

CH local mode overtone excitations in benzyl chloride— A conformational study

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Abstract. The CH local mode overtone spectrum of benzyl chloride in the visible and NIR regions studied by laser induced thermal lens and conventional NIR absorption is presented. The analysis shows that the $-\text{CH}_2\text{Cl}$ group is symmetrically oriented with respect to the benzene ring, thus finalizing one of the two possible conformational models predicted by electron diffraction studies. The aryl CH bonds have a slightly larger force constant than that in benzene.

Keywords. Overtone spectroscopy; conformation; thermal lens technique.

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1. Introduction

Vibrational overtone spectroscopy of molecules containing $X\text{-H}$ oscillators ($X = \text{C}, \text{N}, \text{O}$) is an area of recent interest [1–3]. The local mode (LM) model in which the $X\text{-H}$ oscillators are considered to be loosely coupled anharmonic Morse oscillators, has been widely used for interpretation of overtone spectra. The overtone transition energies obey the relation

$$\Delta E_{v-0} = AV + BV^2$$

where V is the quantum level of excitation, $A = X_1$ is the mechanical frequency and $B = X_2$ is the anharmonicity of the $X\text{-H}$ bond. A plot of $\Delta E/V$ vs V yields the local mode parameters, X_1 and X_2 . In a molecule containing non-equivalent $X\text{-H}$ bonds, different overtone progressions are formed due to their differing mechanical frequency and/or anharmonicity values. Thus overtone spectroscopy has become an effective tool for structural studies of organic molecules pertaining to nonequivalent CH bonds; the nonequivalence may arise due to factors like structural difference, conformational difference, anisotropic environments created by lone pair and/or π electron interactions etc. [4–13]. Overtone spectroscopy has also been used to study the influence of various substituents on benzene ring CH bonds [8, 9, 14–19].

In the present paper we report the CH overtone spectrum of liquid phase benzyl chloride recorded by the dual beam thermal lens ($\Delta V = 6$) and conventional NIR absorption ($\Delta V = 2\text{--}4$) techniques. The analysis of the structure of chloromethyl CH overtones leads to the conclusion that the $-\text{CH}_2\text{Cl}$ group is oriented symmetrically with respect to the benzene ring, thus finalizing one of the two structures compatible with electron diffraction data. The aryl CH bonds in this molecule are found to have a slightly larger force constant than that in benzene.

2. Experimental

High purity (99%) benzyl chloride (E Merck India) is used for the present experiments. The dual beam thermal lens technique [20] uses a rhodamine 6G dye laser (Spectra Physics 380 A) pumped by an argon laser (Spectra Physics 171-17) as the pump source. The chopped dye laser beam (50-100 mW) creates a pulsating thermal lens in the sample (path length 1 cm). The intensity modulations on a probe He-Ne laser beam (2 mW) passing through the sample are synchronously detected and normalized for pump laser power variation. The details of our thermal lens experimentation are given elsewhere [13]. The near infrared absorption spectrum is recorded in a Hitachi 3410 spectrophotometer from pure liquid with air as reference and path length 1 cm. All spectra are recorded at $25 \pm 2^\circ\text{C}$.

3. Results

The thermal lens and near infrared absorption spectra are shown in figures 1-4. The thermal lens absorption spectrum (figure 1) shows only the fifth overtone of the aryl

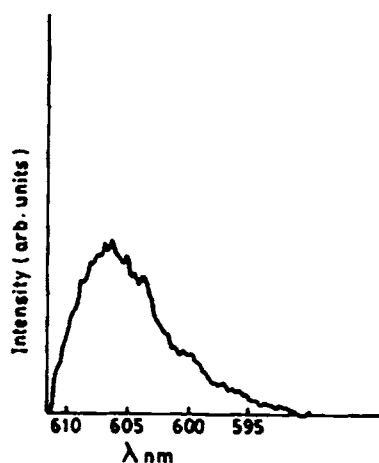


Figure 1. Fifth overtone absorption spectrum of aryl CH bonds in benzyl chloride recorded from pure liquid by dual beam thermal lens technique.

Table 1. Observed overtone energies (cm^{-1}) their assignments, mechanical frequencies $X_1(\text{cm}^{-1})$ and anharmonicities $X_2(\text{cm}^{-1})$ of aryl and chloromethyl CH local modes in benzyl chloride. Data for benzene [23] is also given for a comparison.

Molecule	$\Delta V=2$	$\Delta V=3$	$\Delta V=4$	$\Delta V=5$	$\Delta V=6$	X_1	X_2
Benzene	5983	8760	11442	14015	16467	3148.1	-57.6
Benzyl chloride							
Aryl CH	5988	8775	11464		16475	3175.4 ± 7	-61.6 ± 2
Chloro- methyl CH	5806	8553	11191	3062.7 ± 2	-53.0 ± 0.5

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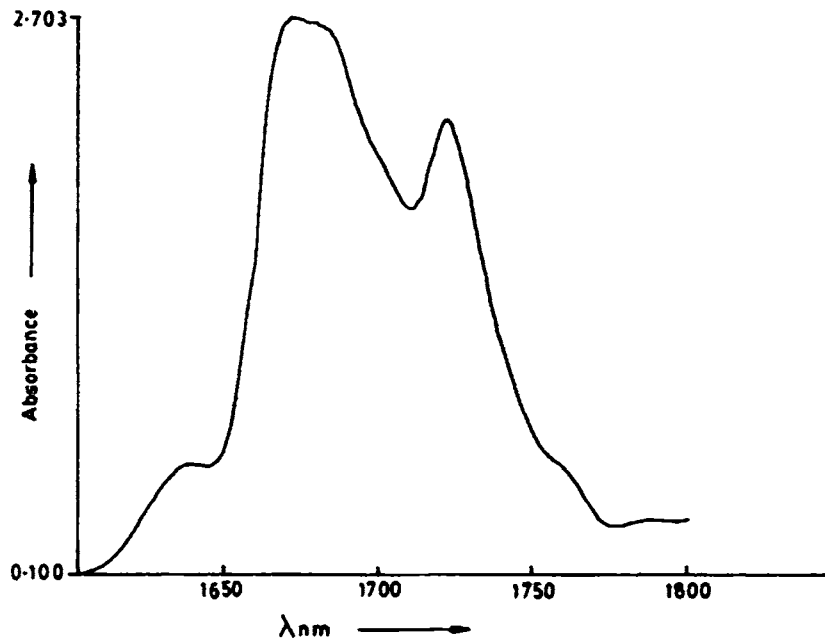


Figure 2. First overtone spectrum of benzyl chloride recorded from pure liquid. Reference-air.

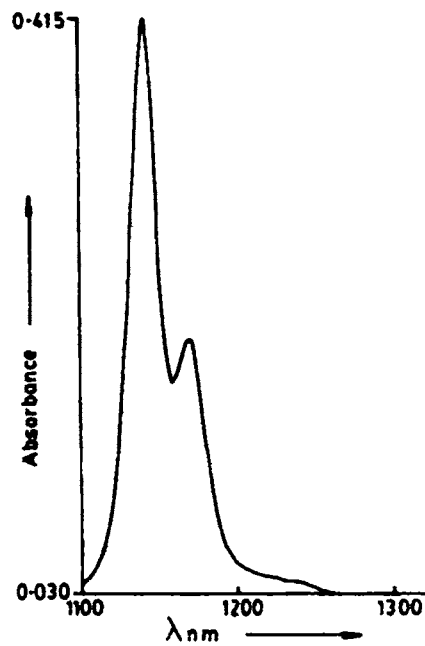


Figure 3. Second overtone spectrum of benzyl chloride recorded from pure liquid. Reference-air.

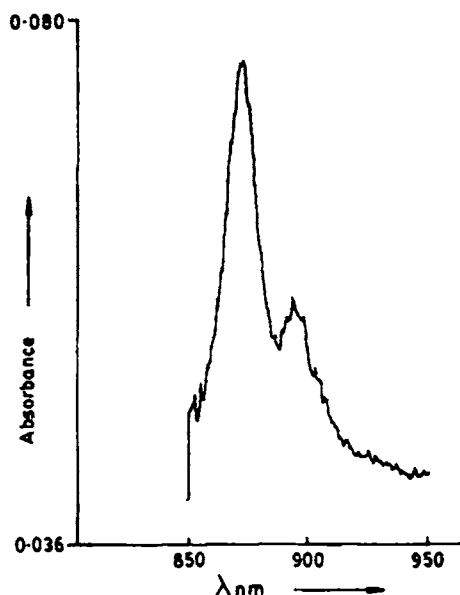


Figure 4. Third overtone spectrum of benzyl chloride recorded from pure liquid. Reference-air.

CH bond due to the limited tuning range of the dye laser. The first through third overtone spectra show bands due to aryl and alkyl local mode excitations. The fourth overtone spectrum is not presented due to the poor signal to noise ratio of the spectrophotometer in that region. The peak positions, their assignments and the local mode parameters obtained from Birge-Sponer plot are given in table 1.

4. Discussion

4.1 Chloromethyl CH overtones

The overtone spectrum in the region $\Delta V = 2-4$ (figures 2-4) shows the chloromethyl CH overtone peaks occurring on the low energy side of the aryl CH overtones. The chloromethyl CH overtones in all these regions give rise to sharp peaks. As explained below the occurrence of these sharp peaks lead to important conclusions regarding the conformation of the $-\text{CH}_2\text{Cl}$ group with respect to the benzene ring.

The electron diffraction studies on benzyl chloride was carried out by Sadova *et al* [21]. The results of their studies are compatible with two possible structures. In one structure, the angle of rotation (as seen in Newman projection) of the $-\text{CH}_2\text{Cl}$ group around the C-C bond is $\phi = 67.5^\circ$ ($\phi = 0$ when the C-Cl bond is the plane of the benzene ring), with relatively large torsional amplitudes (hereafter referred to as structure I). In the other possible structure, the potential for internal rotation is given by $V(\phi) = (V_2/2)[1 - \cos 2(\phi - \phi_0)]$ with $V_2 = 6.3 \text{ kJ mol}^{-1}$ with a minimum at $\phi = \phi_0 = 90^\circ$ and relatively smaller torsional amplitudes (hereafter referred to as structure II). The overtone spectral structure shows that the structure II is the one which is acceptable (see below).

Before discussing the chloromethyl CH overtones in benzyl chloride it is necessary to consider the alkyl CH overtones reported in related compounds like toluene, *p*-xylene,

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m-xylene and *o*-xylene. The liquid phase overtone study of these compounds by Nakagaki and Hanazaki [22] shows that the methyl CH overtones of toluene, *p*-xylene and *m*-xylene are broad flat peaks whereas those of *o*-xylene are resolved doublets. Later the gas phase overtone spectral studies carried out by Gough and Henry [8] have shown that the methyl CH overtone regions of toluene, *p*-xylene and *m*-xylene consist of three peaks corresponding to in-plane CH, out of plane CH and free rotor states above the torsional potential barrier. The gas phase *o*-xylene overtone spectra again shows only two peaks which correspond to the in-plane and out-of plane CH bonds of the methyl group. The difference occurs for *o*-xylene compared to toluene, *p*-xylene and *m*-xylene due to the fact that the methyl groups in the latter molecules are almost free rotors whereas it is not so in *o*-xylene (barrier-6.3–9.2 kJ mol⁻¹).

The present case of benzyl chloride is similar to *o*-xylene since the -CH₂Cl group is not at all a free rotor in both the possible structures [21]. For *o*-xylene, the non-equivalent methyl CH overtones have frequency separations of 100 cm⁻¹ ($\Delta V = 3$) and 150 cm⁻¹ ($\Delta V = 4$) and are well resolved in liquid and gas phase spectra. The stable conformation of this molecule is such that one of the three CH bonds is in the plane of the benzene ring while the other two are out of plane, i.e., they are at 60° to the ring. Thus we have a frequency shift of 100 cm⁻¹ ($\Delta V = 3$) and 150 cm⁻¹ ($\Delta V = 4$) for an orientation angle variation of 60° for the CH bonds. In benzyl chloride, if structure I is valid then one of the CH bonds will be at 7.5° while the other CH bond will be at 52.5° with respect to the benzene ring. Thus we have an orientation angle variation of 45° and hence we expect two peaks in the chloromethyl CH overtone region of the spectrum. But the overtone spectrum shows only one sharp peak at all the quantum levels. This shows that the two CH bonds in the -CH₂Cl group of benzyl chloride are equivalent. This result is in perfect agreement with structure II in which the C-Cl bond is at 90° and the two CH bonds are at 30° with respect to the ring (as seen in Newman projection). We thus conclude that structure II is the one which is acceptable.

4.2 Aryl CH overtones

The major peaks observed in the overtone spectra are due to the aromatic CH bonds in the benzene ring. The peak positions and the local mode parameters obtained from Birge-Sponer plot are given in table 1. Mizugai and Katayama [14] have reported the fifth overtone peak position of aryl CH in benzyl chloride to be 16490 cm⁻¹. We believe that our value 16475 cm⁻¹ is more accurate than the data obtained from point-by-point thermal lens measurement of these authors. The most reliable overtone data of liquid benzene reported [23] is also given in table 1 for a comparison. The aryl CH overtone peak positions of benzyl chloride are slightly blue shifted with respect to those of benzene. It can be seen from table 1 that this blue shift in overtone energy is due to an increased mechanical frequency of the ring CH bonds compared to that in benzene. It is well established from extensive overtone studies of substituted benzenes [8, 9, 14–19], that an electron withdrawing group causes shortening of the ring CH bonds (thereby increasing overtone frequency) and an electron donating group causes lengthening of the ring CH bonds thereby decreasing overtone frequency. Correlation between shift in overtone energy and inductive part of Hammett $\sigma(\sigma_1)$ and correlation between overtone energy and bond length are also established from these earlier studies.

The small blue shift with respect to benzene overtone positions resulting from increased mechanical frequency is in line with the small electron withdrawing power of the $-\text{CH}_2\text{Cl}$ group $\sigma_1 = 0.11$ [14]. As is true in many other molecules [14–18] the electron withdrawing group reduces the electron density at the ring carbon atoms. This results in a net positive charge on them thus increasing the force constant of the ring CH bonds.

5. Conclusions

The analysis of the CH overtone spectrum of benzyl chloride has shown that, out of the two different conformational models compatible with electron diffraction data, the one symmetric conformation in which C–Cl bond is perpendicular to the benzene ring plane (as seen in Newman projection) is acceptable. Also the aryl CH bonds in benzyl chloride is found to have slightly larger force constant than that in benzene.

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