symmetry. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix and the 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [25]. In this study, the electronic dipole moment, molecular polarizability, anisotropy of polarizability and molecular first hyperpolarizability of the title compound have been investigated. The polarizability and hyperpolarizability tensors (α_{xx} , α_{xy} , α_{yy} , α_{xz} , α_{yz} , α_{zz} and β_{xxx} , β_{xxy} , β_{xyx} , β_{xyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{zzz} , β_{yzz} , β_{zzz}) can be obtained by a frequency job output file of Gaussian. However, the first hyperpolarizability (β) value of Gaussian output are in atomic units (a.u.) so they have been converted into electronic units (esu) (1 a.u. = 8.6393×10^{-33} esu). The mean polarizability (α), anisotropy of polarizability ($\Delta\alpha$) and the average value of the first hyperpolarizability (β) can be calculated using the following equations:

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

It is well known that the higher values of dipole moment, first hyperpolarizability are important for more active NLO properties. The calculated value of dipole moment is found to be 2.1952 Debye. The calculated first hyperpolarizability value (β) of benzyl fluoride by B3LYP/ 6-311++G(d,p) method is equal to 0.607428×10^{-30} e.s.u. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular. The first hyperpolarizability of the title compound is 1.6 times larger than those of urea. According to the magnitude of the first hyperpolarizability, the title compound may be a potential applicant in the development of NLO materials.

Conclusion

The vibrational properties of benzyl fluoride are investigated by FTIR and FT Raman spectroscopy. The various modes of vibrations are unambiguously assigned based on the TED output. The calculated wavenumbers are found in good agreement with the experimental values. NLO property is also observed by predicting the first hyperpolarizability for the title molecule due to the substitution in the benzene, NBO study reveals that lone pair orbital participates in electron donation to the stabilize the molecule.

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