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

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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

$F_{ii}L_{i\alpha}^2/ \lambda_\alpha$ (1)

where F_{ii} the diagonal force constant matrix element

Where F_{ii} is the diagonal force constant matrix element and $L_{i\alpha}$ is the eigen vector matrix element.

$S_i = \Sigma L_{i\alpha}Q\alpha$ -(2) (2)

And λ_α his 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 Sayvetz 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 $k_i = 4\pi^2\tilde{\nu}_i^2c^2\mu_i$ since $\nu_i = \frac{1}{2\pi}\sqrt{\frac{k_i}{\mu_i}}$.

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.

Figure 1: Structure of Beta Asarone

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	41.2293	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	τHCCC
955.4193769	5.05	2.9409	40.9242	12.3467	17,-67	τHCOC, 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

1023.690835	1.5279	1.0215	9.8782	11.6406	13,14,-15	γOC, νCC
1053.507686	1.7782	1.2591	38.6308	4.4583	24,18	γOC, τHCOC
1131.999187	1.277	1.044	4.0404	7.124	33,-33	τHCOC,
1133.903985	1.2726	1.0439	1.799	6.4599	33,-31	τHCOC
1135.516543	1.2584	1.0351	5.0281	15.1027	38,-25	βHCH, τHCOC
1150.562632	1.6049	1.3554	133.4229	13.5779	15,-15	βHCH
1160.168019	2.1748	1.8675	267.7766	3.7201	-25	τHCCC, βHCH
1177.413933	1.6074	1.4216	114.2754	26.6235	57	τHCCC, βHCH
1188.305426	2.1403	1.9281	388.8327	9.9252	20	γOC
1215.447045	1.4921	1.4063	35.044	36.5337	17,-13	γOC
1269.670125	2.4518	2.5215	123.5613	459.2547	56	βHCH
1316.768927	5.6158	6.2121	37.4039	213.4382	59	γCC
1348.557077	1.2434	1.4427	20.0133	91.2726	88	βHCH
1372.803011	3.0015	3.6088	89.6711	73.6382	14	βCCO
1416.74637	1.1447	1.4658	49.4944	83.5254	62	βHCH
1426.413261	1.0617	1.3782	0.3242	68.3673	-12	βHCH
1427.071258	1.055	1.3707	20.1205	39.4494	40	βHCH
1428.555618	1.0719	1.3956	30.4658	51.8309	17,-74	τHCCC, βHCH
1431.704815	1.2106	1.5831	12.2083	127.2269	70	βHCH
1436.567668	1.0573	1.392	47.7965	46.2391	75,-14	βHCH, τHCOC
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, τHCOH
1448.197305	1.0814	1.447	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	6.602	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
3028.89902	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	1.751	274.6743	99	γCH

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

Table 1 Vibrational Assignments

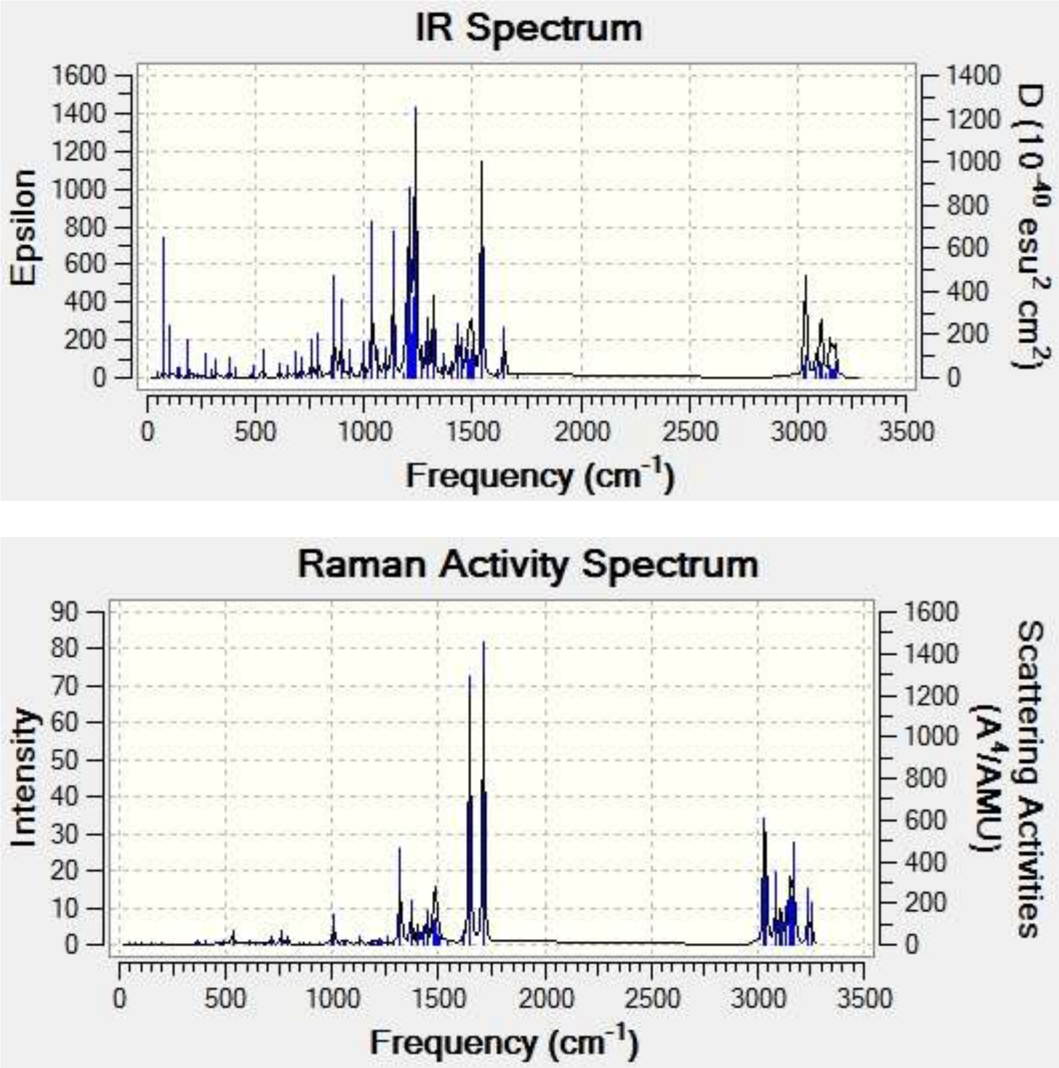

Figure 2 IR Spectrum and Raman Spectrum of Beta Asarone

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%. 3037cm^{-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 2912cm^{-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 Tiwari1 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, 1316cm^{-1} with PED value of 59 and the band is assigned to the Raman activity.

OH stretching is observed at 1215cm^{-1} and it has one symmetric assignment with 17% and anti symmetric at -13%. OH stretching is also observed at 1188cm^{-1} with high IR activity and the PED assignment is 20%. At 1096cm^{-1} the PED assignments stand at 24 and 18%, at 1065cm^{-1} with 13 ,14% and antisymmetric -15% assignments. 1065cm^{-1} 3 bands with PED assignments at 25 and the antisymmetric -22 and -38%. At 997cm^{-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 1583cm^{-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 1442cm^{-1} with PED assignments at 62 and 21% and exhibits a reasonable IR activity. HCH bending is also observed at 1436cm^{-1} with a higher 71% and a considerably lower anti symmetric at -14%. At 1431cm^{-1} the PED is found to be 70% with a high Raman activity.1427cm^{-1} and 1426cm^{-1} frequencies exhibit HCH bend at 40 and anti symmetric -12% respectively. 1416cm^{-1} and 1348cm^{-1} have PED assignments at 62 and 88% and both exhibit good Raman activity. At 1269cm^{-1} with a PED assignment of 56 % the Raman activity is found to be very high with a reasonable IR intensity. 1150cm^{-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 1372cm^{-1}, 712cm^{-1}, 583cm^{-1} with PED assignments of 14, 37 and anti symmetric -47%.CCO bending is also exhibited at a frequency of 364cm^{-1} with degenerate bands at 12 and -64. CCC bending is found at 464cm^{-1} with PED assignments of 20 and -13%.

Out of the plane CCC bending is exhibited at 618cm^{-1} at 22,13 and -10% and also at 464cm^{-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 1442cm^{-1} at with a small PED of 21%. HCOC torsional vibrations are found at 1436 cm^{-1}, 1133 cm$^{-1,}$ 1131 cm^{-1} and 955 cm^{-1} with most of the PED assignments being antisymmetric at -14, -35, -31, -33, 17% respectively. The band at 955cm^{-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.

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