Calculation of the infrared spectrum of 4-Cyanostyrene by Hartree-Fock (HF) and Density Functional Theory (DFT)

Kani ARICI 1, 2,  Rafet Yılmaz2

1Department of Physics, Faculty of Science and Arts, Kilis 7 Aralık University, Kilis, Turkey
2Department of Physics, Faculty of Science and Arts, Yüzüncü Yıl University, Van Turkey

ABSTRACT

In this study, the molecular geometry of 4-Cyanostyrene molecule was optimized by using the Hartree–Fock (HF) and density functional theory (DFT/B3LYP) with 6-311G(d,p) basis set in the ground state. After the optimization, infrared vibration bands of 4-Cyanostyrene molecule were calculated by using the Hartree–Fock (HF) and density functional theory (DFT/B3LYP) with 6-311G(d,p) basis set. The theoretically calculated vibrational frequencies were multiplied by a scalar factor to correlate to experimental results. These theoretically obtained frequencies were compared exactly with the experimental results of 4-Cyanostyrene. All calculated frequencies were discussed. Finally, the correlation graphs of the theoretical and experimental results were obtained. The results were seen to be quite compatible with each other.

Keywords: 4-Cyanostyrene, Hartree-Fock (HF), density functional theory (DFT), infrared (IR).

INTRODUCTION

Styrene is most commonly found in cigarette smoke, polluted atmosphere and working areas. Styrene and styrene-7,8-oxide are used in plastic reinforcement and rubber industry. Styrene-7,8-oxide molecule is the basic metabolite of styrene in the human body. Many researchers have revealed that styrene and styrene-7,8-oxide substances cause various cancers, and increase risk of cancer in groups working in the plastics industry. Styrene model is studied on the rotation of a vinyl group attached to the benzene ring. Thus, many scientists have worked on this topic. Hollas and co-workers have accepted the structure of styrene as planar and determined its vibrations with the help of the electronic absorption spectrum. Zilberg and Haas have studied the fluorescence spectra of the styrene, and also they have investigated trans-β-methyl styrene substances in both the ground state and twice-excited state, finally carried out the theoretical ab initio study. The rotational constant of the vinyl group in the planar structure of the styrene has been calculated by Bock and co-workers based on ab initio calculations. In the literature, although there are many experimental and theoretical studies about styrene and trans-β-methyl oxide substances cause various cancers
styrane, it is seen that 4-Cyanostyrane, a derivative of styrane, has not been studied both experimentally and theoretically. Therefore, in this study, it is aimed to calculate the infrared vibration frequencies of the planar 4-Cyanoster molecule using HF and DFT methods.

2. CALCULATIONS

Infrared vibration calculations were carried out using the Gaussian 09 software on a windows system. As mentioned above, the shape of the molecule was considered as plane, and the input data was created by using Gauss View molecular visualization program. The data created above was reused in HF/6-311G (d, p) and DFT/B3LYP/6-311G (d, p) to find optimization, that is, the lowest energy level of the molecule. In this case, bond lengths, bond angles and dihedral angles in the molecule were calculated. Thus, by optimizing the molecule, negative vibrations were prevented. All the vibration frequencies in the basic state of the molecule were obtained using the same HF/6-311G (d, p) and DFT/6-311G (d, p) calculation methods. The theoretically calculated number of vibrations is considerably greater than that observed experimentally. This means that the compound is large and the calculations are done in gas phase. Since the 4-Cyanostyrane molecule is planar and has a C$_2$ symmetry, all vibrations are both raman and infrared active. Considering the method mentioned above, a total of 45 vibrations were calculated as 31 in-plane (A') and 14 out-of-plane (A$^\prime$). The frequencies obtained were multiplied by scalar factors of 0.9085 and 0.9669, respectively. All the frequencies are assigned in terms of fundamental, overtone and combination bands. As shown in Figure 1, the 4-Cyanostyrane molecule has 17 atoms.

The infrared vibration frequencies obtained from the calculations and the experimental data are given in Table 1. As seen in Figure 2, the bands between 2100 cm$^{-1}$ - 1700 cm$^{-1}$ are the combinations of the benzene ring. For example, in Figure 2, the band at 1846 cm$^{-1}$ is determined as the sum of the 536 cm$^{-1}$ and 3100 cm$^{-1}$ bands. The bands between 3100 cm$^{-1}$ - 4000 cm$^{-1}$ are the overtone bands. The band at 3392 cm$^{-1}$ is designated as the overtone band, which is four times the 848 cm$^{-1}$ band.

3. RESULTS AND DISCUSSION

3.1. Combination and overtone bands

The experimental infrared vibrational spectra of 4-Cyanostyrane molecule are shown in Figure 2. The infrared vibration frequencies in the basic state of the molecule, negative vibrations were multiplied by scalar factors of 0.9085 and 0.9669, respectively.

In general, in the infrared spectrum, C = C tensile vibration bands of vinyl, vinylidine and cis alkenes are observed in the range of 1600 cm$^{-1}$ to 1635 cm$^{-1}$. However, this C = C tensile vibration band was observed at 1627 cm$^{-1}$ with medium intensity. This band was calculated as 1677.4357 cm$^{-1}$ in HF and 342.5710 cm$^{-1}$ in DFT. The calculation of HF deviated from the experimental value by approximately 150 cm$^{-1}$. In general, in the infrared spectrum, C = C tensile vibration bands of vinyl, vinylidine and cis alkenes are observed in the range of 1600 cm$^{-1}$ to 1635 cm$^{-1}$. However, this C = C tensile vibration band was observed at 1627 cm$^{-1}$ with medium intensity. This band was calculated as 1677.4357 cm$^{-1}$ in HF and 342.5710 cm$^{-1}$ in DFT.

In-plane bending vibrations of the vinyl molecule appear between 1075 cm$^{-1}$ and 1415 cm$^{-1}$. In the spectrum, the band observed at 1423 cm$^{-1}$ with medium intensity was marked as symmetrical in-plane bending (scissoring) vibration of the CH$_2$ group in vinyl. In Figure 2, the band that appears to be rather weak at 1310 cm$^{-1}$ was marked as the C-H in-plane bending vibration. The band observed at 1014 cm$^{-1}$ with medium intensity was marked as rocking in the plane. It is understood from Table 1 that these three bands marked are in harmony with the calculated values.

The out-of-plane C-H bending vibrations in the vinyl group are generally observed in the range of 985 cm$^{-1}$ to 915 cm$^{-1}$. A closer look at the spectrum revealed that the band at 991 cm$^{-1}$ was very intense and marked as out-of-plane C-H bending vibration. Likewise, the band which was observed to be very strong at 922 cm$^{-1}$ was marked as out-of-plane wagging. It is understood from Table 1 that these bands are in agreement with the theoretically calculated results. As a consequence, these values are compatible with many experimental and theoretical results.
Figure 2. The experimental infrared vibrational spectra of 4-Cyanostyrene molecule.

3.3. C≡N vibrations

In the infrared spectrum, C≡N tensile vibration bands of benzonitriles between 2220 cm\(^{-1}\) and 2240 cm\(^{-1}\) are observed to be strong. This C≡N stretch band may slide higher or lower depending on the condition of the groups attached to the benzene ring.\(^{27-29}\) Looking at the infrared spectrum, it was observed as a very strong at 2225 cm\(^{-1}\), and it was assigned as C≡N strain vibration. The peak observed at 536 cm\(^{-1}\) was marked as the C-N out-of-plane bending band. From Table 1, it seems that the experimental results and the theoretical results are highly compatible with each other.

3.4. Ring vibrations

3.4.1. C-H vibrations

The peaks observed between 3000-3100 cm\(^{-1}\) are aromatic C-H tensile vibrations\(^{30}\) and they are pure. Looking at the spectrum, the peak that appear at 3066 cm\(^{-1}\) with medium intensity was marked as aromatic C-H stretch band. This peak was calculated at 2873.7293 cm\(^{-1}\) in HF and 3066.5823 cm\(^{-1}\) in DFT. In-plane and out-of-plane C-H bending vibrations are observed at 1000-1300 cm\(^{-1}\) and 950-800 cm\(^{-1}\), respectively.\(^{31-33}\) Looking at the spectrum, the bands observed at 1284 cm\(^{-1}\), 1207 cm\(^{-1}\), 1176 cm\(^{-1}\) and 1119 cm\(^{-1}\) at medium intensity were marked as in-plane bending. These bands were calculated as 1315.5468 cm\(^{-1}\), 1216.6726 cm\(^{-1}\), 1197.0028 cm\(^{-1}\) and 1078.4971 cm\(^{-1}\) in HF and 1284.7295 cm\(^{-1}\), 1191.5421 cm\(^{-1}\), 1189.9749 cm\(^{-1}\) and 1104.8523 cm\(^{-1}\) in DFT, respectively. However, as seen in Table 1, it can be said that the calculated HF values deviate slightly from the experimental values. The band that appears to be very strong at 848 cm\(^{-1}\) in the spectrum is marked as out-of-plane bending and is compatible with DFT calculation.

3.4.2. C-C vibrations

In the infrared spectrum, aromatic C-C stretch vibrations generally occur between 1620 cm\(^{-1}\) and 1400 cm\(^{-1}\).\(^{34}\) Looking at the spectrum, the bands at 1627 cm\(^{-1}\), 1605 cm\(^{-1}\), 1552 cm\(^{-1}\), 1504 cm\(^{-1}\), 1423 cm\(^{-1}\) and 1404 cm\(^{-1}\), which appear to be strong and very weak in this range, were marked as C-C ring strain vibrations. The bands observed very weak at 745 cm\(^{-1}\) and medium strength at 419 cm\(^{-1}\) were marked as out-of-plane C-C bending vibration. From Table 1 these signs seem to agree with the theoretical results.

Although the observed bands are compatible with the literature, there is some difference in calculation. This may be due to the calculation of the molecule in the gas phase. It is also known from the literature that the frequencies calculated by the HF method are higher than other methods.\(^{34,35}\)
Table 1. Frequencies obtained from the calculations and the experimental data along with their assignment

| Calculation | Frequency | IR Int. | Scaled | Assignment |
|-------------|-----------|---------|--------|------------|
| HF/6-311G(dp) | 3292.6445 | 0.6598 | 61.0356 | (CH₃)₂ torsion |
| DFT/B3LYP/6-311G(dp) | 3220.0649 | 0.2983 | 61.0356 | (CH₃)₂ torsion |

Scaled: 0.9085, scaled: 0.9669, A: asymmetric, A': in-plane, A'': out-of-plane, Sc.: scissoring, S.: symmetric, Cy.: cyano, V.: vinyl, v: in plane stretch, β: in plane bending, γ: out of plane bending, T: type, N: number, c: Ref.16.
Some vibration types of the 4-Cyanostyrene molecule are listed in Figure 3.

3090 cm\(^{-1}\) asymmetric \(\nu(CH)\)

3066 cm\(^{-1}\) \(\nu(CH)\)

3012 cm\(^{-1}\) symmetric \(\nu(CH)\)

2225 cm\(^{-1}\) \(\nu(C\equiv N)\)

1504 cm\(^{-1}\) \(\nu(CC)\)

1423 cm\(^{-1}\) scissoring (CH\(_2\))

1228 cm\(^{-1}\) \(\beta(CH)\)

1014 cm\(^{-1}\) rocking (CH\(_2\))

922 cm\(^{-1}\) wagging (CH\(_2\))

848 cm\(^{-1}\) \(\gamma(CH)\)

745 cm\(^{-1}\) \(\gamma(CC)\)

436 cm\(^{-1}\) \(\gamma(CCN)\)

Figure 3. Vibration types of the 4-Cyanostyrene molecule.

4. CONCLUSIONS

The IR frequencies and intensities of the fundamental vibrational bands of 4-Cyanostyrene were calculated using HF and DFT/B3LYP methods with 6–311G(dp) basis set. The infrared absorption and intensities, computed by B3LYP method, are in reasonable agreement with the experimental data. The results confirm the ability of the methodology applied for interpretation of the vibrational spectrum of the 4-Cyanostyrene molecule in the solid state. It is important to do such a study first time on the 4-Cyanostyrene molecule.

ACKNOWLEDGEMENT

The Gaussian 09 program used in this study was provided by The Scientific Research Projects Council of Kilis 7 Aralık University, project number: 2010/02/08.

Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

REFERENCES

1. Rappaport, S. M.; Yeowell-O’Connell, K.; Bodell, W.; Yager, J. W.; Symanski, E. Cancer Res. 1996, 56 (23), 5410-5416.

2. Kogevinas, M.; Ferro, G.; Andersen, A. et al. Scand. J. Work Env. Hea. 1994, 20 (4), 251-261.

3. Coggon, D.; Ntani, G.; Harris, E. C.; Palmer, K. T. Occup. Environ. Med. 2015, 72 (3), 165-170.

4. Christensen, M. S.; Vestergaard, J. M.; d’Amore, F. et al. Epidemiology 2018, 29 (3), 342-351.

5. Collins, J. J.; Bodner, K. M.; Bus, J. S. Epidemiology 2013, 24 (2), 195-203.

6. Nissen, M. S.; Stokholm, Z. A.; Christensen, M. S.; Schlinnssen, V.; Vestergaard, J. M.; Iversen, I. B.; Kolstad, H. A. Occup. Environ. Med. 2018, 75 (6), 412-414.

7. Cruzan, G.; Bus, J. S.; Banton, M. I.; Sarang, S. S.; Waite, R.; Layko, D. B.; Raymond, J.; Dodd, D.;
Andersen, M. E. *Toxicol. Sci.* 2017, 159 (2), 413-421.

8. Cruzan, G.; Cushman, J. R.; Andrews, L.S.; et al. *J. Appl Toxicol.* 2001, 21 (3), 185–198.

9. Ponomarkov, V.; Tomatis, L. *Scand. J. Work Environ. Hea.* 1978, 4 (2), 127–135.

10. Conti, B.; Maltoni, C.; Perino, G.; Ciliberti, A. *Ann. NY Acad. Sci.* 1988, 534 (1), 203-234.

11. Hollas, J. M.; Khalilipour, E.; Thakur, S. N. *J. Mol. Spectrosc.* 1978, 73 (2), 240-265.

12. Zilberg, S.; Haas, Y. *J. Chem. Phys.* 1995, 103 (1), 20-36.

13. Bock, C. W.; Trachtman, M.; George, P. *Chem. Phys.* 1985, 89 (5), 2738–2742.

14. Frisch, A.; Nielsen, A. B.; Holder, A. J. *Gauss 09 View User Manual* (Pittsburg: Gaussian Inc.) 2009.

15. Frisch, A.; Nielsen, A. B.; Holder, A. J. *Gauss 09 View User Manual* (Pittsburg: Gaussian Inc.) 2009.

16. https://www.acros.com/DesktopModules/Acros_SearchResults/Acros_Search_Results.aspx?search_type=CatalogSearch&searchString=4-Cyanostyrene (accessed 01.05.2020).

17. Smith, B. C. *Infrared Spectral Interpretation: A Systematic Approach*; CRC Press, New York, 1998.

18. Rao, J. M. *Organic Spectroscopy Principles and Applications*, Narosa Publishing House, New Delhi, 2000.

19. Kanamori, H.; Endo, Y.; Hirota, E. *J. Chem. Phys.* 1990, 92 (1), 197-205.

20. Kim, E.; Yamamoto, S. *J. Chem. Phys.* 2002, 116 (24), 10713-10718.

21. Tanaka, K.; Toshimitsu, M.; Harada, K.; Tanaka, T. *J. Chem. Phys.* 2004, 120 (8), 3604-3618.