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Vibrational Assignments and Normal Coordinate
Analysis of 2-Hydroxy-4-methoxybenzophenone

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The FTIR and FT Raman spectra of 2-hydroxy-4-methoxybenzophenone have been recorded. The observed frequencies were assigned to various modes of vibrations on the basis of normal coordinate calculations, assuming Cs point group symmetry. The potential energy distribution associated with normal modes is also reported here. The assignment of fundamental vibrations agrees well with the calculated frequencies.

Key Words: Vibrational spectra, 2-Hydroxy-4- methoxybenzophenone, Normal coordinate analysis.

INTRODUCTION

Benzophenone is a common photosensitize in photo-chemistry. It crosses from the S_1 state into the triplet state with nearly 100 % yield. The resulting diradical will abstract a hydrogen atom from a suitable hydrogen donor to form a ketyl radical. Benzophenone can be used as a photo initiator in UV-curing applications such as inks, imaging and clear coatings in the printing industry. Benzophenone prevents ultraviolet (UV) light form damaging scents and colours in products such as perfumes and soaps. It can also be added to the plastic pack-aging as a UV blocker. This allows manufacturers to package the product in clear glass or plastic. Without it, opaque or dark packaging would be used. Benzophenone is often used to generate such a soluble drying agent. An advantage to this application is the intense blue colour of the ketyl radical anion. Thus, benzo-phenone can be used as an indicator of air-free and moisture-free conditions in the purification of solvents by distillation[1].

Consideration of these factors motivated to record infrared and Raman spectra of 2-hydroxy-4-methoxybenzophenone. Normal coordinate analysis of 2-hydroxy-4-methoxybenzo-phenone was carried out to obtain a more complete description of the molecular motions involved in the fundamental vibrations of 2-hydroxy-4- methoxybenzophenone to study the interesting nature of industrial activity. It appears that no work has been reported on the complete vibrational analysis of this molecule. Hence in the present investigation, an effort has been made to record the spectra and to assign the observed fundamental modes of vibrations. The assignment is supported by normal coordinate analysis with a simplified general valence force field. The calculated frequencies are in good agreement with experiment. The PED (potential energy distribution) obtained in the analysis provide some insight into the nature of normal modes of 2-hydroxyl-4-methoxybenzophenone.

EXPERIMENTAL

The fine sample of 2-hydroxy-4-methoxybenzophenone was provided by Lancaster Chemical Company, UK and used as such without further purification for the spectral measure-ments. The 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^{-1} using Nd: YAG laser operating at 200 mW power continuously with 1064 nm excitation. The room temperature mid infrared spectrum of 2-hydroxy-4-methoxybenzophenone was measured in the region 4000-400 cm^{-1} at a resolution of $\pm$ 1 cm^{-1} using Perkin-Elmer FTIR spectrum RX1 model spectrometer equipped with an MCT detector, a KBr beam splitter and globar source. Boxcar apodization was used for the 250 averaged interferogrames collected for the samples. The FT-IR spectrum was recorded at Archbishob Casimir Instrumentation Centre (ACIC), St. Joseph's College (Autonomous) Trichirappalli-620 002. The FT-Raman spectrum was recorder at ICP Centre, Central Electro-chemical Research Institute (CECRI), Karaikudi-630 006.

Structure and symmerty: The structural point of 2-hydroxy-4-methoxybenzophenone molecule belongs to Cs

point group symmetry. The title compound has 78 normal mode vibrations, these can be classified into

$$\Gamma 3N - 6 = 52A' + 26A''$$

according to symmetry species of Cs point group symmetry. The A' and A" species represent the in-plane and out-of-plane vibrations, respectively.

Method of calculation: The orthonormal set of symmetry coordinates are obtained, by transforming the characters of irreducible representations of the Cs point group. The S vectors have been derived by expression the symmetry coordinates in terms of Cartesian displacement coordinates. The elements of B matrix are obtained by transforming the Cartesian displacement coordinates into internal coordinates. The inverse kinetic energy matrix G is obtained by using the relation.

$$G = B\mu B'$$

where B' is a transpose of B matrix and μ is a diagonal matrix of the reciprocal masses of the atoms in the molecule. The summarized force constant matrix F is constructed by transferring the force constants form similar type of molecules with similar environments. In order to obtain the force constants the secular equation |FG - Eλ| = 0 is to be solved, by Cyvin's W-matrix method[2] it is not convenient to diagonalize the unsymmetrical FG matrix. Cyvin's W-matrix method is a convenient practical way of computing F matrix. The elements of G matrix are factorised using the relation.

$$G = PP'$$

where P is a lower triangular matrix and P' is a transpose of P. Diagnolizing the W matrix, λ values are obtained. The process of refining the force constant has been carried out by least square fit method until all the λ values agree fairly well with the observed values. This method introduces several non-vanishing off- diagonal elements in F; which is very useful to calculate the interaction force constants. Redundant coordinates arising during the computation of force constants can be eliminated, by diagonalizing the summarized G matrix. The structural parameters employed in the evaluation of force constants are taken from Sutton's table[3]. Computer programs of Schachtschneider[4] with necessary changes were used to solve the vibrational secular equation.

Normal coordinate analysis: A normal coordinate analysis of 2-hydroxy-4-methoxybenzophenone has been carried out, using the observed frequencies from the recorded spectra. The evaluation of force constants are made on the basis of general valence force filed, by applying Wilson's FG matrix mechanism[5].

Using the final set of force constants so calculated, the potential energy distribution has been calculated using the relation:

$$PED = \frac{F_{ii}L_{ia}^2}{\lambda a}$$

where F_{ii} = potential constant, L_{ia} = L matrix element and $\lambda a = 4\pi^2 C^2 va$.

Force constants: The best fit force constants obtained in the study for the 2-hydroxy-4-methoxybenzophenone listed in the Table-1. The objective of this investigation is to find out the stretching, bending and interaction force constants corresponding to each substitutent and its position in the ring. The stretching force constants observed in the study for f_p(C-C)

TABLE-1 POTENTIAL ENERGY CONSTANTS OF 2-HYDORXY-4-METHOXYBENZOPHENONE (THE UNITS OF m, dyne Å, m dyne rad⁻¹ AND m dyne rad⁻²)			
Types of constants	Parameters	Coordinates involved	Values
Stretching	f_p	C-C	2.975
	f_α	C=C	6.385
	f_r	C-H	4.536
	f_s	C=O	10.368
	f_T	C-F	3.988
Bending	$f_{\alpha\delta}$	CCC	0.543
	$f_{\beta\sigma}$	CCH	0.266
	$f_{\gamma\psi}$	CCO	1.563
	$f_{\theta\Phi}$	CCF	0.565
Stretching-stretching	f_{pp}	CC CC	0.187
	f_{pT}	CC CF	0.393
	f_{pr}	CC CH	0.244
	f_{ps}	CC CO	0.380
Stretch-bend	$f_{p\delta}$	CC CCC	0.215
	$f_{r\delta}$	CH CCC	0.201
	$f_{p\sigma}$	CC CCH	0.185
	$f_{p\Phi}$	CO CCF	0.209
	$f_{T\sigma}$	CF CCH	0.313
	$f_{P\psi}$	CC CCO	0.223
	$f_{S\delta}$	CO CCC	0.193
Bend-bend	$f_{\delta\delta}$	CCC CCC	0.083
	$f_{\delta\psi}$	CCC CCO	0.037
	$f_{\delta\sigma}$	CCC CCH	0.043
	$f_{\delta\Phi}$	CCC CCF	0.079

atoms are found to be 2.975 m dyne A⁻¹. The potential energy constants between carbon and oxygen f_s(C=O) is found to be 10.368 m dyne A⁻¹ and f_T(C-F) is found to be 3.988 m dyne A⁻¹ for 2-hydroxy-4-methoxybenzophenone. 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.

RESULTS AND DISCUSSION

The observed frequencies of 2-hydroxy-4-methoxybenzophenone together with relative intensities, probable assignments, calculated frequencies and PEDs are presented in Table-2.

O-H vibrations: The FT-IR band observed at 3437 cm⁻¹ in 2-hydroxy-4-methoxy benzophenone, is due to O-H stretching mode of vibration. The assignment of this region is made in accordance with the literature[6] Moreover the OH group interacts with π cloud systems to give a hydrogen bond.

C-H vibrations: The aromatic structure shows the presence of CH stretching vibrations in the region 3100-3000 cm⁻¹ which is the characteristic region for the ready identification of CH stretching vibrations[7,8]. Accordingly, the Raman bands observed in this study at 3082, 3065, 3047, 3012, 2996 and 2949 cm⁻¹ while IR bands at 3020 and 3003 cm⁻¹ are assigned to CH stretching modes of vibrations for 2-hydroxy-4-methoxy-benzophenone. The in-plane and our-of plane bending vibrations are listed in the Table-2.

TABLE-2
FUNDAMENTAL FREQUENCIES (cm⁻¹) OF 2-HYDROXY-4-METHOXYBENZOPHENONE

Species	Observed frequencies		Calculated frequencies	Assignment (PED %)
	FTIR	FT Raman		
A'	3437	–	3419	CH Stretching (99)
A'	–	3082	3070	CH Stretching (98)
A'	–	3065	3058	CH Stretching (98)
A'	–	3047	3041	CH Stretching (98)
A'	3020	–	3007	CH Stretching (99)
A'	–	3012	3000	CH Stretching (97)
A'	3003	–	2985	CH Stretching (95)
A'	–	2996	2981	CH Stretching (97)
A''	–	2949	2941	CH Stretching (97)
A'	2939	–	2927	CH$_3$ asymmetric stretching (85)
A'	2849	–	2831	CH$_3$ asymmetric stretching (84)
A'	2733	–	2717	CH$_3$ asymmetric stretching (84)
A'	1633	–	1623	C=O Stretching (86)
A'	–	1626	1619	C=C Stretching (85)
A''	1595	1594	1584	C=C Stretching (84)
A'	–	1572	1594	C=C Stretching (82)
A'	–	1550	1543	C=C Stretching (82)
A'	–	1526	1517	C=C Stretching (83)
A'	1506	1508	1501	CH$_3$ asymmetric deformation (82)
A'	–	1492	1483	C=C Stretching (84)
A'	–	1450	1440	C-C Stretching (82)
A'	–	1441	1429	CH$_3$ asymmetric deformation (77)
A'	1434	1433	1420	C-C Stretching (81)
A'	–	1411	1400	C-C Stretching (82)
A'	–	1382	1371	C-C Stretching (82)
A'	1348	1348	1333	O-H in plane bending (69)
A'	–	1317	1309	C-C Stretching (82)
A'	–	1305	1295	C-C Stretching (80)
A'	1260	1260	1251	C-C Stretching (82)
A'	1220	1225	1211	CH in-plane bending (72)
A'	–	1202	1195	CH in-plane bending (72)
A'	–	1180	1172	CH in-plane bending (71)
A'	–	1163	1160	CH in-plane bending (72)
A'	–	1115	1113	CO stretching (72)
A'	1109	–	1102	CO stretching (72)
A'	–	1100	1093	CO stretching (72)
A'	–	1076	1080	CH in-plane bending (61)
A'	–	1050	1043	C=O in-plane bending (62)
A'	–	1029	1024	CH in-plane bending (61)
A'	1021	–	1017	CH in-plane bending (61)
A'	–	998	993	CH in-plane bending (61)
A''	–	978	972	O-H out-of-plane bending (52)
A''	–	969	965	CH$_3$ asymmetric deformation (52)
A''	958	–	957	C-H out-of-plane bending (52)
A''	–	950	948	C-H out-of-plane bending (52)
A'	–	940	933	CH$_3$ in-plane rocking (54)
A''	–	931	930	C-H out-of-plane bending (52)
A''	911	–	910	C-H out-of-plane bending (54)
A''	–	888	885	C-H out-of-plane bending (54)
A''	–	855	852	C-H out-of-plane bending (52)
A''	–	840	837	C-H out-of-plane bending (52)
A''	–	831	829	C-H out-of-plane bending (52)
A'	822	–	820	Ring in-plane bending (66)
A'	–	812	813	Ring in-plane bending (62)
A'	–	801	803	Ring in-plane bending (65)
A'	–	794	793	CH$_3$ in-plane rocking (62)
A'	–	786	786	C-C in-plane bending (67)
A'	748	750	751	C-C in-plane bending (64)
A'	–	735	734	Ring in-plane bending (63)
A'	–	709	710	Ring in-plane bending (63)
A'	700	–	700	Ring in-plane bending (62)
A''	–	692	690	C=O out-of-plane bending (52)
A'	–	676	675	C-O in-plane bending (67)

A'	–	650	653	C-O in-plane bending (68)
A'	–	617	615	C-O in-plane bending (66)
A''	–	608	609	Ring out-of-plane bending (52)
A''	598	–	598	Ring out-of-plane bending (54)
A''	–	591	593	Ring out-of-plane bending (54)
A''	–	580	578	Ring out-of-plane bending (52)
A''	529	532	530	Ring out-of-plane bending (52)
A''	–	450	449	CCC out-of-plane bending (50)
A''	–	438	438	CO out-of-plane bending (53)
A''	–	423	423	CO out-of-plane bending (54)
A''	410	413	412	CO out-of-plane bending (53)
A''	–	310	311	CC out-of-plane bending (50)
A''	–	260	261	CC out-of-plane bending (50)
A''	–	248	246	CH₃ torsion (51)
A''	–	221	220	Ring out-of-plane bending (52)

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[9] occur in the region 1750-1700 cm^{-1}.

Accordingly in the present study the FTIR band observed at 1633 cm^{-1} for 2-hydroxy-4-methoxybenzophenone have been designated to C=O stretching vibration. The FT-Raman bands observed at 1050 and 692 cm^{-1}, respectively, is due to in-plane and out-of-plane bending vibrations of carbon and oxygen modes. The assignments of C=O in-plane and out-of-plane bending vibrations made in this study are also supported by the literature[8,10].

CH₃ vibrations: The CH₃ stretching and bending modes appear to be quite pure group vibrations. Considering the assignment of CH₃ group frequencies, it is expected that nine fundamentals can be associated to each CH₃ group, namely the symmetrical and asymmetrical in-plane stretching modes" the symmetrical and asymmetrical, deformation modes; the in-plane rocking and out-of-plane rocking and twisting bending modes. The asymmetric stretching and asymmetric deformation modes of the methyl group is expected to be depolarized for A" symmetry species. The band found at 2939 and 2849 cm^{-1} in IR were assigned to CH₃ asymmetric stretching vibration. The infrared bands observed at 2733 cm^{-1} was due to asymmetric modes were also well established. The band observed at 1506 cm^{-1} in infrared was attributed to asymmetric deformation of methyl group. The symmetrical methyl deformation modes were found at 1441 cm^{-1} in Raman spectrum. The CH₃ deformational modes mainly coupled with the in-plane bending vibrations[11]. The in-plane, out-of-plane modes and torsion modes of the CH₃ group vibrational modes were depicted in the Table-2.

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-hydroxy-4-methoxybenzophenone have been carried out. A normal coordinate analysis has 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. Force constants in internal coordinate representation are compared well with their characteristic values. The assignment of most of the fundamentals provided in this work is believed to 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 to the vibrational spectra of 2-hydroxy-4-methoxybenzene in the solid phase.

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