Potential Energy Distribution Study Of Beta Asarone and its Vibrational Spectrum and Force Constants

M.B.Bindu¹, Linu Sam², Amrutha R³*
¹Department of Mathematics, KCG College of Technology, Chennai
²,³Department of Physics, KCG College of Technology, Chennai
¹email: hodsh@kcgcollege.com
²email: linu@kcgcollege.com
³email: amrutha@kcgcollege.com *
*Corresponding Author

List of Tables and Figures
Figure 1: Structure of Beta Asarone
Table 1 Vibrational Assignments
Figure 2 IR Spectrum and Raman Spectrum of Beta Asarone
Potential Energy Distribution Study Of Beta Asarone and its Vibrational Spectrum and Force Constants

Abstract
The PED assignments are analysed for the title molecule. The Force Constants and Reduced masses are presented for reference. Vibrational assignments are made to the title molecule Beta Asarone. The analysis of Vibrational Assignments is done with an intention to deduce the various properties of Beta Asarone that should aid in analysing the reported toxicity of Beta Asarone.

Keywords: Beta Asarone, Force Constants, PED, Vibrational
Introduction

Vibrational spectroscopy is widely being used as a means to provide information about composition and structure of molecular systems. Both FTIR spectroscopy and Raman Spectroscopy play an important role in characterizing the molecule.

In already published work various properties such as Structural parameters, SCF energy, Charge distribution and MEP of Beta Asarone have been discussed. [1] In this work a comprehensive study on Raman Spectroscopy, PED and Force constants is carried out. The Raman intensity is a function of the polarizability and symmetry and therefore probes the bonding covalence and structure, it is calculated here. The Potential Energy Distribution (PED) gives the relative contribution of each displacement of each coordinate to the total change of potential energy during normal vibration. The description of a normal mode is often given by the potential energy distribution (PED), which is defined by the relative contribution of each displacement coordinates to the total change in potential energy during the normal vibration $Q$. The fractional contribution of each coordinate is given by

$$F_{ii} = L_{ii} \lambda_{ii}$$  \hspace{1cm} (1)

where $F_{ii}$ is the diagonal force constant matrix element and $L_{ii}$ is the eigenvector matrix element.

$$S_i = \sum L_{ii} Q_i$$  \hspace{1cm} (2)

And $\lambda_{ii}$ is the eigenvalue. (Contributions of off-diagonal elements, which can be negative as well as positive, are typically small and are usually neglected in this representation.) [2] Force constant is the second derivative with respect to a normal mode displacement and the units for the normal mode force constant Gaussian prints out is different. The different masses of the atoms leads to a different set of Sayetx conditions, which in turn, change the internal coordinate system the force constants are transformed to, and ultimately the resulting force constant.

The coordinates used to calculate the force constants, the reduced mass and the cartesian displacements are all internally consistent. The force constants $k_i$ are given by

$$k_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}$$

Computational Details

The DFT/B3LYP presents better results pertaining to energies, vibrational frequencies and geometries of organic compounds. Furthermore, the 6-31G(d) basis set calculations approximate the observed fundamental frequencies much better than the other basis sets results. The small difference between experimental and calculated vibrational modes is observed. This discrepancy may be due to intermolecular interactions in the solid state and the calculations may be performed in the gas phase. [3]

Materials and Methods

Acorus Calamus (Vacha) is a herb with reported medicinal values for decades. Acorus Calamus is used as a medicine only on aging. Hence the dried species of Acorus Calamus is only used for medicinal purpose.

Several phytochemical studies on Acorus Calamus has been carried out and various chemicals have been identified. Beta Asarone is a main component of Acorus Calamus and seems to extend a mentionable influence on the activity of the herb. It has been listed toxic by FDA. Continuous work is being carried out to establish the medical efficacy of Acorus Calamus and the modified toxicity of Beta Asarone.
The structure of Beta Asarone is generated using Gaussview 05 software.[4] The generated coordinates were optimised using in Gaussian 09 software[5] with B3LYP/6-31G** basis set and the optimised parameters were used to carry out the vibrational calculations. The PED assignments were made using the VEDA software.[6] The Structure of Beta Asarone is given in Fig 1.

Results and Discussions

IR spectra and Raman spectra were recorded for Beta Asarone with their intensities. The frequency was scaled by a factor of 0.961. The Force Constants, Potential Energy Distributions(PED), and Reduced Masses are presented here. The compound has 87 modes of vibration. The appropriate vibrational assignments are made and the PED assignments are also listed. The relevant Force Constants and Reduced Masses are presented for reference. The values are listed in Table 1. The spectrum is given in Fig 2.

| Scaled Frequencies | Red. masses | Frc consts | IR Inten | Raman Activ | PED | Assignments |
|--------------------|-------------|------------|----------|-------------|-----|-------------|
| 364.1014697        | 4.8104      | 0.4068     | 9.1453   | 4.641       | 12,-54 | βCOC        |
| 464.4060369        | 4.7784      | 0.6575     | 2.2971   | 9.7836      | 20,-13 | βCCC        |
| 583.7154362        | 3.9544      | 0.8596     | 10.0455  | 18.785      | 47   | βCCO        |
| 618.2512776        | 5.9972      | 1.4624     | 8.993    | 8.6399      | 22,-33,-10 | ρCCCC    |
| 664.271069         | 5.7468      | 1.6178     | 3.7665   | 7.6124      | 72,-16 | τHCCC       |
| 685.1850237        | 2.1882      | 0.6554     | 16.4936  | 41.2929     | 11,11,37 | γCC,βCCC   |
| 729.5724605        | 4.6835      | 1.5904     | 32.9433  | 63.8325     | 53,-18 | ρCCCC       |
| 829.4456348        | 3.4573      | 1.5175     | 102      | 7.1463      | 78   | πHCCC       |
| 955.4193769        | 5.05        | 2.9409     | 40.9242  | 12.3467     | 17,-67 | πHCOC, τHCCC |
| 970.9676842        | 1.1891      | 0.7152     | 4.5257   | 140.1434    | 11,22,16 | γOC       |
| 997.8955769        | 7.8256      | 4.9716     | 188.3183 | 8.5479      | 25,-22,-38 | γOC    |

Figure 1: Structure of Beta Asarone
| Wavenumber | Intensity | Compound | Assignments |
|------------|-----------|----------|-------------|
| 1023.690835 | 1.5279 | 1.0215 | 9.8782 | 11.6406 | 13.14, 15 | γOC, νCC |
| 1053.507686 | 2.7708 | 1.2591 | 38.6308 | 4.4583 | 24, 28 | γOC, τHOC |
| 1131.999187 | 1.2770 | 1.0440 | 4.0404 | 7.1240 | 33, 33 | τHOC, νCC |
| 1133.903985 | 1.2726 | 1.0439 | 1.9799 | 6.4599 | 33, 33 | βHCH, τHOC |
| 1135.516543 | 1.2584 | 1.0351 | 5.0581 | 15.1027 | 38, 25 | βHCH |
| 1150.562632 | 1.6049 | 1.3554 | 133.4229 | 13.5779 | 31, 31 | τHCCC, βHCH |
| 1153.205426 | 1.2344 | 1.4427 | 20.0133 | 91.2345 | 17, 32 | γOC |
| 1158.305426 | 1.2106 | 1.5831 | 122.0832 | 127.2269 | 70 | γOC |
| 1160.168019 | 2.1748 | 1.8675 | 267.7766 | 3.7201 | -25 | γOC |
| 1177.413933 | 1.6074 | 1.4216 | 114.2754 | 26.6235 | 57 | γOC |
| 1180.305426 | 2.1403 | 1.9281 | 388.8327 | 9.9205 | 20 | γOC |
| 1215.447045 | 1.2434 | 1.4427 | 20.0133 | 91.2345 | 17, 32 | γOC |
| 1269.470125 | 2.4518 | 2.5215 | 123.5613 | 45.2547 | 56 | βHCH |
| 1316.768927 | 5.6158 | 6.2121 | 37.4039 | 213.4382 | 59 | γCC |
| 1348.557077 | 1.2434 | 1.4427 | 20.0133 | 91.2345 | 88 | βHCH |
| 1372.803011 | 3.0015 | 3.6088 | 89.6711 | 73.6382 | 14 | βCCO |
| 1416.746370 | 1.1447 | 1.4658 | 49.4944 | 83.5254 | 62 | βHCH |
| 1426.413261 | 1.0617 | 1.3782 | 0.3242 | 68.3673 | -12 | βHCH |
| 1427.071258 | 1.0550 | 1.3707 | 20.1205 | 39.4494 | 40 | βHCH |
| 1428.555618 | 1.0719 | 1.3956 | 30.4658 | 51.8391 | 17, 74 | βHCH |
| 1431.704815 | 1.2106 | 1.5831 | 122.0832 | 127.2269 | 70 | βHCH |
| 1436.567668 | 1.0573 | 1.3920 | 47.7965 | 46.2391 | 75, 14 | βHCH |
| 1440.415031 | 1.2422 | 1.6443 | 8.6518 | 25.8541 | 38 | βHCH |
| 1442.669729 | 1.0896 | 1.4468 | 53.8177 | 21.534 | 62, 21 | βHCH |
| 1448.197305 | 1.0814 | 1.4470 | 8.4982 | 41.5524 | 33 | βHCH |
| 1483.272075 | 2.6969 | 3.7853 | 360.4385 | 9.8767 | 34 | γCC |
| 1555.041958 | 8.9637 | 13.8285 | 10.9966 | 43.5467 | 63 | γCC |
| 1583.288727 | 6.3292 | 10.1222 | 97.4859 | 288.8838 | 51, 13 | βHCC |
| 1644.401312 | 6.6020 | 11.3892 | 3.6763 | 456.9437 | 60, 12 | γCC |
| 2962.836324 | 1.0957 | 6.1363 | 34.5552 | 347.2396 | 99 | γCH |
| 2983.612856 | 1.1067 | 6.2852 | 57.975 | 113.7963 | 100 | γCH |
| 3027.624926 | 1.1039 | 6.4554 | 43.1305 | 276.5946 | 79 | γCH |
| 3028.99902 | 1.0867 | 6.3602 | 21.1805 | 145.514 | 75 | γCH |
| 3037.426069 | 1.1031 | 6.4926 | 29.4691 | 222.624 | 15, 75 | γCH |
| 3112.789803 | 1.0911 | 6.7445 | 1.7510 | 274.6743 | 99 | γCH |

γ- Stretch, β- Bend, τ- Torsion, ρ- out of plane bending

Table 1 Vibrational Assignments
Vibrational Assignments

Stretching Vibrations

CH stretching was observed at several frequencies. It is observed at 3112 cm\(^{-1}\) with a quite a high Raman intensity and a PED of 99\%. 3037 cm\(^{-1}\) exhibits degeneracy with PED of 15 and 75\%. CH stretching is also observed at 3028 cm\(^{-1}\), 3027 cm\(^{-1}\), 2983 cm\(^{-1}\), 2962 cm\(^{-1}\), 2915 cm\(^{-1}\), 2912 cm\(^{-1}\) with PED of 75, 79, 100, 99 and degenerate bands with 11 and 82 and 13 and 86 respectively. In all the above frequencies CH stretching exhibits more of Raman Intensity as compared to the IR intensity. The most intense Raman band is observed at 2912 cm\(^{-1}\) with an intensity of 610. This is attributed to anti symmetric stretching and this methyl group is said to exhibit anti symmetric C-H stretching around 2700 to 2900 cm\(^{-1}\) comparable to those observed by Neha Tiwari et al.[7]

CC stretching vibrations are observed at 1644 cm\(^{-1}\) with 2 bands with PED of 60 and 12\% respectively. This band has a high Raman intensity contribution. CC Stretching is also observed at 1555 cm\(^{-1}\) again with 2 assignments at 60 and 12\%, 1483 cm\(^{-1}\) with PED of 34\% and this has more of IR intensity, 1316 cm\(^{-1}\) with PED value of 59 and the band is assigned to the Raman activity.

OH stretching is observed at 1215 cm\(^{-1}\) and it has one symmetric assignment with 17\% and anti symmetric at -13\%. OH stretching is also observed at 1188 cm\(^{-1}\) with high IR activity and the PED
assignment is 20%. At 1096 cm\(^{-1}\) the PED assignments stand at 24 and 18\%, at 1065 cm\(^{-1}\) with 13 \,14\% and antisymmetric -15\% assignments. 1065 cm\(^{-1}\) 3 bands with PED assignments at 25 and the antisymmetric -22 and -38\%. At 997 cm\(^{-1}\) a high level of IR activity is observed with a degeneracy again with 11 and 12\% PED. OH stretching is also observed at 970 with a high Raman activity and PED assignments if 12 and 16 respectively.

**Bending assignments**

HCC bending is observed at 1583 cm\(^{-1}\) with PED assignments of 51 and 13 with a high Raman Activity.

HCH bending is observed at 1448 cm\(^{-1}\) with a PED of 33\% and exhibits reasonable Raman activity and at 1442 cm\(^{-1}\) with PED assignments at 62 and 21\% and exhibits a reasonable IR activity. HCH bending is also observed at 1436 cm\(^{-1}\) with a higher 71\% and a considerably lower anti symmetric at -14\%. At 1431 cm\(^{-1}\) the PED is found to be 70\% with a high Raman activity. 1427 cm\(^{-1}\) and 1426 cm\(^{-1}\) frequencies exhibit HCH bend at 40 and anti symmetric -12\% respectively. 1416 cm\(^{-1}\) and 1348 cm\(^{-1}\) have PED assignments at 62 and 88\% and both exhibit good Raman activity. At 1269 cm\(^{-1}\) with a PED assignment of 56 \% the Raman activity is found to be very high with a reasonable IR intensity. 1150 cm\(^{-1}\) has 2 bands in the IR region with a symmetric 15\% and an anti symmetric -15\%. At 685 cm\(^{-1}\) 3 bands are found at 11, 11, and 37\%.

The CCO bending vibrations are found at 1372 cm\(^{-1}\), 712 cm\(^{-1}\), 583 cm\(^{-1}\) with PED assignments of 14, 37 and anti symmetric -47\%. CCO bending is also exhibited at a frequency of 364 cm\(^{-1}\) with degenerate bands at 12 and -64. CCC bending is found at 464 cm\(^{-1}\) with PED assignments of 20 and -13\%.

Out of the plane CCC bending is exhibited at 618 cm\(^{-1}\) at 22, 13 and -10\% and also at 464 cm\(^{-1}\) at 20 and -13\% indicating distortion of the ring.

**Torsional vibrations**

HCOH torsion is observed at one of the H-C-O-H nearer to the methyl group at 1442 cm\(^{-1}\) at with a small PED of 21\%. HOCO torsional vibrations are found at 1436 cm\(^{-1}\), 1133 cm\(^{-1}\), 1311 cm\(^{-1}\) and 955 cm\(^{-1}\) with most of the PED assignments being antisymmetric at -14, -35, -31, -33, 17\% respectively. The band at 955 cm\(^{-1}\) exhibits a small IR intensity. HCCC vibrations are observed at 1428 cm\(^{-1}\), 1177 cm\(^{-1}\), 1160 cm\(^{-1}\), at 955 cm\(^{-1}\), 829 cm\(^{-1}\) and 664 cm\(^{-1}\) at 17, 57, -25, -67, 78, 72 and -16, with 1177 and 1160 cm\(^{-1}\) intense IR bands.

**Force Constants**

The higher values of force constants mostly relate to the higher assignments of Raman spectrum. A force constant value of around 6 X 10\(^2\) N/m ensures a PED of 50 \% or above.

**Conclusion**

Vibrational assignments have been made to Beta Asarone with the relevant PED assignments, Force Constants and Reduced Masses. The Raman activity analysed here and the PED assignments may throw more light into the structure activity relationship of Beta Asarone and also would help assess its reported toxicity. Further studies would involve reading the Raman spectra in solution and also generating the Potential Energy Surfaces for enhanced analysis.

**References**

[1] L. Sam, R. Amrutha, P. Chandran, Computational Analysis of Physico Chemical Properties of Beta Asarone, 10 (2018) 61–71.

[2] W. Qian, S. Krimm, Dipole derivative distribution: A useful adjunct to the potential energy
distribution, J. Phys. Chem. 97 (1993) 11578–11579. https://doi.org/10.1021/j100147a003.

[3] Ö. Dereli, S. Sudha, N. Sundaraganesan, Molecular structure and vibrational spectra of 4-phenylsemicarbazide by density functional method, J. Mol. Struct. 994 (2011) 379–386. https://doi.org/10.1016/j.molstruc.2011.03.054.

[4] GaussView, Version 6, Dennington, Roy; Keith, Todd A.; Millam, John M. Semichem Inc., Shawnee Mission, KS, 2016.

[5] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, E. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[6] M.H.JamaRoz, Vibrational Energy Distribution Analysis, VEDA 4 Program, Warsaw, 2004-2010.

[7] N. Tiwari, A. Mishra, G. Bhatt, A. Chaudhary, Isolation of Principle Active Compound of Acorus Calamus. In Vivo Assessment of Pharmacological Activity in the Treatment of Neurobiological Disorder (Stress), Jmscr. 2 (2014) 2201–2212. www.jmscr.igmpublication.org.