

Overtone spectroscopy of salicylaldehyde (*o*-hydroxy benzaldehyde)

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Abstract. The overtone spectra of the C–H stretch vibrations in salicylaldehyde (*o*-hydroxy benzaldehyde) at room temperature have been studied in the 200–12000 cm^{-1} region. Vibrational frequencies and anharmonicity constants for the aryl and alkyl C–H stretch vibrations have been determined. It is noted that the O–H stretch vibration does not appear in the structure at all due to strong intramolecular hydrogen-bonding. The effect of OH substitution on the C–H stretch vibrations has been studied.

Keywords. Overtone spectroscopy; local mode model; thermal lensing; anharmonicity; vibrational frequency.

1. Introduction

The overtone spectra of polyatomic molecules have been a subject of interest for several years¹. Most of the earlier studies are limited to the bands involving low vibrational quanta due to their poor sensitivity. The development of new sensitive techniques such as long path absorption², photoacoustics^{3–6}, thermal-lensing^{7–11}, addition of signal by repeated scan etc. have enabled researchers to measure even weak overtone transitions accurately and provide interesting information about the structure of the molecules. Recently, we¹² studied the higher overtones of C–H stretch vibrations in benzaldehyde using conventional IR and thermal-lens techniques. In the present note we report our studies on the overtone spectra of salicylaldehyde where both the aldehyde and the hydroxyl groups are attached to the benzene ring. It is seen that the OH band which appears very strongly in phenol¹³ is totally absent in this case. It is probably due to strong intramolecular hydrogen-bonding. The vibrational frequencies corresponding to the C–H aryl group remain nearly unaffected. However for the alkyl group it is slightly increased with respect to benzaldehyde.

2. Experimental

The sample of salicylaldehyde used (99.9% pure) was obtained from Riedel. It was doubly distilled and filtered using Glaxo 5 μm filter paper before recording the

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spectra. IR spectra were recorded using a Perkin-Elmer IR spectrophotometer (model no. 883) and NIR spectra on a U-3501 spectrophotometer.

3. Results and discussion

Salicylaldehyde is a molecule with the hydroxyl group in an ortho-position to the aldehyde group, as shown in figure 1. The hydrogen of the hydroxyl group is bonded to the oxygen of the aldehyde group by an intramolecular hydrogen-bond. Therefore the peak expected in the region $3200\text{--}3600\text{ cm}^{-1}$ due to the OH-stretching mode does not appear in the structure. Two very sharp peaks due to the fundamental band of C-H bond of aldehyde (alkyl) group appear at 2760 and 2840 cm^{-1} , the first being slightly weaker than the second. These are the characteristic bands of the aldehyde group. Three broad peaks superposed on each other due to the C-H vibrations (aryl) of the benzene ring are observed in the $3020\text{--}3180\text{ cm}^{-1}$ region. A broad peak is observed in the region $1620\text{--}1680\text{ cm}^{-1}$ due to the C-O stretch vibration. There are a large number of other peaks in the $200\text{--}1600\text{ cm}^{-1}$ region. The most prominent of these are at 1458 , 1376 , 1322 , 1227 , 1150 , 882 and 776 cm^{-1} . They are tabulated in the atlas by Schrader¹⁴ and are well assigned and verified by normal coordinate studies¹⁵.

The spectrum in the NIR region again shows a large number of bands, the intensities decreasing at higher frequencies (see figure 2). The first, second and third

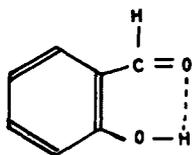


Figure 1. Structure of salicylaldehyde

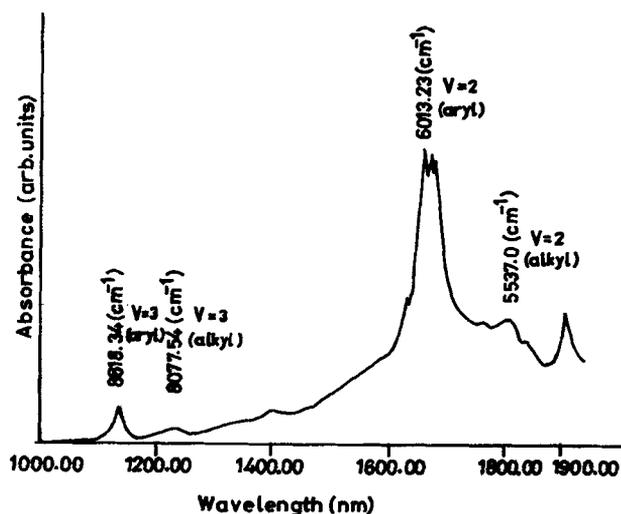


Figure 2. Absorption spectrum of salicylaldehyde in the NIR region

overtone of the C–H stretch (aryl as well as of alkyl) are expected to lie in this region. The other bands may be due to a combination of fundamentals or to fundamentals with different overtones. An analysis of these indicates that the first overtones due to the alkyl group lie at 5426 and 5537 cm^{-1} . These two peaks are much weaker and broader though they still follow the same intensity pattern amongst themselves as in the fundamental. The intensity ratios of peaks are changed from 35:18 to 9:4. The second overtones of these appear very broad and weak and their doublet character cannot be seen any more. The third harmonics of these can also be seen though they are extremely weak.

The first overtone due to the aryl C–H group lies at 6013 cm^{-1} and seems to have more than one component (as also in benzaldehyde). In the second and third overtones, only one peak is observed. It seems that the intensity corresponding to the other peaks is concentrated in only one peak and indicates the necessity of the use of local mode description for higher overtones. Thus, while vibrations corresponding to lower frequency bands can be described on the basis of normal modes, the higher peaks need a local mode model. The frequencies of the harmonics for the alkyl and the aryl peaks are given in table 1. Three more bands are observed for this molecule in the NIR region at 5260, 5681 and 7107 cm^{-1} . The bands at 5260 and 7107 cm^{-1} are quite intense whereas the third one is weak. The assignment of these bands is given in table 2. These bands also appear in the benzaldehyde molecule.

The appearance of double peaks for the alkyl C–H stretch band in the aldehydes is a common feature for all aldehyde compounds. There are three hypotheses proposed in the literature for this.

- (i) It is believed that the two peaks are due to Fermi resonance between C–H fundamental and the combination band of C–H deformation with C=O stretch¹⁶.
(ii) The two peaks are due to symmetric and asymmetric stretch of the C–C bond with the C–H bond¹⁷.

Table 1. Transition frequencies of fundamental and different overtones for CH stretch vibrations in salicylaldehyde.

Group	$\nu = 1$ (cm^{-1})	$\nu = 2$ (cm^{-1})	$\nu = 3$ (cm^{-1})	$\nu = 4$ (cm^{-1})
Alkyl	(2840.0)*	(5537.0)	(8077.0)	(10471.0)
	2842.2	5534.8	8077.7	10471.0
Aryl	(2760.0)	(5426.0)	(8077.0)	(10471.0)
	2777.6	5452.4	8024.2	10493.1
Aryl	(3071.0)	(6013.2)	(8818.0)	(11534.0)
	3065.0	6008.0	8830.0	11529.0

*Observed values in parentheses

Table 2. Assignment of the combination bands.

Peak frequencies (cm^{-1})	Assignment of band
5260.0	Aryl CH stretch and two quanta of CH in plane bending
5681.0	Alkyl CH stretch and two quanta of CC stretch
7107.0	First overtone of alkyl CH stretch and of CO stretch

Table 3. Vibrational frequencies, anharmonicity constants and dissociation energies for alkyl and aryl CH stretch vibrations in salicylaldehyde.

Group	B (cm ⁻¹)	$C \sim -\omega_e x_e$ (cm ⁻¹)	$\omega_e \sim B + C$ (cm ⁻¹)	$\Delta G_{1/2}$ (cm ⁻¹)	D_e (eV)
Alkyl	2917.0	74.8	2991.8	2842.2	3.69
	± 1.7	± 0.5	± 2.2	± 1.2	± 0.02
		(75.3)	(2952.7)		
		± 2.9	± 13.0		
Aryl	2829.1	51.4	2880.5	2777.6	5.23
	± 34.9	± 10.2	± 45.1	± 24.7	± 1.19
		(56.3)	(2862.9)		
		± 7.1	± 31.6		
Aryl	3126.5	61.1	3187.6	3065.3	5.16
	± 7.8	± 2.3	± 10.1	± 5.5	± 0.22
		(61.2)	(3187.8)		
		± 1.2	± 7.4		

*Values in parentheses are for benzaldehyde

(iii) They are due to the presence of two conformers of the CHO group, one in the plane of the molecule and the other perpendicular to the plane.

The second hypothesis does not appear reasonable as the C–C stretch frequency is very different from the C–H stretch. A coupling of these two frequencies will be very weak. Moreover a normal coordinate analysis totally discards this coupling¹⁵. The idea of two conformers also does not appear satisfactory as higher harmonics of the two peaks also appear with appreciable intensity. Thus, the idea of Fermi resonance seems more justified. Our measurements support this view.

The separation between the two peaks corresponding to the first overtone is slightly larger than in their fundamentals. The increase in level separation weakens the Fermi interactions. So the two peaks appear with different intensities. This is exactly what we observe in the structure. We calculated the vibrational stretching frequencies and the anharmonicity constants for the two C–H groups (alkyl and aryl) using a least squares fit to the quadratic equation,

$$E_{v,0} = Bv + Cv^2,$$

where $E_{v,0}$ is the energy separation of the fifth level from its zeroth level. B and C are the fitting constants. They are related to the vibrational frequency as $\omega_e \sim (B-C)$ and the anharmonicity constant $\omega_e x_e \sim -C$. A least squares fit procedure given by Birge¹⁸ was used to evaluate the values of B and C and ω_e and $\omega_e x_e$ in turn could be evaluated from these. We also estimated the errors in these constants. The frequency values calculated using these constants are also compared with the measured values in table 1. As is clear from the table the bands of the aryl group and the peak corresponding to the higher frequency component of the alkyl group show excellent fit with < 1% error. However the fit for another alkyl peak here is again poor. The $\omega_e x_e$ values for the two alkyl peaks are very different from each other. It appears that the higher frequency component of the two is due to the C–H stretch of the CHO,

and the lower one is due to the combination band, while the doublet occurs due to Fermi-resonance. The constants thus obtained in the two cases are compared in table 3.

$\Delta G_{1/2}$ values have also been calculated for both the cases (aryl and alkyl) and are compared with the respective fundamental transition frequencies in table 3. We also estimated the dissociation energies for the aryl and alkyl groups using the Morse relation ($\omega_e^2/4\omega_e x_e$). The values thus obtained are 5.16 ± 0.22 eV for the aryl and 3.69 ± 0.017 eV and 5.23 ± 1.19 eV for the two alkyl groups. A similar observation is seen in the case of the benzaldehyde molecule as well.

Comparison of the molecular constants and dissociation energies for the two C–H vibrations in benzaldehyde with those of salicylaldehyde indicates that for the aryl group the vibrational frequency, anharmonicity constant and the dissociation energy remain nearly unaffected. However, the vibrational frequency for the two vibrations of the alkyl group in salicylaldehyde appears slightly larger than in benzaldehyde. This is probably due to a slight increase in the angle between the C=O and the C–H bonds of the CHO group due to hydrogen bonding with the hydroxyl group. The interaction between oxygen of the C=O group and the hydrogen of the hydroxyl group has become stronger. The C–H bond of CHO is thus more free for oscillations in salicylaldehyde.

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