

The Fifth Overtone Spectra of Aryl C–H Stretching Vibrations in $C_6H_5CH_{3-n}Cl_n$

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Synopsis. The fifth overtone frequencies of the aryl C–H vibration of $C_6H_5CH_{3-n}Cl_n$ were observed by means of the thermal-lens technique. The shifts of their vibrational frequencies from that of benzene were found to be proportional to the inductive contribution of the Hammett σ , thus supplying information on the reactivity of the chemical bond.

Since the development of dye lasers, the opto-acoustic and thermal-lens techniques have been powerful methods for studying overtone spectroscopy in polyatomic molecules, where high vibrational levels are excited by means of very weak single photon absorption rather than by multiphoton absorption.^{1,2)} The experimental study of highly excited vibrational transitions in the ground electronic state offers valuable information on the photodissociation and radiationless transitions of molecules.

In the present article we wish to report our observation of the fifth ($\Delta v_{CH}=6$) overtones of the aryl C–H stretching vibrations of toluene and its chlorinated derivatives, $C_6H_5CH_{3-n}Cl_n$ ($n=0,1,2,3$), in the liquid state. The spectra of the fundamental vibrations, which are mainly attributable to the oscillation of the aryl C–H bond, show relatively complicated structures, and it is difficult to deduce the properties of their C–H bonds from the differences in the fundamental vibrational spectra. However, in their fifth C–H overtone spectra, single broad bands with a bandwidth of about 300 cm^{-1} are observed. The frequencies of their band centers exhibit systematic differences, demonstrating that the change in the electronic properties of $CH_{3-n}Cl_n$ ($n=0,1,2,3$) groups gives rise to the variation in the nature of the aromatic C–H bonds.

The measurements of the C–H overtone spectra were performed by means of the thermal-lens technique. A flashlamp pumped dye laser (Chromatix CMX-4) was used for the exciting light source, and a He–Ne laser with an average power output of 5 mW was operated in the TEM₀₀ mode. We can measure the absorption of the exciting laser by observing the decrease in the transmission of the He–Ne laser through

the pinhole which is put after the absorption cell. The thermal blooming of the He–Ne laser was observed by means of photodiode.

The observed results for $C_6H_5CH_{3-n}Cl_n$ ($n=0,1,2,3$) and benzene are listed in Table 1. As is shown in this table, the frequencies of the fifth C–H overtone increase with the number of substituted chlorine atoms in the CH_3 group. The aryl C–H overtone of toluene is on the lower side of benzene, while those of the chlorine substituted molecules are at higher frequencies than that of benzene.

It has been found that the frequencies of the overtone spectra are represented quite adequately by this simple two-parameter equation:

$$G_{v,0} = v(A + vB) \quad (1)$$

where A and B are the constants and where v is the vibrational quantum number. At least for high-frequency modes, the experimental results can well be described as corresponding to the excitation of localized modes of vibration rather than a set of symmetry-allowed combination of anharmonic normal modes.^{3–5)} Thus, it can be understood that the frequencies of the higher overtone of molecular vibrations can give information on the nature of individual isolated chemical bonds.

The overtone spectra of the aryl C–H stretching vibrations of $\Delta v=2–5$ for toluene and α,α,α -trichlorotoluene could be observed by means of a Cary 14 spectrophotometer, but not those of their fifth overtone spectra ($\Delta v=6$). Both the frequencies of the fifth overtone as measured by the thermal-lens technique and the overtone spectra of $\Delta v=2–5$ obtained by the conventional method can be well expressed by the following equations:

$$G_{v,0} = 3094v - 59v^2 \quad \text{for toluene} \quad (2)$$

$$G_{v,0} = 3113v - 58.5v^2 \quad \text{for } \alpha,\alpha,\alpha\text{-trichlorotoluene} \quad (3)$$

where $G_{v,0}$ is expressed in cm^{-1} . On the other hand, the overtone spectra of benzene are represented by:⁵⁾

$$G_{v,0} = 3095v - 58.4v^2. \quad (4)$$

The second terms in these equations, i.e., the B constants in the above three equations, are almost the same. Therefore, it would be reasonable to assume that the B constants in Eq. 1 are the same in benzene and $C_6H_5CH_{3-n}Cl_n$ ($n=0,1,2,3$). Thus, the increase in the number of the substituted Cl atoms in the CH_3 group gives rise to a slight increase in the A constant of Eq. 1, indicating that the strength of the aryl C–H bonds increases with the number of substituted Cl atoms. The experimental results show that the fifth-overtone frequency of $C_6H_5CCl_3$ is the highest and that of $C_6H_5CH_3$ is the lowest, demonstrating that the strength of the local mode of the aryl C–H stretching

TABLE 1. THE FIFTH OVERTONE SPECTRA OF ARYL C–H STRETCHING VIBRATIONS IN $C_6H_5CH_{3-n}Cl_n$ ($n=0,1,2,3$) MOLECULES; THE FREQUENCIES, THE SHIFTS FROM THAT OF BENZENE, AND THE LINE WIDTHS

| Molecule | Frequency | Shift | Width(fwhm) |
|----------------|------------------------|----------------------|----------------------|
| $C_6H_5CH_3$ | 16460 cm^{-1} | -15 cm^{-1} | 275 cm^{-1} |
| C_6H_6 | 16475 | 0 | 235 |
| $C_6H_5CH_2Cl$ | 16490 | +15 | 270 |
| $C_6H_5CHCl_2$ | 16520 | +45 | 280 |
| $C_6H_5CCl_3$ | 16555 | +80 | 310 |

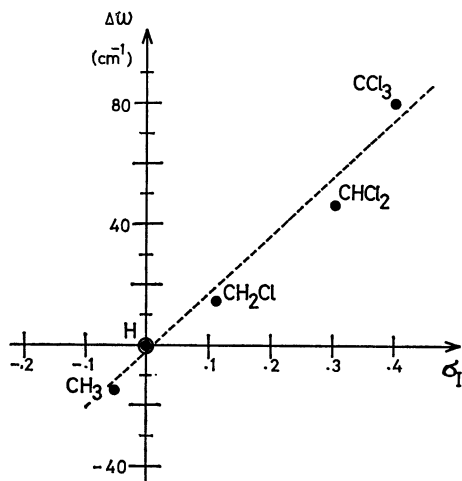


Fig. 1. The relation between the frequencies of the fifth overtone spectra of aryl C-H stretching vibration and the values of σ_1 , the inductive contribution in Hammett σ , in $C_6H_5CH_{3-n}Cl_n$ ($n=0,1,2,3$) molecules.

vibration in $C_6H_5CCl_3$ is the strongest among the four molecules of $C_6H_5CH_{3-n}Cl_n$ ($n=0,1,2,3$) and the benzene molecule. It was also found that the shifts of the fifth-overtone frequencies from that of benzene are proportional to the σ_1 values of Hammett, as is shown in Fig. 1.⁶⁾ Therefore, the shifts of the frequencies of the higher-overtone spectra provide quantitative measures of the inductive contribution of the Hammett σ , supplying information on the chemical reactivity of a certain bond. This is because the highly excited vibration is well represented by the local mode, *i.e.*, the vibrational mode of an individual

isolated bond. Therefore, the nature of its chemical bond is appropriately represented by the frequency of its higher-overtone vibration.

It should be noted that the linewidths of the fifth C-H overtone of $C_6H_5CH_{3-n}Cl_n$ are wider than that of benzene. This is brought about by the fact that the $C_6H_5CH_{3-n}Cl_n$ molecules have non-equivalent aryl C-H local modes with slightly different vibrational frequencies. Although it is desirable to observe the overtone frequencies in the gas phase for the more accurate measurement of their center frequencies, the power output of our laser is not large enough for us to obtain a good signal for the gas phase. Nevertheless, the liquid-state spectra may be expected to provide reliable information on the band center of the overtones.

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