Infrared Spectrum and STM images of Cyclohexene-2-Ethanamine: First Principle Investigation

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We have investigated the structure of cyclohexene-2-ethanamine molecule both theoretically and experimentally. Theoretical investigation is based on a first principle technique Density Functional Theory (DFT) using plane wave basis sets and ultrasoft pseudo-potentials while the experimental technique is infrared (IR) spectroscopy. Exchange-correlation potential of DFT was approximated in the frame of both local density approximation (LDA) and generalized gradient approximation (GGA) schemes. Vibrational properties of this molecule are given by the assignments in the range for wavenumber 4000 – 400 cm⁻¹. Stable equilibrium structure of the molecule was also obtained by using LDA and GGA. Obtained optimized geometrical structure was used to calculate vibrational properties and STM images. A remarkable agreement was obtained between theory and experiment, especially in the symmetric and asymmetric vibrations of NH groups.

Keywords: Cyclohexene-2-ethanamine, First Principle, IR spectrum, STM images.

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I. INTRODUCTION

The design and synthesis of strong organic bases have long been an active field of research [1, 2, 3, 4]. Infrared spectroscopy is a valuable tool in order to obtain information about the molecular structure and properties of the molecules. This technique is used widely in qualitative and quantitative molecular analysis. IR spectrum of interatomic vibrations can be used as structural probes for determining weak changes of structure or chemical bonding in molecules. Cyclohexene-2-ethanamine molecule consists of cyclohexene C₆H₁₀ group attached to the carbon of ethylamine (C₂H₇N). There are previous works on the cyclohexene and ethylamine structures. Some studies showed that the lowest energy conformations of cyclohexene are in a half-chair form and a boat structure. Basically, the cyclohexene ring can interconvert from one twisted form to the other over the boat conformation with Cs symmetry [5]. The point symmetry group for trans-ethylamine ion is Cs whereas there is no such symmetry for gauche-ethylamine [6]. Cyclohexene-2-ethanamine (CyHEA) has also important industrial applications, that is used as chemical intermediate in rubber industry. They demonstrated prototypical non-conjugated olefinic substrate CyHEA which was not only a highly active substrate but also a mechanism-based inhibitor for DBM. CyHEA was also used as a substrate and oxidizing agent for Ru complex. Sirimanne and May reported that dopamine β-monoxygenase (DBM) catalyzed stereo-selective allylic hydroxylation of CyHEA [7]. CyHEA was first synthesized by İzgi et al. [8] and some of IR and NMR properties of this compound were reported by them.

Density functional theory (DFT) is a widely used and very precise ab initio technique which is used to provide vibrational frequencies of organic compounds perfectly [11, 12, 13, 14, 15, 16]. The vibrational modes and STM images of this molecule have not been investigated by an ab initio theoretical method. In this study, the molecule has been investigated by using planewave pseudopotential calculation based on DFT. Exchange-correlation potential of DFT scheme was taken into account within the LDA and GGA which are the commonly used approximations and both are used in calculation process. The stable conformation of the molecule is obtained by following a relaxation procedure within the framework of DFT under periodic boundary conditions.

II. METHOD

The normal modes and STM images of the molecule were calculated with both LDA and GGA by using the freely available DFT program PW-SCF (Plane Wave Self Consistent Field) [10] which uses plane wave basis sets for

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FIG. 1: The stable configuration of the Cyclohexene-2-ethanamine.

electronic wavefunctions. For all calculations, we have used Perdew-Zunger [18] and Perdew-Burke-Ernzerhof [19] exchange-correlation parameterizations for LDA and GGA, respectively and Vanderbilt [17] ultrasoft pseudopotentials. The electronic wavefunctions were expanded in terms of plane waves with kinetic energy cut-off up to 25 Ry. The special k-points of the molecule in the cubic cell is selected as $q = 0$ gamma point. The lattice constant of cubic cell is 20 bohr(au).

For experimental work, the pure Cyclohexene-2-ethanamine in liquid form was obtained from Aldrich Chemical Co., USA and was used without further purification. The IR spectra of the molecule in liquid form was recorded to be in the range of 4000 – 400 cm$^{-1}$ using Perkin Elmer FT-IR 2000 spectrometer with a resolution of 4 cm$^{-1}$.

III. RESULTS AND DISCUSSIONS

The calculated stable structure of CyHEA is shown in Fig.1 which was drawn by XCrySDen (Crystalline Structures and Densities) program [9]. The vibrational assignments and frequencies of cyclohexene-2-ethanamine was reported experimentally by Izgi et al. [8]. The spectral properties of the molecule were evaluated through the calculated vibrational frequencies of the free ligand molecule. The calculated and experimental infrared spectra data of the molecule are given in Table.I. The experimental, GGA and LDA results are also compared in Fig.2.

The strong N-H asymmetric and symmetric stretch bands seen in Table.I are due to the contribution of ethylamine (see Fig.3). C-H stretch bands between 3000 – 3100 cm$^{-1}$ are attributed to cyclohexene group and the very strong C-H stretch bands at 2926 cm$^{-1}$ and 2835 cm$^{-1}$ result from ethylamine. The very strong bands are attributed to the attachment of ethylamine and cyclohexene and appear between 2830 – 2920 cm$^{-1}$. Most of the modes below the 1300 cm$^{-1}$ arise from cyclohexen. If the vibrational assignments of the molecule involving these groups are investigated, it is seen that the assignments obtained for the molecule also involve the group frequencies. Furthermore, the observed medium broad band appears at 829 cm$^{-1}$ is an N-H bending band as well as a group frequency. There is also a good agreement between the experimental and the theoretical vibrational frequencies in the region of 4000 – 400 cm$^{-1}$ except some GGA and LDA results. The ground state energy of the molecule was obtained to be -128.66 ryd and -128.53 ryd for GGA and LDA, respectively. Finally, we examined the electronic properties by using calculated STM images for cyclohexene-2-ethanamine. In Fig.4 and Fig.5 which were drawn by using XCrySDen, we calculated the STM images at constant current and bias voltage -2.5 eV and 2.5 eV, respectively. These results supply a microscopic model for STM images and can serve as a source for STM experiments for organic molecules.

IV. CONCLUSION

The experimental and the theoretical investigation of CyHEA molecule have been performed successfully by using FT-IR and density functional theory calculations. For all calculations, it is shown that the results of GGA and LDA methods are in excellent agreement with all experimental findings. Thus, density functional theory (DFT) methods are suitable for the calculation of ground state properties and potential energies. Hence, DFT is an excellent method for calculating vibrational spectra and STM images from first principles.
| mode | Assignments | Experimental [8] | Calculated |
|------|-------------|------------------|------------|
| $\nu_1$ | $N-Ha-str$ | 3366s 3447 3436 | LDA GGA |
| $\nu_2$ | $N-Hs-str$ | 3288s 3353 3347 |  |
| $\nu_3$ | $\nu_{23}$ | 3097vw 3015 3045 |  |
| $\nu_4$ | $\nu_1$ | 3043m 2979 2998 | |
| $\nu_5$ | $C-Hstr(CH_3)$ | 2995m 2954 2971 |  |
| $\nu_6$ | $\nu_2 + C-Hstr(CH_3)$ | 2926vs 2925 2921 |  |
| $\nu_7$ | $\nu_{25} + C-Hstr(CH_2)$ | 2894vw 2896 2899 |  |
| $\nu_8$ | $\nu_{26}$ | 2877vw 2880 2897 |  |
| $\nu_9$ | $\nu_{27} + C-Hstr(CH_3)$ | 2857vs 2856 2879 |  |
| $\nu_{10}$ | $\nu_5 + C-Hstr(CH_3)$ | 2836vs 2827 2857 |  |
| $\nu_{11}$ | $\nu_6$ | 1666 m 1712 1693 |  |
| $\nu_{12}$ | $NH_2sciss$ | 1600mb 1562 1594 |  |
| $\nu_{13}$ | $CH_2sciss$ | 1505vw - - |  |
| $\nu_{14}$ | $C-Hbend(CH_3)$ | 1473vw - - |  |
| $\nu_{15}$ | $\nu_{28} + C-Hbend(CH_3)$ | 1448vw 1439 1442 |  |
| $\nu_{16}$ | $\nu_8$ | 1438s 1431 1425 |  |
| $\nu_{17}$ | $CH_2wag$ | 1384w 1391 1384 |  |
| $\nu_{18}$ | $\nu_9 + C-Hbend(CH_3)$ | 1370vw 1376 1359 |  |
| $\nu_{19}$ | $\nu_{10}$ | 1344m 1352 1338 |  |
| $\nu_{20}$ | $\nu_{30}$ | 1334w 1328 1334 |  |
| $\nu_{21}$ | $NH_2twist$ | 1307w 1320 1309 |  |
| $\nu_{22}$ | $\nu_{12}$ | 1269m 1285 1298 |  |
| $\nu_{23}$ | $\nu_{11} + CH_2twist$ | 1242w 1248 1247 |  |
| $\nu_{24}$ | $\nu_{12}$ | 1215w 1212 1227 |  |
| $\nu_{25}$ | $\nu_{34}$ | 1136m 1131 1139 |  |
| $\nu_{26}$ | $(C-C,C-N)a-str$ | 1086w 1101 1092 |  |
| $\nu_{27}$ | $\nu_{15}$ | 1066w - - |  |
| $\nu_{28}$ | $\nu_{25}$ | 1049w 1045 1042 |  |
| $\nu_{29}$ | $\nu_{36} + CH_3rock$ | 1022w 1014 1023 |  |
| $\nu_{30}$ | $\nu_{16}$ | 966w 976 975 |  |
| $\nu_{31}$ | $\nu_{37}$ | 919m 921 920 |  |
| $\nu_{32}$ | $\nu_{17}$ | 906vw 919 903 |  |
| $\nu_{33}$ | $\nu_{28}$ | 857w 834 843 |  |
| $\nu_{34}$ | $\nu_{18} + CH_2rock$ | 829m 824 818 |  |
| $\nu_{35}$ | $\nu_{19}NH_3wag$ | 800m - - |  |
| $\nu_{36}$ | $\nu_{38}$ | 726sh 733 734 |  |
| $\nu_{37}$ | $\nu_{40}$ | 647w 680 686 |  |
| $\nu_{38}$ | $\nu_{20}$ | 497vw 518 512 |  |
| $\nu_{39}$ | $\nu_{41}$ | 448s 417 411 |  |

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$^a$ Ass., assignments; Exp., experimental; Freq., frequency; v, very; s, strong; m, medium; w, weak; sh, shoulder; b, broad; str, stretching; bend, bending; sciss, scissoring; twist, twisting; wag, wagging; s, symmetric; a, asymmetric.

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FIG. 2: The comparison of experimental data with GGA and LDA results.

\[ \omega = 3436 \text{ cm}^{-1} \text{ (GGA)} \]
\[ \omega = 3347 \text{ cm}^{-1} \text{ (LDA)} \]

FIG. 3: Calculated N-H asymmetric and symmetric stretch.

\[ \omega = 3436 \text{ cm}^{-1} \text{ (GGA)} \]
\[ \omega = 3447 \text{ cm}^{-1} \text{ (LDA)} \]

\[ \omega = 3347 \text{ cm}^{-1} \text{ (GGA)} \]
\[ \omega = 3353 \text{ cm}^{-1} \text{ (LDA)} \]

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FIG. 4: Calculated STM images for HOMO.

FIG. 5: Calculated STM images for LUMO.

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