Overtone spectroscopy of benzaldehyde

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Abstract. The vibrational overtone spectra of aryl and alkyl C–H stretch vibrations in benzaldehyde have been studied using conventional IR and thermal lensing technique at room temperature. The stretching vibrational frequency ω_e, anharmonicity constant $\omega_e x_e$ and the dissociation energies of the two C–H bonds have been calculated. The bond length of C–H bond in aryl position has been estimated.

Keywords. Overtone spectroscopy; Benzaldehyde.

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1. Introduction

Overtone spectroscopy of polyatomic molecules is of fundamental importance in understanding the photochemical reactions and non-radiative energy transfers. The normal coordinate description of molecular vibrations fail to describe satisfactorily the higher overtones in these molecules and the local mode model proposed by Henry [1] is used to describe the appearance of these bands. Recently we [2] have studied the higher harmonics of C–H stretch vibrations in several substituted benzenes using conventional IR and dual beam thermal lens technique. The carbon atom in the C–H bond in these molecules belong to the parent ring and C–H group known as aryl group have been studied. In the present note we have studied the overtone spectra of C–H stretch vibration in benzaldehyde which contains two C–H stretch vibrations, the aryl group and the other alkyl group (the C–H bond of the aldehyde group). A detailed study of the same are presented here.

2. Experimental

The experimental method used has been described in our earlier paper [2]. In brief, for IR spectrum we have used Perkin Elmer IR spectrophotometer (Model No. 883). The NIR spectra were recorded using Cary 2390, Varian Associates. The fifth overtone of aryl group and the sixth overtone of alkyl group lie in our dye laser region $(17550–15650\,\text{cm}^{-1})$ and they have been studied using dual beam thermal lens technique. We have used benzaldehyde (Riedel) of 99·99% purity. Pure benzaldehyde shows beautiful needle-like crystals if left in the open. The liquid was doubly distilled and filtered with a 2–5 μm filter (Glaxo India) to avoid any dust or crystal in the sample. The fundamental, first, second and third overtones could be recorded using earlier mentioned spectrometers. The higher harmonics beyond this could not be recorded using spectrophotometers due to their weak intensities. This fifth overtone

of the aryl group and the sixth overtone of the alkyl group could be recorded using dual beam thermal lens technique. Several sets of spectra were recorded here. The maximum uncertainty in this case is $\sim 15\,\text{cm}^{-1}$ whereas the IR or NIR measurements involve large errors (up to $25\,\text{cm}^{-1}$).

3. Results

The structure of benzaldehyde molecule is shown in figure 1. The CHO group in the molecule lies in its molecular plane. The angle between C–H and C=O bond is of the order of 130°, so there is no interaction between oxygen and hydrogen atom. Thus there should not be any intermolecular O–H bond in the structure. However there may be intermolecular hydrogen bonding and a weak peak of small frequency due to this should appear in the structure. In fact peak due to weak O–H bond has been observed in the far IR region in this molecule. The aldehyde group C–H stretching fundamental band lies in between $2700\text{–}2750\,\text{cm}^{-1}$ and gives a very sharp peak in this region. The C–O-stretch vibration on the other hand, gives a quite broad peak near $1700\,\text{cm}^{-1}$. The IR spectrum also shows a strong broad peak with several components merged together in the range of $3000\text{–}3100\,\text{cm}^{-1}$. These peaks are due to aryl C–H vibrations.

The NIR spectrum corresponding to different harmonics of C–H aryl group is shown in figure 2. Whereas the first overtone peak appears to have several components, the higher overtones show only one peak. It appears that the intensity which is distributed in several CH modes are now localized in only one C–H mode (symmetric mode). This clearly indicates that whereas the fundamental and the first overtone of C–H stretch vibration can be described satisfactorily under normal mode description, for the second, third overtones, the local mode consideration is essential. The thermal lensing spectrum corresponding to fifth overtones of aryl group is also shown in the same figure.

The fundamental peak for alkyl group appears at $2730\,\text{cm}^{-1}$. This peak is very sharp and intense. A broad intense peak appears near $5332\,\text{cm}^{-1}$ and a weak peak at $5376\,\text{cm}^{-1}$. Initially it was thought that the intense peak belonged to second harmonics of alkyl group. However it is found that the weak peak fits better than the intense one. The intensity of the third harmonic peak is larger than the weak peak taken as second harmonic (see figure 3). It appears that the second harmonic peak of this is perturbed by some combination band. The fourth harmonics appear with very weak intensity. Though we could not observe the fifth and sixth harmonics, the seventh harmonics which lie in our dye laser region could be marked by dual beam thermal lens technique at $17018\cdot4\,\text{cm}^{-1}$. We noted that the intensity of the
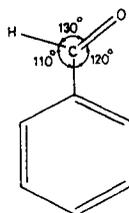
STRUCTURE OF BENZALDEHYDE

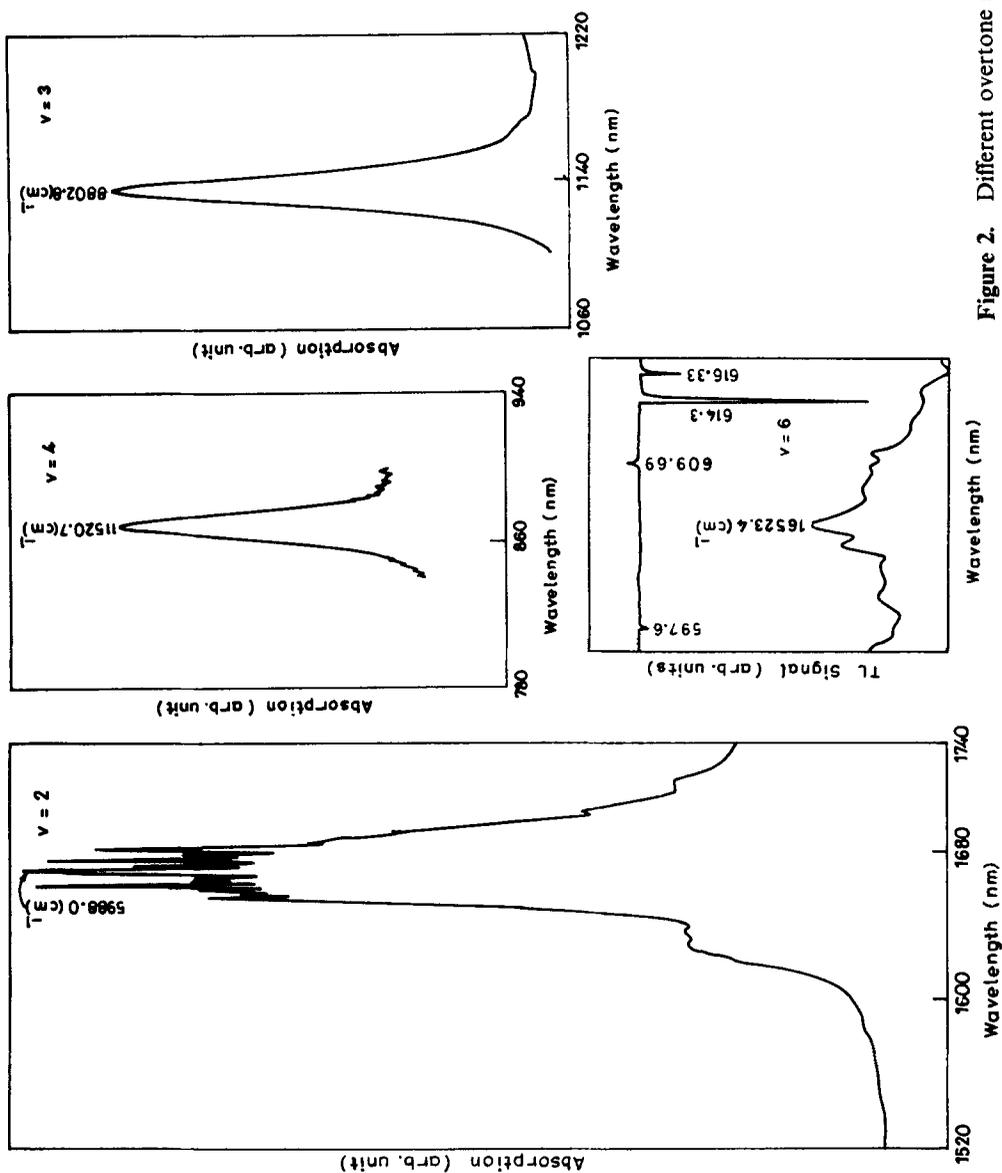**Figure 1.** Structure of benzaldehyde.

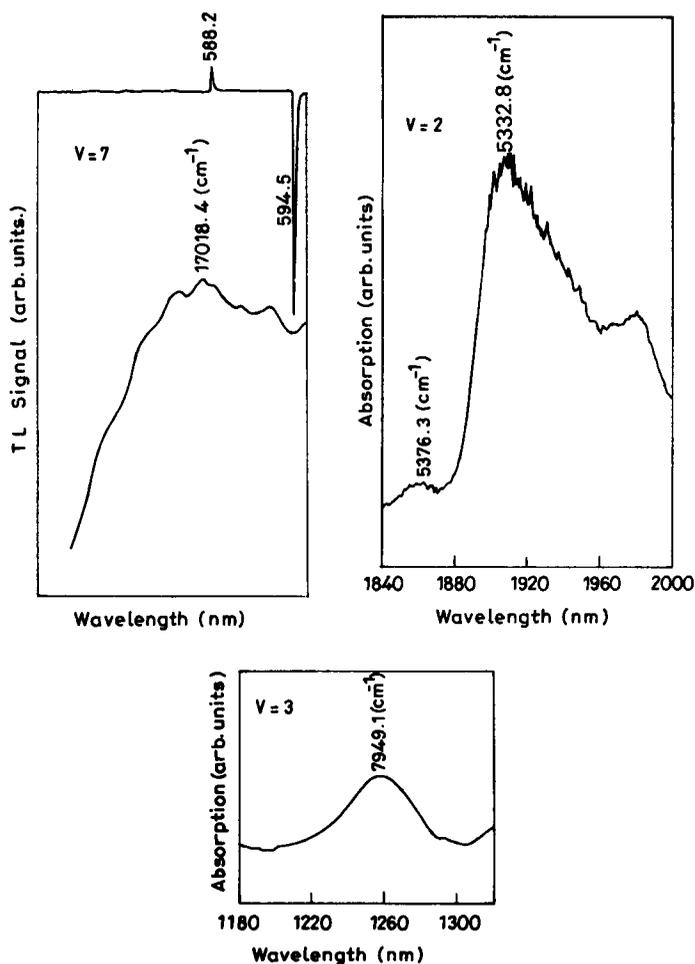**Figure 2.** Different overtone spectra of CH aryl group.

Figure 3. Different overtone spectra of CH alkyl group.

different peaks decreases rapidly as we go to higher harmonics. The intensities of the different peaks with respect to fundamental in the aryl group are 1/5, 1/50, 1/90, 1/200. This indicates that the absorption coefficients for higher harmonics decrease rapidly. We have also measured the width (FWHM) of different peaks in both the cases. The width of the peaks increases as we go to higher energies. The absorption frequencies corresponding to different peaks along with their full width at half maxima for both the C–H vibrations are given in table 1. Mizugai and Katayama [3] have also reported the lensing spectrum of this molecule and have given a value of 16525 cm^{-1} for the fifth overtones or aryl group. We get this peak at 16523 cm^{-1} in our thermal lensing spectrum which is the same. To determine the stretching frequency and anharmonicity constant, the frequencies corresponding to different harmonics for the two CH groups were fitted separately to the quadratic equation

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

where $E_{v,0}$ represents the energy separation of the vth level of CH vibration in the ground state from its 0th vibrational level. The terms B and C are the constants of

Table 1. Transition frequencies of different overtones in benzaldehyde for aryl and alkyl groups.

	Frequency (cm^{-1})						
	$v = 1$	$v = 2$	$v = 3$	$v = 4$	$v = 5$	$v = 6$	$v = 7$
Aryl group	3075 (60)	5988·0 (122)	8802·8 (155)	11520·7 (186)	— —	16523·0 (126)	
Alkyl group	2730 (25)	5376·0 (26)	7949·1 (228)	10309·0 (254)	— —	— —	17018·4 (142)

Quantities in parentheses represent the FWHM of the peaks.

Table 2. Vibrational frequency and anharmonicity constant for the CH stretch vibration of benzaldehyde (cm^{-1}).

Group	B	$C(= \omega_e x_e)$	$B - C$ $(= \omega_e)$	$\Delta G_{1/2}$ $(\omega_e - 2\omega_e x_e)$	$\Delta G_{1/2}$ value from IR spectra
Aryl	3121·6 ± 6·2	− 61·2 ± 1·2	3182·8 ± 7·4	3060·4 ± 8·7	3075
Alkyl	2791·6 ± 10·6	− 51·6 ± 1·8	2843·2 ± 12·4	2740·1 ± 14·2	2730

fitting which are related to the vibrational frequency and the anharmonicity constant by

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

In order to determine the values of B and C a least square fit procedure given by Birge [4] was used. The values of B and C for the CH stretch vibration for the alkyl and aryl groups are given in table 2. This enabled us to determine separately the ω_e and $\omega_e x_e$ values and the error in these for the alkyl and aryl CH stretch vibrations. The values thus obtained are also given in table 2. The two sets of values are very different from one another. The frequency of the first overtone of alkyl group calculated using present constants (5378 cm^{-1}) match very well with the weak band observed for this. It appears that the combination band lying near this at 5332 cm^{-1} has borrowed its intensity without shifting the second harmonic peak. We have also calculated the $\Delta G_{1/2}$ value using our ω_e and $\omega_e x_e$ values in the two cases. The $\Delta G_{1/2}$ values thus obtained are compared with the fundamental IR values in table 2. It is interesting to note that the two $\Delta G_{1/2}$ values are in good agreement with the first harmonic frequencies of the two CH groups. We also estimated the dissociation energy of the C–H bond in the two cases using Morse empirical relation $\omega_e^2/4\ \omega_e x_e$. The values of De thus obtained for the alkyl and aryl groups respectively are 39224·69 ± 1027 cm^{-1} and 41388 ± 648 cm^{-1}. The De value for aryl group is larger than that of free CH radical (28048 cm^{-1}, calculated using Morse relation) as well as of alkyl group. This indicates that the alkyl group CH bond is weaker compared to aryl group. However both are stronger than free CH radical.

The CHO group in benzaldehyde molecule is electron withdrawing type substituent. Thus when CHO is substituted on benzene ring by replacing hydrogen, it affects the charge-distribution at the neighbouring carbon atoms in the benzene ring. This influences the bond length of the aryl C–H bond. Mizugai and Katayama [5, 6] has given an empirical relation to calculate the change in bond length of aryl type C–H bond with respect to benzene molecule. The aryl C–H bond length for fifth overtone in the new compound is

$$r_{CH} = 1 \cdot 084 - \frac{8 \times 10^{-5} \times \Delta v (\text{cm}^{-1})}{v}$$

where $1 \cdot 084$ refers to the bond length of the C–H bond in benzene and Δv is the shift in frequency of the particular overtone with respect to benzene, v is the vibrational quantum number of the upper level involved in the transition. The bond length of the C–H aryl group in benzaldehyde is found to be $(1 \cdot 0833 \pm 0 \cdot 0001 \text{ Å})$.

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