

Overtone spectroscopy of some benzaldehyde derivatives

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Abstract. Overtone spectrum of *o*, *m* and *p*-nitrobenzaldehydes and *p*-chlorobenzaldehyde has been studied in 2000–12000 cm^{-1} region. Vibrational frequencies and anharmonicity constants for aryl as well as alkyl CH stretch vibrations have been determined. We have also determined the internuclear distances for the aryl CH bond in the different molecules. The small variation observed in these distances is an indication of the substitution effect.

It is observed that in the case of *p*-disubstituted benzenes, the shift in aryl CH bond is proportional to sum of the Hammett σ of the substituents. However in the case of *o*-disubstituted benzenes it is only 80% of the para-substituted shift.

Keywords. Overtone spectroscopy; aryl CH; alkyl CH; Hammett σ ; inductive effect.

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1. Introduction

The overtone spectrum of benzaldehyde and *o*-hydroxybenzaldehyde has been studied recently [1,2 and references therein]. It is observed that in the spectral region of the alkyl CH stretch vibration two peaks are seen due to Fermi resonance. The resonance doubling is seen to persist even in the region of the harmonics. In many other benzaldehyde compounds no such doubling is observed.

It is well-known that frequencies of the vibrational modes undergo changes when substitutions are introduced at the position of the hydrogens in benzene. Such shifts have been extensively documented in mono substituted benzenes but are less studied in multisubstitutions. Mizugai and Katayama [3–5] have shown that such shifts in the case of *p*-disubstituted benzenes are approximately equal to the sum of the frequency shifts in the corresponding monosubstituted benzenes. For the case of ortho- and meta-disubstitutions and when the two substituents are dissimilar no such simple rules remain valid. The present studies on the overtone spectroscopy of *o*, *m* and *p*-nitro and *p*-chlorobenzaldehyde have been undertaken with the following objectives:

1. To see if the Fermi resonance seen in the alkyl CH stretch region for benzaldehyde, ortho hydroxy and methoxy benzaldehydes is present in the present group of compounds.

2. To see if the observation made by Mizugai and Katayama about the frequency shifts in the disubstituted benzenes remain valid in these cases.
3. To use the local mode treatment to assess the molecular parameters e.g. harmonic frequencies, anharmonic constants and the dissociation energy for the CH bond both in the alkyl and in the aryl groups.

2. Experimental

The samples of *p*-chlorobenzaldehyde as well as of *o*, *m* and *p*-nitrobenzaldehydes were obtained from M/s. E Merck, India with a reported purity of 99.8%. No further purification was made. The spectra of these solid samples were recorded either in the form of a nujol mull or a KBr pellet. The relative concentration of the sample were optimized to obtain good spectra. The NIR spectra (5000–12000 cm^{-1}) were recorded using a Cary 2390 double beam spectrophotometer while the IR spectra (200–4000 cm^{-1}) were recorded on a Perkin Elmer 883 spectrophotometer. The NIR spectra particularly above 10,000 cm^{-1} were found very weak and broad. We therefore made repeated scans in order to ensure their realities.

3. Results

3.1 IR spectrum

As mentioned earlier, the IR spectrum of benzaldehyde shows two sharp peaks one at 2730 and other at 2815 cm^{-1} in the region 2700–2850 cm^{-1} i.e. where the fundamental band ($\sim 2750 \text{ cm}^{-1}$) of the CH stretch vibration of the aldehyde group is expected. Two peaks in this region are also observed for *o*-hydroxy, dihydroxy and methoxybenzaldehyde [2,6]. The appearance of two peaks is explained as due to Fermi resonance between the alkyl CH stretching fundamental mode and a combination mode consisting of CH deformation and C=O stretch. However, in *p*-dichlorobenzaldehyde; and *o*, *m* and *p*-nitrobenzaldehydes only a single peak is observed at 2856, 2857, 2865 and 2849 cm^{-1} respectively. Since these observed frequency values are similar to the higher frequency components of the Fermi resonance doublet in other molecules, it is possible that this interaction is present in these compounds also, but the lower frequency component is too weak to be observed.

Along with the alkyl CH peak, an absorption peak due to the aryl CH group also appears in the above region of the spectrum. Thus in the case of *p*-chlorobenzaldehyde two absorption peaks at 3095 cm^{-1} and a weak one at 3050 cm^{-1} are seen. For *o*-nitrobenzaldehyde a strong peak is observed at 3104 cm^{-1} accompanied with two relatively weak peaks. Meta and parabenzenaldehyde show a strong peak at 3098 cm^{-1} and 3106 cm^{-1} respectively along with several close lying components in each case.

3.2 NIR spectrum

The NIR spectrum of these molecules show harmonics corresponding to $v' = 2, 3$ and 4 of both aryl and alkyl CH stretching modes. One also observes several combination bands in this region (see figures 1 and 2). As can be seen from these figures, the intensity of the

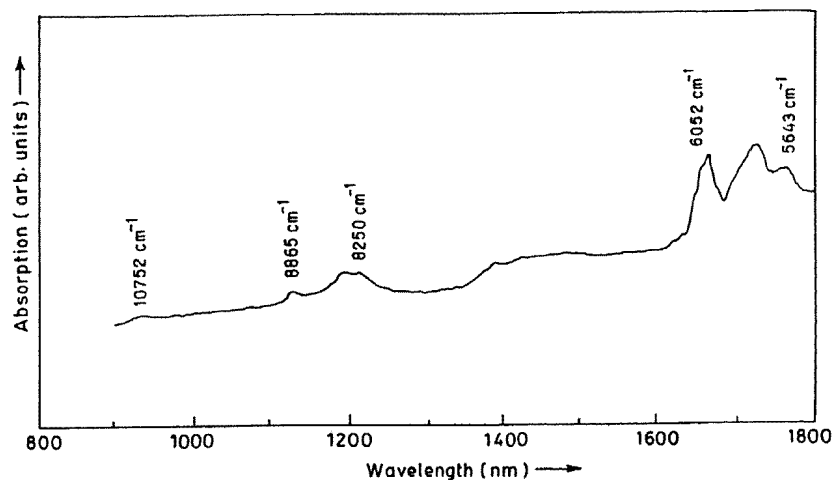


Figure 1. Absorption spectrum of *p*-chlorobenzaldehyde in NIR region.

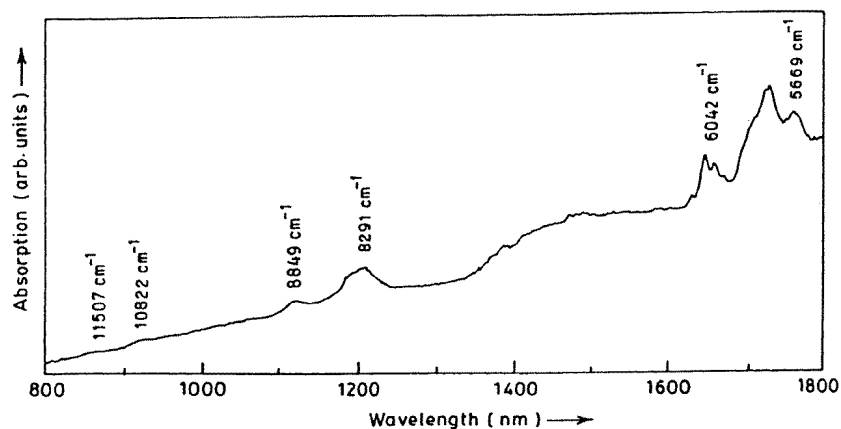


Figure 2. Absorption spectrum of 3-nitrobenzaldehyde in NIR region.

bands decreases very rapidly as Δv increases. For example, the NIR spectrum of *o*-nitrobenzaldehyde shows absorption peaks at 5678, 5806, 6046, 8298, 8865, 10823 and 11534 cm^{-1} of which the peaks at 5678, 8298 and 10823 correspond to $0 \rightarrow 2$, $0 \rightarrow 3$ and $0 \rightarrow 4$ transitions of the alkyl CH vibration whereas the bands at 6046, 8865 and 11534 cm^{-1} belong to the corresponding transitions of the aryl CH vibration. The strong band observed at 5806 cm^{-1} is perhaps due to a combination mode. The band observed at 8298 cm^{-1} appears to be a doublet. Similar spectrum is observed for the meta and para nitrobenzaldehyde molecules also except that in these molecules the $\Delta v = 2$ band due to the aryl group also appears as double.

Table 1. Transition frequencies (cm^{-1}) for different aryl CH overtones in benzaldehyde and substituted benzaldehyde.

Sample	$\Delta v = 1$	$\Delta v = 2$	$\Delta v = 3$	$\Delta v = 4$	$\Delta v = 5$	$\Delta v = 6$
Benzaldehyde	3075 (60) *3060 # –	5988 (122) 5998 5995	8802 (155) 8813 8799	11521 (186) 11507 11468	– – –	16523 (126) 16525 16541, 16525 ⁺
Salicylaldehyde	3071 (64) *3065	6013 (160) 6008	8818 (177) 8830	11534 – 11529	– –	– –
<i>p</i> -Chloro benzaldehyde	3095 (34) *3096	6052 (51) 6051	8865 (164) 8865	– – 11539	– –	– –
2-Nitro benzaldehyde	3104 (36) *3099	6046 (57) 6052	8865 (166) 8860	11534 – 11521	– –	– –
3-Nitro benzaldehyde	3098 (29) *3095	6042 (44) 6045	8849 (193) 8848	11507 – 11507	– –	– –
4-Nitro benzaldehyde	3106 (34) *3103	6060 (52) 6064	8888 (181) 8887	11560 – 11561	– –	– –

() → FWHM values; * → calculated values; # → ref. [12]; + → ref. [4].

Table 2. Transition frequencies (cm^{-1}) for different alkyl CH overtones in benzaldehyde and substituted benzaldehydes.

Sample	$\Delta v = 1$	$\Delta v = 2$	$\Delta v = 3$	$\Delta v = 4$
Benzaldehyde	2815 *2802	5446 5454	7949 7954	10309 10305
Salicylaldehyde	2840 *2842	5537 5535	8077 8078	10471 10471
<i>p</i> -Chloro benzaldehyde	2856 *2875	5643 5626	8250 8254	10752 10753
2-Nitro benzaldehyde	2857 *2852	5678 5654	8298 8300	10823 10826
3-Nitro benzaldehyde	2865 *2884	5669 5659	8291 8296	10822 10821
4-Nitro benzaldehyde	2849 *2878	5672 5640	8271 8283	10810 10809

* → Calculated value.

The NIR spectrum of *p*-chlorobenzaldehyde is very similar to that for nitrobenzaldehyde. However, the bands in this case are relatively sharper. The absorption bands in all

these molecules appear at somewhat higher wave number as compared to the corresponding bands in benzaldehyde. The frequency of the different peaks for the alkyl and aryl CH bands are listed in tables 1 and 2. For the sake of comparison the frequencies of the corresponding bands in benzaldehyde and *o*-hydroxybenzaldehyde are also given.

4. Discussion

We have calculated the mechanical frequency and the anharmonicity constant for the aryl and the alkyl CH stretch vibrations for all these four molecules using the local mode model [7–9]. According to this model the transition energy for the $0 \rightarrow v$ absorption is expressed as

$$\Delta E_{v,0} = Av + Bv^2,$$

where A and B are the characteristic constants for the molecule. They are related to the vibrational frequency ω_e and the anharmonicity constant $\omega_e x_e$ as

$$\omega_e x_e = -B \quad \text{and} \quad \omega_e = A - B.$$

The constants A and B were evaluated using least squares fitting of the observed transition frequencies. Since the bands involving $v = 0 \rightarrow 4$, transition nearly in all the molecules are very weak and broad and involve large uncertainty, therefore at first we disregarded these particular bands in our fit and estimated the vibrational constants with the remaining bands. Only after we are reasonably sure of our fit, we extrapolated to the next higher overtone. When we find that the extrapolations match with weak and broad features within the estimated errors, we took these data and included in the final estimation of the constants. The goodness of the fit is seen from a comparison of the observed frequencies with those calculated using these constants. The molecular constants ω_e and $\omega_e x_e$ along with the estimated errors in these values are listed in tables 3 and 4. The dissociation energies for alkyl and aryl CH bonds estimated using the relation $D_e = \omega_e^2 / 4\omega_e x_e$ are also listed.

From table 3 it is noted that the vibrational frequencies of the aryl CH stretch vibrations follows the trend.

ω_e (benzaldehyde) < ω_e (*o*-hydroxybenzaldehyde) < ω_e (*p*-chlorobenzaldehyde) < ω_e (nitrobenzaldehyde).

This is in accordance with the values of the inductive part of the Hammett σ for the different substituents [4,10,11]

$$\text{OH}(0.28) < \text{CHO}(0.35) < \text{Cl}(0.51) < \text{NO}_2(0.70).$$

This indicates that the inductive effect plays a predominant role in causing the frequency shift and the contribution of the resonance effect is small. Mizugai and Katayama [4] and later on Gough and Henry [10] in their studies on monosubstituted benzenes have shown that the shift in the frequency of the CH vibrations are proportional to the Hammett σ of the substituents. In the case of the *p*-disubstituted benzenes the shift is linearly proportional to the sum of the Hammett σ of the two substituents. These studies are limited to mostly identical substituents. From our measurements we note that in the case of *p*-disubstituted benzenes the same relation holds even when the two substituents are different. A curve representing the frequency shift (for $\Delta v = 3$) versus sum of the Hammett σ is shown in figure 3 and the values are listed in table 5.

Table 3. Vibrational frequencies, anharmonicity constants and dissociation energies for aryl CH bond in benzaldehyde and substituted benzaldehydes.

Sample	A (cm^{-1})	$-B(\sim \omega_e x_e)$ (cm^{-1})	$A - B(\sim \omega_e)$ (cm^{-1})	$\Delta G_{1/2}$ (cm^{-1})	D_e (cm^{-1})
Benzaldehyde	3121.6 ± 6.2	61.2 ± 1.2	3182.8 ± 7.4	3060.4 ± 8.6	41388 ± 648
Salicylaldehyde	3126.5 ± 7.8	61.1 ± 2.3	3187.6 ± 10.1	3065.4 ± 12.4	41644 ± 1831
<i>p</i> -Chloro benzaldehyde	3166.4 ± 1.6	70.4 ± 0.6	3236.8 ± 2.2	3095.9 ± 3.3	37197 ± 361
2-Nitro benzaldehyde	3172.3 ± 5.17	73.1 ± 1.5	3245.0 ± 6.7	3099.5 ± 8.2	36056 ± 888
3-Nitro benzaldehyde	3167.9 ± 2.1	72.8 ± 0.6	3240.6 ± 2.7	3095.1 ± 3.3	36072 ± 362
4-Nitro benzaldehyde	3174.5 ± 3.6	71.1 ± 1.1	3245.6 ± 4.7	3103.5 ± 5.8	37070 ± 660

Table 4. Vibrational frequencies, anharmonicity constants and dissociation energies for alkyl CH bond in benzaldehyde and substituted benzaldehydes.

Sample	A (cm^{-1})	$-B(\sim \omega_e x_e)$ (cm^{-1})	$A - B(\sim \omega_e)$ (cm^{-1})	$\Delta G_{1/2}$ (cm^{-1})	D_e (cm^{-1})
Benzaldehyde	2877.4 ± 10.1	75.3 ± 2.9	2952.7 ± 13.0	2802.1 ± 15.9	29001 ± 1383
Salicylaldehyde	2917.0 ± 1.7	74.8 ± 0.5	2991.8 ± 2.2	2842.2 ± 2.7	29917 ± 244
<i>p</i> -Chloro benzaldehyde	2938.0 ± 13.8	62.4 ± 4.0	3000.5 ± 17.8	2875.7 ± 21.8	36248 ± 2764
2-Nitro benzaldehyde	2947.2 ± 20.6	60.2 ± 6.0	3007.5 ± 26.6	2887.0 ± 32.6	38007 ± 4467
3-Nitro benzaldehyde	2944.6 ± 14.8	59.7 ± 4.3	3004.3 ± 19.1	2884.9 ± 23.4	38007 ± 3230
4-Nitro benzaldehyde	2937.9 ± 24.3	58.9 ± 7.0	2996.8 ± 31.3	2878.9 ± 38.3	38774 ± 5445

From the measurements of *o*-hydroxybenzaldehyde and *o*-nitrobenzaldehyde we noted that the shifts in these cases are smaller ($\sim 80\%$) of the shift in the case of the *p*-disubstituted molecules. Gough and Henry [10] also found similar results from their studies of disubstituted benzenes. No such general conclusion is arrived at for *m*-disubstituted benzenes.

It seems that in the case of *p*-disubstituted benzene, the substituents interact very little with each other and the total effect is the sum of the individual contribution. However, in the case of *o*- and *m*-disubstituted benzenes, their interaction causes a departure from the additivity.

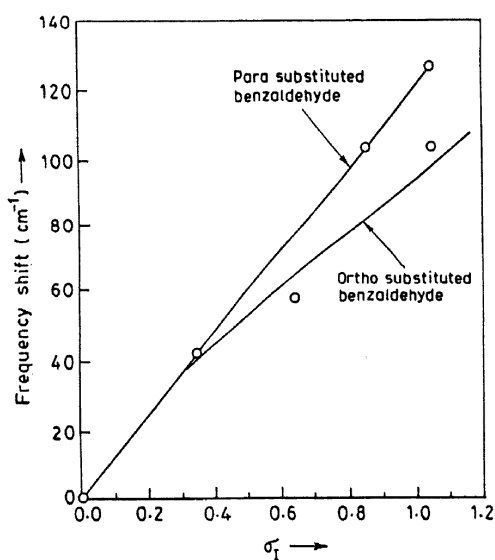


Figure 3. A plot of Hammett σ_1 versus frequency shift in $\Delta\nu = 3$ region in benzaldehyde and substituted benzaldehydes.

Table 5. Frequency shift ($\Delta\nu$) with respect to benzene in $0 \rightarrow 3$ transition and corresponding σ Hammet value for different substituents.

Compound	Frequency (cm ⁻¹)	Shift (cm ⁻¹)	Group	σ_1 ref. [5]	σ_{eff} ($\sigma_1 + \sigma_2$)
Benzene	8760	—	H	0.00	0.00
Benzaldehyde	8803	+43	CHO	0.35	0.35
Salicylaldehyde	8818	+58	CHO, OH	0.35 0.28	0.63
<i>p</i> -Chloro benzaldehyde	8865	+105	CHO, Cl	0.35 0.51	0.86
2-Nitro benzaldehyde	8865	+105	CHO, NO ₂	0.35 0.71	1.06
3-Nitro benzaldehyde	8849	+89	CHO, NO ₂	0.35 0.71	1.06
4-Nitro benzaldehyde	8888	+128	CHO, NO ₂	0.35 0.71	1.06

We have also estimated the CH bond length (r_{CH}) of the aryl bond for these molecules using the relation

$$r_{\text{CH}} = 1.0833 - [8 \times 10^{-5}(\Delta\nu/v)],$$

where 1.0833 corresponds to CH bond length in benzaldehyde and $\Delta\nu$ is the frequency shift in cm⁻¹. The values thus obtained for the different molecules are given in table 6.

Table 6. Bond length (Å) for benzaldehyde and substituted benzaldehydes.

Compounds	r_{CH} (Å)
Benzaldehyde	1.0833
Salicylaldehyde	1.0829
<i>p</i> -Chlorobenzaldehyde	1.0816
2-Nitro benzaldehyde	1.0816
3-Nitro benzaldehyde	1.0821
4-Nitro benzaldehyde	1.0810

5. Conclusion

For *p*-disubstituted benzenes the shift in frequency is the sum of the shifts caused by the individual substituents whether they are similar or dis-similar. However, a departure is observed in the case of *m* and *o*-disubstitution perhaps due to interaction amongst the substituents. The peak observed for alkyl CH stretch vibration in *o*, *m* and *p*-nitrobenzaldehydes and *p*-dichlorobenzaldehyde are shifted by Fermi resonance. The other peak towards the lower energy side is perhaps too weak to be observed.

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