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The Infrared Absorption Spectrum of Hydrogen Chloride in Solution

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The near infrared absorption bands of HCl in nonionizing solvents in the neighborhood of 3.5μ and 1.8μ, measured with a 3600 line per inch grating, have the following characteristics; they show no rotational structure; they usually have two components of unequal intensities; the absorption region is displaced towards lower frequencies compared with the gas. The displacement is independent of concentration up to mole fraction 0.1, but increases with diminishing temperature in certain solvents. The interval between the components varies directly with the dielectric constant of the solvent. In solution, the relative displacement of the more intense component from the origin of the gas band is approximately the same for the 3.5μ and 1.8μ bands, as is also the interval between components. A simple relation exists approximately between the frequency displacement from the gas origin and the dielectric constant of the solvent, of the form $\Delta\nu/\nu = C[(D-1)/(2D+1)]$, a deduction of which formula has been made by J. G. Kirkwood. The more intense component, whose relative shift from the gas origin is within the limits of error the same as the corresponding shift in the Raman spectrum, is interpreted as originating in the internuclear vibration, and it is tentatively suggested that the other component represents a combination between such vibrational transitions and some slow intermolecular vibration between HCl and solvent molecules. The effect of the medium on the anharmonic character of the mechanical and electrical vibrations in the HCl molecule is qualitatively discussed.

THIS investigation was undertaken for the sake of confirming with greater precision the results of the previous communication on the influence of solvents on the vibrational frequencies of simple polar molecules and to extend the observations to higher vibrational transitions than the first. Absorption spectra are also much more sensitive at low concentrations than Raman spectra, making it possible to use much lower concentrations of solute, and therefore to study the influence of solvent on solute uncontaminated by possible interactions between the solute molecules themselves; and finally, as it has turned out, new information on the structure of the HCl absorption bands, of which no hint was given by the Raman spectra, has been secured. The nature of absorption spectra, however, places more limitations on the choice of solvent than are presented by Raman spectra; for while the Raman lines of a pure liquid are often quite sharp, absorption bands increase greatly in intensity and width as the thickness and concentration of absorbing layer increases, with the result that, while it is relatively easy to find compounds with no lines too near the HCl Raman line, most organic compounds interfere in the infrared. The "C−H bands" centered about 3.3μ and their overtones at 1.7μ may easily spread so as to cover the HCl absorptions centered at about 3.5μ and 1.76μ. Even if very thin layers of concentrated HCl solutions in organic compounds are used, the HCl absorption is, at best, superposed on a region of rapidly varying solvent absorption, a condition not conducive to accuracy in the determination of the maximum or of any structure in the solute band. Except, then, in cases in which we purposely wished to measure the absorption of thin layers of concentrated solutions, we have avoided organic solvents containing more than one hydrogen atom, but, at the same time, the smaller concentrations necessary for absorption have enabled us to use certain inorganic solvents whose freezing points did not permit cooling to a sufficiently low temperature to obtain an adequate concentration of solute for Raman work.

Besides the Raman results of the previous paper, the information from previous work relevant to the investigation of HCl solutions is to the effect that the fundamental of liquid HCl has a single maximum displaced by about 100 cm^{-1} to lower frequencies than the origin of the gas band;[1] that the first overtone of liquid HCl has a single maximum similarly displaced by 125 cm^{-1};[2] no absorption corresponding to gaseous absorption of HCl is present in aqueous solution,[3] while recently, with fluorite prism dispersion, Plyler and Williams have found a

[1] G. Hettner, Zeits. f. Physik 89, 234 (1934).
[2] E. O. Salant and W. West, Phys. Rev. 37, 108 (1931).
[3] E. K. Plyler and E. S. Barr, J. Chem. Phys. 2, 306 (1934).

single maximum for HCl dissolved in benzene at about 3.4μ.[4]

APPARATUS

A grating spectrometer was used along with a rough prism monochromator for removal of higher orders of wave-lengths shorter than those under investigation. The grating, ruled by Professor R. W. Wood to concentrate light in the first order of 3.5μ, had 3600 lines per inch and a ruled surface 5 in.$\times$4 in. The light from the entrance slit was collimated and thrown on the grating, and the diffracted light focused on the exit slit by separate mirrors, of 50 cm focal length and aperture $f/3$. A single junction thermopile was used, made by Dr. J. D. Hardy of the Russell Sage Institute of Pathology, New York. The galvanometer was a Leeds and Northrup HS, sometimes used in conjunction with a Moll thermorelay amplifier. The monochromator prism for work on the first overtone was a 30° glass prism, and for the fundamental two 20° rocksalt prisms were used through which the light was passed twice. The whole instrument was enclosed in a galvanized iron box covered with Celotex. As light source, a 500-watt tungsten-filament projection lamp was used at 1.7μ, and a Nernst glower, consuming about 70 watts, at 3.5μ. In the course of the investigation of the fundamental it developed that special care had to be taken to prevent the entrance into the grating slit of spurious light of wavelength 1.7μ, which, in the light from the Nernst glower, is far more intense than light of wavelength 3.5μ. For this purpose a Pfund filter of zinc oxide on mica of the required transmission characteristics was interposed near the monochromator slit,[5] and the efficacy of the filter-monochromator arrangement proved by our obtaining the theoretical intensity relationships between the P and R rotational lines of the gas.

The instrument was calibrated by measuring the HCl gas rotational-vibrational lines with the use of Meyer and Levin's values for the frequencies.[6] Slit widths covering a spectral range of 4 cm^{-1} were used at 1.7μ and 6 cm^{-1} at 3.5μ.

In the region of the first overtone, glass windows were used on the absorption cells, in some cells fused on, in others clamped liquid tight without the use of grease or cements. According to the experiment, the cell length for solutions in this region varied from about 5 to 25 cm; the diameter was 5 cm. The overtone of liquid hydrogen chloride was observed in a quartz cell 1 mm thick and 5 cm diameter. This cell was made like a Baly cell by fusing windows to quartz tubes, one sliding within the other, separating the two windows by a ring of platinum wire 1 mm in diameter, and fusing together the two tubes at the end remote from the windows. Inlet and outlet tubes were fused to the outer tube. The length of the absorption path can be altered by cutting open the seal, separating the windows to the desired distance, and resealing.

Quartz windows were used at 3.5μ. The cell here was 1 cm long and 4 cm in diameter provided with inlet and outlet tubes. Such cells can easily be made by cutting Pyrex rings of the desired length, drawing out with the help of a pointed flame a small cone in the side which can be fashioned into a small hole, on which is fused, without subsequent working, the very hot end of a narrow bore side tube. The ends are now ground and polished and the windows pressed on by clamping (Fig. 1).

In low temperature experiments, condensation of ice on the windows was prevented in the manner illustrated in the diagram (Fig. 2). The P_2O_5 prevented condensation on the cell windows, and the heating wire prevented cooling of the other two below the dew point. Sufficiently constant temperature of $-65°C$ was secured in the cell by packing the vessel with dry ice and occasionally replenishing during an experiment. Temperatures were read by means of a copper-constantan couple inclosed in a tube immersed in the solution.

Transmissions were determined by evaluating immediately after each other at a given grating setting the galvanometer deflections for the substance under investigation and for a blank in an identical cell; the blank was air in determining the transmission of the pure solvents, and in calibrating by means of HCl gas, and the

[4] E. K. Plyler and D. Williams, Phys. Rev. 49, 215 (1936).
[5] A. H. Pfund, Phys. Rev. 36, 71 (1930).
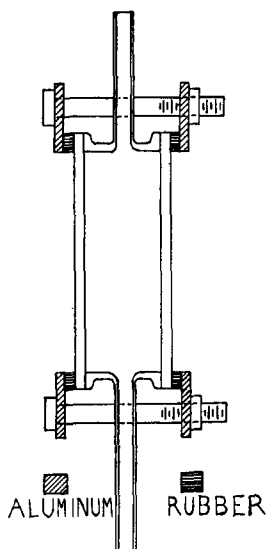[6] C. F. Meyer and A. A. Levin, Phys. Rev. 34, 44 (1929).

FIG. 1. 1 cm cell.

FIG. 2. Low temperature apparatus.

solvent in the case of solutions. The two cells were mounted on a carriage sliding on ways perpendicularly to the direction of the light beam so that first one and then the other was in the path. With the exception of chloropicrin, $CH(NO_2)_3$, all the nonionizing solvents used had a practically uniform transmission of 85 percent to 100 percent in the region of HCl absorption.

Solvents were distilled into the absorption cell from an efficient rectifying column in an all-glass apparatus. Purity was checked by boiling point, and refractive index determinations. Special attention was paid to preventing the entrance of traces of water to the solution. Hydrogen chloride was prepared by dropping concentrated sulphuric acid on hydrochloric acid and drying the gas.

The concentration of HCl in solutions in non-hydrolyzing solvents was measured by direct titration; in other cases the concentration has been estimated from the amount of infrared absorption. All results reported have been checked at least twice, and most of them more often. The maxima of absorption in the solution are flatter than those of HCl gas lines, in whose wave-lengths the limit of reproducibility is set by the reproducibility of grating settings; we judge the maxima reported for the solution spectra correct to within 2 cm^{-1}.
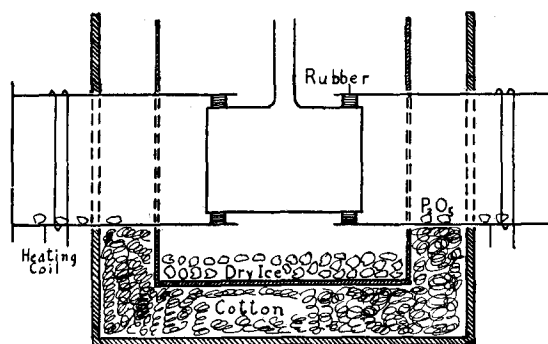
EXPERIMENTAL RESULTS

A glance at the diagrams (Figs. 3, 4, 5) shows the general nature of the absorption of HCl in nonionizing solvents. There is no sign of a structure analogous to the rotational structure of the gas. Except in carbon disulphide solution and in liquid hydrogen chloride two maxima of absorption are present, of which the low frequency one is the more intense. This latter band is of lower frequency, the other of higher than the origin of the gas band. (In the subsequent discussion of frequency differences between solution and gas absorption, these will be with reference to the gas band origin of HCl^{35}.) The interval between these maxima varies from solvent to solvent. In liquid hydrogen chloride, although only one maximum appears, the band is strongly asymmetrical, falling off much more rapidly in intensity towards the low frequencies from the maximum than towards the high frequencies. Compared with the gas absorption there is in solution a general shift to lower frequencies.

In the single case for which we have yet obtained data on both fundamental and harmonic, CCl_4 solutions, the appearance of the HCl absorption bands is similar in both regions and the separation between the two components almost the same.

EFFECT OF CONCENTRATION

The figures for CCl_4 solutions for the fundamental show no effect of concentration on the position of the maxima for a twofold change, and similarly, in the overtone in PCl_3 solution at $-67°$, a fivefold change in concentration is without effect.

EFFECT OF TEMPERATURE

There is a distinct shifting of the absorption of HCl in PCl$_3$ solution to lower frequencies with diminishing temperature. Also, the short wave satellite maximum becomes less distinct. The interval between the two maxima does not change appreciably at low temperatures. The asymmetric appearance of the liquid HCl absorption band, observed at −100°C, along with the tendency of the short wave maximum to

FIG. 3.

FIG. 4.
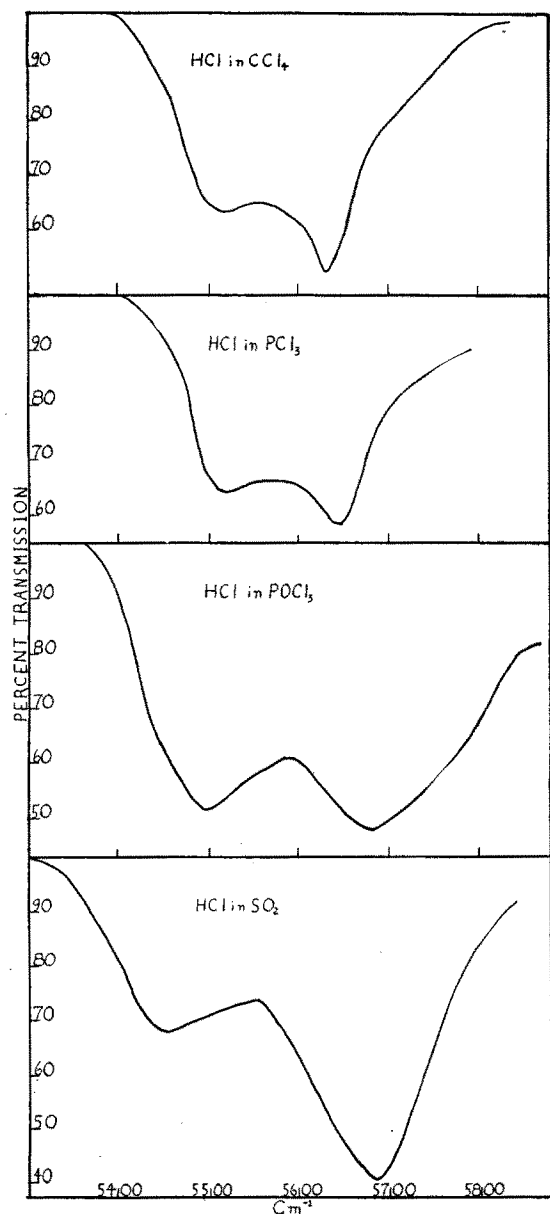
FIG. 5.
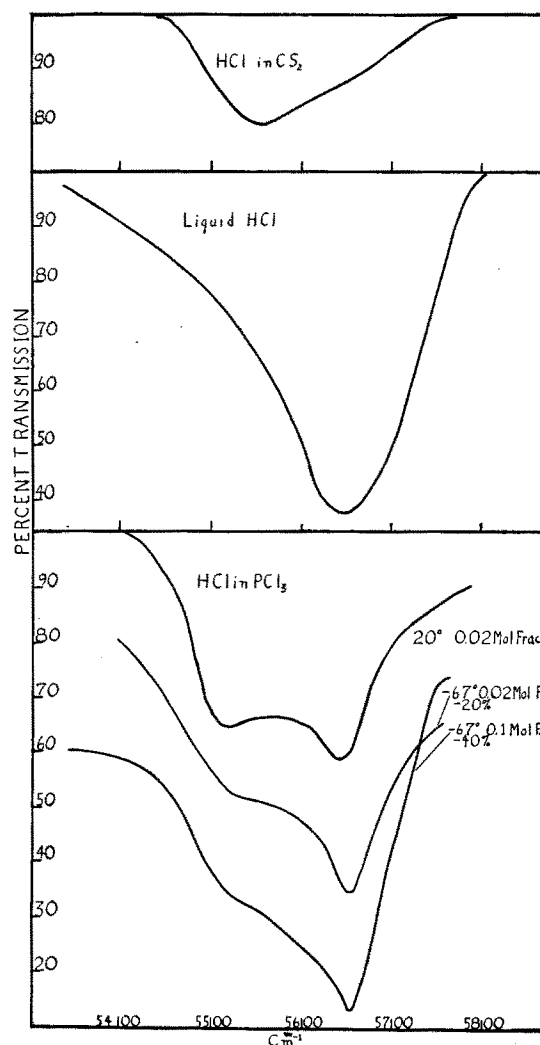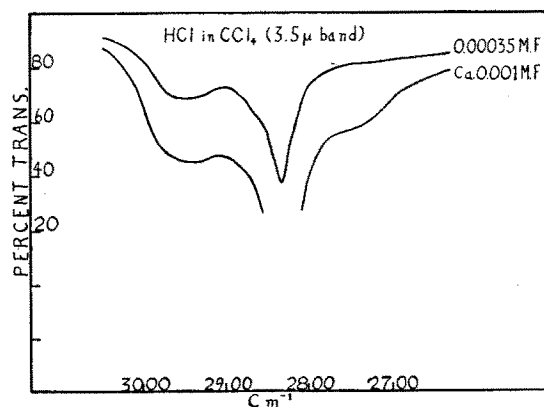
TABLE I. *0→1 vibration of HCl.*

SOLVENT	$T°C$	CONC. HCl (MOLE FRACTION)	ν_1	ν_2	$\nu_2 - \nu_1$
HCl GAS			2886		
CCl$_4$	20°	0.00035	2833	2939	106
	20°	.0007	2833	2939	106
HCl LIQUID (HETTNER)	−100°		2780		

disappear in solution at low temperatures suggests that the liquid band may also be composite and that if it were observed at sufficiently high temperatures two maxima might appear.

RELATIVE INTENSITIES OF GAS AND SOLUTION ABSORPTION

In solution in the various nonionizing solvents examined the maximum absorption in the solution band at 1.7μ was approximately the same as the absorption of the most intense lines of the gas containing the same number of molecules in the light path. The total width of the overtone in the two cases is also about the same. At 3.5μ, in carbon tetrachloride solution, the number of HCl molecules in the light path required to produce a given absorption at the maximum was less than one-tenth of that required to produce the same absorption in the most intense gas lines. The ratio of intensities of first overtone to fundamental is thus considerably smaller in this solution than in the gas. A similar considerably greater apparent absorption of the HCl fundamental in benzene solution over that of the gas has been observed by Plyler and Williams.[4]

IONIZING SOLVENTS

In addition to the solutions in nonionizing solvents, we have investigated the absorption of the electrically conducting solutions of HCl in ether and ethyl alcohol in the neighborhood of wave-length 1.7μ. Thin layers (1 mm) of concentrated solutions were used; and, although the absorption bands of the solvents in this region, the first overtones of the C−H bands, were somewhat intensified and broadened by the HCl, no suggestion of an absorption maximum due to HCl molecules was observed, a result in accord

with all published investigations of the absorption and Raman spectra of HCl in such solvents.

DISCUSSION OF RESULTS

While the lack of rotational structure in the solution bands was to be expected, the appearance of the solution bands, especially in sulphur dioxide and phosphorus oxychloride, at first sight, recalls the envelope of the P and R branches of the gas bands, such as would be observed if in solution the individual rotational lines of the branches were merged together but at the same time the significance of the branches as indicating negative and positive rotational transitions, respectively, were maintained. The separation between the two maxima in the solutions is in some solutions indeed comparable with that between the maxima of the P and R envelopes in the gas, nevertheless it seems very improbable that the two solution bands are to be interpreted in this way. 1. The high frequency band in solution is always of lower intensity than the other, in some cases, much lower, the opposite intensity relation to that for the R and P branches of a gas absorption band. As these intensity relations are determined practically by the statistical weights of the rotational levels and the Boltzmann distribution law, it is difficult to see how an inversion could take place in going from gas to solution. 2. Liquid HCl and HCl in CS_2 show only one band with a maximum of lower frequency than the origin of the gas band. Evidently these solvents are exceptional on any

TABLE II. *0→2 vibration of HCl.*

SOLVENT	$T°C$	CONC. HCl (MOLE FRACTION)	ν_1	ν_2	$\nu_2 - \nu_1$
HCl GAS			5668		
CS$_2$*	20°	0.009	5644		
CCl$_4$	20°	.018	5570	5675	105
PCl$_3$	20°	.02	5556	5678	122
	−67°	.02	5534	5660	126
	−67°	.10	5534	5660	126
HCl LIQUID	−100°	1.00	5551		
CH(NO$_3$)$_2$	20°	.02	5541	5668	127
POCl$_3$	20°	.02	5518	5702	184
SO$_2$	−65°		5513	5744	231

* Since the anomalous behavior of the HCl absorption in CS$_2$ as compared with that of other solutions might be associated with the low concentration of the saturated solution at 20°, we attempted to increase the concentration by lowering the temperature to −65°C. The experiment was not completely satisfactory, as the solution became cloudy, but the nature of the absorption was the same as at 20°.

interpretation of the solution doublet, but an exception consisting of the absence of an R branch, if it is normally exhibited, is very difficult to understand. 3. Although the interval between the two solution bands is for a number of solutions comparable with the "doublet separation" in the gas (125 cm^{-1}) it varies a good deal with the solvent, from 105 cm^{-1} in CCl$_4$ to 231 cm^{-1} in SO$_2$. To interpret the bands as produced in the same way as the P and R branches of the gas would involves the conclusion that the moment of inertia of dissolved HCl is greater in CCl$_4$ than in SO$_2$ in the ratio of $(\Delta\nu_{SO_2}{}^2 \cdot T_{CCl_4})/(\Delta\nu_{CCl_4}{}^2 \cdot T_{SO_2})$, approximately 6.5, where $\Delta\nu$ is the frequency interval between the two components at an absolute temperature T; and this would mean, if the reduced masses were the same in the two solvents, that the equilibrium internuclear distance in CCl$_4$ was about $2\frac{1}{2}$ times greater than in SO$_4$, a most improbable conclusion. 4. Lowering the temperature from 20°C to $-65°$ in PCl$_3$ solution makes the high frequency band relatively less intense, and no very accurate determination of its frequency can be made, but definitely the separation between the two bands at the lower temperature is not more than a few cm^{-1} different from that at 20°. If the two bands had been P and R branches, the separation would have diminished from 122 to 102 cm^{-1} at the lower temperature, which is certainly not true.

Our conclusion, therefore, is that the appearance of two maxima of absorption in the regions of the fundamental and first overtone vibrational bands of these solutions does not represent the liquid phase analog of the two branches of the gas absorption bands. How they do originate is a problem which is not unambiguously answered by our present data, but the high intensity of the long wave band and the fact that in certain solutions it alone is present suggest that it is the band originating in the internuclear vibration of the dissolved HCl molecule; and it is true that the relative displacement of the maximum of this solution band from the origin of the gas band agrees with the corresponding displacement of the Raman band. As only one internal vibration can exist in a hydrogen chloride molecule, the short wave satellite to the main band seems to originate in some other kind of motion not existing in the gas and called up in solution. Arguments have recently been advanced from studies both of the spectral and dielectric properties of liquids that polar molecules in the liquid state undergo more or less regular torsional oscillations about relatively slowly moving positions of equilibrium.[7] Thus, liquid water has frequencies of 500 cm^{-1} and 167 cm^{-1} which are absent in the vapor, and which have been attributed by Cartwright to a torsional oscillation of the water molecule and an intermolecular vibration respectively, and Ellis[8] had previously suggested as explanation of some features of the water spectrum peculiar to the liquid that they were combination bands between intramolecular vibrations and a low frequency vibration of about 500 cm^{-1}. It is perhaps possible that an HCl molecule in a solvent medium may be disposed in such a way as to carry out similar oscillations, and we tentatively make the suggestion that the short wave component of the near infrared absorption bands of HCl in solutions is a combination frequency between the intramolecular nuclear vibration which gives rise to the long wave component and a torsional vibration of the HCl molecule or perhaps some other kind of intermolecular solute-solvent vibration of frequency varying between 100 cm^{-1} and 230 cm^{-1} according to the solvent. The approximate identity of the frequency difference between the two components in the fundamental and first overtone of HCl in CCl$_4$, which, on the hypothesis advanced, is equal to the slow intermolecular vibration, is in accord with this explanation; and such a motion would also depend on the nature of the force field due to the solvent molecules acting on the solute and lead to a different frequency in different solvents. Fig. 6 shows indeed that the interval between the two components of the first overtone of HCl is approximately directly proportional to the dielectric constant of the solvent.

[7] M. Magat, J. de phys. et rad. **5**, 347 (1934), which see, for reference to previous work by Segrè and by Bolla, J. D. Bernal and G. Tamm, Nature **135**, 229 (1935); P. Debye, Zeits. f. Physik **36**, 100 (1935); J. H. Cartwright, Phys. Rev. **49**, 470 (1936).
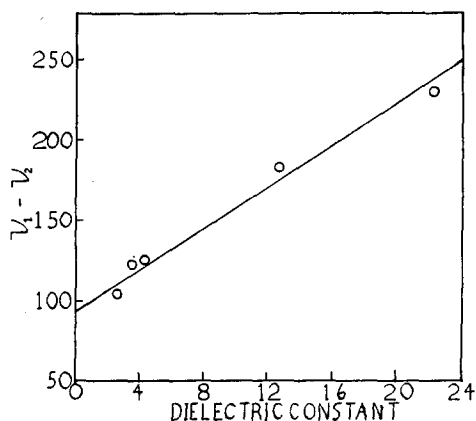
[8] J. W. Ellis, Phys. Rev. **38**, 693 (1931).

FIG. 6. Separation of maxima as a function of dielectric constant.

FREQUENCY SHIFT

It is evident that if the stronger maximum is taken to represent the internuclear $H - Cl$ vibration in the dissolved molecules it is displaced from the origin of the gas band in the same way as the Raman frequencies. Table III, in which $(\Delta\nu/\nu)_{01}$ represents the relative displacement of the fundamental in solution, from Raman data, except for CCl_4, and $(\Delta\nu/\nu)_{02}$ of the first overtone shows that the relative displacements of the two bands are about the same. The figures of Jung and Gude[9] show a similar approximate constancy in the relative displacement of the frequency of the 4th, 5th and 6th harmonics of 22 normal aqueous ammonia solution.

A very general treatment of the changes in vibrational frequency suffered by molecules in dispersive media has been made by G. Breit and E. O. Salant.[10] A displacement of the absorption frequency is found at high density of the dispersive medium, describable in terms of at least three effects; one analogous to the classical Lorentz-Lorenz pressure damping, one originating in electrostatic interaction of the molecule with its neighbors, due to its excitation, and one originating in overlapping of the electronic wave functions, an electronic "exchange effect." Beyond showing that the observed diminution in frequency produced by liquefying HCl and HBr was much too large to be ascribed to the Lorentz-Lorenz interaction, these authors

made no attempt to evaluate the contributions of the various actions.

J. G. Kirkwood, using the model of a point dipole in a continuous dielectric he employed in his calculations of the chemical potential of ionic dipoles in dielectric media,[11] has deduced an expression for the change in vibrational frequency of a dipole caused by the change in energy consequent on the electrostatic interaction of medium and dipole, in a calculation to be offered by him for publication at a later date. The expression for the relative frequency shift is $(\Delta\nu/\nu) = C[(D-1)/(2D+1)]$, where C is a constant and D the dielectric constant of the medium. This function is seen to reproduce qualitatively the observed variation of frequency of HCl and HBr with dielectric constant of the solvent—it reaches a limiting value of $C/2$ at high dielectric constants, and in fact, practically at moderate values of D. Taking for HCl the empirical limiting value of 0.03 for $\Delta\nu/\nu$, we find $C = 0.06$; in Fig. 7, the curve represents the function $0.06[(D-1)/(2D+1)]$ and the only experimental points seriously off the curve are for CS_2 and liquid HCl. The constant C depends on the details of the model; for a point dipole at the center of the sphere of radius b occupied by the molecule, it has the value α/b^3, where $\alpha = (10^{28}(\mu_1^2 + 2\mu_0\mu_2))/((2\pi\nu_0c)^2I)$, with μ_0 the electric moment of the dipole at the equilibrium position r_0, in units of 10^{-18} e.s.u.

$$\mu_1 = [(\partial\mu)/(\partial r)]_{r_0}, \quad \mu_2 = [(\partial^2\mu)/(\partial r^2)]_{r_0}$$

and I the moment of inertia in units of 10^{-40}. Substituting Bourgin's[12] value for the first derivative, 1.06, and Dunham's[13] smaller value, ap-

TABLE III. *Relative displacements of fundamental and first overtone frequencies HCl solution.*

SOLVENT	D	$(\Delta\nu/\nu)_{01}$	$(\Delta\nu/\nu)_{02}$
$CS_2(20°)$	2.64		0.0042
$CCl_4(20°)$	2.24	0.0187	.0173
$PCl_3(20°)$	3.43		.0198
$PCl_3(-65°)$	4.2	.022	.0236
$POCl_3(20°)$	12.7		.0264
$SO_2(-65°)$	22.4	.030	.0274
LIQUID HCl $(-90°)$	8.85	.030	.0206

[9] G. Jung and H. Gude, Zeits. f. physik. Chemie **B18**, 380 (1932).
[10] G. Breit and E. O. Salant, Phys. Rev. **36**, 871 (1930).
[11] J. G. Kirkwood, J. Chem. Phys. **2**, 351 (1934).
[12] D. G. Bourgin, Phys. Rev. **29**, 815 (1927).
[13] J. L. Dunham, Phys. Rev. **35**, 1347 (1930); J. E. Rosenthal, Proc. Nat. Acad. **21**, 281 (1935).

proximately zero, for the second, and using Zahn's value of the electric moment as μ_0 one finds $\alpha = 0.0146$ and $b = 0.62$A, to be compared with a reasonable value of about 2A. Kirkwood, however, argues that since the electrical center of the HCl molecule is probably displaced towards the proton, the point dipole in the model must be displaced a distance a from the center of the sphere of radius b, making

$$C = (\alpha/b^3)[(1+a^2/b^2)/(1-a^2/b^2)^3].$$

If a is assumed 1.27A, i.e., the point dipole, of moment equal to the observed, imagined to exist in the HCl molecule to account for its dielectric actions on its surroundings, is placed near the proton, the reasonable value of 1.7A for b will satisfy the observations.

This theory of Kirkwood's is also qualitatively correct in predicting the same relative shift for overtones as for the fundamental. It may also be pointed out that this relation between frequency and dielectric constant can account for the greater displacement of the HCl absorption in PCl$_3$ at lower temperatures, as the dielectric constant of this polar solvent increases considerably with diminishing temperature.

E. Cremer and M. Polanyi[14] have attempted to see in the diminution in frequency of HCl produced by liquefaction that loosening in binding, as a result chiefly of the electronic exchange interactions with other systems, which is a preliminary to chemical action between homopolar molecules, the third effect deduced by Breit and Salant as effective to the first order at high densities. The frequency shift thus calculated amounts to a diminution of a few per thousand, against the observed change of a few percent. The situation seems to be then that the electrostatic forces make the largest contribution to the energy charges when HCl and HBr are liquefied or dissolved in nonreactive solvents, and that Kirkwood's calculation of their magnitude is, in principle, correct. The Raman experimental data for SO$_2$ in solution, and also our knowledge of the electric moment derivatives are inadequate for a test of the theory, though there is a tendency of the shift to increase with dielectric constant of solvent, while for ammonia

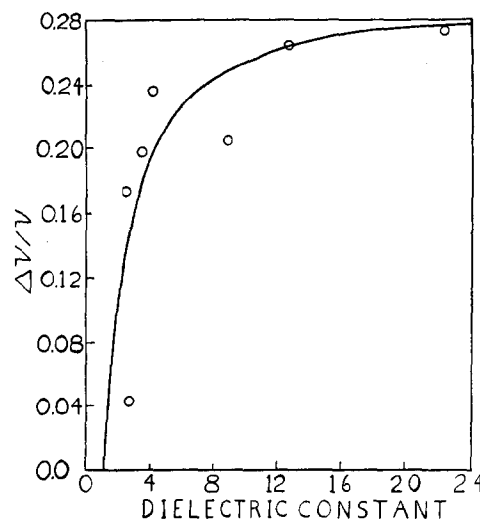[14] E. Cremer and M. Polanyi, Zeits. f. physik. Chemie, Bodenstein Festband, 770 (1931).

FIG. 7. Relative shift as a function of dielectric constant.

our Raman and Jung and Gude's absorption results cannot be accounted for by the electrostatic effect alone.

ANHARMONIC NATURE OF VIBRATION IN SOLUTIONS

If we apply the theory of the anharmonic oscillator to the maxima of absorption of the $0 \rightarrow 1$ and $0 \rightarrow 2$ bands of HCl dissolved in carbon tetrachloride, we find an $\omega_0 x$ factor of 48 cm^{-1}, not very different from the gas value of 52 cm^{-1}. The less accurate Raman values for the $0 \rightarrow 1$ vibration along with the absorption for the $0 \rightarrow 2$ in PCl$_3$ and SO$_2$ also lead to anharmonic factors near that of the gas. Hettner's figures for the absorption of the fundamental of liquid HCl with ours for the overtone give an anharmonic factor of 10 cm^{-1}, much smaller than that of the gas. It is apparent that in dilute solutions of HCl in the solvents we have examined, the potential energy function differs from harmonic in approximately the same way as in the gas. On the other hand, the considerable increase in the intensity of the $0 \rightarrow 1$ vibration of HCl in carbon tetrachloride, compared with that of the gas as estimated in the way indicated in the section on results, and the approximate equality of the absorption of the $0 \rightarrow 2$ vibration in the two phases point to rather considerable changes in the coefficients of the electric moment

as a function of internuclear distance.[15] In this connection it is perhaps interesting to recall the peculiar intensity relations in the harmonics of the liquid hydrogen halides.[2] Although gaseous HI absorbs very feebly in the fundamental and

[15] We can make no statement from our measurements as to the relative magnitudes of the true absolute intensities in gas and solution. The gas measurements being made with slit widths of 4–6 cm^{-1}, amply adequate to resolve the rotational structure and for calibration with sufficient accuracy for our purpose, but very large compared with the natural width of the lines, indicate an apparent absorption at the maxima of the lines much less than corresponds to the true absorption coefficient. In solution, on the other hand, rotational structure having disappeared, and the variation of absorption coefficient over the region covered by the slit being small, the apparent absorptions are much closer approximations to the true, and our measurements here should give a fairly accurate value of the mean transition probability for the 0→1 vibrational transition according to the method employed by E. Bartholomé (Zeits. f. physik. Chemie **B23**, 131 (1933)). But at present it does not seem profitable to discuss the absolute magnitude of the absorption intensity in solution until the difficulty presented by the serious discrepancy between the results of Bourgin and Dunham, on the one hand and of Bartholomé, on the other, has been resolved. See especially E. C. Kemble, J. Chem. Phys. **3**, 316 (1935).

first overtone, the liquid absorbs as well as liquid HCl and HBr in the first overtone, and in fact, the 0→3 transition was found in HI at a thickness of absorbing layer at which this transition was unobservable in the other two halides. In these changes of intensity between the dilute gas and liquid and solution we are evidently dealing with effects of the medium on the electric moment-internuclear distance curve, which could take the forms of shifting the equilibrium distance on the curve and of altering its shape, from the investigation of which it may ultimately be possible to gain further insight into molecular interactions in the condensed state.

We are greatly indebted to Professor John G. Kirkwood of Cornell University for his discussing with us his theory of the frequency shifts, and to the Physics Department of Washington Square College for the use of much of the equipment employed.

The Absorption Spectra of Salts of Ytterbium in Crystals and Solutions Compared with Those of Cerium

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The absorption spectra of salts of ytterbium [the chloride $YbCl_3 \cdot 6H_2O$, the acetate $Yb(C_2H_3O_2)_3 \cdot 4H_2O$ and the ethylsulfate $Yb(C_2H_5SO_4)_3 \cdot 9H_2O$] were found to resemble those of cerium very closely, especially in their diffuseness even at low temperatures. This is in marked contrast with the sharp spectra of the other rare earths. The resemblance was anticipated on the supposition that the thirteen electrons in the $4f$ shell of Yb^{+++}, one short of the maximum the shell can hold, would give rise to but one term ^2F, the same term as the one electron of Ce^{+++} gives rise to. That is, activations aside from fine structure, are impossible when the thirteen electrons remain in the $4f$ shell. This prohibition is derived from the Pauli exclusion principle as it has been applied in gases. The lattice, however, may possibly modify the application of this principle. It was thought likely that the activated states of the ions in crystals would respond to any change in the application of the principle the lattice might impose. The spectra show that the principle holds for these ions in crystals in exactly the same way as it does in gases. Strong confirmation is obtained that the sharp spectra of the other rare earths consist of "forbidden transitions," arising from a change in coupling among the electrons of the $4f$ shell.

T HIS work is concerned with whether the Pauli exclusion principle can be applied to spectra of ions in crystals and solutions in precisely the same way as it has been applied to ions in gases. Even if it be granted that the Pauli principle is valid for ions in crystals, there yet remains the uncertainty that the usual operation of the principle may be modified by the influences

in the lattice which have no parallel in gases. Such influences if they exist are most likely to be revealed at present with ions of the rare earths in their activated states.

The basic electronic states of these ions, with possibly one or two exceptions, are known definitely[1] from their magnetic susceptibilities. The

[1] F. Hund, Zeits. f. Physik **33**, 855 (1926).