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Available online at www.elixirpublishers.com (Elixir International Journal)

**Computational Physics** 

Elixir Computational Physics 106 (2017) 46509-46512



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### **ARTICLE INFO**

Article history: Received: 10 March 2017; Received in revised form: 28 April 2017; Accepted: 8 May 2017;

# ABSTRACT

The molecular vibrations of 2-methylnaphthalene was investigated by FT-IR and FT-Raman spectroscopies. Normal coordinate calculations of 2-methylnaphthalene have been carried out using Wilson's FG matrix mechanism on the basis of General Valence Force field (GVFF) for both in-plane and out-of-plane vibrations. The potential energy constants obtained in this study are refined using numerical methods.

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2229-2122

### Keywords

FT-IR, FT-Raman, 2-methylnaphthalene, Normal coordinate analysis, Potential energy distribution.

### 1. Introduction

Naphthalene is a white solid that evaporates easily. It is also called mothballs, mothflakes, white tar and tar camphor. 2-methylnaphthalene is a polycyclic aromatic hydrocarbon. It is found naturally in crude oil and coal. It is a white crystalline solid. It is also called beta methylnaphthalene. 2methylnaphthalene is incompatible with strong oxidizing agents. It is used to make other chemicals such as dyes and resins. It is also used to make vitamin K. The main uses of methylnaphthalene are as a raw material for dyestuff dispersants and heat transfer oils and as a solvent for agricultural chemical.

In the present paper, an effort has been made to record spectra and to assign the observed fundamental modes of vibrations. The evaluation of potential energy constant has been made on the basis of General valence Force Field (GVFF) by applying Wilson's FG matrix mechanism [1].

#### 2. Experimental Details

Pure chemical of 2-methylnaphthalene is obtained from Lancaster chemical company, England and used as such without any further purification.

The FT-IR spectrum of the title compound was recorded in the region 4000-400cm<sup>-1</sup> using KBr pellet. The Bruker IFS 66V model FT-IR spectrometer was used for the spectral measurements. The globar and mercury arc sources, KBr beam splitters are used while recording FT-IR spectrum of the title compound.

The FT-Raman spectrum was recorded on a Bruker IFS 66V model interferometer equipped with an FRA-106 FT-Raman accessory. The spectrum eas recorded in the stokes region (4000-100cm<sup>-1</sup>) using the 1064nm line of a Nd: YAG laser for excitation operating at 200 mW of power.

# 3. Results and Discussion

### 3.1. Structure and symmetry

The molecular structure of 2-methylnaphthalene is shown in fig. 1. Form the structural point of view the molecule is assumed to have  $C_s$  point groups symmetry.

The 57 fundamental modes of vibrations arising for this molecule are distributed into 38A' and 19A'' species. The A' and A'' species represent the in-plane and out-of-plane vibrations.



#### Fig. 1: Molecular structure of 2-methylnaphthalene 3.2. Normal Coordinate Analysis

The evaluation of potential energy constants are made on the basis of GVFF by applying Wilson's FG matrix mechanism. The structural parameters were taken from the sutton's table [2]. The vibrational secular determinants have been solved using the computer programmes with the SIMPLEX optimization procedure [3]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature [4]. All the force constants have been refined via a non-linear square fit analysis between the calculated and observed frequencies. The refinement converged smoothly in three cycles.

#### 3.3. Symmetry Coordinates

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 79 standard internal valence coordinates (containing 22 redundancies) were defined in Table 1. From these a non-redundant set of local internal coordinates were constructed (Table 2) much like the natural internal coordinates recommended by IUPAC [5,6].

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Theoretically calculated force fields were transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

 
 Table 1.Definition of internal coordinates of 2methylnaphthalene.

NT (*)	0 1 1		D. C. 14
No (1)	Symbol	Туре	Definition
Stretchin	g		1
1-12	ri	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C6-C7, C7-C8, C8-C9, C9-C10, C10-C5, C2- C18
13-19	R <sub>i</sub>	С-Н	C1-H15, C3-H16, C4-H17, C10-H11, C9-H12, C8-H13, C7-H14
20-22	R <sub>i</sub>	C-H (Methyl)	С18-Н19, С18-Н20, С18-Н21
In-Plane	bending	()-)	L
23-24	αί	C-C-C	C1-C2-C18, C3-C2-C18
25-38	αί	С-С-Н	C2-C1-H15, C6-C1-H15, C2-C3-H16, C4-C3-H16, C3-C4-H17, C5-C4-H17, C5-C10-H11, C9-C10-H11, C10-C9-H12, C8-C9-H12, C9-C8-H13, C7-C8-H13, C8-C7-H14, C6-C7-H14,
39-44	βi	Ring1	C1-C2-C3, C2-C3-C4, C3-C4- C5, C4-C5-C6, C5-C6-C1, C6-C1- C2
45-50	βi	Ring2	C7-C6-C5, C6-C5-C10, C5- C10-C9, C10-C9-C8, C9-C8-C7, C8-C7- C6
51-53	$\delta_i$	C-C- H(methyl)	C2-C18-H19, C2-C18-H20, C2- C18-H21
54-56	σ	Н-С-Н	H19-C18-H20,H19-C18-H21, H21-C18-H20
Out-of-p	ane bendi	ng	
57-63	ωi	С-Н	H17-C4-C5-C3, H16-C3-C4- C2, H15-C1-C2-C6, H14-C7-C6-C8 H13-C8-C7-C9, H12-C9-C8- C10 H11-C10-C9-C5
65-70	$\frac{\pi_i}{t_i}$	τ-C τRing1	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2.
71-76	ti	τRing2	C6-C1-C2-C3 C7-C6-C5-C10, C6-C5-C10-C9, C5-C10-C9-C8 C10-C9-C8-C7, C9-C8-C7-C6, C8-C7-C6-C5
77	t <sub>i</sub>	τ-C-CH <sub>3</sub>	(C3-C1)-C2-C18- (H19 H20 H21)
78-79	t <sub>i</sub>	Butterfly	C4-C5-C6-C7, C10-C5-C6-C1

For numbering of atoms refer Fig. 1.

 

 Table 2. Definition of local symmetry coordinates of 2methylnaphthalene.

No. (i)	Туре	Definition
1-12	CC	r <sub>1</sub> ,r <sub>2</sub> ,r <sub>3</sub> ,r <sub>4</sub> ,r <sub>5</sub> ,r <sub>6</sub> ,r <sub>7</sub> ,r <sub>8</sub> ,r <sub>9</sub> ,r <sub>10</sub> ,r <sub>11</sub> ,r <sub>12</sub>
13-19	СН	$R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}$
20	CH <sub>3</sub> ss	$(R_{20}+R_{21}+R_{22})/\sqrt{3}$
21	CH <sub>3</sub> ips	$(2R_{20}-R_{21}-R_{22})/\sqrt{6}$
22	CH <sub>3</sub> ops	$(R_{21}-R_{22})/\sqrt{2}$

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2	3	bCC	$(\alpha_{23}-\alpha_{24})/\sqrt{2}$
2	4-30	bCH	$(\alpha_{25}-\alpha_{26})/\sqrt{2}$ , $(\alpha_{27}-\alpha_{28})/\sqrt{2}$ ,
			$(\alpha_{29}-\alpha_{30})/\sqrt{2}$ , $(\alpha_{31}-\alpha_{32})/\sqrt{2}$
			$(\alpha_{33}-\alpha_{34})/\sqrt{2}$ , $(\alpha_{35}-\alpha_{36})/\sqrt{2}$ , $(\alpha_{37}-\alpha_{34})/\sqrt{2}$
			$(\alpha_{38})^{/}\sqrt{2}$
3	1	R1trigd	$(\beta_{39}-\beta_{40}+\beta_{41}-\beta_{42}+\beta_{43}-\beta_{44})/\sqrt{6}$
3	2	R1 symd	$(-\beta_{39}-\beta_{40}+\beta_{41}-\beta_{42}-\beta_{43}+2\beta_{44})/\sqrt{6}$
3	3	R1asymd	$(\beta_{39}-\beta_{40}+\beta_{41}-\beta_{42})/\sqrt{2}$
3	4	R2trigd	$(\beta_{45}-\beta_{46}+\beta_{47}-\beta_{48}+\beta_{49}-\beta_{50})/\sqrt{6}$
3	5	R2symd	$(-\beta_{45}-\beta_{46}+\beta_{47}-\beta_{48}-\beta_{49}+2\beta_{50})/\sqrt{6}$
3	6	R2asymd	$(\beta_{45}-\beta_{46}+\beta_{47}-\beta_{48})/\sqrt{2}$
3	7	CH <sub>3</sub> sb	$(-\delta_{51}-\delta_{52}-\delta_{53}+\sigma_{54}+\sigma_{55}+\sigma_{56})/\sqrt{6}$
3	8	CH <sub>3</sub> ipb	$(-\sigma_{54}-\sigma_{55}-2\sigma_{56})/\sqrt{6}$
3	9	CH <sub>3</sub> opb	$(\sigma_{54} - \sigma_{55})/\sqrt{2}$
4	0	CH <sub>3</sub> ipr	$(2\delta_{51}-\delta_{52}-\delta_{53})/\sqrt{6}$
4	1	CH <sub>3</sub> opr	$(\delta_{52}-\delta_{53})/\sqrt{2}$
4	2-48	ωCH	@57 <b>,</b> @58 <b>,</b> @59 <b>,</b> @60,@61,@62,@63
4	9	πCC	π64
5	0	tR1trig	$(\tau_{65} - \tau_{66} + \tau_{67} - \tau_{68} + \tau_{69} - \tau_{70})/\sqrt{6}$
5	1	tR1sym	$(\tau_{65} - \tau_{67} + \tau_{68} - \tau_{70})/\sqrt{2}$
5	2	tR1asy	$(-\tau_{65}+2\tau_{66}-\tau_{67}-\tau_{68}+2\tau_{69}-\tau_{70})/\sqrt{12}$
5	3	tR2trig	$(\tau_{71}-\tau_{72}+\tau_{73}-\tau_{74}+\tau_{75}-\tau_{76})/\sqrt{6}$
5	4	tR2sym	$(\tau_{71}-\tau_{73}+\tau_{74}-\tau_{76})/\sqrt{2}$
5	5	tR2asy	$(-\tau_{71}+2\tau_{72}-\tau_{73}-\tau_{74}+2\tau_{75}-\tau_{76})/\sqrt{12}$
5	6	tCH <sub>3</sub>	τ77
5	7	Butterfly	$(\tau_{78}-\tau_{79})/\sqrt{2}$

#### **3.4. Vibrational Band Assignments**

The FT-IR and FT-Raman spectra of the title compound are shown in figs. 2-3.



Fig 2.FT-IR spectrum of 2-methylnaphthalene .



Fig 3. FT-Raman spectrum of 2-methylnaphthalene.

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*R. Ramasamy and P. Chandra / Elixir Computational Physics 106 (2017) 46509-46512* Table 3.Vibrational frequencies and assignments of 2-methylnaphthalene.

S. No.	Species	Observed	Frequency (cm <sup>-1</sup> )	Calculated Frequency (cm <sup>-1</sup> )	Assignment (% PED)
	-	FT-IR	FT-Raman		
1	A'	-	3068	3059	C-H Stretching (97)
2	A'	3061	-	3053	C-H Stretching (99)
3	A'	3036	-	3026	C-H Stretching (98)
4	Α'	-	3022	3011	C-H Stretching (96)
5	Δ'	3016	-	3006	C-H Stretching (97)
5	A \	5010	2008	2080	C H Stretching (98)
7	A A'	-	2330	2989	C-II Stretching (98)
/	A	2991	-	2980	C-H Stretching (99)
8	A	2967	-	2959	$CH_{3}(97)$
9	A	2946	-	2936	CH <sub>3</sub> ops (89)
10	A	2919	-	2911	CH <sub>3</sub> ss(98)
11	A'	1648	-	1637	C-C Stretching (70)
12	A'	1632	-	1621	C-C Stretching (71)
13	A'	-	1611	1601	C-C Stretching (72)
14	A'	1601	-	1592	C-C Stretching (71)
15	A'	-	1581	1573	C-C Stretching (70)
16	A'	1509	-	1499	C-C Stretching (72)
17	A'	-	1467	1455	C-C Stretching (72)
18	A'	1454	-	1444	C-C Stretching (71)
19	Α'	1446	-	1437	C-C Stretching (70)
20	Δ'	1432	-	1424	C-C Stretching (71)
20	Δ'	1452	1427	1/17	C-C Stretching (71)
21	A A'	- 1402	1427	1411	C C Stretching (70)
22	A A'	1403	-	1411	CU inh (94)
25	A	-	15//	1380	$CH_{3}(p)$ (84)
24	A	1300	-	13/6	$CH_3SD(88)$
25	A	1273	-	1284	C-H in-plane bending (70)
26	A'	1266	-	1274	C-H in-plane bending (72)
27	A'	1173	-	1183	C-H in-plane bending (71)
28	A'	1166	-	1174	C-H in-plane bending (70)
29	A'	-	1132	1124	Ring1 deformation in-plane bending (51)
30	Α″	1124	-	1113	CH <sub>3</sub> opb (87)
31	A'	-	1078	1068	C-H in-plane bending (72)
32	A'	1037	-	1026	C-H in-plane bending (71)
33	A'	-	1025	1016	C-H in-plane bending (70)
34	A'	1018	-	1009	CH <sub>3</sub> ipr (79)
35	Α΄	1006	-	994	Ring1 deformation in-plane bending (52)
36	Δ"	962	_	970	CH <sub>2</sub> opr (77)
37	Δ'	953	-	962	Ring2 deformation in-plane bending (53)
38	A"	995	-	808	C H out of plane bending (60)
20	A A'	880	-	878	C C in plane bending (00)
39	A ^"		802	872	C-C III-plane bending (90)
40	A	830	-	839	
41	A	812	-	803	C-H out-of-plane bending (66)
42	A	/92	-	/82	C-H out-of-plane bending (65)
43	Α"	773	-	762	C-H out-of-plane bending (64)
44	A″	765	-	756	C-H out-of-plane bending (66)
45	Α″	741	-	730	C-H out-of-plane bending (65)
46	A'	-	703	712	Ring2 deformation in-plane bending (52)
47	A'	-	668	679	Ring2 deformation in-plane bending (51)
48	A'	622	-	631	Ring1 deformation in-plane bending (53)
49	Α″	514	-	522	Ring2 deformation out-of-plane bending (57)
50	A″	474	-	484	Ring1 deformation out-of-plane bending (59)
51	Α″	-	460	451	Ring2 deformation out-of-plane bending (58)
52	Δ"	_	439	431	Ring? deformation out-of-plane bending (50)
52	Δ"		405	395	Ring1 deformation out_of_plane bending (57)
5/	Λ /		318	306	Ring1 deformation out of plane bending (57)
54	A	-	262	252	Ringi deformation out-of-plane bending (58)
55	A	-	203	232	
56	A	-	242	232	CH <sub>3</sub> torsion (56)
57	A″	-	162	153	C-C out-of-plane bending (63)

Abbreviations used: ss-symmetric stretching; sb-symmetric bending; ipb-in-plane bending; opb-out-of-plane bending; ipr-in-plane rocking; opr-out-of-plane rocking.

The observed frequencies of the title compound together with probable assignment, calculated frequencies and PEDS are presented in Table 3.

#### **3.4.1.** C-H vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3000-3100cm<sup>-1</sup> which is the characteristic region for the ready identification of C-H stretching vibrations [7,8]. In this region the bands are not affected appreciably by the nature of the substituents. Hence, in the present investigation, C-H vibrations have found at 3061, 3036, 3016, 2991cm<sup>-1</sup> in IR and 3068, 3022, 2998cm<sup>-1</sup> in Raman.

#### **3.4.2.** C-C vibrations

The bands between 1400 and 1650cm<sup>-1</sup> in benzene derivatives are due to C-C stretching vibrations [9]. Therefore, the C-C stretching vibrations of the title compound are observed at 1648, 1632, 1601, 1509, 1454, 1446, 1432, 1403cm<sup>-1</sup> in IR and 1611, 1581, 1467, 1427cm<sup>-1</sup> in Raman.

#### **3.4.3.** Methyl Group vibrations

The methyl group substituted at the first position of the title compound given raise to asymmetric and symmetric stretching vibrations. We have observed the symmetrical methyl deformation modes  $CH_3$ sb at 1366cm<sup>-1</sup> in IR and inplane bending methyl deformation modes  $CH_3$ ipb at 1377cm<sup>-1</sup> in Raman. The band at 1124cm<sup>-1</sup> in IR is attributed to  $CH_3$ opb in the A" species. The bands obtained at 1018cm<sup>-1</sup> in IR and 962cm<sup>-1</sup> in IR are assigned to  $CH_3$  in-plane and out-of-plane rocking modes. These assignments are also supported by the literature [10].

#### 4. Conclusion

Based on the normal coordinate analysis a complete vibrational analysis was performed on 2-methlnaphthalene. A systematic set of symmetric coordinates have been constructed. The closer agreement obtained between the calculated and the observed frequencies and the PED calculations are also supporting the assignments made for the various functional groups present in the molecule. **References** 

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