The Fifth Overtone Spectra of C-H Stretching Vibrations of C_6H_5X in Nonpolar Solvents

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The fifth overtone spectra of aryl C–H stretching vibrations of fluorobenzene, chlorobenzene, and bromobenzene in nonpolar solvents were observed using photoacoustic spectroscopy. In a nonpolar solvent, such as hexane, the three components of the overtones of the *o*-, *m*-, and *p*-C–H stretching vibrations could be easily decomposed owing to line-width narrowing. We could therefore obtain more detailed information concerning the chemical properties of these C–H bonds.

A number of investigations on the high overtone spectra of C–H stretching vibrations have elucidated that the spectra can be interpreted on the basis of a local mode model.[1,2] According to the local mode model, equivalent C–H bonds have the same vibrational frequency. For example, all of the six C–H bonds of benzene are equivalent, and their high overtones are observed at the same frequencies. On the other hand, for molecules of monosubstituted benzene having the three types of C–H bonds (*o*-, *m*-, and *p*-) three different frequencies must be observable in the region of the high overtone of the C–H stretching vibrations. It is, however, rather difficult to determine their frequencies.

As far as we know, there have been few reports in which the different frequencies of the three components of the overtone of the C–H stretching vibrations have been observed in the neat liquid states of monosubstituted benzenes. Mizugai and Katayama previously observed the frequency shifts of the overtones of monosubstituted benzene from that of benzene; they found that the shifts are related to the chemical and physical properties of the C–H bonds.[3] Furthermore, a doublet structure was observed in the overtone spectra of para-substituted benzenes.[4] However, it was impossible to distinguish the three components of the overtone spectra in monosubstituted benzenes, since the line width of the overtone spectrum becomes wider in the neat liquid state due to an intermolecular interaction.

In the present article we report on the experimental results of the high overtone spectra of the C–H vibrations of halobenzenes in nonpolar solvents using a photoacoustic technique; the observed results for the fifth overtone spectra of the C–H stretching vibrations elucidated that it is possible to distinguish the frequencies of three components of the overtones which correspond to the *o*-, *m*-, and *p*-C–H bonds.

Because the fifth overtone spectra of the C–H stretching vibrations are very broad and have almost 100 cm^{-1} width, even in the vapor phase,[5] the overtone spectra which we observed using a nonpolar solvent, did not split into three components, though considerable changes of the spectral shape upon dilution were observed. We can thus distinguish the three frequencies by means of a least-square method using the fifth overtone spectra of benzene in a nonpolar solvent as an elemental spectral line shape. Linear relations were found between the frequency shifts of the overtones from that of benzene $\Delta\tilde{\nu}_{\mathrm{I}}$, $\Delta\tilde{\nu}_{\mathrm{II}}$, or $\Delta\tilde{\nu}_{\mathrm{III}}$ and the inductive contribution of Hammett σ of halogen atoms. The values of $\Delta\tilde{\nu}_{\mathrm{I}}/\Delta\tilde{\nu}_{\mathrm{II}}$ and $\Delta\tilde{\nu}_{\mathrm{III}}/\Delta\tilde{\nu}_{\mathrm{II}}$ were found to be 1.7 and 0.43, respectively, and were independent of F, Cl, and Br substituents.

Our results indicate that we can measure the frequencies of the overtone spectra rather precisely in a nonpolar solvent, and that more detailed information concerning the chemical and physical properties of *o*-, *m*-, and *p*-C–H bonds in monosubstituted benzenes can easily be obtained.

Experimental

The extremely weak absorption of the fifth overtone of the C–H vibrations of benzene or substituted benzenes in various solvents can be observed relatively easily using photoacoustic spectroscopy with a pulsed dye laser light source and a piezoelectric transducer detector.[6]

Figure 1 shows our experimental arrangement. A flash lamp-pumped dye laser (Chromatix CMX-4) was used to excite the liquid samples. A laser pulse of 3—5 mJ output, 1 μs width and 5 Hz repetition rate was incident on the quartz cell which was loaded with the sample. The piezoelectric transducer (obtained from TOKIN Co., Ltd.) was attached to one side of the cell with thin layer of vacuum grease. The photoacoustic signal was detected by using the piezoelectric detector; after being amplified with a low-noise amplifier and gated through a box car averager, the signal intensity was normalized through a signal from the power monitor. The samples were either spectrograde or guaranteed reagent grade and were obtained from Tokyo Kasei Co., Ltd.

Results and Discussion

Figure 2 shows changes in the fifth overtone spectra of the C–H stretching vibrations of fluorobenzene

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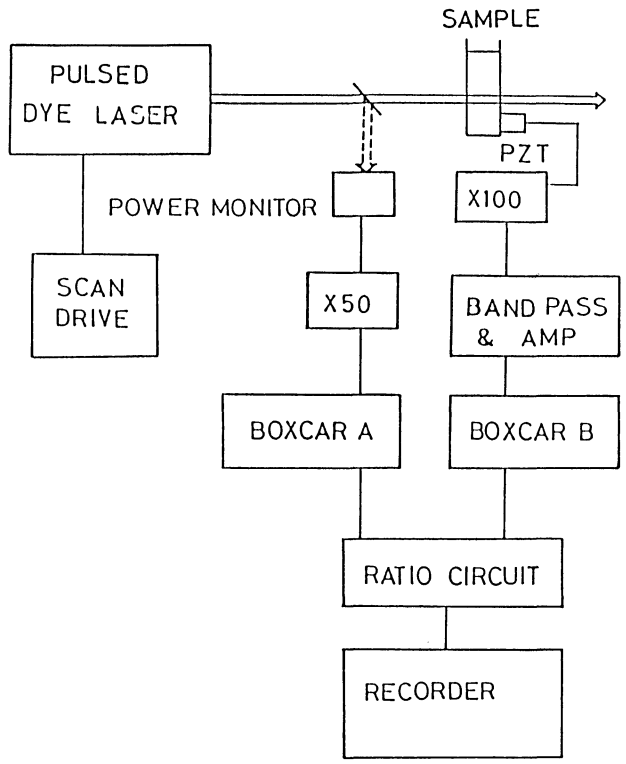

Fig. 1. Experimental arrangement.

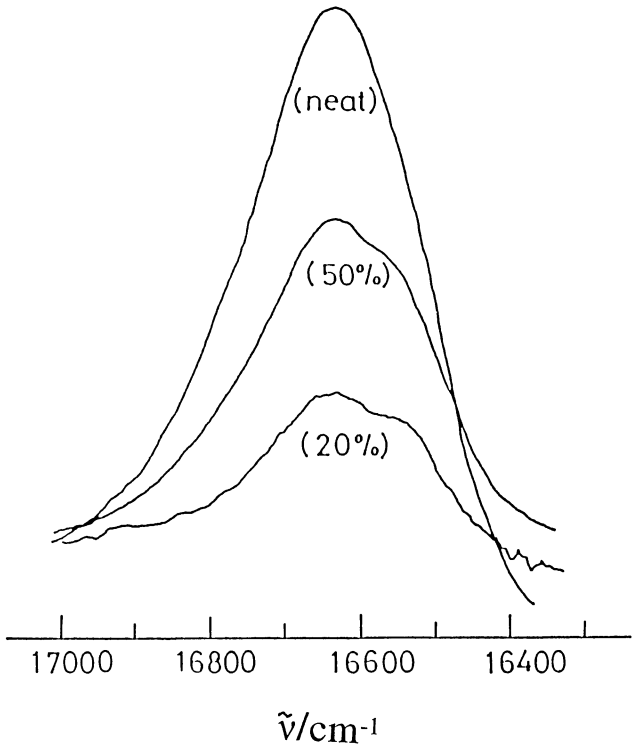

Fig. 2. The fifth overtone spectra of the C–H stretching vibrations of fluorobenzene diluted with hexane.

Table 1. Frequencies and the Line Widths of the Fifth Overtones of C–H Stretching Vibrations of Benzene in the Neat Liquid State and in Hexane Solutions of Various Concentrations

Concentration	Frequency	Linewidth
%	cm^{-1}	cm^{-1}
Neat	16475	270
50	16475	260
30	16480	250
10	16485	235
5	16485	230

when diluted with hexane. Though the spectrum in the neat liquid state conprises a single broad band centered at 16620 cm^{-1}, its line shape at 50% dilution with hexane exhibits a shoulder on the lower frequency side. In a 20% solution, the shoulder becomes more prominent and shifts by about 10 cm^{-1} to the blue side. The spectra of the fifth overtone of the C–H stretching vibrations of benzene in hexane also change upon dilution. The width becomes narrower and the peak of the spectrum is observed at the higher frequency when diluted. Table 1 represents our experimental results. Patel and Tam have also reported similar data for a CCl_4 solution.[6] The decrease in the interaction between the molecules gives rise to linewidth narrowing, and shifts of the the absorption frequency are induced by a change in the refractive index of the solution.[7]

Although fluorobenzene has three nonequivalent aryl C-H bonds, the frequency differences of their vibrational overtones are far smaller than the absorption linewidth in the neat liquid, and it is impossible to determine the frequencies of the three components of the overtone. When diluted with hexane, however, a decrease in the molecular interaction gives rise to a narrowing of the spectrum width and , hence, the rather complex absorption spectra are obtained (Fig. 2). The structures of the spectra correspond to the overtones of the three components of the C–H stretching vibrations. It must be mentioned that the shift of the peak of the overtone spectra of fluorobenzene in a hexane solution is not so evident, presumably because the difference in the refractive indices between hexane and fluorobenzene is relatively small, i.e., 1.3723 and 1.4683, respectively.

In order to analyze the observed overtone spectra, the shape of the spectra was calculated using appropriate assumptions: (1) the widths of the fifth overtone spectra of the *o*-, *m*-, and *p*-C–H stretching vibrations of fluorobenzene in hexane solutions are somewhat smaller than those of the corresponding overtones of benzene in its neat liquid state, and (2) the intensity ratio of the overtones of the *o*-, *m*-, and *p*-C–H stretching vibrations is 2:2:1. Furthermore, the peaks of the absorptions are assumed to be at 16665, 16580,

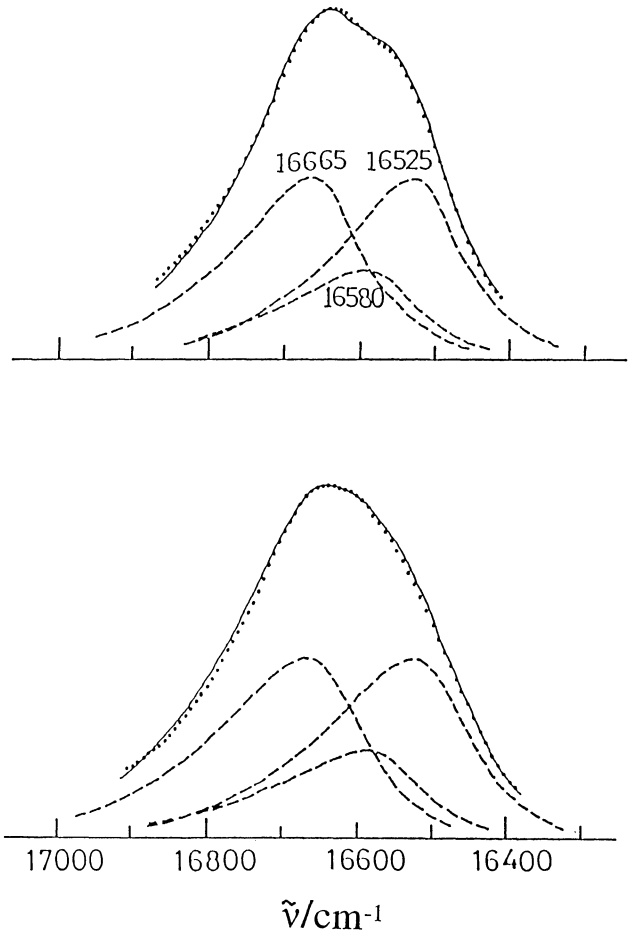

Fig. 3. Observed line shape of the spectra of the fifth overtone of the C–H stretching vibration of fluorobenzene and the calculated results, upper; 50% in hexane, lower; neat liquid state. Dashed curves; the calculated spectra of *o*-, *m*-, and *p*-components, solid curve; whole spectrum, dotted line; the observed spectrum.

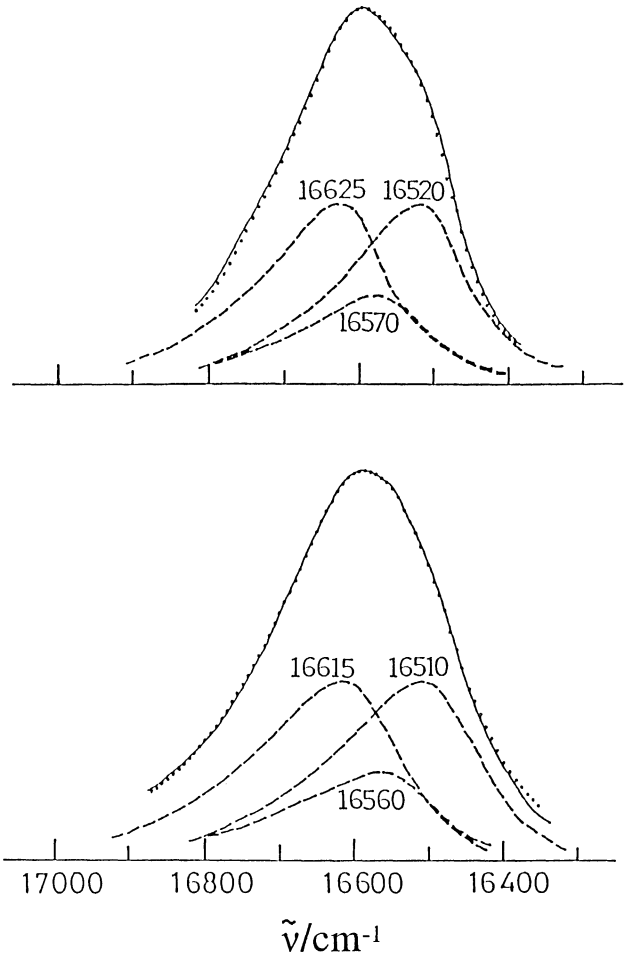

Fig. 4. Observed line shape of the spectra of the fifth overtone of the C–H stretching vibration of chlorobenzene and the calculated results, upper; 20% in hexane, lower; neat liquid state. Dashed curves; the calculated spectra of *o*-, *m*-, and *p*-components, solid curve; the whole spectrum, dotted line; the observed spectrum.

and 16525 cm^{-1} with an intensity ratio of 2:1:2; the width (fwhm) of the absorption is considered to be 235 cm^{-1}, as is shown by the dashed curves in the upper part of Fig. 3. The calculated shape of the entire spectrum was obtained as exhibited by the solid line of this figure; the results are in good agreement with those observed.

If we assume that each component has a width wider than 265 cm^{-1} in the neat liquid state, the superposed spectrum would not show any structure. Substantial agreement between the calculated and observed spectra was obtained, as is shown in the lower part of Fig. 3.

The overtone spectra of chlorobenzene slightly varies with the concentration in a hexane solution; though little change was observed in a 50% solution, we could see a slight modification of the line shape in a 20% solution. The observed line shapes are indicated by the dotted lines in Fig. 4; the solid curves indicate the calculated line shapes of the overtone of chlorobenzene, the upper part for a 20% solution in hexane, the lower part for the neat liquid state. In a hexane solution of chlorobenzene the frequency shift is not negligible; in a 20% solution the blue shift is about 10 cm^{-1}.

The overtone spectra of bromobenzene and iodobenzene in hexane solutions were also observed. Though for bromobenzene, quite similar results to the fluorobenzene case were obtained, for iodobenzene the line shape did not show any appreciable vibration with dilution up to a concentration of 5%, and we were unable to determine the frequencies of their three components.

The frequencies of the three components of the fifth overtones of fluorobenzene, chlorobenzene, and bromobenzene determined by the present analysis are listed in Table 2; the frequency shifts from that of

Table 2. Frequencies and the Shifts of Three Components of the Fifth Overtones of C–H Stretching Vibrations of Halobenzens and σ_I Values of Halogen Atoms

Molecules		Frequencies / cm^{-1}	Shift / cm^{-1}	σ_I values
Fluorobenzene	$\tilde{\nu}_I$	16665	190	0.56
	$\tilde{\nu}_{II}$	16580	105	
	$\tilde{\nu}_{III}$	16525	50	
Chlorobenzene	$\tilde{\nu}_I$	16615	140	0.51
	$\tilde{\nu}_{II}$	16560	85	
	$\tilde{\nu}_{III}$	16510	35	
Bromobenzene	$\tilde{\nu}_I$	16605	130	0.50
	$\tilde{\nu}_{II}$	16550	75	
	$\tilde{\nu}_{III}$	16505	30	

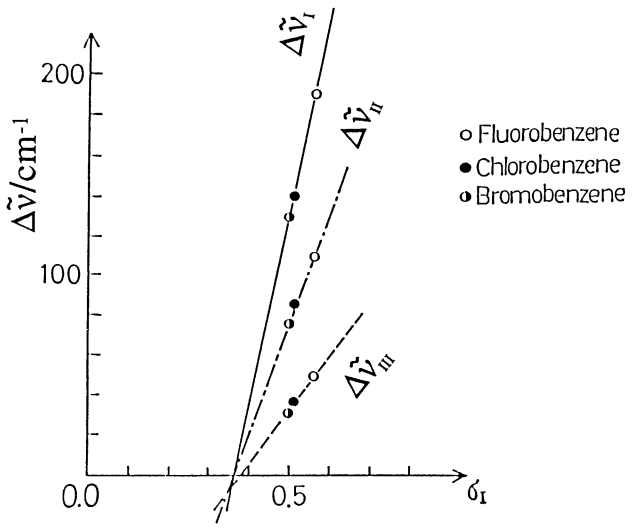

Fig. 5. The relation between the frequency shifts and σ_I of the substituents.

benzene, $\Delta\tilde{\nu}_I$, $\Delta\tilde{\nu}_{II}$, and $\Delta\tilde{\nu}_{III}$ are also presented.

Though it is obvious that the three components are due to the *o*-, *m*-, and *p*-C–H bonds, it is not easy to assign the frequency of each component to individual bonds. However, the results of the calculation mentioned above indicate that the component $\Delta\tilde{\nu}_{II}$ can be ascribed to the *p*-C–H vibration. With regard to the other components, it was difficult from the present analysis to determine to what type of C–H bond the $\tilde{\nu}_I$ and $\tilde{\nu}_{III}$ frequencies can be ascribed, though we may tentatively assume that $\tilde{\nu}_I$, the higher frequency vibration, results from the *o*-C–H bond.

Mizugai and Katayama[3] have reported that the shift of the $\Delta\tilde{\nu}$ frequency is proportional to σ_I, an inductive contribution of the Hammett σ. Having determined the frequencies of the three components of the C–H overtone in halobenzenes, we plotted the $\Delta\tilde{\nu}_I$, $\Delta\tilde{\nu}_{II}$, and $\Delta\tilde{\nu}_{III}$ frequency shifts as a function of σ_I, respectively. Figure 5 shows their relations. The present results indicate that a linear relation can be established between the frequency shift of each component and σ_I of the substituent. The straight lines for $\Delta\tilde{\nu}_I$ $\Delta\tilde{\nu}_{II}$, and $\Delta\tilde{\nu}_{III}$ in Fig. 5 intersect at around 3.5 of the σ_I value, but not at the origin of the figure, in contrast with the results for the overtone spectra of the aryl C–H vibration of $C_6H_5CH_{3-n}Cl_n$;[8] almost the same results were obtained in our previous report[3] concerning the C–H overtone spectra of the neat liquid state of C_6H_5X. Our present proposition is, however, an extension of the conclusion derived by Mizugai and Katayama. Since the σ_I value of an I atom is 0.43, the relative frequency shifts of the overtone spectra of iodobenzene are expected to be small. This is the reason that we were unable to resolve the three components of the C–H overtone vibration in the present experiment. It is reasonable to assume that since the inductive contribution of the substituent to the *o*-C–H bond is larger than that to the *m*-C–H bond, the higher frequency $\tilde{\nu}_I$ of the overtone of the C–H vibration may be attributed to the *o*-C–H bond and that the lower frequency $\tilde{\nu}_{III}$ belongs to the *m*-C–H bond.

We can derive another conclusion from the results of Fig. 5, that the ratio $\Delta\tilde{\nu}_I:\Delta\tilde{\nu}_{II}:\Delta\tilde{\nu}_{III}$ is independent of the substituents; the following two relations were obtained:

$$\Delta\tilde{\nu}_I/\Delta\tilde{\nu}_{II} = 1.7$$

and

$$\Delta\tilde{\nu}_{III}/\Delta\tilde{\nu}_{II} = 0.43\,.$$

These relations indicate that the relative shifts of the three components of the overtone frequencies are independent of the substituted atoms; we thus confirmed from the observed results of the high overtone of the C–H stretching vibrations that almost the same behavior can be expected in certain types of C–H bonds of the halobenzenes. Consequently, we can see that the specific C–H bonds of halobenzenes have the same chemical and physical properties.

Conclusion

We have demonstrated that the frequencies of the three components of the fifth overtone of aryl C–H vibrations of halobenzenes can be distinguished by using hexane as a solvent. These results can help us to understand the properties of the *o*-, *m*-, and *p*-C–H bonds respectively.

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