# Substituent Effect on the Fifth Overtones of the Aryl C–H Stretching Vibrations in Disubstituted Benzenes

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**Abstract:** The fifth overtone spectra of the aryl C–H stretching vibrations of a number of disubstituted benzenes, $XC_6H_4Y$, in the liquid state were observed by a thermal-lens technique. If the two substituents in $p$-$XC_6H_4Y$ have opposite polarities, the doublet structure of the spectrum is observed. On the other hand, an unresolved single absorption is obtained when the substituents of the molecules have the same nature of polar effect. The frequency shifts of the overtones from that of benzene, $\Delta\omega$, were proportional to the sum of the inductive contribution of the Hammett $\sigma$ of the substituents X and Y, $\sigma_I^X + \sigma_I^Y$. Our results support that a local-mode model is much superior to a normal-mode model for the description of high overtones.

Numerous investigations of overtone spectra of the C–H stretching vibrations in hydrocarbons have been reported since the earliest work in liquid benzene by Elis.[1] Recently, new techniques to measure the highly excited overtone of molecular vibration in the liquid state have been developed, one of the techniques used most widely being the thermal blooming spectroscopy.[2] Those studies provide valuable information on infrared multiphoton dissociations, radiationless transition of molecules, and chemical reactivity of the bond relevant to the observed vibration. The spectra are well interpreted from a local-mode point of view.[3–5] Since the principal bands in the spectra correspond to excitation of C–H stretching motion with all of the energy localized in a single C–H stretching oscillation, the frequency of higher overtone of molecular vibration manifests the property of an isolated chemical bond.

Previously we reported that the frequency shifts of the fifth overtones of the aryl C–H stretching vibrations of monosubstituted benzenes from that of benzene, $\Delta\omega$, are proportional to the inductive contribution of the Hammett $\sigma$.[6] Futhermore, it was found that the frequency shifts in some heterocyclic compounds, benzene and fluorobenzene, are proportional to the decrease in the relevant C–H bond lengths from that of benzene.[7] These results strongly support the local-mode picture for the representation of highly excited molecular vibration rather than a conventional normal-mode picture.

In the present article we wish to report on the relationship between the frequencies of the fifth overtones of the aryl C–H stretching vibrations in some disubstituted benzenes and their properties of the relevant chemical bonds; the frequency shifts are proportional to the sum of $\sigma_I$ of the substituents, accordingly the shift of the disubstituted molecule being the sum of the shifts of the corresponding monosubstituted benzenes. Hence, the high-overtone frequencies of the aryl C–H stretching vibrations in the disubstituted benzenes manifest their chemical properties of the C–H bonds as in the case of the monosubstituted benzenes. Incidentally, the shifts of the overtone frequencies appear to correspond to the chemical shift in NMR.

## Experimental Section

The thermal-lens technique described in the previous paper was used for the measurements of the overtones of the aryl C–H stretching vibrations of the transitions between $v = 0$ and 6, 7 levels.[7] The overtone spectra with $v = 0 \rightarrow 2 \sim 5$ were observed by a Cary 14 spectrophotometer. Spectrograde or guaranteed reagent liquid samples were obtained from Tokyo Kasei Co. Ltd. Further purification was made by distillation.

## Results and Discussion

The observed results of the fifth or sixth overtones of the aryl C–H stretching vibrations in several disubstituted and trisubstituted benzenes measured by the thermal-lens technique in the liquid state will be described in the following.

Since the overtone spectra of the aryl C–H stretching vibrations in para-disubstituted benzenes are rather simple, we will discuss mainly the overtone spectra of these molecules. The structure of the fifth overtone spectra depends on the nature of the two substituents; the doublet structure of the spectrum was observed in the molecule having the substituents with opposite polarities, i.e., the electron-withdrawing and electron-donating substituents. On the other hand, those with the same nature of polar substituents exhibit the single broad absorptions.

Molecules such as $p$-chlorotoluene, $p$-methylanisole, and $p$-toluic acid methyl ester belong to the former group; the substituents Cl, $OCH_3$, and $COOCH_3$ are electron-withdrawing, while the $CH_3$ group is the electron-donating substituent. Figure 1 shows the fifth overtone spectra of the aryl C–H stretching vibrations in $p$-chlorotoluene observed by the thermal-lens technique. The spectrum is composed of a doublet with almost equal intensity at the frequencies of 166 610 and 16 420 $cm^{-1}$. Because of its symmetry, $p$-chlorotoluene has two kinds of aryl C–H bonds, which give rise to the doublet structure in their high-overtone spectrum as expected from the local-mode picture of the molecular vibrations.

Figure 2 shows the fundamental and overtone spectra of the aryl C–H stretching vibrations of $p$-chlorotoluene. The common features and simplicity of the $\Delta v \geq 4$ overtone bands of $p$-chlorotoluene can be interpreted in terms of the localized model rather than a set of symmetry-allowed combinations of anharmonic normal modes. The frequencies of the overtones of the C–H stretches are expressed as follows:

$$G_{v,0} = 3115v - 58v^2 \qquad (1)$$

$$G_{v,0} = 3095v - 61v^2 \qquad (2)$$

for the high- and low-frequency components, respectively. Here, $G_{v,0}$ is expressed in $cm^{-1}$. The fifth overtone spectrum of the aryl C–H stretches in $p$-chlorotoluene is assumed with a rough approximation to be composed of superposed spectra of chlorobenzene and toluene. Although the high-frequency component of the doublet of $p$-chlorotoluene is about 20 $cm^{-1}$ higher than that of chlorobenzene, we can conclude that those frequencies are practically coincide with each other. Therefore, the high-frequency component of the doublet is ascribed to the aryl C–H bond nearest to the substituent Cl; this is because the effect of the substituent in benzene is largest on the $o$-CH bond as will be seen in a later

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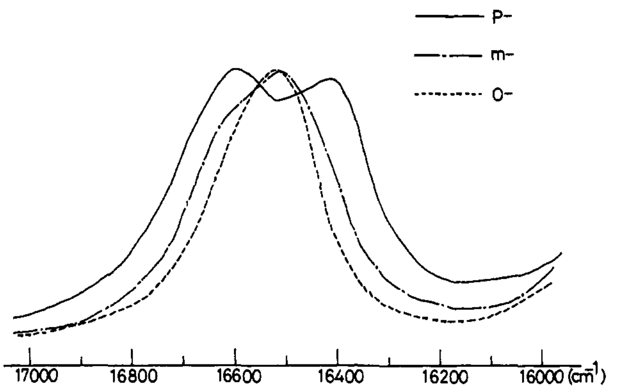

**Figure 1.** The fifth overtone spectra of the aryl C–H stretching vibrations of chlorotoluenes.

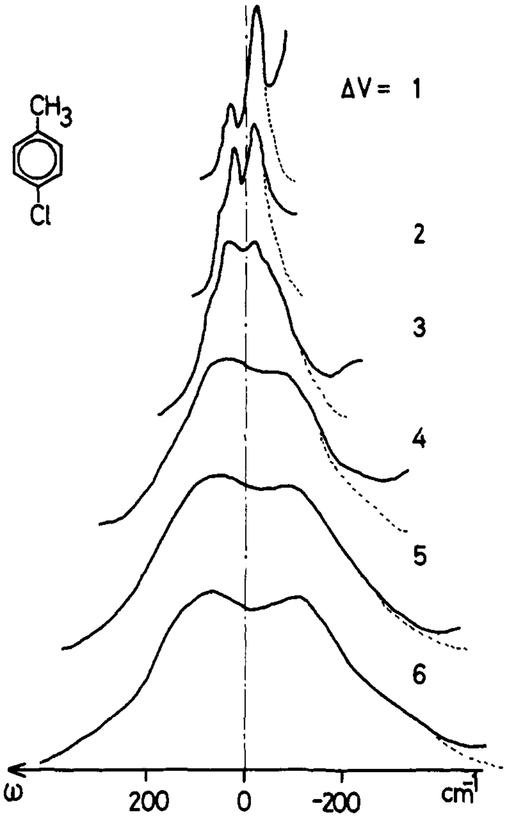

**Figure 2.** The fundamental and overtone spectra of the aryl C–H stretching vibrations of *p*-chlorotoluene.

discussion on the overtone spectra of $CH_3$-substituted benzenes. On the other hand, the low-frequency component corresponds to the vibration of the aryl C–H nearest to the substituent $CH_3$, although its frequency is about 40 $cm^{-1}$ lower than the fifth overtone frequency of toluene.

Similar spectra were obtained in the fifth overtone of the aryl C–H stretching vibrations of *p*-methylanisole and *p*-toluic acid methyl ester as shown in Figure 3. The frequencies of the peaks of the doublet spectra are 16 530 and 16 355 $cm^{-1}$ in *p*-methylanisole and 16 600 and 16 400 $cm^{-1}$ in *p*-toluic acid methyl ester, respectively. By comparing the spectra with those of $C_6H_5OCH_3$ and $C_6H_5COOCH_3$, the low-frequency components of the doublet are ascribed to the aryl C–H stretch nearest to the substituent $CH_3$.

For *o*- and *m*-chlorotoluene, single broad spectra of the fifth overtone of the aryl C–H stretching vibrations were obtained and their frequencies of the peaks are almost the same with the center frequency of the doublet in *p*-chlorotoluene.

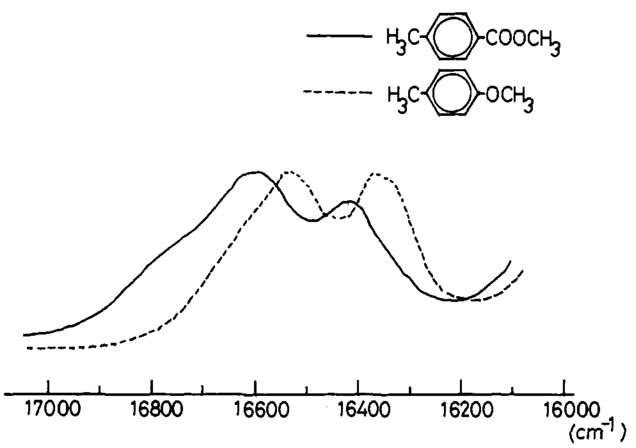

**Figure 3.** The fifth overtone spectra of the aryl C–H stretching vibrations of *p*-methylanisole and *p*-toluic acid methyl ester.

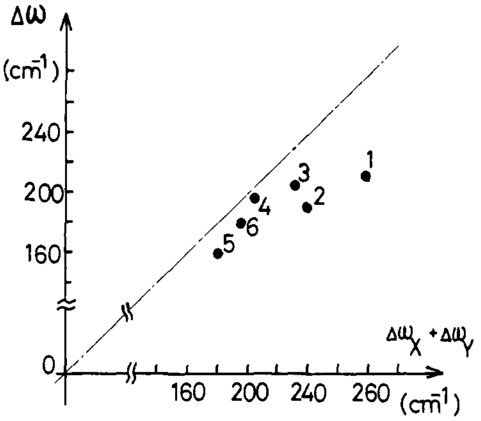

**Figure 4.** Additivity on the frequency shifts of the halogenated benzenes, *p*-$XC_6H_4Y$ and $C_6H_5X$—X and Y: 1, F, Cl; 2, F, Br; 3, Cl, Cl; 4, Cl, Br; 5, Br, Br; 6, Cl, $CCl_3$.

Table I. Frequencies of the Fifth Overtones of the Aryl C–H Stretching Vibrations of *p*-$XC_6H_4Y$ and Their Frequency Shifts from that of Benzene and Frequency Shifts of the Monosubstituted Benzenes

| substituent | | freq, | shift | | | |
|---|---|---|---|---|---|---|
| X | Y | $cm^{-1}$ | $\Delta\omega_{X,Y}$, $cm^{-1}$ | $\Delta\omega_X$, $cm^{-1}$ | $\Delta\omega_Y$, $cm^{-1}$ | $\Delta\omega_X + \Delta\omega_Y$, $cm^{-1}$ |
| F | Cl | 16 685 | 210 | 145 | 115 | 260 |
| F | Br | 16 665 | 190 | 145 | 90 | 235 |
| Cl | Cl | 16 680 | 205 | 115 | 115 | 230 |
| Cl | Br | 16 670 | 195 | 115 | 90 | 205 |
| Br | Br | 16 630 | 155 | 90 | 90 | 180 |
| Cl | $CCl_3$ | 16 655 | 180 | 115 | 80 | 195 |

For disubstituted para-halogenated benzene, *p*-$XC_6H_4Y$, in which the two substituents have the same nature of the polar effects as in the case of *p*-dichlorobenzene or *p*-chlorofluorobenzene, the high-overtone spectra are composed of single lines with the spectral width of 230–300 $cm^{-1}$. The frequency shifts of the fifth overtone of the aryl C–H vibrations in these molecules from that of benzene, $\Delta\omega$, are almost coincide with the sum of those values of the corresponding monosubstituted benzenes, $\Delta\omega_X$ and $\Delta\omega_Y$, indicating that an additivity rule,

$$\Delta\omega_{X,Y} = \Delta\omega_X + \Delta\omega_Y \qquad (3)$$

holds fairly well among the frequency shifts of monosubstituted benzenes and disubstituted para-halogenated benzene, as shown in Figure 4. Those values of the shifts are listed in Table I.

In the previous paper we have reported that the frequency shifts of the fifth overtone of the aryl C–H stretching vibrations in monosubstituted benzenes from that of benzene are proportional to the value of $\sigma_I$, the inductive contribution of the Hammett $\sigma$. The experimental results of the high-overtone of the aryl C–H stretching vibrations and the analysis for the para-disubstituted

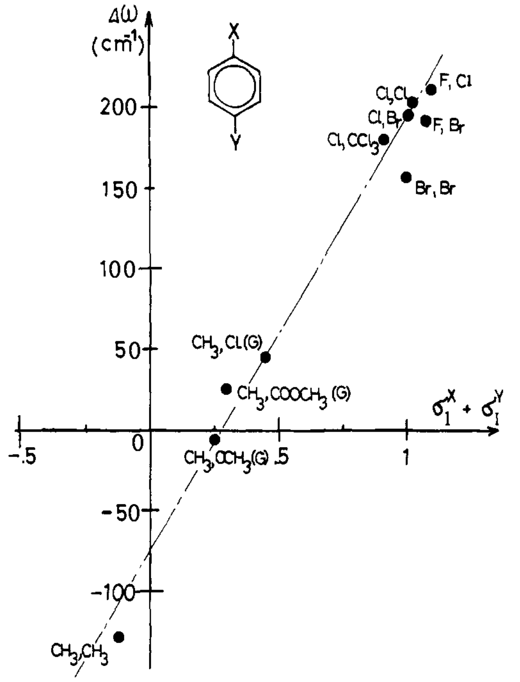

**Figure 5.** The relation between the frequency shifts of the fifth overtones of the aryl C–H stretching vibrations of para-disubstituted benzenes and the $\sigma_I$ values of the substituents.

benzenes suggest that the frequency shifts are proportional to the sum of $\sigma_I$ of the substituents, i.e.,

$$\Delta\omega \propto \sigma_I^X + \sigma_I^Y \tag{4}$$

The observation of the overtone frequency in a number of para-disubstituted benzenes supports that relation 4 is satisfied as shown in Figure 5. For the molecules in which the doublet overtone spectra are obtained, the shifts of the center frequency of the doublet are plotted. The present study shows that the additivity of $\sigma_I$ of the substituents holds in disubstituted benzenes; hence relationship 3 is satisfied.

The additivity rule of the frequency shifts of the high-overtone is violated in the cases of the fifth overtone of the aryl C–H stretches of toluene and *p*-xylene, the frequency shifts, $\Delta\omega$, being -15 and -135 cm$^{-1}$, respectively. There are three nonequivalent aryl C–H bonds in toluene; hence the three overtone frequencies should be observable. However, the frequency differences among these three overtones are too small to be observed separately. Consequently, the absorption line width is broader than that of benzene. The absorption line widths (fwhm) of the fifth overtone of the aryl C–H stretching vibrations of toluene and benzene are 275 and 235 cm$^{-1}$. Its line shape of toluene is asymmetrical, because the spectrum is composed of *o*-CH, *m*-CH, and *p*-CH overtones. The effect of the substituent $CH_3$ is the largest on the *o*-CH bonds. This is presumed from the fifth and sixth overtone frequencies of *o*-, *m*-, and *p*-xylene and 1,3,5-trimethylbenzene as listed in Table II, in which the fifth overtones of *o*-, *m*-, and *p*-dichlorobenzene and 1,2,4-trichlorobenzene are also tabulated. For toluene, therefore, the frequency shift of the overtone of the *o*-CH stretching vibration must be larger than the observed value listed in Table II. The failure of the additivity rule for toluene and *p*-xylene is partially explained by an ambiguity of the fifth overtone frequency of the *o*-CH stretching vibration in toluene.

**Table II.** Fifth and Sixth Overtone Frequencies of $CH_3$ or Cl Substituted Benzenes

| | $\Delta\nu_{CH} = 6$ | | | $\Delta\nu_{CH} = 7$ |
|---|---|---|---|---|
| substance | freq, cm$^{-1}$ | shift $\Delta\omega$, cm$^{-1}$ | width (fwhm), cm$^{-1}$ | freq, cm$^{-1}$ |
| toluene | 16 460 | −15 | 275 | 18 750 |
| *o*-xylene | 16 410 | −65 | 290 | 18 720 |
| *m*-xylene | 16 390 | −85 | 280 | 18 680 |
| *p*-xylene | 16 340 | −135 | 240 | 18 640 |
| 1,2,3-trimethylbenzene | 16 375 | −100 | 315 | |
| 1,2,4-trimethylbenzene | 16 330 | −145 | 290 | |
| 1,3,5-trimethylbenzene | 16 305 | −170 | 235 | |
| *o*-dichlorobenzene | 16 615 | +140 | 260 | |
| *m*-dichlorobenzene | 16 640 | +165 | | |
| *p*-dichlorobenzene | 16 680 | +205 | 230 | |
| 1,2,3-trichlorobenzene | 16 685 | +210 | | |

The experimental fact, that the overtone spectra illustrated in Figure 1 are not exactly the superposed spectra of toluene and chlorobenzene, can be explained by our conclusion that the overtone spectrum of chlorotoluene represents the vibrations of *o*-CH bonds with respect to the substituents Cl and $CH_3$. On the other hand, the overtone spectra of monochlorobenzene and toluene are due to three groups of C–H bonds, i.e., *o*-, *m*-, and *p*-CH bonds, respectively.

For the overtone spectra of *p*-methylanisole and *p*-toluic acid methyl ester, the frequency separations between the doublet components are too large to interprete their spectra as the superposition of the monosubstituted benzenes. It indicates that the effect of the disubstitution of $CH_3$ and $OCH_3$ or $COOCH_3$ is quite different from those of monosubstituted benzenes because of their different nature of the conjugation among the substituents and the benzene ring.

In conclusion, we have demonstrated that the high-overtone of the aryl C–H stretching vibrations manifests the chemical property of the isolated C–H bond.

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