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# Quantum Chemical Studies on Structures of 1-Isopropyl -4-Methylbenzene

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**ABSTRACT**

The vibrational spectroscopy of 1-isopropyl-4-methyl benzene [IMB] by means of quantum chemical calculation has been studied. The FT-Raman and FT-IR spectra of IMB have been recorded in the region 3500-50cm$^{-1}$ and 4000-400cm$^{-1}$ respectively. The fundamental vibrational frequencies and intensity of vibrational bands have been evaluated using HF and density functional theory (DFT) with standard B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) basis set combinations for optimized geometries. The observed FT-IR and FT-Raman vibrational frequencies have been anlaysed and compared with theoretically predicted vibrational frequencies. The assignments of bands to various normal modes of molecule have also been carried out. The electric dipole moment (μ) and the first hyperpolarizability (β) values of the investigated molecule have been computed using DFT calculations. The calculated HOMO and LUMO energies show that charge transfer occur with in the molecule.



## 1.Introduction

Benzene is mainly used as an intermediate to make other chemicals. Its most widely produced derivatives include styrene, which is used to make polymers and plastics, phenol for resins and adhesives, and cyclohexane, which is used in the manufacture of Nylon [1]. Nitrobenzene, the simplest nitro aromatic compound, is the parent compound of a range of important compounds, including explosives; 2,4,6-trinitrotoluene. It is also related to nitro phenols, including the biologically important nitro tyrosine, whose presence in proteins is often the result of damage by peroxynitrite [2-4]. A full theoretical understanding of the molecular properties of nitrobenzene can therefore inform on the properties of these other larger compounds. The vibrational spectroscopy of nitrobenzene has been the subject of numerous studies [5,6].

Benzene and its derivatives do not undergo most of the usual addition reactions of alkenes. Instead, they undergo reactions in which another group substitutes ring hydrogen. Such substitution reaction can be used to prepare a variety of substituted benzene from benzene itself. One of the most characteristic reactions of benzene and many of its derivatives is substitution of ring hydrogen by an electrophile and reactions of this type are often called as electrophilic aromatic substitution reactions. Both activating/deactivating and directing effects of substituents come into play in planning an organic synthesis that involves electrophilic substitution reactions.

Hence the understanding of molecular properties as well as the nature of reaction mechanism they undergo has great importance. The substituted benzene derivatives with high optical non-linearity are very promising materials for future optoelectronics and non-linear optical applications. Non-linear optical effects of compound depend on the polarizability of organic material is generally contribution from the lattice components because of the weak intermolecular bonding and hence posses the high degree of delocalization. By combining all these facts into account, the present study has been aimed, to investigate the vibrational spectra of 1-Isopropyl-4-methylbenzene (**IMB**). Investigations have also been carried out to analyse the HOMO-LUMO energy gap and NLO property (first-hyperpolarizability). All these investigations have been done on the basis of the optimized geometry by using Hartree fock and density functional theory (DFT) at HF/B3LYP/6-311++G(d,p) level.

## 2. Experimental details

The pure sample of 1-Isopropyl-4-methylbenzene (**IMB**) was obtained from Lancaster Company, UK that is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FT-IR spectra of IMB was measured in the BRUKER IFS 66V spectrometer in the range 4000–400 cm$^{-1}$. The FT-Raman spectra of IMB was also recorded in FT-Raman BRUKER RFS 100/S instrument equipped with Nd:YAG laser source operating at 1064 nm line widths with 150 mW powers. The spectrum is recorded in the range 3500–50 cm$^{-1}$. The spectral resolution is ±4 cm$^{-1}$.

## 3. Methods of Computation

The initial geometries of IMB were optimized using the HF/B3LYP/6-311++G(d,p) level of Gaussian 09W program package [7]. The vibrational frequency analysis was computed using HF/B3LYP/6-311++G(d,p) method to determine the nature of a stationary point found by geometry optimization. HOMO–LUMO analysis has been carried out to explain the charge transfer within the compounds. The chemical hardness (η) and chemical potential (μ) have been calculated using the Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO) energies. NBO analysis has also been performed using B3LYP/6-311++G(d,p) level in order to elucidate the intermolecular hydrogen bonding, intermolecular charge transfer (ICT), rehybridization, delocalization of electron density.

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**Table 1. Optimized geometrical parameters of 1-isopropyl -4- methyl benzene obtained by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods and basis set.**

| Bond length | Value (Å) | | Bond angle | Value (°) | | Dihedral angle | Value (°) | |
|---|---|---|---|---|---|---|---|---|
| | 6-31+G(d,p) | | | 6-31+G(d,p) | | | 6-31+G(d,p) | |
| | HF | B3LYP | | HF | B3LYP | | HF | B3LYP |
| C1-C2 | 1.3896 | 1.4039 | C2-C1-C6 | 117.4823 | 117.608 | C6-C1-C2-C3 | -0.0008 | 0.002 |
| C1-C6 | 1.3969 | 1.4088 | C2-C1-C7 | 120.7726 | 120.8405 | C6-C1-C2-H8 | 180.0002 | 179.9991 |
| C1-C7 | 1.522 | 1.5267 | C6-C1-C7 | 121.7451 | 121.5515 | C7-C1-C2-C3 | 179.9991 | 179.9999 |
| C2-C3 | 1.3925 | 1.4024 | C1-C2-C3 | 121.372 | 121.2876 | C7-C1-C2-H8 | 0.0001 | -0.0031 |
| C2-H8 | 1.0749 | 1.0875 | C1-C2-H8 | 119.5217 | 119.3433 | C2-C1-C6-C5 | 0.0002 | -0.0005 |
| C3-C4 | 1.3887 | 1.4037 | C3-C2-H8 | 119.1063 | 119.3691 | C2-C1-C6-H12 | 179.9996 | 179.9998 |
| C3-H9 | 1.0747 | 1.0872 | C2-C3-C4 | 121.0622 | 121.0597 | C7-C1-C6-C5 | -179.9998 | -179.9984 |
| C4-C5 | 1.3961 | 1.4084 | C2-C3-H9 | 119.2625 | 119.4726 | C7-C1-C6-H12 | -0.0004 | 0.0019 |
| C4-C10 | 1.5104 | 1.5141 | C4-C3-H9 | 119.6753 | 119.4677 | C2-C1-C7-H13 | -0.0018 | 0.0007 |
| C5-C6 | 1.3855 | 1.398 | C3-C4-C5 | 117.6756 | 117.7229 | C2-C1-C7-C17 | 117.3347 | 117.4345 |
| C5-H11 | 1.0754 | 1.0877 | C3-C4-H10 | 121.6029 | 121.4598 | C2-C1-C7-C18 | -117.3378 | -117.429 |
| C6-H12 | 1.0742 | 1.0868 | C5-C4-H10 | 120.7215 | 120.8172 | C6-C1-C7-H13 | -180.0018 | 179.9985 |
| C7-H13 | 1.0869 | 1.1002 | C4-C5-C6 | 121.2242 | 121.1818 | C6-C1-C7-C17 | -62.6653 | -62.5677 |
| C7-H17 | 1.5386 | 1.5471 | C4-C5-H11 | 119.457 | 119.3945 | C6-C1-C7-C18 | 62.6621 | 62.5688 |
| C7-H18 | 1.5386 | 1.5472 | C6-C5-H11 | 119.3188 | 119.4237 | C1-C2-C3-C4 | 0.0003 | -0.0024 |
| C10-H14 | 1.0831 | 1.0951 | C1-C6-C5 | 121.1837 | 121.1399 | C1-C2-C3-H9 | 180.0006 | 179.9986 |
| C10-H15 | 1.0851 | 1.0978 | C1-C6-H12 | 119.9532 | 119.8341 | H8-C2-C3-C4 | -180.0007 | -179.9994 |
| 10-H16 | 1.0851 | 1.0978 | C5-C6-H12 | 118.8631 | 119.026 | H8-C2-C3-H9 | -0.0004 | 0.0016 |
| C17-H19 | 1.084 | 1.096 | C1-C7-H13 | 106.9208 | 106.9766 | C2-C3-C4-C5 | 0.0009 | 0.0012 |
| C17-H20 | 1.0847 | 1.0972 | C1-C7-H17 | 111.9997 | 111.9889 | C2-C3-C4-C10 | 179.9973 | 179.9985 |
| C17-H21 | 1.0854 | 1.0973 | C1-C7-H18 | 111.9993 | 111.9874 | H9-C3-C4-C5 | -179.99944 | -179.9998 |
| C18-H22 | 1.084 | 1.096 | H13-C7-H17 | 107.3566 | 107.4135 | H9-C3-C4-C10 | -0.003 | -0.0025 |
| C18-H23 | 1.0854 | 1.0973 | H13-C7-H18 | 107.3564 | 107.4109 | C3-C4-C5-C6 | -0.0016 | 0.0003 |
| C18-H24 | 1.0847 | 1.0972 | C17-C7-C18 | 110.9027 | 110.7725 | C3-C4-C5-H11 | 180.0003 | 179.9994 |
| | | | C4-C10-H14 | 111.1605 | 111.2556 | C10-C4-C5-C6 | 180.002 | -179.997 |
| | | | C4-C10-H15 | 111.2242 | 111.4124 | C10-C4-C5-H11 | 0.0038 | 0.002 |
| | | | C4-C10-H16 | 111.2237 | 111.4124 | C3-C4-C10-H14 | 0.0213 | 0.0327 |
| | | | H14-C10-H15 | 107.757 | 107.6886 | C3-C4-C10-H15 | 120.0977 | 120.2139 |
| | | | H14-C10-H16 | 107.7566 | 107.687 | C3-C4-C10-H16 | -120.0543 | -120.1463 |
| | | | H15-C10-H16 | 107.5429 | 107.1785 | C5-C4-C10-H14 | 180.0176 | -179.97 |
| | | | C7-C17-H19 | 111.0398 | 111.1225 | C5-C4-C10-H15 | -59.9059 | -59.7889 |
| | | | C7-C17-H20 | 111.2985 | 111.075 | C5-C4-C10-H16 | 59.942 | 59.8509 |
| | | | C7-C17-H21 | 110.4536 | 110.51 | C4-C5-C6-C1 | 0.001 | -0.0006 |
| | | | H19-C17-H20 | 107.9207 | 107.879 | C4-C5-C6-H12 | -179.9984 | 179.9991 |
| | | | H19-C17-H21 | 108.2194 | 108.3163 | H11-C5-C6-C1 | -180.0008 | -179.9997 |
| | | | H20-C17-H21 | 107.7792 | 107.8125 | H11-C5-C6-H12 | -0.0002 | 0.0 |
| | | | C7-C18-H22 | 111.0395 | 111.1219 | C1-C7-C17-H19 | -55.9128 | -56.1381 |
| | | | C7-C18-H23 | 110.4535 | 110.5096 | C1-C7-C17-H20 | 64.3395 | 63.967 |
| | | | C7-C18-H24 | 111.2983 | 111.0734 | C1-C7-C17-H21 | -175.9786 | -176.4174 |
| | | | H22-C18-H23 | 108.2196 | 108.3178 | H13-C7-C17-H19 | 61.1622 | 61.0337 |
| | | | H22-C18-H24 | 107.9209 | 107.8792 | H13-C7-C17-H20 | -178.5855 | -178.8612 |
| | | | H23-C18-H24 | 107.7793 | 107.8137 | H13-C7-C17-H21 | -58.9035 | -59.2456 |
| | | | | | | C18-C7-C17-H19 | 178.1585 | 178.0578 |
| | | | | | | C18-C7-C17-H20 | -61.5892 | -61.8371 |
| | | | | | | C18-C7-C17-H21 | 58.0927 | 57.7785 |
| | | | | | | C1-C7-C18-H22 | 55.9125 | 56.1534 |
| | | | | | | C1C7-C18-H23 | 175.9783 | 176.4338 |
| | | | | | | C1-C1-C18-H24 | -64.3398 | -63.9505 |
| | | | | | | H13-C7-C18-H22 | -61.1623 | -61.0159 |
| | | | | | | H13-C7-C18-H23 | 58.9035 | 59.2644 |
| | | | | | | H13-C7-C18-H24 | 178.5855 | 178.8802 |
| | | | | | | C17-C7-C18-H22 | -178.1586 | -178.0417 |
| | | | | | | C17-C7-C18-H23 | -58.0928 | -57.7613 |
| | | | | | | C17-C7-C18-H24 | 61.5892 | 61.8544 |

For numbering of atoms refer Fig. 1

**Table 2. Vibrational assignments of fundamental modes of 1-isopropyl -4- methyl benzene along with calculated IR intensity (km mol$^{-1}$), Raman activity (Å$^4$ amu$^{-1}$) and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using HF and B3LYP methods.**

| S. No. | Species | Observed fundamentals (cm$^{-1}$) | | Calculated frequencies (cm$^{-1}$) | | | | | | | | Assignments with TED (%) among types of internal coordinates |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | HF/6-311++G(d,p) | | | | B3LYP/6-311+ +G(d,p) | | | | |
| | | FTIR | FT-Raman | Unscaled $\nu_i$ | Scaled | IR intensity | Raman activity | Unscaled $\nu_i$ | Scaled | IR intensity | Raman activity | |
| 1. | A | 3490 | - | 3363 | 3498 | 3.9465 | 213.3752 | 3197 | 3493 | 2.2265 | 255.8313 | γCH(99) |
| 2. | A | 3120 | - | 3358 | 3127 | 54.5583 | 31.3756 | 3192 | 3122 | 57.2060 | 22.6741 | γCH(98) |
| 3. | A | - | 3080 | 3337 | 3087 | 14.9095 | 61.4771 | 3173 | 3081 | 10.5113 | 86.1609 | γCH(97) |
| 4. | A | 3050 | - | 3335 | 3058 | 19.7879 | 54.8271 | 3173 | 3055 | 23.6617 | 41.8642 | γCH(98) |
| 5. | A | 3030 | - | 3261 | 3039 | 27.9113 | 64.0723 | 3117 | 3033 | 23.1260 | 64.1289 | γCH(98) |
| 6. | A | - | 3020 | 3259 | 3031 | 51.3253 | 61.8687 | 3115 | 3026 | 38.0974 | 82.8452 | γCH(98) |
| 7. | A | - | 2970 | 3255 | 2972 | 28.7072 | 35.0827 | 3112 | 2971 | 26.7513 | 35.3992 | $CH_3$ips(80)+γCH(20) |
| 8. | A | 2960 | - | 3249 | 2968 | 111.5487 | 182.6562 | 3106 | 2962 | 100.4246 | 188.4326 | $CH_3$ ips(79)+γCH(21) |
| 9. | A | - | 2940 | 3240 | 2947 | 1.9255 | 10.6103 | 3098 | 2943 | 0.0248 | 10.3072 | $CH_3$ips(79)+γCH(21) |
| 10. | A | 2930 | - | 3237 | 2937 | 25.8377 | 87.8883 | 3087 | 2933 | 21.0853 | 95.7567 | γCH(85)+$CH_3$ss(15) |
| 11. | A | - | 2890 | 3185 | 2899 | 29.4688 | 414.6668 | 3036 | 2895 | 35.8240 | 388.1811 | $CH_3$ss(97) |
| 12. | A | 2880 | - | 3183 | 2887 | 64.4610 | 111.7078 | 3033 | 2882 | 54.4523 | 197.0593 | $CH_3$ss(89)+γCH(11) |
| 13. | A | - | 2750 | 3179 | 2756 | 40.1210 | 2.4680 | 3031 | 2751 | 36.6581 | 4.1551 | $CH_3$ss(89)+γCH(11) |
| 14. | A | 2740 | - | 3173 | 2746 | 21.4724 | 58.3876 | 3018 | 2744 | 20.9171 | 76.4338 | $CH_3$ops(89) |
| 15. | A | 2600 | - | 1812 | 2613 | 0.2955 | 37.2078 | 1664 | 2611 | 0.3111 | 52.1084 | $CH_3$ops(89) |
| 16. | A | 1900 | - | 1761 | 1911 | 0.4636 | 8.4807 | 1621 | 1907 | 0.6802 | 6.5837 | $CH_3$ops(89) |
| 17. | A | 1790 | - | 1693 | 1799 | 31.5672 | 0.7888 | 1565 | 1794 | 31.2731 | 1.2414 | γC=C(90) |
| 18. | A | 1700 | - | 1657 | 1707 | 7.7936 | 3.1486 | 1543 | 1703 | 7.1706 | 2.7490 | γC=C(89)+$CH_3$ipb(12) |
| 19. | A | 1640 | - | 1654 | 1648 | 8.7755 | 23.3190 | 1539 | 1645 | 9.6436 | 20.1127 | γC=C(87)+$CH_3$ipb(13) |
| 20. | A | 1620 | - | 1648 | 1629 | 17.1363 | 7.8840 | 1532 | 1626 | 16.5763 | 9.9203 | γC-C(87) |
| 21. | A | - | 1610 | 1643 | 1615 | 6.8684 | 14.7346 | 1528 | 1613 | 8.6731 | 12.4100 | γC-C(89) |
| 22. | A | - | 1580 | 1643 | 1586 | 5.9124 | 0.9348 | 1527 | 1582 | 5.6131 | 1.5808 | $CH_3$ipb (89) |
| 23. | A | 1570 | - | 1639 | 1577 | 0.0634 | 20.4010 | 1526 | 1574 | 0.0004 | 16.4125 | $CH_3$ipb (90)+γC-C(10) |
| 24. | A | 1510 | - | 1583 | 1518 | 6.6379 | 1.5544 | 1464 | 1513 | 2.9658 | 1.1854 | γC-C(89) |
| 25. | A | - | 1470 | 1579 | 1475 | 5.0850 | 11.5757 | 1457 | 1471 | 4.6308 | 25.2825 | γC-C(78) |
| 26. | A | 1460 | - | 1578 | 1464 | 1.2620 | 1.1885 | 1455 | 1462 | 4.8377 | 0.3384 | γC-C(76) |
| 27. | A | 1410 | - | 1559 | 1419 | 9.6269 | 0.8377 | 1437 | 1415 | 9.2086 | 1.3808 | $CH_3$ipb (79) |
| 28. | A | 1380 | - | 1519 | 1387 | 1.9118 | 0.9852 | 1404 | 1385 | 2.2061 | 1.4621 | bCH(78)+ $CH_3$ipb (12) |
| 29. | A | - | 1370 | 1483 | 1374 | 1.5596 | 9.2471 | 1368 | 1373 | 2.7535 | 1.9338 | bCH(78) |
| 30. | A | 1360 | - | 1463 | 1366 | 5.9132 | 2.2046 | 1366 | 1364 | 2.7250 | 8.3212 | bCH(78) |
| 31. | A | 1330 | - | 1372 | 1341 | 1.0681 | 2.2496 | 1333 | 1335 | 3.2412 | 1.0016 | bCH(79) |
| 32. | A | 1310 | - | 1348 | 1314 | 0.7469 | 8.1881 | 1260 | 1311 | 0.0480 | 4.7245 | $CH_3$sb(79) |
| 33. | A | - | 1300 | 1333 | 1309 | 0.0117 | 2.3807 | 1245 | 1306 | 3.5289 | 30.6312 | $CH_3$sb(80) |
| 34. | A | - | 1280 | 1332 | 1288 | 4.4903 | 19.4434 | 1238 | 1285 | 1.7848 | 15.3921 | $CH_3$sb(81) |
| 35. | A | 1270 | - | 1284 | 1276 | 0.6142 | 1.6713 | 1200 | 1271 | 0.9446 | 0.5002 | bCH(90) |
| 36. | A | 1240 | - | 1235 | 1248 | 8.0827 | 1.4298 | 1158 | 1246 | 7.4782 | 2.8855 | bCH(90) |
| 37. | A | - | 1210 | 1233 | 1217 | 1.2710 | 6.8054 | 1135 | 1214 | 1.4888 | 6.2581 | bCH(91) |
| 38. | A | 1220 | - | 1210 | 1229 | 4.4356 | 0.1634 | 1099 | 1225 | 4.9888 | 0.0053 | RSymd(82)+$CH_3$ipr(18) |
| 39. | A | 1200 | - | 1185 | 1205 | 15.8010 | 12.2998 | 1097 | 1201 | 17.8313 | 13.2627 | $CH_3$ipr(85)+ RSymd(15) |
| 40. | A | - | 1190 | 1153 | 1194 | 0.0187 | 0.0017 | 1055 | 1193 | 3.7198 | 0.0462 | $CH_3$ipr(85) |
| 41. | A | 1180 | - | 1139 | 1187 | 2.2685 | 0.0726 | 1029 | 1182 | 0.2188 | 0.7635 | RSymd(85) |
| 42. | A | 1150 | - | 1128 | 1155 | 1.6745 | 0.0595 | 1002 | 1153 | 0.0001 | 0.0808 | $CH_3$ipr(87) |
| 43 | | 1130 | - | 1106 | 1137 | 0.0508 | 1.0904 | 989 | 1135 | 0.4894 | 0.0089 | Rtrigd (87) |
| 44 | | - | 1110 | 1054 | 1121 | 0.0435 | 7.7454 | 981 | 1118 | 0.1148 | 6.3274 | $CH_3$opb(85) |
| 45 | | 1100 | - | 1032 | 1109 | 1.1895 | 3.2701 | 954 | 1107 | 0.7881 | 2.2396 | $CH_3$opb(84) |
| 46 | | - | 1060 | 982 | 1066 | 0.0754 | 0.7347 | 904 | 1064 | 0.5685 | 6.9761 | $CH_3$opb(84) |
| 47 | | 1050 | - | 966 | 1055 | 0.270 | 8.6683 | 869 | 1052 | 0.0475 | 0.4883 | ωCH(75) |
| 48 | | 1010 | - | 959 | 1017 | 58.0740 | 0.5427 | 852 | 1013 | 43.2835 | 0.1875 | ωCH(79)+bCC(21) |
| 49 | | - | 960 | 883 | 969 | 0.0849 | 45.3606 | 828 | 964 | 0.0343 | 37.1796 | ωCH(79)+bCC(21) |
| 50 | | 920 | - | 838 | 924 | 5.9488 | 0.8852 | 756 | 922 | 5.2716 | 0.6725 | ωCH(78)+bCC(22) |
| 51 | | 900 | - | 748 | 906 | 0.0710 | 0.5883 | 702 | 903 | 0.2776 | 0.4633 | bCC(79) |
| 52 | | - | 890 | 725 | 898 | 0.0323 | 6.1676 | 673 | 895 | 0.0362 | 5.6959 | bCC(79)+ ωCH(21) |
| 53 | | 870 | - | 619 | 877 | 36.3973 | 0.0634 | 560 | 872 | 26.9794 | 0.0066 | ωCH(80) |
| 54 | | - | 820 | 589 | 829 | 0.0664 | 2.0326 | 548 | 821 | 0.0943 | 1.5410 | ωCH(80) |
| 55 | | 810 | - | 486 | 814 | 0.1598 | 8.1082 | 454 | 813 | 0.1176 | 5.8639 | $CH_3$OPr(84) |
| 56 | | - | 800 | 471 | 807 | 0.0383 | 0.0320 | 427 | 802 | 0.0429 | 0.0801 | $CH_3$opr(82)+ ωCH(18) |
| 57 | | - | 730 | 432 | 738 | 1.5290 | 0.8659 | 395 | 735 | 1.4192 | 1.0425 | ωCH(79) |
| 58 | | 710 | - | 389 | 715 | 0.2314 | 0.4068 | 363 | 711 | 0.2574 | 0.6247 | $CH_3$opr(79) |
| 59 | | - | 690 | 317 | 694 | 0.1179 | 3.0728 | 296 | 692 | 0.1275 | 2.9138 | tRsymd(82) |
| 60 | | - | 640 | 273 | 643 | 0.1107 | 0.0744 | 259 | 642 | 0.1486 | 0.0962 | tRsymd(82) |
| 61 | | 560 | - | 252 | 568 | 0.2795 | 1.1264 | 235 | 564 | 0.1386 | 0.5304 | ωCC(79) |
| 62 | | 540 | - | 236 | 548 | 0.2199 | 0.8902 | 218 | 544 | 0.3087 | 1.3684 | tRtrigd(74)+ ωCC(26) |
| 63 | | - | 450 | 206 | 457 | 0.3295 | 0.3744 | 189 | 452 | 0.2500 | 0.3640 | ωCC(82) |
| 64 | | - | 390 | 105 | 396 | 1.1038 | 1.2406 | 95 | 393 | 0.8254 | 1.5986 | $CH_3$twist(70)+ ωCC(30) |
| 65 | | - | 300 | 47 | 308 | 0.0664 | 2.9753 | 38 | 303 | 0.0578 | 3.6299 | $CH_3$twist(70)+ ωCC(20) |
| 66 | | - | 220 | 32 | 226 | 0.1611 | 0.2360 | 32 | 222 | 0.2467 | 0.3692 | $CH_3$twist(70)+ ωCC(20) |

**Abbreviations:** ν-stretching; ss-symmetric stretching; ips-in-plane stretching; sb-symmetric bending; ipr-in-plane rocking; opr-out-of-plane rocking; ops-out-of-plane stretching; b-bending; ω-out-of-plane bending; R-ring; trigd-trigonal deformation; symd-symmetric deformation; asymd-antisymmetric deformation; t-torsion.

In order to improve the agreement of theoretically calculated frequencies with experimentally calculated frequencies, it is necessary to scale down the theoretically calculated harmonic frequencies. Hence, the vibrational frequencies theoretically calculated at B3LYP/6-311++G(d,p) are scaled down by using MOLVIB 7.0 version written by Tom Sundius [8,9].

## 4. Results and Discussion

### 4.1. Optimized Geometry

The optimized molecular structure and the scheme of atoms numbering of IMB is represented in Fig.1. The geometries of IMB under investigation is considered as possessing $C_1$ point group symmetry. The calculated optimized geometrical parameters of IMB is presented in Table .1 and analyzed as follows.

Several authors have explained the changes in bond length of the C–H bond on substitution due to a change in charge distribution on the carbon of the benzene ring. The substituents may be either of the electron withdrawing type (Cl, F, Br...) or electron donating type ($CH_3$, $C_2H_5$....). The carbon atoms are bonded to the hydrogen atoms with an σ bond in benzene and the substitution of a halogen for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atoms in substituted benzenes exert a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C–H forces constant and a decrease in the corresponding bond length would be influenced by the combined effects of the inductive-mesomeric interaction and the electric dipole field of the polar substituent.

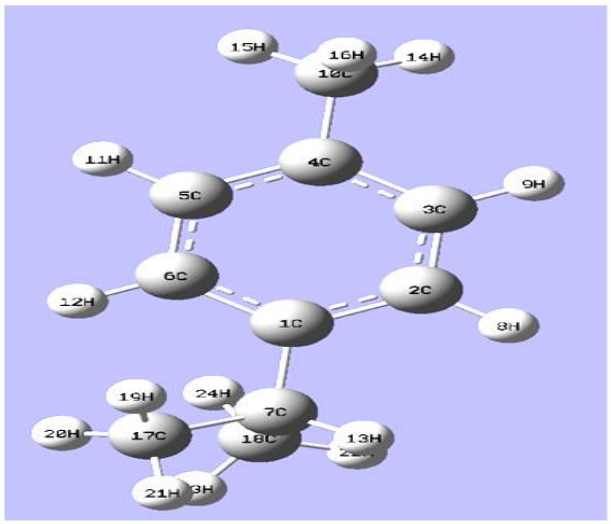


**Fig 1. Molecular structure of 1-Isopropyl 4-Methylbenzene.**

### 4.2. Vibrational assignments analysis

The molecule consists of 24 atoms and gives 66 fundamental modes of vibrations. All the vibrational assignments of IMB along with the experimentally and theoretically calculated frequencies are presented in Table 2. The FT-IR and FT-Raman spectra of **IMB** is shown in Figs. 2-3. The assignments of vibrational frequencies are interpreted as in the following sections.

Since the identification of all normal modes of vibration of compound is not trivial, so to simplify the problem by considering each compound as substituted benzene. Such an idea has already been successfully utilized by several workers for vibrational assignment of compounds containing multiple homo and heteroaromatic rings [10-14].

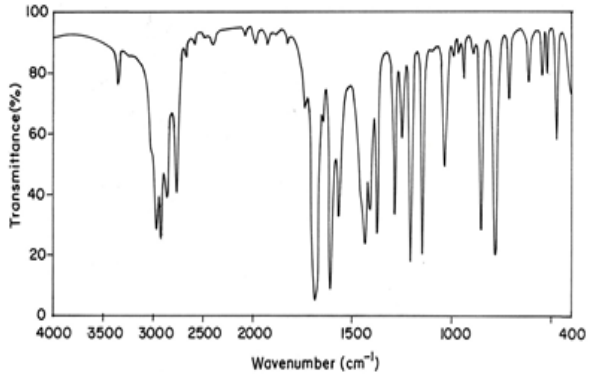


**Fig 2. FTIR spectrum of 1-Isopropyl 4-Methylbenzene.**

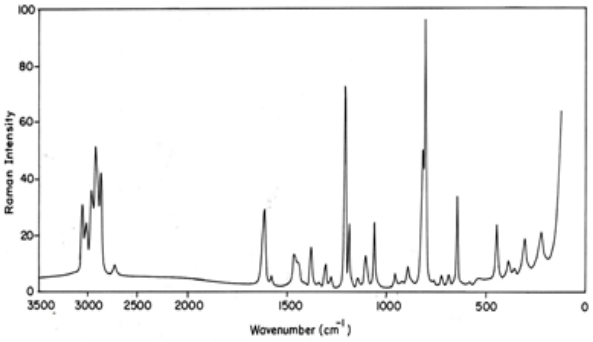


**Fig 3. FT-Raman spectrum of 1-Isopropyl 4-Methylbenzene.**

**C-H vibrations**

The heteroaromatic structure shows the presence of C-H stretching vibrations in the region 3100-3000 $cm^{-1}$ [15-17]. This is the characteristic region for the ready identification of C-H stretching vibrations. In this region, the bands are not affected appreciably by the nature of the substitutions. In the present investigation, the C-H stretching vibrations are observed at 3490,3120,3050,3030, and 2930 $cm^{-1}$ in the FT-IR spectrum and at 3080 and 3020 $cm^{-1}$ in the Raman for IMB. The C-H in-plane and out-of-plane bending vibrations of the IMB have also been identified and listed in Table 2.

**C-C vibrations**

The benzene possesses six stretching vibrations of which the four with highest wave numbers occurring near 1650-1400 $cm^{-1}$are good group vibrations [18].

With heavy substituents, the bonds tend to shift to somewhat lower wave numbers and greater the number of substituents on the ring, broader the absorption regions. In the title molecule, the FT-IR bands observed at 1640, 1620, 1510 ,1460 $cm^{-1}$ and 1610, 1470 $cm^{-1}$ in FT-Raman have been assigned to C-C stretching vibrations are due to the substituents in benzene ring. The higher percentage of total energy distribution (TED) obtained for this group encouraging and confirms the assignments proposed in this study for C-C stretching vibrations. The in-plane and out-of-plane bending vibrations of C-C group are also listed in Table 2.

**Methyl group vibrations**

For the assignments of $CH_3$ group frequencies, basically nine fundamentals can be associated to each $CH_3$ group namely, $CH_3$ ss – symmetric stretch; $CH_3$ ips – in-plane stretch (i.e., in-plane hydrogen stretching modes); $CH_3$ ipb – in-plane-bending (i.e., hydrogen deformation modes); $CH_3$ sb – symmetric bending; $CH_3$ ipr – in-plane rocking; $CH_3$ opr – out-of-plane rocking and t $CH_3$– twisting hydrogen bending modes. In addition to that, $CH_3$ops – out-of-plane stretch and $CH_3$ opb – out-of-plane bending modes of the $CH_3$ group

would be expected to be depolarised. In the present investigations, the $CH_3$ ss frequencies are established at 2880 and 2980,2750 $cm^{-1}$ in IR and Raman Spectrum respectively. The $CH_3$ips are assigned at 2960 $cm^{-1}$ and 2970,2940 $cm^{-1}$ in IR and Raman respectively for IMB. These assignments are also supported by the literature [19,20] in addition to TED output.

The two in-plane methyl hydrogen deformation modes are also well established. We have observed the symmetrical methyl deformation mode $CH_3$sb, at 1310 and 1300,1280 $cm^{-1}$ in the infrared and Raman, respectively. The in-plane-bending methyl deformation mode observed at 1570,1410 and 1580 $cm^{-1}$ in the IR and Raman spectrum respectively. The band at 2740,2600, 1900 $cm^{-1}$ in infrared is attributed to $CH_3$ ops and $CH_3$ opb is observed at 1100 $cm^{-1}$ and 1110,1060 $cm^{-1}$ respectively. The methyl deformation modes mainly coupled with the in-plane-bending vibrations.

**5. Homo-Lumo Analysis**

This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [21,22]. The LUMO as an electron acceptor (EA) represents the ability to obtain an electron and HOMO represents ability to donate an electron (ED). The ED groups to the efficient EA groups through π-conjugated path. Many organic molecules containing conjugated π electrons are characterized hyperpolarizabilities are analyzed by means of vibrational spectroscopy [23,24]. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman Spectrum are weak in the IR spectrum and vice versa. But the intramolecular charge transfer from the donor to acceptor group through a single-double bond conjugate path can include large variations of both molecular dipole moments and molecular polarizability making IR and Raman activity at the same time. The experimental spectroscopic behaviour described above is well accounted for DFT calculations in π-conjugated systems that predict exceptionally large Raman and infrared intensities in IR and Raman spectra are comparable resulting from the electron cloud movement through π-conjugated frame work electron donor to electron acceptor groups. The analysis of wave function indicates that the electron absorption corresponds to the transition from the ground to first excited stated and is mainly described by one electron excitation from the HOMO to LUMO. The atomic orbital compositions of the frontier molecular orbital and few MOS for IMB is sketched in Fig. 4.

$E_{HOMO}$ = -0.23547 a.u.
$E_{LUMO}$ = -0.00901 a.u.
Energy gap = 0.2265 a.u.

The energy gap reflects the chemical activity of the molecules. LUMO as electron acceptor represents the ability to obtain an electron, HOMO represent the ability to donate the electron. Moreover the lower in HOMO–LUMO energy gap explains the eventual charge transfer interactions taking place within the molecules, which influences the biological activity of the molecule.

**6. First Hyperpolarizability Calculation**

The electronic and vibrational contributions to the first hyperpolarizability have been studied theoretically for many organic and inorganic systems. The values of the first hyperpolarizability were found to be quite large for the so-called push-pull molecules, i.e. p-conjugated molecules with the electron donating and the electron withdrawing substituents attached to a ring, compared to the mono substituted systems [25]. This type of functionalization of organic materials, with the purpose of maximizing NLO properties, is still commonly followed route.

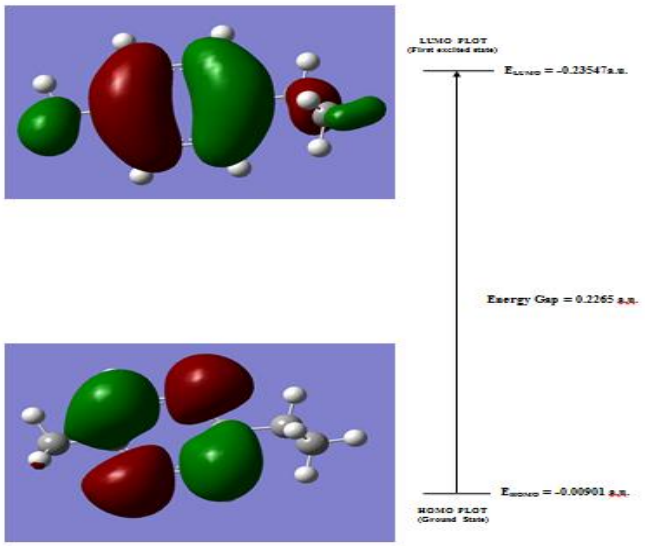


**Fig 4. The atomic orbital of HOMO-LUMO composition of frontier molecular orbital for 1-Isopropyl-4-Methylbenzene.**

The first hyperpolarizability of title compound is calculated using DFT and HF methods with 6-311++G(d,p) basis set. In the presence of an applied electric field, the energy of a system is a function of the electric field. First order hyperpolarizability (β) is a third rank tensor that can be described by 3 × 3 × 3 matrices. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + \ldots \quad (1)$$

where $E^0$ is the energy of the unperturbed molecule, $F_\alpha$ is the field at the origin, and $\mu_\alpha$, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first order hyperpolarizability, respectively. The total static dipole moment (μ) and the mean first hyperpolarizability (β) using the x, y, z components, they are defined as:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$

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

where

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

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

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

Since the value of hyperpolarizability (β) of the GAUSSIAN 09W output is reported in atomic units (a.u.), the calculated values should have been converted into electrostatic units (esu) (β: 1 a.u. = $8.639 \times 10^{-33}$ e.s.u). The total molecular dipole moment and first hyperpolarizability are 0.0641 Debye and $0.7336\times 10^{-30}$ e.s.u, respectively and are depicted in Table 3.

**Table 3.The calculated first hyperpolarizability (β) of 1-isopropyl -4- methyl benzene using DFT/ B3LYP/6-311++G(d,p) method and basis set.**

| Parameters | 1-Isopropyl -4- methyl benzene |
|---|---|
| $\beta_{xxx}$ | 5.7434157 |
| $\beta_{xxy}$ | -26.4915551 |
| $\beta_{xyy}$ | -45.4421044 |
| $\beta_{yyy}$ | -44.0642854 |
| $\beta_{xxz}$ | 12.6781007 |
| $\beta_{yyz}$ | -9.106822 |
| $\beta_{xzz}$ | -16.6890597 |
| $\beta_{yzz}$ | -17.0475786 |
| $\beta_{zzz}$ | -7.0345488 |
| β | $0.7336\times 10^{-30}$ |
| Dipole moment | 0.0641 Debye |

## 7. Thermodynamical Parameters

Several calculated thermodynamical parameters, rotational constants, rotational temperature and vibrational temperature have been presented in Table 4. The zero-point vibration energies, the entropy and the molar capacity at constant volume were calculated. The variations in the zero-point vibration energies seem to be insignificant. The changes in the total entropy of IMB at room temperature at DFT/6-311++G(d,p) and HF/6-311++G(d,p) methods are only marginal [26].

**Table 4. The thermodynamical parameters 1-Isopropyl -4- methyl benzene calculated at the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods and basis set.**

| Parameters | 1-Isopropyl-4-methylbenzene | |
|---|---|---|
| | HF | B3LYP |
| | 6-311++G(d,p) | 6-311++G(d,p) |
| Zero point vibrational energy (Kcal/Mol) | 143.28838 | 134.31455 |
| Rotational constants (GHZ) | | |
| A | 3.28881 | 3.23443 |
| B | 0.72619 | 0.71789 |
| C | 0.68570 | 0.67703 |
| Entropy (Cal/Mol-Kelvin) | 98.941 | 101.591 |
| Specific heat capacity at constant volume (Cal/Mol-Kelvin) | 35.974 | 38.888 |
| Total (Thermal) energy (KCal/Mol) | 149.456 | 140.873 |
| Translational energy (KCal/Mol) | 0.889 | 0.889 |
| Rotational energy (KCal/Mol) | 0.889 | 0.889 |
| Vibrational energy (KCal/Mol) | 147.679 | 139.096 |
| Dipole moment (Debye) | 0.0370 | 0.0641 |

## 8. Conclusion

The FT-IR and FT-Raman spectra of 1-isopropyl-4-methylbenzene have been studied. The equilibrium geometries, harmonic wavenumbers and HF and DFT calculations for IMB is carried out for the first time. Optimized geometrical parameters of the title compound are calculated. B3LYP/6-311++G(d,p) calculations are shown better correlation with the experimental data than other calculations. The calculated vibrational values are in good agreement when they are compared with IR and Raman experimental data. Frontier molecular orbital analysis, and NLO properties and other molecular properties of the title compound are also studied at DFT/6-311++G(d,p) and HF/6-311++G(d,p) levels. The results of this study will help researches to design and synthesis of new materials. Decrease in HOMO and LUMO energy gap, explains the eventual charge transfer within the molecule which is responsible for the chemical reactivity of the molecule. These calculations are carried out in ground state by using *ab initio* and Density functional theory.

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