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The Infrared Absorption Spectra of HCl in Benzene

E. K. Plyler and Dudley Williams, *Department of Physics, University of North Carolina*

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The infrared absorption of benzene and a solution of HCl in benzene has been measured in the region from 2.5μ to 4.2μ. The absorption band of benzene at about 3.38μ is increased in intensity and shifted to longer wave-lengths in the solution for the same cell thickness. Other benzene bands in the region from 2μ to 3μ did not show an appreciable change in intensity or position. It was concluded that the absorption in the region of 3.4μ was due to the HCl in solution. When the ratio of the absorption of the solution to the absorption of the benzene is found, there appears a band with center at about 3.49μ. The relation of the absorption to the dipole moment is discussed.

THE spectra of hydrogen chloride in the gaseous state have been studied by a number of investigators.[1] Under the resolution obtained with the grating spectrometer there appears a strong band at 3.46μ consisting of the lines of the positive and negative branches, the zero branch being absent. The first harmonic of this band has also been observed at 1.76μ and it is found to have the same general characteristics. In solid hydrogen chloride[2] the fundamental band appears at 3.74μ with a series of broad lines equally spaced about a zero line. In aqueous solution hydrogen chloride is highly ionized, whereas in substances like benzene ionization does not take place. In this investigation the infrared absorption spectra of both types of solutions were studied to observe the effects of distortions of HCl molecules in the benzene and to detect the possible presence of undissociated HCl molecules in water.

A large type Hilger infrared spectrometer with a fluorite prism was used as the resolving instrument. The effective slit width at 3.4μ was 0.03μ. Fluorite windows were used in preparing the cells, their thickness being 0.03 mm. The cells were made by placing mica washers of this thickness between the fluorite plates.

In the case of aqueous solutions of HCl no absorption other than that due to water was observed in the region from 3μ to 3.6μ, the concentration being 5 normal. When thicker cells were used, the 3μ water band was greatly broadened for the HCl solution, but no separate absorption band was observed. This change in the 3μ water band is probably due to hydration effects. However, there was no absorption band in this region which could be attributed to undissociated HCl molecules, showing that if molecules are present in aqueous solution their number is insufficient for the cell thickness used to produce an observable band.

In the investigation of the benzene solution it was necessary to obtain water free materials. A sample of Baker's chemically pure benzene was

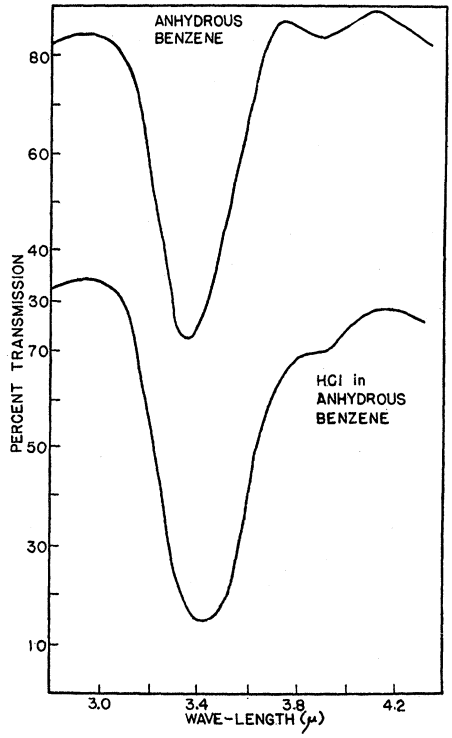

FIG. 1. The transmission of anhydrous benzene and HCl in benzene, the cell thickness being 0.03 mm.

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[1] W. Burmeister, Vesh. d. D. Phys. Ges. **15**, 589 (1913); E. v. Bahr, Vesh. d. D. Phys. Ges. **15**, 1154 (1913); H. M. Randall and E. S. Imes, Phys. Rev. **15**, 152 (1920); E. S. Imes, Astrophys. J. **50**, 25 (1919).

[2] P. E. Shearin, Phys. Rev. **48**, 299 (1935).

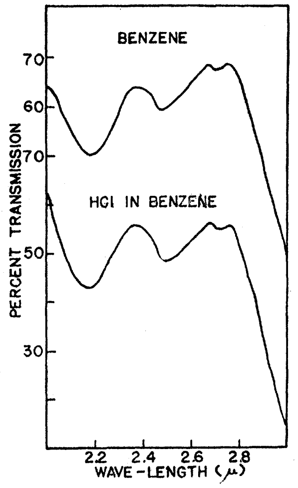

FIG. 2. The transmission of HCl in benzene and benzene in the region from 2μ to 3μ, the cell thickness being 0.6 mm.

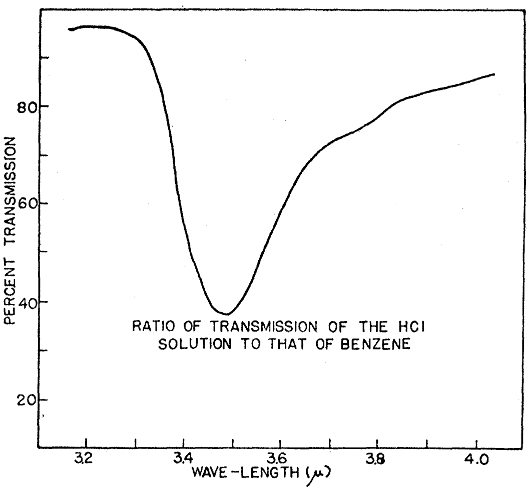

FIG. 3. The ratio of transmission of the HCl solution to that of benzene in the region from 3.2μ to 4.0μ. The band center is at about 3.4μ.

dried over fresh sodium chips for three days before the solution was prepared. The hydrogen chloride gas was passed through three drying towers containing concentrated sulphuric acid before it was bubbled into the benzene. The benzene solution was saturated at 25°C.

Since the strong absorption band of HCl in the gaseous state occurs at 3.46μ, the solutions were studied over the range from 2.5μ to 4.2μ. The bands observed in this region are shown in Fig. 1. The upper curve represents the transmission of anhydrous benzene for a cell thickness of 0.03 mm. The second curve shows the transmission of hydrogen chloride in the benzene solution for the same cell thickness. It is seen that the widening of the observed absorption band in the lower curve takes place entirely on the long wavelength side of the band. In order to ascertain if the presence of HCl in benzene produced any appreciable change in the other parts of the benzene spectrum, the absorption was studied in the region from 2μ to 3μ with a cell thickness of 0.6 mm. The results are shown in Fig. 2. It is observed that the two transmission curves are very similar, indicating that no modification is produced by the presence of HCl in the solution.

The characteristic band in the sample of anhydrous benzene used in this work appears at 3.38μ. The position of this broad band has been shown by Barnes[3] to vary with cell thickness. He observed that the benzene absorption band consisted of eight maxima lying between 3.23μ and 3.51μ.

In Fig. 3 is shown the ratio of the transmission of the HCl solution to that of pure benzene for various wave-lengths. This curve, which represents the absorption of the hydrogen chloride, has its maximum at about 3.49μ, this being in the same general region as the band for gaseous HCl. The position of the HCl absorption cannot be determined very accurately from this curve on account of the fact that benzene varies rapidly in its absorption in this region. This change in absorption of benzene in this region may produce a distortion and a shift in the band when calculating the ratio of transmission. The band as observed in this work shows a slight shift to the longer wave-lengths as compared with the gaseous state. This diminution of the vibrational frequency indicates a slight decrease in the binding energy between the hydrogen and chlorine nuclei. This change may be connected with the increase of electric moment of HCl from 1.08 $\times 10^{-18}$ e.s.u. in the gas to about 1.3×10^{-18} e.s.u. in benzene, as reported by Fairbrother.[4] It is interesting to note that this intense absorption obtained in the infrared spectra does not appear

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[3] R. B. Barnes, Phys. Rev. **36**, 296 (1930).

[4] F. Fairbrother, J. Chem. Soc., Part I, 43 (1932).

in the Raman spectra. Woodward[5] has reported his inability to observe the Raman spectrum of HCl dissolved in benzene, pointing out that the negative result was probably due to the low solubility of HCl in this solvent. In the case of certain other organic solvents,[6] West and Arthur have overcome this difficulty by studying the Raman spectra at a temperature of −65°C. They were able to observe the Raman spectra of HCl in solution at this temperature for several solvents. Evidently the coefficient of absorption in the infrared of HCl in solution is greater than the coefficient for HCl in the gaseous state, as can be seen from the magnitude of the observed band as shown in Fig. 3. An approximate calculation reveals that the coefficient of absorption of HCl in solution is three to four times greater than in the gaseous state. On account of the variation in concentration with temperature and errors in cell thickness the coefficient of absorption could not be determined very accurately. This indicates that the change in the electric moment causing absorption in solution is greater than the corresponding change in the gaseous state. These results are in accord with the observation of Fairbrother for the increase of the total dipole moment of HCl when in benzene solution. This increase in change of dipole moment may explain the difficulty of observing the Raman spectra at room temperature.

On account of intense bands of benzene occurring in the regions of 1.76μ and 3.46μ it is difficult to observe the absorption bands of HCl in a benzene solution accurately. However, there are other organic solvents which do not have bands in these regions that may be used. Then the position of the HCl solution band can be determined with greater accuracy than in the present work.

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[5] L. A. Woodward, Physik. Zeits. **32**, 777 (1931).

[6] W. West and P. Arthur, J. Chem. Phys. **2**, 215 (1934).

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Note on a Band System of Caesium

P. KUSCH AND F. W. LOOMIS, *University of Illinois*

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A further attempt is made to analyze a band system of Cs_2 at 6250A. It has been possible to arrange a number of bands, degraded to the red, into a square array and to assign quantum numbers to the lower state. An assignment reported for this system by Matuyama is shown to be incorrect.

THE molecule Cs_2 gives rise to several band systems in absorption. An analysis has been given[1] for several of these systems, but an extremely complex system whose maximum intensity lies at about 6250A has not been satisfactorily analyzed. Rompe[2] has observed this system in absorption and Matuyama[3] has reported an analysis on the basis of Rompe's data. While the data of Rompe agree in a rough way with those of Loomis and Kusch, many close groups of bands are not resolved by him, nor does he make any reference to the blue degraded bands which appear in this system and were reported by Loomis and Kusch.

It has been possible to find several progressions among the bands degraded to the red and to assign the quantum numbers of the lower state to the bands in these progressions by reference to the accurately known ground state of caesium. These progressions have been fitted into a square array. As was the case with the previously reported[1] bands in this system, degraded to the blue, it has been impossible to follow the system to its origin and therefore to assign quantum numbers to the upper state. Matuyama reports an origin of the system at 15,801 cm^{-1} but this assignment is believed to be incorrect. For, certain of Matuyama's progressions may be iden-

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[1] Loomis and Kusch, Phys. Rev. **46**, 292 (1934).

[2] Rompe, Zeits. f. Physik **74**, 175 (1932).

[3] Matuyama, Tohoku Imp. Univ. Sci. Rep. **23**, 322 (1934).