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*International Journal of Current Research*
*Vol. 4, Issue, 02, pp.324-332, February, 2012*

**INTERNATIONAL JOURNAL OF CURRENT RESEARCH**

**ISSN: 0975-833X**

## RESEARCH ARTICLE

# SPECTROSCOPIC AND QUANTUM CHEMICAL (HF/DFT) ANALYSIS ON LEVAMISOLE

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**ARTICLE INFO**

***Article History:***
Received 13th November, 2011
Received in revised form
20th December, 2011
Accepted 10th January, 2011
Published online 29th February, 2012

***Key words:***

FTIR and FT Raman spectra;
ab initio and DFT;
Levamisole; vibrational analysis.

**ABSTRACT**

Quantum chemical calculations of molecular geometries, vibrational wavenumbers and thermodynamical properties of Levamisole was carried out using Hartree-Fock (HF) and density functional theory (DFT) using hybrid functional B3LYP with 6-31G(d,p) as basis set. The study is extended to calculate the HOMO-LUMO energy gap, polarizability, ionization potential, electron affinity, global hardness and electro negativity of Levamisole. The optimized geometrical parameters obtained by HF and DFT calculations are in good agreement with the experimental FTIR and FT Raman spectral data. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed spectrograms.

## INTRODUCTION

Levamisole is an anthelminthic and immunomodulator belonging to a class of synthetic imidazothiazole derivatives. Levamisole has been used in humans to treat parasitic worm infections, and has been studied in combination with other forms of chemotherapy for colon cancer, melanoma, and head and neck cancer. Levamisole is a cancer (antineoplastic) medication which interferes with the growth of cancer cells and slows their growth and spread in the body. As an anthelmintic, it probably works by targeting the nematode nicotinergic acetylcholine receptor. As an immunomodulator, it appears that Levamisole is an immunostimulant which has been shown to increase NK cells and activated T-cells in patients receiving this adjuvantly along with 5FU for Stage III colon cancer. Chemically it is called as (6S)-6-phenyl-2,3,5,6-tetrahydroimidazo[2,1-b][1,3] thiazole. Density functional theory (DFT), accepted by the ab initio quantum chemistry community is a cost-effective general procedure for studying physical properties of the molecules. DFT calculations of vibrational spectra of many organic systems (Johnson et. Al, 1993 and Handy et. Al, 1993) have shown promising conformity with experimental results. Therefore, in this present investigation ab initio and DFT techniques are employed to study the complete vibrational spectra of the title compound and to identify the various normal modes with greater wave number accuracy. Several other investigations have been carried out on the title compound Fun *et al.,* 2008) and its derivatives (Janciene *et al.,* 2008). Literature survey reveals that to the best of our knowledge no ab initio HF/DFT frequency calculations of Levamisole have been reported so far. It may be due to difficulty in interpreting the spectra of these molecules because of their complexity and low symmetry. Due to the absence of Raman spectra and vapour phase infrared spectra, a complete vibrational assignment is not available in the literature. Hence the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wave number accuracy. Assuming $C_1$ point group symmetry the band assignments have made ab initio and Density Functional Theory (DFT) calculations have been performed to support our wave number assignments. The theoretically predicted IR and Raman intensities are well in agreement with that of experimental spectral data.

## EXPERIMENTAL

The compound Levamisole in the solid form was purchased from Sigma-Aldrich Chemical Company with a stated purity of greater than 98% and it was used as such without further purification. A projection of Levamisole is shown in Fig. 1. The FT-Raman spectrum of Levamisole has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 100 – 3500$\text{cm}^{-1}$ on a Nexus 670 spectrophotometer equipped with FT-Raman module accessory. The FTIR spectrum of this compound was recorded in the range 400 – 4000 $\text{cm}^{-1}$ Nexus 670 spectrophotometer using KBr pellet technique with scanning speed of 30$\text{cm}^{-1}$ $\text{min}^{-1}$ and the spectral resolution of 4.0 $\text{cm}^{-1}$. The observed theoretical and experimental FTIR and FT-Raman spectra are shown in Figs. 2 & 3.

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## COMPUTATIONAL DETAILS

The entire calculations conducted in the present work were performed at Hartree-Fock (HF) and B3LYP levels included in the Gaussian 03W package (Frisch *et al.,*2004) program together with the 6-31G(d,p) basis set function of the density functional theory (DFT) utilizing gradient geometry optimization (Schlegel, 1982). The geometries were first determined at the Hartree Fock level of theory employing 6-31G (d,p) basis set by assuming $C_1$ point group symmetry. All the geometries were then optimized using 6-31G (d,p) basis sets using density functional theory (Hohenberg, 1964) employing the Becke's three-parameter hybrid functional (Becke, 1993) combined with Lee-Yang-Parr correlation (Lee *et al.,*1988) functional (B3LYP) method. The DFT partitions the electronic energy as $E = E_T+E_V+E_J+E_{XC}$, where $E_T$, $E_V$, and $E_J$ are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The electron correlation is taken into account in DFT via the exchange correlation term $E_{XC}$, which includes the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure (Foresman et. al, 1996). The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of Levamisole is used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The DFT hybrid B3LYP functional also tends to overestimate the fundamental modes in comparison to the other DFT methods; therefore, scaling factors have to be used to obtain considerably better agreement with experimental data. Thus according to the work of Rauhut and Pulay (Rauhut *et al.,*1995), a scaling factor of 0.963 has been uniformly applied to the B3LYP calculated wavenumbers. Similarly, the vibrational modes studies through HF method were scaled by a value of 0.891. Finally, calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics. Zero point vibrational energy was also calculated in the present work. By combining the results of the Gauss view program (Frisch *et al.,*2000) with symmetry considerations, vibrational frequency assignments were made with high degree of accuracy. The transformation of force field, calculations of potential energy distribution (PED), IR and Raman intensities were done on a personal computer (PC) with a version V7.0-G77 of the MOLVIB program written by Tom Sundius (Sundius, 1991). There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the Gauss view program. To achieve a close agreement between observed and calculated frequencies, the least square fit refinement algorithm was used. For the plots of simulated IR and Raman spectrum, pure Lorentzian band shapes were used with a bandwidth of 10 cm$^{-1}$.

**Table 1 Optimized geometrical parameters of Levamisole, bond length(Å), Interaxial angles(°)**

| Parameters | Expt. | HF/6-31 G(d,p) | B3LYP/6-31G(d,p) |
|---|---|---|---|
| $C_8$-$H_{20}$ | 1.113 | 1.067 | 1.078 |
| $C_8$-$H_{21}$ | 1.113 | 1.069 | 1.079 |
| $C_8$-$N_3$ | 1.470 | 1.418 | 1.432 |
| $N_3$-$C_4$ | 1.470 | 1.475 | 1.480 |
| $N_3$-$C_2$ | 1.466 | 1.419 | 1.447 |
| $C_4$-$H_{16}$ | 1.113 | 1.080 | 1.092 |
| $C_4$-$H_{15}$ | 1.113 | 1.083 | 1.095 |
| $C_4$-$C_5$ | 1.504 | 1.518 | 1.513 |
| $C_5$-$H_{18}$ | 1.113 | 1.083 | 1.093 |
| $C_5$-$H_{17}$ | 1.113 | 1.081 | 1.091 |
| $C_5$-$S_1$ | 1.790 | 1.809 | 1.784 |
| $C_2$-$S_1$ | 1.759 | 1.789 | 1.768 |
| $C_2$-$N_6$ | 1.460 | 1.436 | 1.448 |
| $N_6$-$C_7$ | 1.290 | 1.267 | 1.308 |
| $C_7$-$H_{19}$ | 1.113 | 1.081 | 1.092 |
| $C_7$-$C_9$ | 1.497 | 1.485 | 1.496 |
| $C_7$-$C_{10}$ | 1.337 | 1.394 | 1.311 |
| $C_{10}$-$H_{22}$ | 1.100 | 1.077 | 1.087 |
| $C_9$-$C_{14}$ | 1.337 | 1.393 | 1.321 |
| $C_{14}$-$H_{26}$ | 1.100 | 1.075 | 1.084 |
| $C_{10}$-$C_{11}$ | 1.337 | 1.382 | 1.350 |
| $C_{11}$-$H_{23}$ | 1.100 | 1.076 | 1.086 |
| $C_{11}$-$H_{13}$ | 1.337 | 1.387 | 1.349 |
| $C_{12}$-$C_{13}$ | 1.337 | 1.384 | 1.346 |
| $C_{13}$-$H_{25}$ | 1.100 | 1.076 | 1.086 |
| $C_{12}$-$H_{24}$ | 1.100 | 1.076 | 1.086 |
| $C_{13}$-C-$_{14}$ | 1.337 | 1.385 | 1.353 |
| $H_{20}$-$C_8$-$H_{21}$ | 119.00 | 121.47 | 120.18 |
| $H_{19}$-$C_7$-$C_9$ | 120.00 | 118.34 | 118.54 |
| $H_{19}$-$C_7$-$N_6$ | 119.00 | 118.11 | 118.30 |
| $C_9$-$C_7$-$N_6$ | 124.10 | 126.51 | 125.10 |
| $C_7$-$N_6$-$C_2$ | 124.00 | 126.19 | 125.46 |
| $H_{17}$-$C_5$-$H_{18}$ | 109.40 | 109.79 | 109.54 |
| $H_{17}$-$C_5$-$C_4$ | 109.41 | 109.98 | 109.54 |
| $H_{17}$-$C_5$-$S_1$ | 113.44 | 112.47 | 112.43 |
| $H_{18}$-$C_5$-$C_4$ | 109.41 | 110.90 | 110.46 |
| $H_{18}$-$C_5$-$S_1$ | 109.40 | 110.36 | 110.02 |
| $C_4$-$C_5$-$S_1$ | 102.10 | 102.83 | 102.09 |
| $H_{15}$-$C_4$-$H_{16}$ | 109.40 | 109.58 | 109.08 |
| $H_{15}$-$C_4$-$C_5$ | 109.41 | 110.26 | 109.20 |
| $H_{15}$-$C_4$-$N_3$ | 108.70 | 107.83 | 108.26 |
| $H_{16}$-$C_4$-$C_5$ | 109.41 | 109.07 | 109.69 |
| $H_{16}$-$C_4$-$N_3$ | 108.01 | 108.70 | 108.59 |
| $C_5$-$C_4$-$N_3$ | 112.41 | 110.99 | 111.65 |
| $C_8$-$N_3$-$C_4$ | 120.00 | 118.77 | 119.48 |
| $C_8$-$N_3$-$C_2$ | 124.00 | 126.48 | 125.06 |
| $C_4$-$N_3$-$C_2$ | 108.00 | 110.71 | 110.38 |
| $S_1$-$C_2$-$N_6$ | 126.00 | 126.18 | 126.90 |
| $S_1$-$C_2$-$N_3$ | 124.00 | 123.62 | 123.74 |
| $N_6$-$C_2$-$N_3$ | 111.00 | 111.73 | 111.63 |
| $C_2$-$S_1$-$C_5$ | 104.00 | 104.11 | 104.56 |
| $N_3$-$C_8$-$H_{21}$ | 118.21 | 118.40 | 118.29 |
| $N_3$-$C_8$-$H_{20}$ | 118.00 | 119.10 | 118.29 |
| $C_{14}$-$C_9$-$C_{10}$ | 120.00 | 118.52 | 118.85 |
| $C_7$-$C_9$-$C_{10}$ | 120.00 | 118.13 | 118.58 |
| $C_7$-$C_9$-$C_{14}$ | 121.00 | 122.12 | 121.31 |
| $C_{11}$-$C_{10}$-$C_9$ | 120.00 | 120.86 | 120.58 |
| $H_{22}$-$C_{10}$-$C_9$ | 120.00 | 118.36 | 118.92 |
| $H_{22}$-$C_{10}$-$C_{11}$ | 120.00 | 119.78 | 119.90 |
| $C_{12}$-$C_{11}$-$C_{10}$ | 120.00 | 120.28 | 120.21 |
| $H_{23}$-$C_{11}$-$C_{10}$ | 120.00 | 119.84 | 119.75 |
| $H_{23}$-$C_{11}$-$C_{12}$ | 120.00 | 120.07 | 120.05 |
| $C_{13}$-$C_{12}$-$C_{11}$ | 120.00 | 119.41 | 119.41 |
| $H_{24}$-$C_{12}$-$C_{11}$ | 120.00 | 120.18 | 120.28 |
| $H_{24}$-$C_{12}$-$C_{13}$ | 120.00 | 120.31 | 120.30 |
| $C_{14}$-$C_{13}$-$C_{12}$ | 120.00 | 120.32 | 120.24 |
| $H_{25}$-$C_{13}$-$C_{14}$ | 120.00 | 119.61 | 119.45 |
| $H_{25}$-$C_{13}$-$C_{12}$ | 120.00 | 120.07 | 120.01 |
| $C_9$-$C_{14}$-$H_{26}$ | 120.00 | 119.74 | 119.74 |
| $C_{13}$-$C_{14}$-$H_{26}$ | 120.00 | 119.67 | 119.47 |
| $C_{13}$-$C_{14}$-$C_9$ | 120.00 | 120.58 | 120.47 |

Geometrical parameters determined with X-ray diffraction method from Ref. [19,20]

## RESULTS AND DISCUSSION

### *Molecular geometry*

The optimized structure parameters of Levamisole calculated by ab initio HF and DFT-B3LYP levels with the 6-31G (d,p)

**Table 2. Vibrational Wavenumbers obtained for Levamisole at HF/ 6-31G(d,p) [wavenumber (cm$^{-1}$) IR intensities (km mol$^{-1}$), Raman scattering activities (Å amu$^{-1}$), reduced mass (amu), force constants (m dyne Å$^{-1}$) and Raman depolarisation ratio]**

| $\nu_{cal}$ (cm$^{-1}$) | IR intensity | Raman activity | Reduced mass | Force constants | $\rho$ |
|---|---|---|---|---|---|
| 43 | 1.14 | 11.54 | 4.57 | 0.01 | 0.50 |
| 45 | 2.52 | 12.73 | 5.22 | 0.01 | 0.74 |
| 86 | 2.38 | 5.69 | 4.01 | 0.02 | 0.75 |
| 119 | 1.76 | 7.35 | 4.51 | 0.04 | 0.62 |
| 165 | 10.98 | 19.60 | 4.48 | 0.07 | 0.73 |
| 185 | 7.32 | 36.51 | 5.41 | 0.11 | 0.46 |
| 227 | 2.98 | 1.34 | 3.00 | 0.11 | 0.68 |
| 246 | 3.85 | 27.59 | 4.43 | 0.18 | 0.35 |
| 275 | 0.67 | 8.25 | 3.40 | 0.16 | 0.74 |
| 415 | 3.25 | 17.41 | 3.67 | 0.44 | 0.33 |
| 425 | 0.17 | 21.15 | 3.03 | 0.37 | 0.35 |
| 443 | 13.87 | 38.25 | 4.20 | 0.59 | 0.44 |
| 466 | 0.62 | 1.46 | 3.81 | 0.60 | 0.66 |
| 490 | 0.47 | 20.24 | 4.85 | 0.85 | 0.45 |
| 505 | 0.82 | 3.29 | 3.00 | 0.55 | 0.55 |
| 526 | 8.80 | 17.10 | 1.66 | 0.38 | 0.32 |
| 569 | 14.25 | 149.97 | 3.63 | 0.88 | 0.44 |
| 579 | 69.05 | 96.74 | 2.26 | 0.58 | 0.34 |
| 626 | 14.49 | 3.77 | 5.47 | 1.47 | 0.60 |
| 640 | 11.73 | 10.12 | 4.54 | 1.28 | 0.13 |
| 651 | 65.30 | 38.27 | 5.03 | 1.69 | 0.38 |
| 690 | 23.68 | 8.46 | 2.12 | 0.76 | 0.42 |
| 701 | 11.29 | 9.37 | 2.94 | 1.06 | 0.15 |
| 714 | 67.67 | 50.24 | 1.49 | 0.55 | 0.66 |
| 761 | 49.11 | 19.65 | 1.67 | 0.69 | 0.32 |
| 829 | 87.04 | 44.87 | 3.12 | 1.51 | 0.67 |
| 856 | 67.87 | 12.45 | 1.85 | 0.96 | 0.71 |
| 862 | 0.35 | 13.48 | 1.25 | 0.68 | 0.29 |
| 872 | 14.85 | 164.90 | 1.49 | 0.84 | 0.31 |
| 928 | 8.34 | 4.38 | 1.99 | 1.24 | 0.60 |
| 950 | 12.38 | 22.91 | 1.53 | 1.00 | 0.42 |
| 978 | 0.02 | 110.66 | 6.19 | 4.31 | 0.18 |
| 996 | 9.27 | 14.59 | 2.24 | 1.59 | 0.32 |
| 1010 | 0.73 | 3.75 | 1.37 | 0.99 | 0.37 |
| 1024 | 3.09 | 8.25 | 1.42 | 1.05 | 0.23 |
| 1038 | 0.39 | 14.70 | 1.40 | 1.04 | 0.35 |
| 1049 | 4.04 | 8.61 | 2.09 | 1.56 | 0.14 |
| 1110 | 9.38 | 15.02 | 1.69 | 1.39 | 0.36 |
| 1121 | 11.31 | 15.93 | 2.26 | 1.95 | 0.72 |
| 1169 | 2.99 | 30.95 | 3.51 | 3.20 | 0.66 |
| 1187 | 226.98 | 447.12 | 2.73 | 2.59 | 0.35 |
| 1198 | 3.23 | 57.61 | 1.15 | 1.14 | 0.26 |
| 1210 | 0.77 | 87.52 | 1.35 | 1.34 | 0.29 |
| 1227 | 1.42 | 7.44 | 1.62 | 1.66 | 0.74 |
| 1265 | 336.00 | 137.13 | 1.54 | 1.62 | 0.38 |
| 1311 | 280.14 | 69.04 | 2.45 | 2.64 | 0.66 |
| 1335 | 31.65 | 14.55 | 1.27 | 1.55 | 0.48 |
| 1364 | 12.60 | 16.24 | 1.36 | 1.72 | 0.51 |
| 1373 | 500.60 | 438.13 | 2.03 | 2.61 | 0.31 |
| 1391 | 16.92 | 489.13 | 1.73 | 2.32 | 0.32 |
| 1447 | 531.20 | 410.16 | 1.45 | 2.05 | 0.44 |
| 1469 | 464.25 | 101.10 | 1.66 | 2.48 | 0.63 |
| 1488 | 47.34 | 67.66 | 1.65 | 2.51 | 0.36 |
| 1497 | 37.00 | 31.83 | 1.30 | 1.99 | 0.61 |
| 1507 | 58.39 | 29.74 | 1.12 | 1.75 | 0.37 |
| 1531 | 1.12 | 14.05 | 2.19 | 3.55 | 0.41 |
| 1559 | 436.28 | 388.71 | 2.30 | 3.81 | 0.37 |
| 1572 | 1.36 | 227.39 | 5.15 | 9.54 | 0.39 |
| 1604 | 7.08 | 398.68 | 5.25 | 10.06 | 0.37 |
| 1619 | 38.60 | 249.92 | 10.47 | 20.65 | 0.33 |
| 3073 | 26.97 | 96.46 | 1.06 | 6.54 | 0.22 |
| 3084 | 28.41 | 148.74 | 1.06 | 6.59 | 0.11 |
| 3124 | 36.11 | 103.94 | 1.09 | 6.92 | 0.35 |
| 3137 | 13.27 | 102.44 | 1.11 | 7.09 | 0.50 |
| 3152 | 13.34 | 67.04 | 1.11 | 7.17 | 0.75 |
| 3174 | 5.99 | 35.47 | 1.09 | 7.12 | 0.74 |
| 3182 | 1.65 | 117.63 | 1.09 | 7.17 | 0.70 |
| 3192 | 34.29 | 108.07 | 1.09 | 7.25 | 0.72 |
| 3202 | 52.11 | 218.35 | 1.10 | 7.32 | 0.15 |
| 3218 | 10.21 | 180.92 | 1.10 | 7.37 | 0.09 |
| 3233 | 34.22 | 137.51 | 1.05 | 7.07 | 0.17 |
| 3255 | 8.85 | 119.42 | 1.12 | 8.17 | 0.67 |

Table 3. Vibrational Wavenumbers obtained for Levamisole at B3LYP/ 6-31G(d,p) [wavenumber (cm$^{-1}$) IR intensities (km mol$^{-1}$), Raman scattering activities (Å amu $^{-1}$), reduced mass (amu), force constants (m dyne Å $^{-1}$) and Raman depolarisation ratio]

| Observed wavenumbers | | Calculated using B3LYP/6-31G(d,p) | | | | | |
|---|---|---|---|---|---|---|---|
| $\nu_{IR}$ (cm$^{-1}$) | $\nu_{Raman}$ (cm$^{-1}$) | $\nu_{cal}$ (cm$^{-1}$) | IR intensity | Raman activity | Reduced mass | Force constants | ρ Assignments with PED (%) |
| - | 42 | 0.998 | 15.389 | 4.964 | 0.005 | 0.606 | $R_{puk}$ (24) |
| - | 46 | 1.142 | 4.712 | 5.044 | 0.006 | 0.505 | t $R_{asymm}$ (21), $R_{trigd}$ (19) |
| - | 86 | 2.490 | 4.981 | 3.674 | 0.016 | 0.746 | t $R_{sym}$ (36), ωCH(10) |
| 120 | 119 | 0.956 | 4.802 | 4.748 | 0.040 | 0.746 | γ ring 3 (49) , ι CC(27) |
| 165 | 164 | 0.873 | 27.624 | 4.889 | 0.077 | 0.563 | δ NCH (39), ι CN (25) |
| 180 | 182 | 3.379 | 7.058 | 3.823 | 0.074 | 0.483 | $R_{symd}$ (31), δ NCH (43) |
| 225 | 226 | 2.689 | 1.803 | 3.255 | 0.098 | 0.740 | $R_{asymd}$ (47), δ NCC (33) |
| 250 | 250 | 2.142 | 27.292 | 4.553 | 0.168 | 0.353 | γ NCS (56) |
| 275 | 273 | 1.543 | 24.094 | 3.469 | 0.153 | 0.499 | β CCS (58), δ NCC (28) |
| - | 413 | 5.228 | 2.518 | 3.233 | 0.325 | 0.328 | γ NCN (51), $R_{puk}$ (38) |
| 421 | 422 | 0.232 | 11.668 | 3.071 | 0.322 | 0.368 | $R_{asymd}$ (53), δ NCC $_{ip}$(35) |
| 440 | 442 | 1.681 | 41.563 | 4.412 | 0.509 | 0.380 | ν C- S (63), $\delta_{oop}$ Ring (42) |
| - | 464 | 8.377 | 1.425 | 2.426 | 0.307 | 0.747 | $R_{asymt}$ (59), δ NCC $_{ip}$ (35) |
| 490 | 489 | 14.728 | 7.819 | 3.065 | 0.432 | 0.623 | ι CH$_2$ (42) |
| 505 | 505 | 6.676 | 14.278 | 3.471 | 0.522 | 0.552 | γ CN (69), $\delta_{oop}$ Ring (47) |
| 525 | 526 | 46.514 | 9.326 | 1.821 | 0.297 | 0.493 | δ NCS (61), ω CN (25) |
| 568 | 569 | 19.797 | 37.958 | 3.052 | 0.583 | 0.263 | δ CNC (56) |
| 575 | 577 | 17.413 | 156.214 | 4.217 | 0.829 | 0.366 | δ C NC (52) |
| 625 | 627 | 2.614 | 11.415 | 5.574 | 1.295 | 0.463 | ν CS (58), δ CNH (15) |
| 635 | 637 | 25.891 | 25.880 | 1.722 | 0.412 | 0.453 | ν CS (63), $R_{asymd}$ (33) |
| 645 | 648 | 2.969 | 17.595 | 4.325 | 1.056 | 0.153 | γ NCH (47), $R_{asym}$ (49) |
| 689 | 689 | 5.932 | 3.389 | 3.533 | 1.013 | 0.536 | γ CH (42), $R_{asymd}$ (24) |
| 700 | 702 | 19.802 | 15.390 | 5.672 | 1.648 | 0.201 | δ C=N (55), ω CH(20) |
| - | 713 | 31.428 | 2.037 | 1.907 | 0.572 | 0.708 | t $R_{sym}$ (27) |
| 760 | 760 | 22.994 | 67.270 | 1.660 | 0.565 | 0.354 | t $R_{asym}$ (31) |
| - | 825 | 11.146 | 152.466 | 2.355 | 0.946 | 0.473 | γ CH (61), t $R_{asym}$ (19) |
| 851 | 854 | 2.283 | 7.608 | 1.328 | 0.572 | 0.639 | γ CH (63), t $R_{trigd}$ (23) |
| 860 | 862 | 12.031 | 57.916 | 1.738 | 0.762 | 0.333 | γ CH (57), t $R_{trig}$ (18) |
| - | 871 | 15.183 | 54.452 | 1.861 | 0.832 | 0.155 | γ CH (59), $R_{trigd}$ (21) |
| - | 927 | 8.393 | 5.316 | 1.503 | 0.762 | 0.440 | γ CH (51) |
| 945 | 946 | 11.656 | 4.276 | 2.079 | 1.096 | 0.632 | γ CH (56) |
| 975 | 973 | 0.591 | 11.131 | 1.344 | 0.750 | 0.320 | γ CH (57) |
| 996 | 994 | 1.082 | 1.459 | 1.246 | 0.726 | 0.728 | $R_{symb}$ (45) |
| 1005 | 1010 | 1.392 | 178.280 | 5.806 | 3.490 | 0.223 | $C_5H_{17}$ $H_{18\ rok}$ (37) |
| 1025 | 1025 | 6.087 | 6.047 | 2.216 | 2.216 | 0.353 | ν CC (75), $R_{trigd}$ (52) |
| 1036 | 1037 | 7.026 | 7.160 | 1.465 | 0.911 | 0.298 | ι CH$_2$ (33) |
| 1055 | 1053 | 3.230 | 30.467 | 2.239 | 1.464 | 0.174 | $R_{symd}$ (29) |
| - | 1110 | 15.996 | 45.716 | 3.032 | 2.193 | 0.261 | δ CH$_{2\ ip}$ (32) |
| - | 1123 | 9.873 | 2.428 | 1.643 | 1.195 | 0.269 | δ CCH $_{ip}$ (29) |
| 1168 | 1167 | 10.361 | 91.536 | 1.853 | 1.515 | 0.442 | δ CH$_{2\ ip}$ (21) |
| 1190 | 1186 | 0.062 | 14.274 | 1.097 | 0.909 | 0.725 | δ CCH $_{ip}$ (42) |
| 1196 | 1195 | 4.641 | 320.502 | 1.513 | 1.275 | 0.300 | δ CH$_{2\ ip}$ (23) |
| 1207 | 1208 | 2.964 | 91.129 | 1.178 | 1.013 | 0.284 | δ CCH (45) |
| 1225 | 1226 | 44.166 | 179.690 | 1.660 | 1.471 | 0.317 | ι CH$_2$ (39) |
| 1267 | 1267 | 37.273 | 156.073 | 2.115 | 2.001 | 0.327 | ν C-C(69), δ CCH (24) |
| 1310 | 1310 | 31.689 | 2.836 | 1.223 | 1.237 | 0.741 | ν C-C (74), δ CCH (31) |
| 1335 | 1333 | 1.516 | 247.712 | 2.587 | 2.709 | 0.286 | ν C-C (61), $R_{asymd}$ (22) |
| 1360 | 1360 | 57.570 | 49.940 | 1.834 | 2.000 | 0.270 | δ CH$_{2\ ip}$ (31), υ C-C(62) |
| 1368 | 1370 | 2.290 | 13.947 | 2.147 | 2.361 | 0.656 | $R_{asymd}$ (28), δ CCH (33) |
| 1386 | 1388 | 10.951 | 114.088 | 1.646 | 1.863 | 0.345 | δ CH$_{2\ ip}$ (28) |
| 1445 | 1446 | 18.866 | 13.983 | 1.540 | 1.915 | 0.738 | δ NCH (47) |
| 1467 | 1468 | 107.142 | 77.362 | 1.525 | 1.952 | 0.580 | δ CH$_2$ (54) |
| 1488 | 1489 | 4.047 | 20.498 | 1.161 | 1.524 | 0.439 | ν C=N (88) |
| - | 1496 | 67.691 | 83.217 | 1.716 | 2.265 | 0.323 | δ CH$_2$ (56) |
| 1504 | 1507 | 82.468 | 22.266 | 1.273 | 1.705 | 0.508 | δ CH$_2$ (51) |
| 1530 | 1533 | 7.865 | 81.641 | 2.216 | 3.069 | 0.348 | δ C-H (63) |
| 1556 | 1557 | 566.794 | 32.879 | 3.860 | 5.474 | 0.645 | ν CN (84) |
| 1574 | 1572 | 89.388 | 536.431 | 8.341 | 12.626 | 0.340 | ν CN (89) |
| 1604 | 1602 | 12.145 | 255.175 | 5.307 | 8.256 | 0.300 | δ C-H (59) |
| - | 1619 | 1.006 | 283.803 | 5.866 | 9.472 | 0.470 | δ C-H (48) |
| 3070 | 3069 | 33.852 | 203.766 | 1.061 | 5.896 | 0.131 | $\nu_s$ CH$_2$ (91) |
| 3082 | 3082 | 18.544 | 107.841 | 1.061 | 1.061 | 0.220 | $\nu_s$ CH$_2$ (87) |
| - | 3117 | 29.731 | 131.954 | 1.085 | 6.217 | 0.184 | ν C-H (93) |
| 3129 | 3136 | 12.755 | 104.892 | 1.103 | 6.376 | 0.495 | $\nu_s$ CH$_2$ (92) |
| - | 3156 | 7.448 | 119.881 | 1.106 | 6.487 | 0.615 | $\nu_s$ CH$_2$ (91), $\nu_s$ CH $_{ring}$ (89) |
| 3168 | 3172 | 7.035 | 45.282 | 1.085 | 6.437 | 0.733 | $\nu_s$ CH $_{ring}$ (98) |
| - | 3181 | 0.579 | 109.589 | 1.087 | 6.484 | 0.600 | $\nu_a$ CH $_{ring}$ (94) |
| 3192 | 3190 | 31.932 | 151.533 | 1.092 | 6.553 | 0.635 | $\nu_a$ CH $_{ring}$ (89) |
| 3202 | 3203 | 41.654 | 322.041 | 1.095 | 6.626 | 0.159 | $\nu_a$ CH (99) |
| 3215 | 3214 | 5.594 | 98.781 | 1.093 | 6.658 | 0.083 | $\nu_a$ CH (99) |
| 3225 | 3228 | 19.462 | 230.321 | 1.049 | 6.403 | 0.191 | $\nu_a$ CH$_2$ (99) |
| - | 3250 | 4.049 | 106.838 | 1.124 | 7.439 | 0.640 | $\nu_a$ CH$_2$ (98) |

ω -wagging, trigd -trigonal deformation, symd – symmetric deformation, asymd –asymmetric deformation,
symt – symmetric torsion, asymt – asymmetric torsion, puck –puckering, R – phenyl ring, ν– stretching, s – symmetric stretching, a – asymmetric stretching, oop – out-of-plane, ip –inplane, δ -bending, t – torsion

**Table 4. Theoretically computed energies (a,u), zero point vibrational energies (kcal mol$^{-1}$), rotational constants (GHz) entropies (cal mol$^{-1}$ k$^{-1}$) and Dipole moment (D) (Kcal Mol$^{-1}$ Kelvin$^{-1}$) of Levamisole**

| Parameters | HF / 6-31G (d, p) | B3LYP / 6-31G (d, p) |
|---|---|---|
| Total energy | -929.621382 | - 933.815465 |
| Zero point energy | 140.63382 | 131.05680 |
| Rotational constants | 1.44763 | 1.44449 |
| | 0.36699 | 0.35704 |
| | 0.32318 | 0.31180 |
| Entropy | | |
| Total | 147.883 | 138.843 |
| Translational | 0.889 | 0.889 |
| Rotational | 0.889 | 0.889 |
| Vibrational | 146.105 | 137.065 |
| Dipole moment | 3.1458 | 3.5647 |

**Table 5. Calculated polarizabilities of Levamisole**

| Basis set | $\alpha_{xx}$ | $\alpha_{xy}$ | $\alpha_{yy}$ | $\alpha_{xz}$ | $\alpha_{yz}$ | $\alpha_{zz}$ | $<\alpha>$ |
|---|---|---|---|---|---|---|---|
| HF/6-31G(d,p) | 284.591 | -30.648 | 130.666 | -25.661 | -7.780 | 94.858 | 170.038 |
| B3LYP/ 6-31G(d,p) | 320.437 | -24.562 | 141.388 | -23.877 | -9.663 | 92.015 | 184.613 |

**Table 6. Comparison of HOMO, LUMO, energy gaps (*e*HOMO–LUMO), ionization potentials, Electron affinity, Global hardness and Electro negativity of Levamisole**

| Basis set | ε HOMO eV | ε LUMO eV | Energy gap ($\varepsilon_{HOMO} - \varepsilon_{LUMO}$) eV | Ionisation (I) eV | Electron affinity (A) | Global Hardness $\eta = (I-A)/2$ eV | Electro negativity $\chi = (I+A)/2$ eV |
|---|---|---|---|---|---|---|---|
| HF/6-31G(d,p) | -5.4678 | 2.4765 | 7.9443 | 5.4678 | -2.4765 | 3.9721 | 1.4956 |
| B3LYP/6-31G(d,p) | -3.9568 | -1.3932 | 2.5636 | 3.9568 | 1.3932 | 1.2818 | 2.6750 |

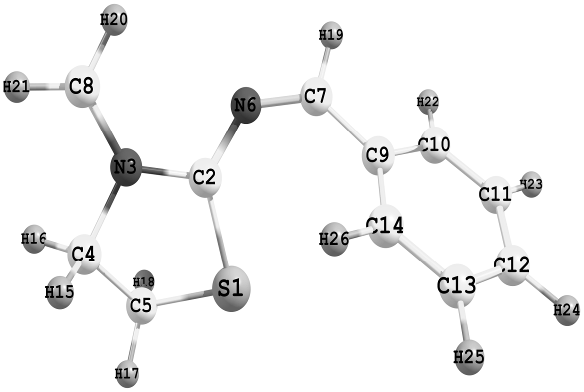

Fig. 1. The atom numbering for Levamisole molecule

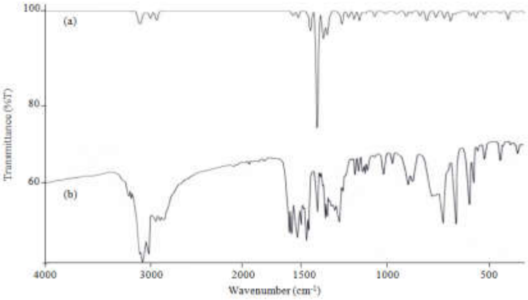

Fig. 2. FTIR spectra of Levamisole (a) Theoretical and (b) experimental

basis set are listed in the Table 1 in accordance with the atom numbering scheme given in Fig.1. The molecular structure, XRD studies have been studied for the compound. Table 1 compares the calculated bond lengths and angles for Levamisole with those experimentally available from X-ray diffraction data (Tang *et al.,* 1985). From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values, due to the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state. Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are on higher side than the latter and the HF calculated values correlates well compared with the experimental results. In spite of the differences, calculated geometric parameters represent a good approximation and they are the basis for calculating other parameters, such as vibrational frequencies and thermodynamic properties.

### *Vibrational assignments*

The vibrational analysis of Levamisole is performed on the basis of the characteristic vibrations of carbonyl and phenyl ring modes. The computed vibrational wavenumbers, their IR and Raman activities, depolarization ratios, the force constants and the atomic displacements as shown in Fig. 4 corresponding to the different normal modes are used for identifying the vibrational modes unambiguously. The harmonic vibrational frequencies calculated for Levamisole at HF and B3LYP levels using the 6-31G (d,p) basis set along with polarization functions have been summarized in Table 2 and 3. It can be noted that the calculated results are harmonic frequencies while the observed frequencies contain anharmonic contribution. The later is generally lower than the former due to anharmonicity. The reproductions of observed fundamental frequencies are more desirable because they are directly observable in a vibrational spectrum. Comparison between the calculated and the observed vibrational spectra helps us to understand the observed spectral features.

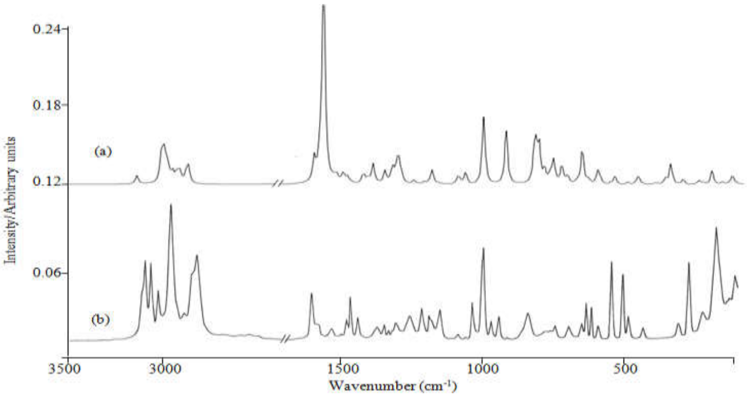

**Fig. 3. FT Raman spectra of Levamisole (a) Theoretical and (b) experimental**

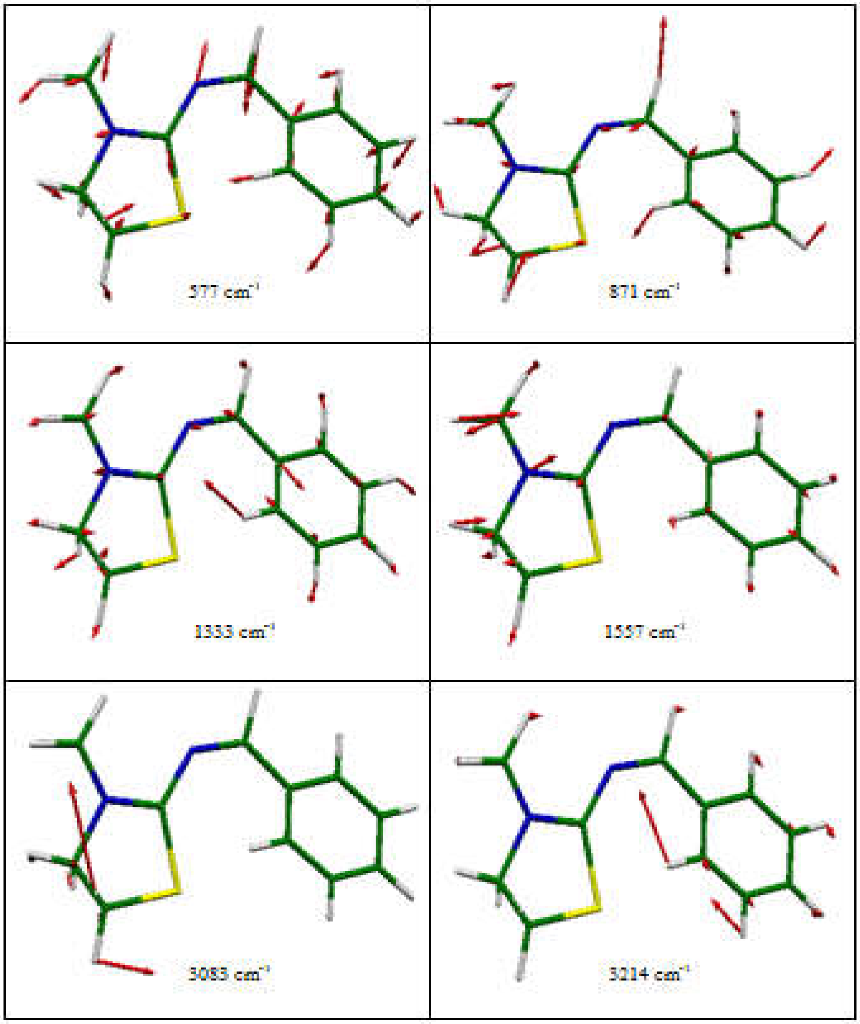

**Fig. 4. Atomic displacements of Levamisole**

Inclusion of electron correlation in density functional theory to a certain extend makes the frequency values smaller in comparison with the HF frequency data. For visual comparison, the observed and calculated FTIR and FT Raman spectra of Levamisole is presented in a common wavenumber scale in Table 3.

### *C-H Vibrations*

The aromatic structure shows the presence of C-H stretching vibrations in the region 3250 cm$^{-1}$ - 2950 cm$^{-1}$ which is characteristic region for the ready identification of C-H stretching vibrations and particularly the regions 3250 cm$^{-1}$ - 3100 cm$^{-1}$ for asymmetric stretching and 3100 cm$^{-1}$ -2950 cm$^{-1}$ for symmetric stretching modes of vibration (Varsanyi, 1973). For most cases, the aromatic compound C-H vibration absorption bands are usually weak; in many cases it is too weak for detection. In this region, the bands are not affected, appreciably by the nature of substituents. In the present work, for the compound Levamisole, the FTIR bands observed at 3230 cm$^{-1}$, 3200 cm$^{-1}$ and FT Raman bands at 3225 cm$^{-1}$,

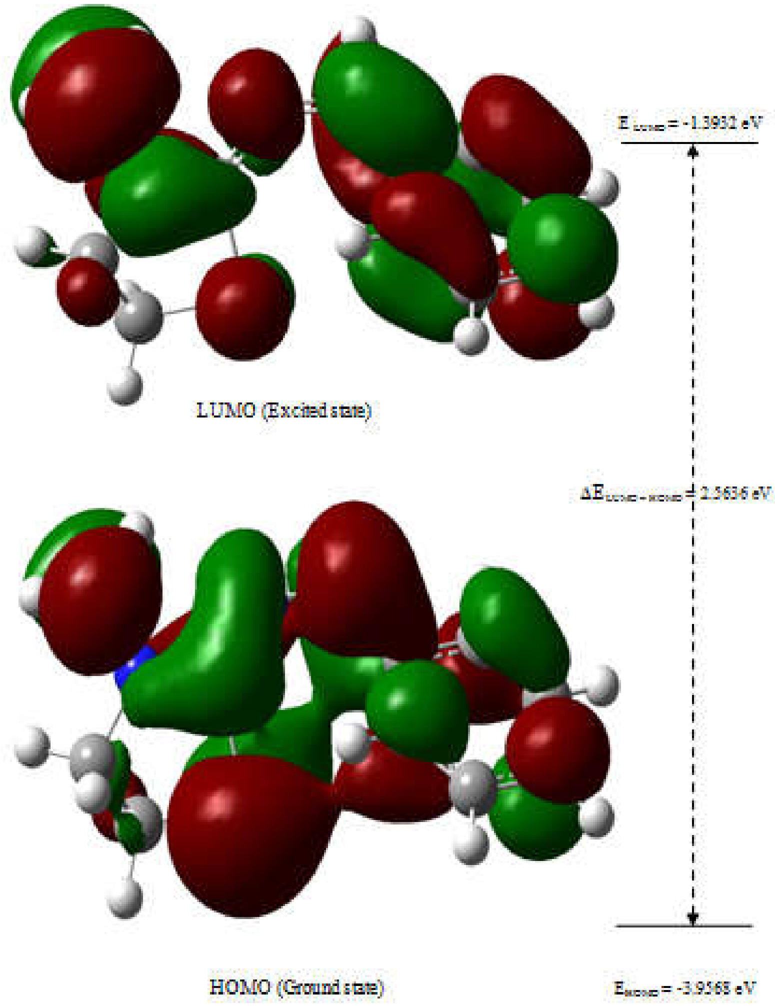

**Fig. 5. The atomic orbital compositions of the frontier molecular orbital for Levamisole**

3202 $cm^{-1}$ have been assigned to C-H asymmetric stretching vibration. Similarly the FTIR bands observed at 3070 $cm^{-1}$, 3083 $cm^{-1}$ and FT Raman bands at 3070 $cm^{-1}$, 3082 $cm^{-1}$ have been assigned to C-H symmetric stretching vibration. The B3LYP level at 6-31G (d,p) gives the same frequency values at 3228 and 3203 $cm^{-1}$ for asymmetric C-H stretching and the values at 3069 and 3082 $cm^{-1}$ for symmetric C-H stretching vibrations as shown in Table 3. For the same vibration the HF/6-31G (d,p) gives a slightly decreased value when compared to experimental data. In general the aromatic C-H stretching vibrations calculated theoretically are in good agreement with the experimentally reported values (Colthup *et al.,* 1964 and Gunasekaran *et al.,* 2008) for di substituted benzene in the region 3200 - 2900 $cm^{-1}$. The title compound Levamisole has both out-of-plane and in-plane aromatic C-H bending vibrations. The out of plane bending mode of C-H vibration of Levamisole is found well in agreement with the experimentally predicted in the region 1000-600 $cm^{-1}$ (Wilson *et al.,* 1995). The observed FTIR band at 947 $cm^{-1}$ is in excellent agreement with band at 946 $cm^{-1}$ of theoretically computed B3LYP/6-31G (d,p) results. The aromatic C-H in-plane bending modes of benzene and its derivatives are observed in the region 1300-1000 $cm^{-1}$ The C-H in plane bending vibrations assigned even though found to be contaminated by C-$CH_2$ stretch is found in literature (Bellamy,1954 and Sundaraganesan *et al.,* 2004), while the experimentally observed values for Levamisole is at 1267 $cm^{1}$. The C-H in-plane bending vibration of Levamisole coincides satisfactorily with the experimentally observed values in this region.

### *C-C vibrations*

The C-C aromatic stretching vibrations gives rise to characteristic bands in both the observed IR and Raman spectra, covering the spectral range from 1600 – 1400 $cm^{-1}$ (Bellamy, 1954 and Varsanyi, 1974) . The IR bands are 1556, 1530, 1506, 1445 $cm^{-1}$; the Raman bands are 1556, 1530, 1504 and 1445 $cm^{-1}$. Of these bands, 1506 and 1556 $cm^{-1}$ have appeared characteristically strong in the IR and Raman spectra, respectively. The calculated bands at B3LYP and HF levels in the same region are in excellent agreement with experimental observations of both in FTIR and FT Raman spectra of Levamisole. The ring in plane vibrations has given rise to weak bands across the low frequency region, that is to say, below 1000 $cm^{-1.}$ The bands at 761 $cm^{-1}$ in Levamisole has been assigned to C-C in- plane bending vibrations. As is seen from Table the predicted frequencies by both RHF and B3LYP agree well with the observed ones.

### *C-S Vibrations*

In general, the assignment of the band due to C-S stretching vibrations in different compounds is difficult. Both aliphatic and aromatic sulphides have weak-to-medium bands due to C-S stretching vibration in the region 78 –510 $cm^{-1}$ (Gunasekaran *et al.,* 2000 and Krishnakumar *et al*., 2005). Double bond conjugation with the C-S bond like vinyl or phenyl lowers the C-S stretching vibration and increases the intensity. In view of this the medium intense bands present at 576 $cm^{-1}$ in the FTIR spectrum and the band at 575 $cm^{-1}$ in the FT Raman spectrum of Levamisole is assigned due to C-S stretching mode of vibration.

### *C-N Vibrations*

The identification of the C-N stretching vibration is a very difficult task since, the mixing of bands are possible in this region (Sortur *et al.,*2006). The C-N stretching band is assigned at 1319 $cm^{-1}$ in 2,6-dibromo-4-nitroaniline by Krishna Kumar (Krishnakumar *et al.,* 2005) and Raja et al 1994 have identified the FTIR band at 1342 $cm^{-1}$ due to C-N in theophylline and (Gunasekaran *et al.,* 2005) have observed the C-N stretching band at 1312$cm^{-1}$ in aminobenzoesaeure. Hence in the present investigation the FTIR and FT-Raman bands observed at 1310$cm^{-1}$ and 1335$cm^{-1}$ of Levamisole are assigned to the C-N stretching mode of vibrations. The calculated value 1310 and 1333 $cm^{-1}$ is in excellent agreement with the observed value for the corresponding mode of vibration.

### *C=N vibrations*

The C=N stretching vibration in Levamisole has a main contribution with HF and B3LYP/6-31G (d,p) predicted vibrational band at 1489 $cm^{-1}$. This is in agreement with the strong experimental bands located at 1486 $cm^{-1}$ and at 1488 $cm^{-1}$ in FTIR and FT Raman spectrum of Levamisole. The C=N stretching vibration calculated with HF level shows slightly lower range of wavenumbers that with the experimental results. The above conclusions are in agreement with the literature value (Silverstein, 1981)

## OTHER MOLECULAR PROPERTIES

On the basis of vibrational analysis at B3LYP/ 6-31G(d,p) and HF/6-31G(d,p) levels, several thermodynamic parameters are calculated and are presented in Table 4 . The zero point vibrational energy (ZPVE) and the entropy, $S_{vib}$ (T) are calculated to the extent of accuracy and the variations in ZPVE seem to be insignificant. The total energy and the change in the total entropy of Levamisole at room temperature at different methods are only marginal. One of the objectives of the present investigation is to study the effect of the basis sets B3LYP/6-31G (d,p) and HF/6-31G (d,p) levels on molecular polarizability of Levamisole using the Gaussian 03W program. In this study, the computation of the molecular polarizability of Levamisole with different basis sets was reported. Here, $\alpha$ is a second-rank tensor property called the dipole polarizability and mean polarizability $< \alpha >$ is evaluated using Eqn.

$$<\alpha> = 1/3\ (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

The calculated polarizabilities using HF and DFT methods for the Levamisole molecule are summarized in Table 5. The largest polarizability was observed for B3LYP/6-31G (d,p) at 100.576. Table 6 lists the calculated values of the first ionization potentials, HOMO & LUMO, energy gaps, Electron affinity (A), Ionisation potential (I), Electro negativity ($\chi$) defined and Global Hardness ($\eta$) of Levamisole. The hardness, defined as the second derivative of the total energy, together with the concept of electronegativity and the principle of quantization of electronegativities has been used to develop the principle of hard and soft acids and bases (Sanderson, 1976).The lowest first ionization potential was obtained by HF/6-31G (d,p). The HOMO–LUMO energy gap is consistent for B3LYP methods and varies erotically to HF methods. It is noted that we have roughly two electrons per occupied level (54 levels for 108 electrons), starting at -88.88208 Hartrees. Fig.5 shows the HOMO (orbital 54) and the LUMO (orbital 220) below and above the zero (0) line, of Levamisole respectively.

## CONCLUSION

Attempts have been made in the present work for the proper frequency assignments for the compound Levamisole from the FTIR and FT Raman spectra. The equilibrium geometries and harmonic frequencies of Levamisole was determined and analyzed both at HF and DFT levels of theories utilizing 6-31G (d, p) basis set. The difference between observed and calculated wavenumber values of the most of the fundamental modes is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made at higher levels of theory with only reasonable deviations from the experimental values seem to be correct. The potential energy distribution made in this study also confirms the assignments proposed for various modes of the title compound.

### Acknowledgement

The authors are thankful to Professor Tom Sundius, University of Helsinki, Helsinki, Finland, for providing necessary help to study PED calculations.

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