



## Vibrational Spectral Studies of 2,3-Dichloro-1,4-naphthaquinone

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Normal coordinate analysis of fundamental vibrations of 2,3-dichloro-1,4-naphthaquinone has been carried out by assuming Cs point group symmetry. The potential energy constants are obtained by applying Wilson's FG matrix method. All the modes of vibrations are assigned and the potential energy distribution calculations are performed.

**Key Words:** Normal coordinate analysis, 2,3-Dichloro-1,4-naphthaquinone, Potential energy.

### INTRODUCTION

Vibrational spectroscopy is used extensively in organic chemistry, besides for the identification of functional group of organic compounds, for studies on molecular conformation, reaction kinetics, *etc.* Assignment for complex systems can be proposed on the basis of frequency agreement between the computed harmonics and the observed fundamentals. Due to the biochemical importance of 1,4-naphthaquinone the normal coordinate analysis and vibrational spectral studies of 2,3-dichloro-1,4-naphthaquinone have been carried out in the present investigation. Consideration of these factors motivated to record infrared and Raman spectra of the compound. Normal coordinate analysis of the compound was carried out to obtain a more complete description of the molecular motions involved in the fundamental vibrations of dichloro naphthaquinone. It appears that no work has been reported on the complete vibrational analysis of this molecule. Hence in the present investigation, an effect has been made to record the spectra and to assign the observed fundamental modes of vibrations. Essentially all the functional frequencies have been assigned. The assignment is supported by normal coordinate analysis with a simplified general valence force field. The interaction force constants have been transferred intact from the *ab initio* force fields of structurally related compounds. The calculated frequencies are in very good agreement with experiment. The PED (potential energy distribution) obtained in the analysis provides some insight into the nature of normal modes of 2,3-dichloro-1,4-naphthaquinone [C<sub>10</sub>H<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>].

**Normal coordinate analysis:** A normal coordinate analysis for 2,3-dichloro-1,4-naphthaquinone have been carried out,

using the observed frequencies from the recorded spectra for the first time during this study. The evaluation of force constants are made on the basis of general valence force field, by applying Wilson's FG matrix mechanism<sup>1,2</sup> using the final set of force constants so calculated, the potential energy distribution has been calculated using the relation

$$PED = \frac{F_{ii} L_{ia}}{\lambda_a}$$

where F<sub>ii</sub> = Potential constant, L<sub>ia</sub> = L matrix element and λ<sub>a</sub> = 4π<sup>2</sup>C<sup>2</sup>va.

### EXPERIMENTAL

The pure sample of 2,3-dichloro-1,4-naphthaquinone was obtained from Lancaster Chemical Company, UK and used as such without further purification for the spectral measurements. FT-Raman spectra was recorded on a computer interfaced BRUKER IFS model interferometer equipped with FRA 106 FT-Raman accessories. The spectra was recorded in the region 3500-100 cm<sup>-1</sup> using Nd:YAG laser operating at 200 mW power continuously with 1064 nm excitation. The room temperature mid infrared spectrum of the compound was measured in the region 4000-400 cm<sup>-1</sup> at a resolution of ± 1 cm<sup>-1</sup> using Perkin-Elmer FTIR Spectrum RX1 model spectrometer equipped with an MCT detector, a KBr beam splitter and global source. Boxcar apozation was used for the 250 averaged interferogrames collected for the samples. The FT-IR spectrum was recorded at Archbishop Casimir Instrumentation Centre (ACIC), St. Joseph's College (Autonomous) Trichirappalli- 620 002. The FT-Raman spectrum was recorded at ICP Centre, Central Electrochemical Research Institute (CECRI), Karaikudi 630 006.

**Force constants:** The best fit force constants obtained in the study for the compound is listed in Table-1. The objective of this investigation is to find out the stretching, bending and interaction force constants corresponding to each substituent and its position in the ring. The stretching force constants observed in the study and the interaction force constants are slowly introduced in force constant refinement process in order to minimize the difference between the observed and calculated frequencies. In general, the values of principal and interaction force constants obtained in the present investigation are fairly in agreement with the literature. The set of force constants reported here reproduces the observed frequency fairly well.

TABLE-1  
VALENCE FORCE CONSTANT OF 2,3-DICHLORO-1,4-NAPHTHAQUINONE (UNITS OF m dyne Å, m dyne rad<sup>-1</sup> AND m dyne rad<sup>-2</sup>)

Types of constants	Parameters	Coordinates involved	Values
Stretching	$f_c$	C-C	3.367
	$f_r$	C=C	7.307
	$f_p$	C=O	11.207
	$f_q$	C-Cl	3.728
	$f_s$	C-H	4.586
Bending	$f_\alpha$	CCC	0.556
	$f_\beta$	CCO	1.063
	$f_\gamma$	CCCl	0.562
	$f_\theta$	CCH	0.325
Stretching-stretching	$f_{tr}$	CC CC	0.278
	$f_{ts}$	CC CH	0.224
	$f_{tp}$	CC CO	0.380
	$f_{tq}$	CC CCl	0.291
	$f_{t\theta}$	CC CCl	0.306
Stretch-bend	$f_{i\alpha}$	CC CCC	0.216
	$f_{i\theta}$	CC CCH	0.185
	$f_{i\beta}$	CC CCO	0.223
	$F_{p\gamma}$	CO CCl	0.269
	$f_{q\gamma}$	CCl CCl	0.285
	$f_{q\alpha}$	CCl CCC	0.099
Bend-bend	$f_{\alpha\alpha}$	CCC CCC	0.037
	$f_{\alpha\theta}$	CCC CCH	0.053
	$f_{\alpha\gamma}$	CCC CCO	0.083
	$f_{\beta\gamma}$	CCO CCl	0.072
	$f_{\beta\theta}$	CCO CCH	0.038

## RESULTS AND DISCUSSION

The structural point of view 2,3-dichloro-1,4-naphthaquinone molecular belongs to Cs point group symmetry. The compound has 48 normal mode vibrations, these can be classified into 33A' and 15A'' according to symmetry species of Cs point group symmetry. The A' and A'' species represent the in plane and out -of-plane vibrations, respectively. The observed frequencies of the compound together with relative intensities, probable assignments, calculated frequencies and PEDs are presented in Table-2. The vibrational assignments are discussed below:

**C-H Vibrations:** The aromatic structure shows the presence of CH stretching vibrations in the region 3100-3000 cm<sup>-1</sup> which is the characteristic region for the ready identi-

fication of CH stretching vibrations<sup>3,4</sup>. Accordingly, the Raman bands observed in this study at 3173, 3081, 3031 and 2988 cm<sup>-1</sup> are assigned to CH stretching modes of vibrations for the compound. The frequency shift is due to inclusion of chlorine atoms in the ring<sup>5</sup>. The in-plane and out-of plane bending vibrations are listed in the Table-2.

**C=O Vibrations:** The carbonyl bonds are the most characteristic bands of infrared and Raman spectra. Both the carbon and oxygen atoms of the carbonyl group move during the vibration and they have nearly equal amplitudes. The carbonyl frequencies can be considerable altered by intra molecular hydrogen bonding. A great deal of structural information can be derived from the exact position of the carbonyl stretching absorption peaks. Normally carbonyl group vibrations<sup>5,6</sup> occur in the region 1750-1500 cm<sup>-1</sup>.

Accordingly in the present study the FTIR band observed at 1671cm<sup>-1</sup> and the IR bend at 1591 cm<sup>-1</sup> for the compound have been designated to C=O stretching vibrations. The FT-Raman bands observed at 1135 and 1122 cm<sup>-1</sup> and FT-IR band at 1133 cm<sup>-1</sup> are due to in-plane bending vibrations of carbon and oxygen modes. The out-of-lane bending modes of C=O vibrations are assigned at 782 and 765 cm<sup>-1</sup> are identified in Raman and infrared spectra, respectively. The assignments of C=O in-plane and out-of-plane bending vibrations made in this study are also supported by the literature<sup>7</sup>.

**C-C Vibrations:** The C-C stretching vibrations appears in the region from 1600-1100 cm<sup>-1</sup> and consequently are of little value for structural study. In 2, 3-dichloro-1,4-naphthaquinone the bands identified at 1586, 1559, 1474, 1165, 1093, 1085 and 1032 cm<sup>-1</sup> in the Raman and 1452, 1382, 1349 and 1050 cm<sup>-1</sup> bands in he infrared spectra have been assigned to C-C stretching vibrations.

**C-Cl Vibrations:** Strong characteristic absorption due to the C-Cl stretching vibration was observed in this study. The position of the band is being influenced by the nature of the halide atoms substituted at the 2nd and 3rd position of the naphthalene derivatives. Chloro compounds absorb strongly in the region 750-650 cm<sup>-1</sup> due to the C-Cl starching vibrations<sup>8</sup>.

The strong FT-Raman bands obtained a 688 and 640 cm<sup>-1</sup> for compound have been designated to carbon-chlorine stretching vibration. The fundamental vibrations arising from C-Cl in-plane and out- of plane bending modes are observed in their respective characteristic regions and they were depicted in Table-2. The C-Cl assignments proposed in this study are also in agreement with the literature<sup>9</sup>.

Vibrational coupling with neighboring carbon atoms may result into a shift in the absorption frequencies of the respective compounds. The predominant values of PED obtained for other groups of vibrations listed in Table-2 are also supporting the assignments proposed in this study.

## Conclusion

A complete vibrational analysis of 2,3-dichloro-1,4-naphthaquinone have been carried out. A normal coordinate analysis has been performed that supports the assignments and reveals the mixing of the symmetric bending vibration of this molecule. A force constant in internal coordinate representation is compared well with their characteristic value. The assignment of most of the fundamental provided in this work if believed to

TABLE-2  
FUNDAMENTAL FREQUENCIES (cm<sup>-1</sup>) OF 2,3-DICHLORO-1,4-NAPHTHAQUINONE

Species	Observed frequencies		Calculated frequencies	Assignment (PED %)
	IR	Raman		
A'	–	3173	3153	CH Stretching (85)
A'	–	3081	3062	CH Stretching (87)
A'	–	3031	3014	CH Stretching (85)
A'	–	2988	2964	CH Stretching (85)
A'	–	1671	1658	C=O Stretching (83)
A'	1591	–	1579	C=O Stretching (83)
A'	–	1586	1570	C-C Stretching (83)
A'	–	1559	1542	C-C Stretching (83)
A'	–	1474	1462	C-C Stretching (83)
A'	1452	–	1443	C-C Stretching (83)
A'	1382	–	1375	C-C Stretching (79)
A'	1349	–	1336	C-C Stretching (80)
A'	–	1290	1281	CH in plane bending (66)
A'	1274	–	1266	CH in plane bending (67)
A'	–	1269	1253	CH in plane bending (66)
A'	–	1237	1226	CH in plane bending (67)
A'	–	1165	1154	C-C Stretching (79)
A'	1133	1135	1123	C=O in plane stretching (67)
A'	–	1122	1110	C=O in plane stretching (67)
A'	–	1093	1081	C-C Stretching (79)
A'	–	1085	1075	C-C Stretching (79)
A'	1050	–	1043	C-C Stretching (84)
A'	–	1032	1028	C-C Stretching (76)
A'	–	955	998	Ring in plane bending (66)
A'	–	950	942	Ring in plane bending (65)
A'	–	885	880	Ring in plane bending (65)
A'	878	–	871	Ring in plane bending (65)
A'	–	840	835	Ring in plane bending (65)
A'	818	820	816	Ring in plane bending (65)
A''	–	797	792	C-H out of plane bending (49)
A''	–	782	778	C=O out of plane bending (49)
A''	765	–	761	C=O out of plane bending (49)
A'	–	688	686	C-Cl Stretching (76)
A'	635	640	638	C-Cl Stretching (76)
A''	–	619	615	C-H out of plane bending (49)
A''	–	520	518	C-H out of plane bending (49)
A''	512	–	510	C-H out of plane bending (49)
A''	–	478	478	Ring out of plane bending (52)
A'	–	420	415	C-Cl in plane bending (65)
A'	–	384	382	C-Cl in plane bending (65)
A''	–	350	348	Ring out of plane bending (52)
A''	–	337	335	Ring out of plane bending (52)
A''	–	281	280	C-Cl out of plane bending (52)
A''	–	260	258	C-Cl out of plane bending (52)
A''	–	245	246	Ring out of plane bending (52)
A''	–	208	208	Ring out of plane bending (52)
A''	–	163	162	Ring out of plane bending (52)
A''	–	117	116	Butterfly (50)

be unambiguous. The calculated and observed frequencies agree well with the better frequency fit. The results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the molecule in the solid phase.

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