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# FT-IR, FT-Raman and computational study of 1,2-cyclohexanediol

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## Abstract

FT-IR and FT-Raman spectra of 1,2-cyclohexanediol were recorded and analyzed. The vibrational wavenumbers were computing at HF and DFT levels. The data obtained from theoretical calculations are used to assign vibrational bands obtained experimentally. The results indicate that DFT method is able to provide satisfactory results for predicting vibrational frequencies. The predicted infrared intensities and Raman activities are reported. The calculated first hyperpolarizability value shows that the title compound is suitable for nonlinear optical studies. The small differences between experimental and calculated vibrational modes are observed. This is due to the fact that experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

*Key words:* FTIR, FT-Raman, DFT, hyperpolarizability

## Introduction

A diol is a chemical compound containing two hydroxyl groups (-OH groups)[1]. This pairing of functional groups is pervasive and many subcategories have been identified. The most common diols in nature are sugars and their polymers, cellulose. The most common industrial diol is ethylene glycol. Cyclohexanone compounds are known for their important biological activities such as herbicidal, antibacterial, antifungal, convulsant, anticonvulsant, anti-implantation and anti-asthmone, besides being useful in organic synthesis and in industry[2-6]. Fan and Khodadadi[7] reported an experimental investigation of enhanced thermal conductivity and expedited unidirectional freezing of cyclohexane base nano particle suspensions utilized as nano enhanced phase change materials. In the present study the FT-IR, FT-Raman and theoretical calculations of the wavenumbers of the title compound are reported.

## Experimental

The FT-IR spectrum (Figure 1) was recorded using a DR/Jasco FT-IR 6300 spectrometer. The spectral resolution was 2 $cm^{-1}$. The FT-Raman spectrum (Figure 2) was obtained on a Bruker RFS 100/s, Germany. For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW.

### *Computational Details :*

Calculations of the title compound were carried out with Gaussian09 software program[8] using the HF/6-31G* and B3LYP/ 6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. The DFT hybrid B3LYP functional method tends to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data[9]. The wavenumber values computed contain known systematic errors and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets[9]. The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. The assignment of the calculated wavenumbers is aided by the animation option of Gaussview program, which gives a visual presentation of the vibrational modes[10].

## Results and Discussion

### *IR and Raman spectra :*

The observed IR, Raman and calculated (scaled) wavenumbers and assignments are given in Table 1. The vibrations of the $CH_2$ group, the asymmetric stretch $\upsilon_{as}CH_2$, symmetric stretch $\upsilon_sCH_2$, scissoring vibration $\delta CH_2$ and wagging vibration $\omega CH_2$ appear in the regions 3000 ± 50, 2965 ± 30, 1455 ± 55 and 1350 ±85 $cm^{-1}$, respectively[11,12]. The DFT calculations give asymmetric and symmetric stretching modes of $CH_2$ at 2987, 2982, 2968, 2967 and 2916, 2908, 2890, 2830 $cm^{-1}$. The bands observed at 2884 $cm^{-1}$ in the IR spectrum and at 2917, 2885, 2833 $cm^{-1}$ in the Raman spectrum are assigned as these modes. The $CH_2$ deformation band which comes near 1463 $cm^{-1}$ in alkenes[12] is lowered to about 1440 $cm^{-1}$ when the $CH_2$ group is next to a double or triple bond. A carbonyl, nitrile or nitro group each lowers the wavenumber of the adjacent $CH_2$ group[12] to about 1425 $cm^{-1}$. The bands at 1488, 1482, 1476, 1475 $cm^{-1}$ (DFT) are assigned as scissoring mode of $CH_2$. The $CH_2$ wagging modes are observed at 1389, 1367 $cm^{-1}$ in the IR spectrum and the DFT calculations give these modes at 1388, 1368, 1343, 1337 $cm^{-1}$. The twisting modes and rocking modes are assigned at 1237, 1197, 1193, 1113 $cm^{-1}$ and 921, 915, 865, 842 $cm^{-1}$ theoretically, which are expected in the regions, 1250 ± 35 and 895 ± 85 $cm^{-1}$, respectively[11].

The OH group provides three normal vibrations $\upsilon OH$, $\delta OH$ and $\gamma OH$. The DFT calculations give the $\upsilon OH$ bands at 3468 and 3454 $cm^{-1}$. Experimentally OH stretching modes are observed at 3406 $cm^{-1}$ in the IR spectrum and at 3309 $cm^{-1}$ in the Raman spectrum.

The in-plane OH deformation[11] is expected in the region 1400 ± 40 $cm^{-1}$ and the band at 1355 $cm^{-1}$ (IR and Raman) and 1363, 1347 $cm^{-1}$ (DFT) are assigned as this mode. The stretching of the hydroxyl group with respect to the phenyl moiety υC-O appears at 1255 $cm^{-1}$ in the IR spectrum, 1279, 1255 $cm^{-1}$ in Raman spectrum and the calculated value is 1265, 1262 $cm^{-1}$. This band is expected[12,13] in the region 1220 ± 40 $cm^{-1}$. The out-of plane OH deformation is observed at 518 $cm^{-1}$ in the IR spectrum, 543 in the Raman spectrum and at 556, 509 $cm^{-1}$, theoretically, which is expected[11] in the region 650 ± 80 $cm^{-1}$. For paracetamol, υ(C-O) and γOH are reported at 1240 and 620 $cm^{-1}$, respectively[14].

The CH stretching modes are assigned[11] at 2964, 2932 $cm^{-1}$ theoretically (DFT) and one band is observed in the IR spectrum at 2934 $cm^{-1}$. The in-plane and out-of-plane deformations of the CH modes are assigned at 1320, 1305 and 826, 773 $cm^{-1}$ theoretically which is in agreement with literature[15]. Experimentally corresponding bands are observed at 1322, 1300, 816, 781 $cm^{-1}$ in the IR spectrum and at 822, 781 $cm^{-1}$ in the Raman spectrum. The ring C-C stretching modes are assigned[11,15] in the range 995-1100 $cm^{-1}$. The ring in-plane and out-of-plane deformation modes are also identified and assigned (table 1).

*First hyperpoplarizability :*

Non-linear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase or other physical properties[16]. Many organic molecules, containing conjugated π-electrons and characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy[17, 18]. Analysis of organic molecules having conjugated π-electron systems and large hyperpolarizability using infrared and Raman spectroscopies has evolved as a subject of research[19]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing and dynamic image processing[17,18]. The first hyperpolarizability ($\beta_0$) of this novel molecular system is calculated using B3LYP/6-31G* method, based on the finite field approach. 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 × 3 × 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry[20]. The calculated first hyperpolarizability of the title compound is 1.06 $10^{-30}$ esu. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

In order to investigate the performance of vibrational wavenumbers of the title compound, the root mean square (RMS) value between the calculated and observed wavenumbers were calculated. The RMS values of wavenumbers were calculated using the following expression[21].

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n}\left(\upsilon_i^{calc} - \upsilon_i^{\exp}\right)^2}$$

. The RMS

error of the observed IR and Raman bands are found to 25.30, 27.39 for HF and 6.46, 8.72 for DFT methods, respectively without considering OH stretch. The small differences between experimental and calculated vibrational modes are observed. This is due to the fact that experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

*Frontier molecular orbitals :*

The analysis of the wavefunction indicates that the electron absorption corresponds to a transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to LUMO. Both the HOMO and the LUMO are the main orbital taking part in chemical reaction. The HOMO energy characterizes the capability of electron giving; LUMO characterizes the capability of electron accepting[22]. The frontier orbital gap helps to characterize the chemical reactivity, optical polarizability and chemical hardness-softness of a molecule[23]. Surfaces for the frontier orbitals were drawn to understand the bonding scheme of the title compound. The calculated HOMO and LUMO energies are -6.878 and -1.526 eV. The chemical hardness and softness of a molecule is a good indication of the chemical stability of the molecule. From the HOMO-LUMO energy gap, one can find whether the molecule is hard of soft. The molecules having large energy gap are known as hard and molecules having a small energy gap are known as soft molecules. The soft molecules are more polarizable than the hard ones because they need small energy to excitation. The hardness value[22] of a molecule can be determined as $\eta$ = (-HOMO+LUMO)/2. The value of $\eta$ of the title molecule is 2.676 eV. Hence we conclude that the title compound belongs to hard material.

## Conclusion

The infrared and Raman spectra of the title compound have been recorded and analysed. Geometry and harmonic vibrational wavenumbers were calculated theoretically using Gaussian09 set of quantum chemistry codes. Calculations were performed at the Hartree-Fock and DFT (B3LYP) levels of theory using the standard 6-31G* basis. The calculated wavenumbers (DFT) agree well with the observed wavenumbers. Calculated infrared intensities, Raman activities and first hyperpolarizability are reported.

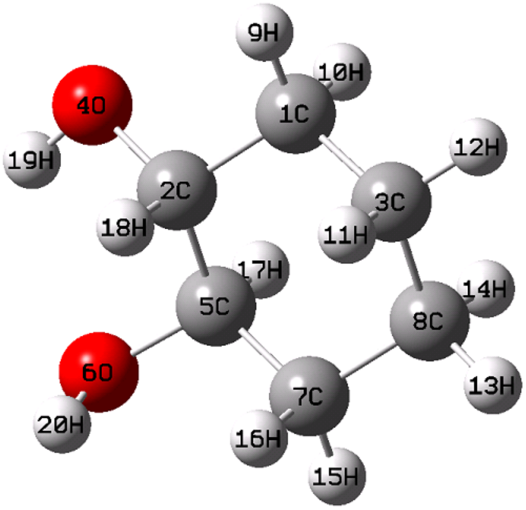

Table 1. Calculated wavnumbers (scaled), observed IR and Raman bands and assignments

| HF/6-31G* | | | B3LYP/6-31G* | | | IR $\upsilon(cm^{-1})$ | Raman $\upsilon(cm^{-1})$ | Assign-ments |
|---|---|---|---|---|---|---|---|---|
| $\upsilon\ (cm^{-1})$ | $IR_I$ | $R_A$ | $\upsilon\ (cm^{-1})$ | $IR_I$ | $R_A$ | | | |
| 3578 | 28.71 | 68.03 | 3468 | 4.43 | 71.17 | 3406 | 3309 | $\upsilon OH$ |
| 3573 | 55.07 | 80.82 | 3454 | 16.75 | 90.27 | | | $\upsilon OH$ |
| 2919 | 66.12 | 56.84 | 2987 | 70.09 | 46.95 | | | $\upsilon_{as}CH_2$ |
| 2910 | 22.28 | 112.69 | 2982 | 18.12 | 151.17 | | | $\upsilon_{as}CH_2$ |
| 2891 | 29.24 | 114.91 | 2968 | 24.65 | 76.97 | | | $\upsilon_{as}CH_2$ |
| 2889 | 70.36 | 66.07 | 2967 | 49.75 | 69.35 | | | $\upsilon_{as}CH_2$ |
| 2886 | 54.80 | 123.60 | 2964 | 43.04 | 125.48 | | | $\upsilon CH$ |
| 2860 | 17.59 | 60.05 | 2932 | 18.43 | 58.06 | 2934 | | $\upsilon CH$ |
| 2841 | 33.71 | 39.58 | 2916 | 32.99 | 28.92 | | 2917 | $\upsilon_{s}CH_2$ |
| 2834 | 29.71 | 141.49 | 2908 | 19.64 | 129.43 | | | $\upsilon_{s}CH_2$ |
| 2818 | 42.13 | 99.90 | 2890 | 27.28 | 88.02 | 2884 | 2885 | $\upsilon_{s}CH_2$ |
| 2803 | 27.97 | 33.59 | 2830 | 51.57 | 64.81 | | 2833 | $\upsilon_{s}CH_2$ |
| 1486 | 4.00 | 4.03 | 1488 | 3.31 | 7.60 | | | $\delta CH_2$ |
| 1481 | 16.15 | 7.03 | 1482 | 13.68 | 6.32 | | | $\delta CH_2$ |
| 1475 | 5.90 | 11.33 | 1476 | 3.40 | 20.34 | | | $\delta CH_2$ |
| 1474 | 1.04 | 24.88 | 1475 | 3.78 | 16.03 | 1464 | | $\delta CH_2$ |
| 1396 | 14.85 | 8.81 | 1388 | 20.58 | 6.05 | 1389 | | $\omega CH_2$ |
| 1385 | 5.00 | 11.72 | 1368 | 12.13 | 7.88 | 1367 | | $\omega CH_2$ |
| 1371 | 19.06 | 2.11 | 1363 | 14.69 | 5.82 | 1355 | 1355 | $\delta OH$ |
| 1360 | 0.57 | 2.38 | 1347 | 3.46 | 4.26 | | | $\delta OH$ |
| 1353 | 10.43 | 3.83 | 1343 | 6.25 | 7.13 | | | $\omega CH_2$ |
| 1347 | 3.96 | 1.65 | 1337 | 2.59 | 4.76 | | | $\omega CH_2$ |
| 1332 | 4.27 | 0.52 | 1320 | 3.28 | 0.33 | 1322 | | $\delta CH$ |
| 1315 | 7.74 | 3.29 | 1305 | 7.26 | 3.23 | 1300 | | $\delta CH$ |
| 1263 | 12.17 | 8.45 | 1265 | 39.06 | 2.75 | | 1279 | $\upsilon CO$ |
| 1258 | 22.86 | 7.28 | 1262 | 8.12 | 12.45 | 1255 | 1255 | $\upsilon CO$ |
| 1238 | 43.32 | 16.90 | 1237 | 18.48 | 17.99 | 1233 | 1240 | $\tau CH_2$ |
| 1203 | 11.73 | 10.34 | 1197 | 8.07 | 7.32 | | | $\tau CH_2$ |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1190 | 17.53 | 2.24 | 1193 | 9.26 | 4.63 | | 1189 | $\tau\mathrm{CH_2}$ |
| 1115 | 20.28 | 2.16 | 1113 | 8.13 | 2.27 | | 1123 | $\tau\mathrm{CH_2}$ |
| 1099 | 29.46 | 4.93 | 1100 | 11.04 | 3.11 | | | υCC |
| 1066 | 23.10 | 7.66 | 1060 | 11.41 | 1.76 | 1070 | 1067 | υCC |
| 1055 | 21.59 | 2.47 | 1050 | 8.15 | 6.25 | 1055 | | υCC |
| 1035 | 90.57 | 7.09 | 1036 | 6.48 | 4.99 | | | υCC |
| 1031 | 2.03 | 8.01 | 1022 | 45.11 | 7.43 | 1022 | 1022 | υCC |
| 1016 | 89.56 | 3.49 | 995 | 116.18 | 1.13 | 988 | 978 | υCC |
| 923 | 17.31 | 1.63 | 921 | 15.53 | 3.43 | 923 | 925 | $\rho\mathrm{CH_2}$ |
| 912 | 6.17 | 2.87 | 915 | 8.50 | 0.10 | 911 | 900 | $\rho\mathrm{CH_2}$ |
| 866 | 3.55 | 2.62 | 865 | 4.11 | 1.73 | 858 | 859 | $\rho\mathrm{CH_2}$ |
| 846 | 24.76 | 0.25 | 842 | 23.81 | 0.35 | | | $\rho\mathrm{CH_2}$ |
| 819 | 10.66 | 4.51 | 826 | 7.38 | 4.38 | 816 | 822 | γCH |
| 769 | 4.06 | 13.50 | 773 | 5.23 | 9.20 | 780 | 781 | γCH |
| 558 | 6.03 | 1.31 | 556 | 5.95 | 1.40 | | 543 | γOH |
| 505 | 10.85 | 10.07 | 509 | 53.87 | 6.53 | 518 | | γOH |
| 450 | 120.69 | 2.66 | 506 | 152.95 | 7.15 | | 505 | δRing |
| 438 | 67.44 | 5.76 | 443 | 4.56 | 3.59 | | | δRing |
| 425 | 85.26 | 2.15 | 430 | 7.62 | 2.58 | | 421 | γRing |
| 357 | 6.41 | 0.43 | 354 | 6.66 | 0.37 | | 360 | δRing |
| 344 | 0.33 | 0.31 | 346 | 4.98 | 0.39 | | | γRing |
| 307 | 1.25 | 0.17 | 312 | 60.76 | 2.56 | | | δRing |
| 251 | 80.30 | 0.61 | 304 | 23.55 | 0.92 | | | γRing |
| 249 | 46.69 | 2.72 | 246 | 7.22 | 0.34 | | 235 | tCOH |
| 180 | 2.78 | 0.06 | 182 | 2.15 | 0.06 | | | tCOH |
| 127 | 4.25 | 0.13 | 129 | 3.15 | 0.13 | | 115 | tRing |

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ω-wagging; ρ-rocking; τ-twisting; -torsion; as-asymmetric; s-symmetric.

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