Scaled Quantum FT-IR and FT-Raman Spectral Analysis of 1-Methoxynaphthalene

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Abstract: The structural and vibrational property of 1-methoxynaphthalene has been studied. The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using B3LYP/6-31G (d, p) basis set and was scaled using various scale factors, which yielded a good agreement between observed and calculated frequencies. The vibrational spectra were interpreted with the aid of normal coordinate analysis. The results of the calculations were applied to simulated spectra of the title compound, which shows excellent agreement with observed spectra. The calculated force constants in vibrational internal coordinates are in closely coincides with the experimentally observed force constants.

Keywords: Scaled quantum FT-IR, FT-Raman Spectra, 1-Methoxynaphthalene, Vibrational property.

Introduction

Vibrational analyses of molecules are more deep study in organic chemistry, for the confirmation of functional groups, molecular structure and reaction kinetics. The naphthalene and its derivatives^{1,2} are the most important class of organic compounds containing two condensed rings. 1-Methoxynaphthalene is used as an intermediate for the synthesis of nonsteroidal anti-inflammatory drugs. It is also used for soap perfumes and in the preparation of non-steroidal anti-inflammatory agents and bromination process. There are series of ladder-like compounds consisting of linearly fused benzene rings^{1,2}, their technological potential³⁻⁵ and their intrinsic value as models for more complex conjugated molecules have been the subjects of many theoretical and experimental investigations⁶⁻¹⁴.

Experimental

The compound under investigation namely 1-methoxynaphthalene was purchased from M/S Aldrich chemicals, U.S.A which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FT-IR spectrum of the compound was recorded in Bruker IFS 66V spectrometer in the range of 4000 to 400 cm^{-1} . The spectral resolution is $\pm 2 \text{ cm}^{-1}$. The FT-Raman spectra of this compound was also recorded in the same instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating at 1.064 μm line widths with 200 mW powers. The spectra were recorded with scanning speed of 30 $\text{cm}^{-1} \text{ min}^{-1}$ of spectral width 2 cm^{-1} . The frequencies of all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$.

Computational methods

The quantum chemical calculations were performed for 1-methoxynaphthalene by applying B3LYP/6-31G (d,p) basis set method using the Gaussian 03 W program¹⁵. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming C_s point group symmetry. Scaling of the force field was performed according to the SQM procedure¹⁶ using selective scaling in the natural internal coordinate representation¹⁷. The optimized bond lengths and bond angles were used for the calculation of vibrational frequencies at the B3LYP levels. The SCF converges to total energy about -500.430925363 and zero point energy 113.19344 (kcal/mol). The rotational constants values are 1.64020, 0.82882 and 0.55253. GAUSSVIEW program¹⁸ is very helpful for visual interpretation of vibrational frequencies assignments with normal mode of vibration.

Results and Discussion

Molecular geometry

The 1-methoxynaphthalene assumed as C_s point group of symmetry and the optimized geometrical parameters of the title compound are calculated according to labeling of atoms as shown in the Figure 1. The most optimized bond lengths and bond angles of this compound were calculated and shown in Table 1.

Figure 1. Molecular structure of 1-methoxynaphthalene.

Table 1. Optimized parameters of 1- methoxynaphthalene.

Bond length	Value (Å ⁰)	Bond angle	Value (°)
C1-C2	1.3769	C2-C1-C6	120.2083
C1-C6	1.4143	C1-C2-H8	120.0527
C1-H8	1.0862	C6-C1-H8	119.739
C2-C3	1.4203	C1-C2-C3	121.0797
C2-H9	1.0869	C1-C2-C9	120.405
C3-C4	1.4309	C3-C2-C9	118.5153
C3-C10	1.4227	C2-C3-C4	118.4281
C4-C5	1.4184	C2-C3-C10	122.0275
C4-C11	1.4336	C4-C3-C10	119.5444
C5-C6	1.378	C3-C4-C5	119.3869
C5-C12	1.0837	C3-C4-C11	118.5468
C6-C13	1.0861	C5-C4-C11	122.0663
H7-C10	1.0861	C4-C5-C6	120.5573
C10-C15	1.3729	C4-C5-H12	118.6985
C11-C14	1.3811	C6-C5-H12	120.7442
C11-O18	1.3652	C1-C6-C5	120.3396
C14-C15	1.417	C1-C6-H13	119.7196
C14-H16	1.083	C5-C6-H13	119.9407
C15-H17	1.0862	C3-C10-H7	119.0627
O18-C19	1.4182	C3-C10- C15	120.1449
C19-H20	1.0973	H7- C10-C15	120.7924
C19-H21	1.0909	C4-C11-C14	120.6224
C19-H 22	1.0973	C4-C11-O18	114.8672
		C14-C11-O18	124.5104
		C11=C14-C15	119.925
		C11-C14-H16	120.9587
		C15-C14-H16	119.1163
		C10-C15-C14	121.2165
		C10-C15-H17	120.1347
		C14-C15-H17	118.6488
		C11-O18-C19	118.2875
		O18-C19-H20	111.5413
		O18-C19-H21	106.0622
		O18-C19-H22	111.5386
		H20-C19-H21	109.2863
		H20-C19-H22	109.0488
		H21-C19-H22	109.2914

Vibrational analysis and theoretical prediction of spectra

The sixty normal modes of vibrations of 1-methoxynaphthalene are distributed by symmetry species as

$$\Gamma_{\text{vib}} = 41A'(\text{in-plane}) + 19A''(\text{out-of-plane})$$

It is in agreement with C_s point group symmetry, all vibrations are active both in FT-Raman and infrared absorption. The detailed vibrational assignments of fundamental modes of 1-methoxynaphthalene along with the calculated frequencies, IR intensities, Raman activities and polarization ratios are reported in the Table 2. The observed and simulated FT-IR and laser Raman spectra are presented in Figures 2 & 3 respectively.

Table 2. Observed and B3LYP 6-31G (d,p) level calculated vibrational frequencies of 1-methoxynaphthalene.

Symmetry	IR	Raman	Unscaled	scaled	Reduced mass	Force constants	IR intensity	Raman activity	Depolar ratio(P)	Depolar ratio(U)	Assignments
A'	3065		3227	3065	1.09	6.69	7.59	201.60	00.11	0.20	C-H stretch
A'		3060	3226	3064	1.09	6.69	12.39	46.33	0.58	0.73	C-H stretch
A'		3055	3201	3040	1.09	6.61	28.85	268.79	0.14	0.24	C-H stretch
A'		3050	3198	3037	1.09	6.59	31.92	212.82	0.39	0.56	C-H stretch
A'		3020	3187	3027	1.09	6.52	15.12	127.75	0.74	0.85	C-H stretch
A'		3010	3180	3021	1.08	6.47	1.76	48.82	0.74	0.85	C-H stretch
A'	3005		3175	3015	1.08	6.44	1.14	42.82	0.63	0.78	C-H stretch
A'		2990	3150	2992	1.10	6.43	22.29	106.12	0.52	0.68	C-H stretch
A'	2940		3080	2925	1.10	6.18	40.46	62.39	0.75	0.85	C-H stretch
A'	2860		3017	2865	1.03	5.54	60.81	136.48	0.03	0.06	C-H stretch
A'		1640	1682	1631	6.29	10.49	7.1218	6.98	0.54	0.70	C-O stretch
A'	1595		1653	1586	5.09	8.20	19.53	1.93	0.28	0.44	C-C stretch
A'		1580	1633	1567	6.75	10.60	64.91	57.52	0.60	0.75	C-C stretch
A'		1505	1562	1499	3.54	5.08	21.39	7.82	0.29	0.46	C-C stretch
A'	1465		1520	1461	1.09	1.49	13.74	8.50	0.59	0.74	C-H in plane bend
A'	1460		1509	1451	2.03	2.73	32.80	14.17	0.49	0.66	C-H in plane bend
A'	1459		1503	1442	1.04	1.39	5.49	24.98	0.75	0.85	C-C stretch
A'	1440		1489	1431	1.50	1.96	3.23	9.00	0.28	0.43	C-H in plane bend
A'		1435	1483	1426	1.81	2.34	19.20	45.48	0.37	0.54	C-H in plane bend
A'		1385	1438	1380	2.21	2.69	97.08	19.94	0.19	0.33	C-C stretch
A'	1325		1418	1325	5.65	6.70	0.99	178.62	0.18	0.31	C-O stretch
A'	1310		1391	1334	3.54	4.04	1.27	4.46	0.34	0.51	C-C stretch
A'		1260	1305	1255	2.56	2.57	149.46	2.00	0.67	0.80	C-H in plane bend
A'	1220		1274	1225	1.73	1.66	51.44	2.65	0.60	0.75	C-C in plane bend
A'	1190		1247	1199	2.08	1.90	3.05	1.81	0.54	0.70	C-H in plane bend
A'	1175		1223	1176	1.41	1.24	4.39	5.11	0.64	0.78	C-H in plane bend
A'	1160		1203	1156	1.42	1.21	6.75	4.90	0.72	0.84	C-H in plane bend
A'		1155	1185	1139	1.14	0.95	8.96	3.12	0.70	0.82	C-H out plane bend
A'		1140	1178	1132	1.27	1.04	0.85	4.56	0.75	0.85	C-H in plane bend
A'	1105		1175	1129	1.33	1.08	2.61	9.79	0.68	0.81	C-H in plane bend
A'	1075		1138	1092	2.66	2.03	74.68	2.95	0.20	0.33	C-C stretch
A'	1025		1101	1042	2.19	1.56	15.22	5.63	0.13	0.24	C-C stretch
A'	995		1052	1011	2.37	1.54	11.00	12.63	0.15	0.27	C-H in plane bend
A'		990	1019	978	6.07	3.72	5.85	1.44	0.74	0.85	C-H out plane bend
A'	974		994	977	1.26	0.73	0.00	0.12	0.75	0.85	C-C-C in plane bend
A'	971		969	952	1.30	0.72	1.70	0.10	0.75	0.85	C-C-C in plane bend
A''		960	960	921	1.29	0.70	0.09	0.39	0.75	0.85	C-H out plane bend
A'		875	888	872	1.57	0.73	0.71	4.91	0.75	0.85	C-C-C in plane bend
A''	863		874	839	4.63	2.08	2.00	4.78	0.11	0.20	C-H out plane bend

Contd...

A''	840	866	831	1.47	0.65	1.28	0.71	0.75	0.85	C-H out plane bend
A'	795	806	792	1.88	0.72	45.95	1.43	0.75	0.85	C-C-C in plane bend
A''	775	802	770	5.23	1.98	1.46	1.73	0.12	0.22	C-H out plane bend
A''	760	788	757	1.68	0.61	40.60	2.43	0.75	0.85	C-H out plane bend
A'	720	746	733	1.36	0.44	0.45	5.57	0.75	0.85	C-C-C in plane bend
A'	710	729	716	5.41	1.69	11.25	24.81	0.10	0.19	C-C-C in plane bend
A''	640	649	638	3.48	0.86	1.97	0.62	0.75	0.85	C-C-C in plane bend
A''	580	615	590	5.47	1.22	4.33	1.91	0.48	0.65	C-H out plane bend
A'	554	585	561	3.38	0.68	4.89	1.86	0.75	0.85	C-H out plane bend
A''	500	541	519	6.45	1.11	0.73	5.50	0.48	0.65	C-H out plane bend
A''	465	494	474	6.45	0.92	2.91	9.92	0.28	0.44	C-C-C out plane bend
A''	460	481	461	3.45	0.47	0.10	0.31	0.75	0.85	C-H out plane bend
A''	430	456	430	5.06	0.61	1.99	6.97	0.42	0.59	C-C-C out plane bend
A''	420	432	407	3.23	0.35	2.15	2.31	0.75	0.85	C-C-C out plane bend
A''	335	341	321	3.71	0.25	0.50	4.16	0.21	0.35	C-C-C out plane bend
A'	280	291	274	2.20	0.11	0.02	0.87	0.75	0.85	C-O in plane bend
A''	220	235	221	1.44	0.04	0.21	0.91	0.75	0.85	C-H out plane bend
A''	195	208	196	3.71	0.09	2.44	1.88	0.72	0.84	C-C-C out plane bend
A''	160	181	170	3.67	0.07	0.03	0.23	0.75	0.85	C-C-C out plane bend
A''		138	130	3.73	0.04	2.38	2.20	0.75	0.84	C-C-C out plane bend
A''		81	76	3.09	0.01	3.84	1.99	0.75	0.85	C-C-O out plane bend

Figure 2. Comparison of observed and calculated FI-Raman 1-methoxynaphthalene.
(a) Observed (b) calculated with B3LYP/6-31G (d,p).

Figure 3. Comparison of observed and calculated FT-Raman 1-methoxynaphthalene (a) Observed (b) calculated with B3LYP/6-31G (d,p).

Root mean square (RMS) values of frequencies were obtained using the relation

$$v_{\text{RMS}} = \sqrt{\frac{1}{n-1} \sum_i^n (v_i^{\text{calcu}} - v_i^{\text{exp}})^2}$$

The RMS error of unscaled frequencies is obtained for 1-methoxy naphthalene and found to be 77.04 cm^{-1} . In order to reproduce the observed frequencies, the refinement through scaling factors was carried out and optimized RMS deviation was reduced to 12.1 cm^{-1} .

C- H Vibrations

In aromatic molecules like 2 naphthalenol C-H vibrations appear¹⁹ in the region $3085\text{--}3040 \text{ cm}^{-1}$ and in 2,4 diisopropylnaphthalene²⁰ in the region $3070 - 3030 \text{ cm}^{-1}$. In this compound the C-H stretch vibrations occur in the region $3065 - 3000 \text{ cm}^{-1}$. The upper limit of frequency comparatively decreases may be due to the presence of oxygen and methyl group. There are seven aromatic C-H stretching vibrations, are observed at $3060, 3055, 3050, 3020$ and 3010 cm^{-1} in FT-Raman and 3065 and 3005 cm^{-1} are in IR region. The maximum and minimum frequencies are lies in the IR region. The mean deviations between experimental and scaled calculated frequencies are nearly 8.57 cm^{-1} . The scaled vibrations are good in agreement with the experimentally reported values of naphthalene derivatives. Optimized C-H bond lengths are clearly shows that the C-H bonds nearer to the methoxy group $\text{C}_5\text{-H}_{12}$ and $\text{C}_{15}\text{-H}_{16}$ having maximum variation with others. This is undoubtedly due to the impact of methoxy group. It is also evident by the farthest bond $\text{C}_2\text{-H}_{13}$ with maximum optimized bond length.

Methyl group vibrations

The methyl group stretching vibrations are in the region $3000\text{--}2980 \text{ cm}^{-1}$. In this compound, there two asymmetric and one symmetric C-H stretching vibrations are appeared at $2990, 2940$ and 2860 cm^{-1} respectively. These assignments are also evidenced by literature values²¹. The calculated frequencies are at $2992, 2940$ and 2865 cm^{-1} . Usually the symmetrical bands are sharper than the asymmetrical bands. The same trend is appeared here also.

2-methoxy-1-naphthaldhyde shows methyl vibrations are in the range 2885-2803 cm^{-1} . This may be indicates that the additional substitutions are pushes down the range of vibration. The asymmetric and symmetric stretching modes of methyl group attached the benzene ring are usually downshifted due to electronic effects and are expected near 2925 and 2865 cm^{-1} asymmetric and symmetric stretching vibration. This evident that the same electronic effect is also applicable in double ring compound like 1-methoxynaphthalene and the vibrations are observed²² at 2940 and 2865 cm^{-1} . Here also the above experimental values coincide with the scaled B3LYP/6-31G (d, p) basis set values. There is an appreciable change in one calculated $\text{C}_{19}\text{-H}_{21}$ bond due to its orientation and very near to the oxygen atom.

The bands due to C-H in-plane bending vibration interact some what with C-C stretching vibrations, are observed as number of bands in the region 1300–1000 cm^{-1} . The C-H out-of-plane bending vibrations occur²³ in the region 900–667 cm^{-1} .

In the present investigation, the bands observed at 1465, 1460, 1440, 1435, 1260, 1220, 1190, 1175, 1160, 1155, 1140, 1105 and 1075 cm^{-1} and 1025 cm^{-1} are assigned to C-H in plane bending vibration. The C-H out of plane bending modes was also assigned at 995, 974, 971, 875, 863, 795, 775, 720, 640, 290 and 220 cm^{-1} within characteristic region except three and is presented.

C–O vibrations

The compounds contain a carbonyl group; the absorption caused by the C–O stretching is generally very strong²⁴. In *p*-anisaldehyde, the C–O vibration with B3LYP/6-31G(d,p) predicated frequencies at 1332 and 1305 cm^{-1} are agreement with experimental frequencies²⁵ at 1322 and 1291 cm^{-1} . The characteristic infrared absorption frequencies of carbonyl group in cyclic ketones are normally strong in intensity and found in the region 1685–1660 cm^{-1} . Carboxylic acids, the C=O stretching observation²⁶ observed at 1725±65. In this compound C=O and C–O stretching vibrations are observed at 1640 and 1325 cm^{-1} . The bands are strong and medium appeared in Raman and IR. The scaled calculated values obtained from B3LYP/6-31G (d,p) are 1631 and 1325 cm^{-1} . The in plane bending vibration is observed at 280 cm^{-1} .

C–C vibrations

Generally the C–C stretching vibrations in aromatic compounds form²⁷ the band in the region of 1430 to 1650 cm^{-1} . In the present case investigation the bands are observed at 1640, 1595, 1580, 1505, 1440, 1325 and 1310 cm^{-1} . The last two bands lie below the expected range, this may be due to the substitution of heavy elements oxygen and methyl group in the present case. The in-plane bending C–C vibrations generally occur at higher frequencies than of out-of-plane bending²⁸. In the present study the bands observed at 760, 720, 580, 500, 465 and 430 are assigned to C–C in plane bending modes. The out of plane bending modes of frequencies are attributed to 554, 460 and 420 cm^{-1} in Raman and 175, 140 and 85 cm^{-1} in IR.

Conclusions

A complete vibrational analysis of 1-methoxynaphthalene was performed on the basis of DFT functional calculations at B3LYP/6-31G (d, p) basis level. The influences of carbon-oxygen, and methyl group in the vibrational frequencies of the title compound were discussed. The observed and stimulated spectra are in agreement and show a good frequency fit. The difference between theoretical and experimental wave numbers within 10 cm^{-1} shows that the assignments of the fundamentals are valid, by the qualitative agreement between the calculated and observed frequencies.

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