[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Infrared Spectra of Iodine Monochloride Charge-transfer Complexes[1]

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This paper reports a study of the changes in the infrared spectrum of the iodine monochloride stretching vibration as the halogen forms complexes of increasing stability. Difficulties due to the chemical reactivity of iodine monochloride were encountered and, to a certain extent, eliminated. The spectrum of this band proved to be very sensitive to the strength of interaction between the halogen and the donor molecule with which it complexed. The frequency decreases regularly from 375 cm.$^{-1}$ for uncomplexed ICl in carbon tetrachloride to 275 cm.$^{-1}$ for the strongest complex, pyridine–ICl. The intensity of the band increases regularly with increasing strength of the complex and for pyridine–ICl complex it is eight times as great as the intensity of the band for uncomplexed halogen. The half-intensity width also increases with the strength of the complex. An attempt is made to explain some of these results in terms of "charge-transfer" theory. The analogy between these experimental results and the changes in the O–H stretching frequency on hydrogen-bond formation is discussed.

Introduction

Numerous investigators have prepared and studied the addition compounds of halogen and interhalogen molecules. In many cases, however, the interaction between the components of such complexes is rather weak and only indirect evidence of the addition reaction can be obtained. The pioneering work of Benesi and Hildebrand[2] showed that spectrophotometric methods provided a powerful tool for the study of weak halogen complexes. The data from such measurements not only established the chemical nature of these complexes but also yielded formation constants. Andrews and Keefer have reported studies on iodine and iodine monochloride complexes with aromatic substances.[3] They found that an increase in the basic character of the benzene molecule resulted in the formation of stronger complexes. Thus, for example, the formation constants for the complexes Ar·IX (X = I or Cl) are ranked in the order mesitylene > xylene > toluene > benzene. Recently the formation constant of the complex $CH_3CN\cdot ICl$ has been measured[4]; it was found that this complex is somewhat more stable than the mesitylene complex. Thus there are a number of complexes of ICl for which formation constants are known.

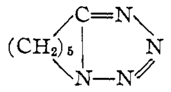
A number of investigations of the infrared spectra of these "charge-transfer" complexes have been made.[5-9] However, much of this work was concerned with the study of changes in the spectrum of the solvent, or donor, molecule on the addition of halogen. Often little change was observed in this spectrum for weak complexes, partly because the concentration of complexed donor was so low.

The theory of this kind of complex formation, proposed in a number of papers by Mulliken,[10-12] indicates that the most profound spectral change should be in the spectrum of the halogen molecule. This is strikingly confirmed in the two papers by Collin and D'Or[7,8] on the spectra of chlorine and of bromine in benzene.

A study of the spectrum of iodine monochloride in solutions where charge-transfer complexes are formed should yield similar striking results. Iodine monochloride complexes are much more stable than the iodine complexes, and thus certainly much stronger than the chlorine–benzene complex. Iodine monochloride has an allowed fundamental absorption at 382 cm.$^{-1}$ in the gas phase.[13] Thus, it can be studied easily with a spectrometer equipped with a cesium bromide prism. For these reasons we decided to study changes in the spectrum of this molecule as a function of strength of complex.

Experimental Part

Chemicals.—Iodine monochloride was prepared by the method of Cornog and Karges,[14] and was purified by repeated fractional crystallization. The melting point of the final product (27.2°) was identical with the literature value.[14] Pentamethylenetetrazole was obtained from Bilhuber-Knoll Corp. It was purified by recrystallization



from ether. The melting point of the purified product was 60–61°. Other solvents and donors are listed in Table I with the source and the method of purification, if applicable.

Pyridine·ICl complex was prepared by the direct reaction of solutions of pyridine and iodine monochloride in carbon tetrachloride. The precipitate was filtered on a sintered glass crucible, washed with solvent, and dried at 80° for two hours. Pentamethylenetetrazole (abbreviated below as PMT) complex was prepared in a similar manner.[15] Cesium iododichloride, iododibromide and tetramethylammonium iododichloride were prepared by standard methods.[16]

The iodine monochloride solutions were prepared by pipetting liquid ICl with a 1-ml. pipet graduated in hundredths of a milliliter. While this method of preparing solutions

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[1] This paper was presented in part at the 132nd Meeting of the American Chemical Society in New York, September 9, 1957. It is also paper XIV of the series "Studies on the Chemistry of Halogens and of Polyhalides."

[2] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[3] L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 4677, 5039, 5170 (1950); **74**, 640, 4500 (1952); **75**, 3561 (1953).

[4] W. Deskin, Ph.D. Thesis, State University of Iowa, 1957. See paper XV of this series to be published.

[5] W. Haller, G. Jura and G. C. Pimental, *J. Chem. Phys.*, **22**, 720 (1954), and references cited there.

[6] D. L. Glusker and H. W. Thompson, *J. Chem. Soc.*, 471 (1955)

[7] J. Collin and L. D'Or, *J. Chem. Phys.*, **23**, 397 (1955).

[8] L. D'Or, R. Alewaeters and J. Collin, *Rec. trav. chim.*, **75**, 862 (1956).

[9] E. E. Ferguson, *J. Chem. Phys.*, **25**, 577 (1956).

[10] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

[11] R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956).

[12] R. S. Mulliken, *J. Chem. Phys.*, **23**, 397 (1955).

[13] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950, p. 542.

[14] J. Cornog and R. A. Karges, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co , Inc., New York, N. Y., 1939, p. 165.

[15] A. I. Popov, to be published.

[16] A. I. Popov and R. E. Buckles, "Inorganic Syntheses," Vol. 5, McGraw-Hill Book Co., New York, N. Y., 1957, p. 172.

Table I

Source and Purity of the Solvents Used in This Research

Solvent	Source	Purification
Acetonitrile	Matheson, Coleman and Bell	Shaken twice with satd. KOH, twice with anhydrous Na_2CO_3, and distilled from P_2O_5, b. at 81°
Benzene	Mallinckrodt Analytical grade	Not purified
Carbon disulfide	Baker analyzed Reagent grade	Not purified
Carbon tetrachloride	Tech. grade	Distilled from BaO, b. 76.8°
Cyclohexane	Arthur S. Lapine Pract. grade	Not purified
Ethylene dichloride	Matheson, Coleman and Bell	Shaken twice with concd. H_2SO_4, twice with water, distilled two times from BaO
n-Heptane	Matheson, Coleman and Bell, 99%	Not purified
n-Hexane	Phillips 66 hydrocarbons, 99 mole % min.	Not purified
Mesitylene	Eastman Chemicals	Not purified
Nitrobenzene	Baker Chemical Co. "purified"	Not purified
Nitromethane	Eastman "spectro"	Distilled from P_2O_5, b. 100°
Pyridine	Eastman "spectro"	Not purified
Toluene	Fisher "purified"	Not purified
p-Xylene	C.P. grade Arthur S. Lapine Co.	Not purified

is not very exact, it is probably accurate enough for this work considering the limitations of other measurements. The error in the concentration for non-reacting solutions is probably less than 5%. Concentrations of solutions studied ranged from 0.01 to 0.2 *M* in ICl.

No special effects, such as are frequently observed in more dilute solutions of interhalogens, were noticed because of water dissolved in the solvents. Usually the solvents were dried before use, as a matter of principle, but no changes were noticed when solvents which had been used without drying were re-studied after drying.

Spectrometer.—The infrared spectra were obtained on a much-converted Perkin-Elmer Model 12C spectrometer, used in double-pass operation, with a CsBr prism. The source optics had been modified so that there was an external focus. Interference from atmospheric water vapor was eliminated completely by blowing dry air through the spectrometer. Spectral slit widths varied from two to three cm.$^{-1}$.

Cells were made of cesium bromide windows, following the design suggested by Lord, McDonald and Miller.[17] An amalgamated lead spacer of appropriate thickness was used. Most of the solutions were studied in a 1 mm. cell.

Other cells also were used in order to eliminate some of the reactions of the halogen with the cell (described in the next section). One of these was constructed from two cesium bromide windows, with no metal in contact with the solution. A hole the size of the light beam and 1 mm. deep was milled into the window. The solution (or solvent) was placed into this hollow, the top window put on, and the entire assembly was clamped tight enough in a demountable cell holder to prevent evaporation. Finally, some studies were made on a thin film of solution in a small polyethylene sack. This work was not quantitative, but direct contact of solution with the CsBr windows was eliminated.

To obtain the spectrum, we first ran a background curve over the region of interest, using the cell filled with solvent. Then the spectrum of the iodine monochloride solution was run, and the spectrum of the complex was obtained by replotting the absorbance against frequency. Readings of log I_0/I were taken every one or two wave numbers and a smooth curve drawn through the points. In order to obtain intensities, the areas of the replotted curves were measured with a planimeter. In most cases, there was little difficulty with the wing absorption.

The spectra almost always were studied as soon as possible (15–20 minutes) after the solutions were prepared. This was done in order to minimize the effects due to possible reactions (next section).

Reactions. I. Low Dielectric Solvents.—We experienced a considerable amount of trouble due to the reactivity of the iodine monochloride. The reactions encountered are conveniently classified according to the nature of the solvent and then according to whether the reaction was with the solvent or with the cell. In this section we shall discuss the solvents with low dielectric constants.

For these solvents, the most troublesome reaction was the halogenation reaction with the solvent (or donor molecules). This reaction often occurred very rapidly, so that reliable spectra could not be obtained. These several donors underwent this reaction: cyclohexane, *n*-heptane, *n*-hexane, toluene, xylene, mesitylene and naphthalene. These reactions are characterized by evolution of a gas (presumably a hydrogen halide) on mixing and a color change from the orange-yellow of the iodine monochloride to the violet or brown color of iodine. Of course, the infrared absorption of the iodine monochloride decreases, or disappears altogether.

These halogenation reactions sometimes could be slowed down enough to obtain the spectrum by diluting the donor. Therefore, these reactive solutions were studied using a mixed solvent of the donor dissolved in carbon tetrachloride as the inert medium. For example, the spectrum of the toluene-ICl complex was obtained by studying a solution of 0.1 *M* ICl and 1.0 *M* toluene in carbon tetrachloride. For the weaker complexes, a 10 to 1 excess of donor was insufficient to complex all of the iodine monochloride. Then two absorption peaks would be observed, one at 375 cm.$^{-1}$ due to the uncomplexed molecules, and one at the lower frequency characteristic of the iodine monochloride in the complex.

Since this dilution technique usually did not prevent the halogenation reaction, but only slowed it down, we still had to estimate the concentration of the unreacted halogen at the time the spectrum was obtained. Often as much as 50% of the original ICl had reacted after 15 minutes. Solutions were prepared in the same way as those whose spectra were studied, and then titrated with standard sodium thiosulfate solution after an appropriate lapse of time. In this way we obtained an estimate, possibly accurate to 10%, of the concentration of unreacted halogen.

This dilution and titration technique enabled us to obtain the spectra of iodine monochloride complexes for all the donors listed above except for mesitylene and naphthalene, where the halogenation reactions were too fast.

Reaction with the cell in low-dielectric solvents appears to be limited to reaction of the iodine monochloride with the stainless steel. The stainless steel parts of standard Perkin-Elmer fixed liquid cells in contact with the iodine monochloride solution reacted immediately to give a dirty black precipitate which absorbed infrared light strongly in the region of interest. In order to prevent this, we made the cesium bromide cells described above, with metal parts of Hastelloy "C"[18] an alloy which completely resisted attack by the halogen.

Reactions. II. High Dielectric Solvents.—In solvents with high dielectric constants, further reactions of the iodine monochloride become important. The most troublesome reaction in these solvents appears to be one between iodine monochloride and cesium bromide from the window to give IBr_2^- and chloride ions. The solubility of cesium bromide in polar solvents results in solutions containing an appreciable amount of bromide ion which then reacts with the

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[17] R. C. Lord, R. S. McDonald and F. A. Miller, *J. Opt. Soc. Amer.*, **42**, 149 (1952).

[18] Obtained from the Haynes Stellite Company, Kokomo, Indiana.

iodine monochloride to give $IClBr^-$ ion. It has been shown previously[19] that in the presence of excess bromide ion the $IClBr^-$ ion reacts to give IBr_2^- and Cl^-. This reaction probably occurs on the surface of the cell windows with solvents which have low dielectric constants, but it is not very extensive due to limited solubility of products and reactants. In the solutions with high dielectric constants, however, the reaction is rapid and complete.

This reaction is characterized by the appearance of the orange IBr_2^- ion. Since many solutions of iodine monochloride are yellow-brown in the solvents under consideration, there is often little change in the appearance of the solution. However, in the infrared spectrum, the sharp iodine monochloride band disappears completely, and is replaced by a very broad intense band. This absorption band is probably due to the IBr_2^- ion, and extends from about 400 cm.$^{-1}$ down to the limit of transmission of our CsBr prism at 280 cm.$^{-1}$. We never were able to obtain satisfactory spectra of $CsIBr_2$ for comparison, either in Nujol mull, or as a pellet in CsBr, but the spectra were similar in appearance. The fact that this band is due to the presence of IBr_2^- ion in these solutions was proven by means of the ultraviolet spectrum. A solution of 0.1 *M* iodine monochloride in acetonitrile which had been standing in a CsBr cell for 20 minutes, was diluted several times and its spectrum was determined. This solution showed an absorbance maximum in the ultraviolet only at 256 mμ, which is characteristic of the IBr_2^- ion.[19] Measuring the absorbance, we estimated the conversion of the iodine monochloride to IBr_2^- ion to be quantitative.

Additional evidence that our difficulty in obtaining the characteristic iodine monochloride peak in these high-dielectric solvents was due to reaction with the cesium bromide and not due to something else (such as ionization) was obtained by studying a solution of 0.1 *M* ICl in acetonitrile in a polyethylene sack. The sharp iodine monochloride peak was observed in this solution, and there was no evidence of the troublesome broad absorption attributed to IBr_2^- ion.

The phenomena which we have just described occurred with solutions of iodine monochloride in acetonitrile, nitromethane, nitrobenzene, 1,2-dichloroethane and pyridine. In order to obtain the spectrum of iodine monochloride complexes with these high dielectric donors, we resorted to the technique of mixed solvents again. We found that solutions of 0.1–0.2 *M* iodine monochloride dissolved in about 10% acetonitrile (or other polar donor) in carbon tetrachloride were relatively stable to reaction with the cesium bromide cell. We verified that solutions of this type which had been in contact with the cesium bromide, and then diluted, did not show any absorption in the ultraviolet characteristic of IBr_2^- ion.

As before, some of the solutions with the weaker donors showed two bands, one at 375 cm.$^{-1}$ due to the uncomplexed iodine monochloride, and one at lower frequency due to the complex.

One other reaction possible in the high dielectric solvents is the reaction between iodine monochloride and the amalgamated lead spacer. We made the cell described above without the amalgam spacers, but the spectra of the solutions studied in it were not much different from the spectra obtained in the cells with spacers. It appears that the principal difficulty with reactions in high dielectric solvents was due to the formation of IBr_2^- ion, although the reaction with the spacer may be possible.

Results

The results are presented in Fig. 1 and Table II. Figure 1 shows the spectra of 0.1 *M* iodine monochloride in carbon tetrachloride, in carbon disulfide, in benzene, and in a 50–50 mixture of carbon tetrachloride and 1,2-dichloroethane, which contains 0.1 *M* PMT as the donor. The cell length is 1 mm. In order to see better the shape of the ICl–PMT spectrum, we have also shown the spectrum of a solution which is 0.04 *M* in ICl–PMT complex.

These four curves illustrate the spectral changes for the four types of interaction observed. These were: (1) no complex formation (carbon tetrachloride, cyclohexane, *n*-heptane, *n*-hexane); (2) weak interaction (carbon disulfide, 1,2-dichloroethane, nitromethane); (3) moderately strong interaction (benzene, nitrobenzene, toluene, *p*-xylene, acetonitrile); and (4) very strong interaction (PMT, pyridine).

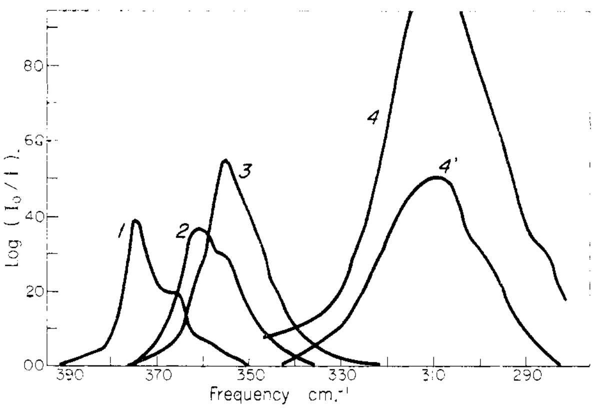

Fig. 1.—Infrared absorption by the I–Cl fundamental stretching vibration in some typical complexes: curve 1, ICl dissolved in carbon tetrachloride; curve 2, ICl dissolved in carbon disulfide; curve 3, ICl dissolved in benzene; curve 4, pentamethylenetetrazole–ICl complex dissolved in a 50-50 mixture of carbon tetrachloride and ethylene dichloride. All spectra were obtained from solutions which were 0.1 *M* in ICl except curve 4′, which was 0.04 *M* in PMT–ICl complex. The cell was approximately one mm. in length.

We have plotted the curve for the PMT–ICl complex rather than for the pyridine–ICl complex because we did not obtain the complete curve for the latter. The absorption of light by the CsBr prism sets a lower limit of 280 cm.$^{-1}$ to our measurements. From the appearance of the absorption band of the pyridine–ICl complex at this frequency, we estimate that the absorption maximum will come around 275 to 270 cm.$^{-1}$, and that the intensity will be of the same order of magnitude as for the weaker PMT complex.

Table II summarizes the results for all the solutions studied. We list the values of the three parameters of the iodine monochloride absorption band: the frequency, ν, the apparent, integrated molar absorption coefficient, *B*, and the half-intensity width, $\Delta\nu_{1/2}$. Where it is resolved, the half-intensity width is given for the ICl^{35} peak. Estimated errors are listed for the intensities. The error in the frequency should be less than 2 cm.$^{-1}$, and the uncertainty in the half-intensity width is about the same. Beer's law plots were made on only three solutions: ICl in carbon tetrachloride, ICl in benzene and PMT–ICl in the 50–50 carbon tetrachloride–1,2-dichloroethane solution. For the other solutions the intensity must be considered to be only semi-quantitative, with the estimated error depending on the number of times the band was studied, the extent of any reaction, etc.

We noticed a small frequency shift between some of the complexes dissolved in carbon tetrachloride, and the frequency of iodine monochloride in pure donor. The values of the frequencies in both cases are reported.

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[19] A. I. Popov and R. F. Swensen, THIS JOURNAL, **77**, 3729 (1955).

TABLE II

SUMMARY OF THE DATA ON THE FUNDAMENTAL ABSORPTION BAND OF IODINE MONOCHLORIDE IN VARIOUS COMPLEXING SOLUTIONS

Donor	K_c[a]	ν[d] (cm.$^{-1}$)	$\Delta\nu_{1/2}$[d] (cm.$^{-1}$)	$(B \times 10^{-3})$[d] (darks[b])
Carbon tetrachloride	...	375	8	1.05 ± 0.10
n-Heptane	...	375	10	0.9 ± .2
n-Hexane	...	375	10	1.1 ± .2
Cyclohexane	...	375	10	....
Nitromethane[e]	(~1)	363	15	1.0 ± .5
Ethylene chloride[e]	(~1)	365	12	1.5 ± .3
Carbon disulfide	...	361	12	1.4 ± .3
Benzene[e]	0.54	355(359)	15	1.9 ± .3
Nitrobenzene[e]	(~2)	358–362	15	2.1 ± .5
Toluene[e]	0.87	356	14	2.1 ± .4
p-Xylene[e]	1.5	350(354)	15	1.5 ± .4
Acetonitrile[e]	6.9	352	15	2.2 ± .5
PMT[e]	~10^3	310	26	7.7 ± .5
Pyridine[e]	5×10^5	~270	~30	~8
Vapor[c]	.....	382	..	0.65 ± .16

[a] From Andrews and Keefer, THIS JOURNAL, **74**, 4500 (1952), except for acetonitrile (ref. 4), pyridine [A. I. Popov and R. H. Rygg, *ibid.*, **79**, 4622 (1957)] and PMT (ref. 15). Values in parentheses are from this research (see text). [b] 1 dark = 1 cm.$^{-1}$ cm.^{2}/mmole. [c] From W. V. F. Brooks and B. Crawford, Jr., *J. Chem. Phys.*, **23**, 363 (1955). [d] Entries in this column are for the ICl absorption in a solution where the donor is the solvent, except for the donors marked *e*. [e] For these, the observation was made for ICl dissolved in a mixed solvent of donor in carbon tetrachloride. In the column of intensities, correction has been made for reaction of ICl by the method described in the experimental section. Solid pyridine–ICl and PMT–ICl were dissolved in benzene for the former and in 50% ethylene dichloride–50% carbon tetrachloride for the latter. For benzene and *p*-xylene, values of ν in parentheses are those observed in carbon tetrachloride solutions, while the other values for ν were obtained in pure donor as solvent.

Equilibrium constants in Table II are calculated from concentrations in moles per liter, and are taken from the literature where possible. For some of the complexes values of the constant are not available. We have, therefore, estimated the order of magnitude of K_c from our measurements.

Discussion

One of the first things to come to our attention was the doublet structure of the iodine monochloride band in carbon tetrachloride (see Fig. 1). This structure, although surprising to us at first, is due entirely to the isotopic effect. The frequency of the iodine monochloride fundamental depends almost entirely on the mass of the chlorine atom. If the frequency for the ICl^{35} vibration is taken to be 375 cm.$^{-1}$, we calculate a frequency of 367 cm.$^{-1}$ for the ICl^{37} vibration, compared to the observed shoulder at 368 cm.$^{-1}$. The high isotopic abundance of Cl^{37} gives a band with appreciable intensity, and leads to this doublet structure. We observed no absorption in the infrared spectrum which indicates any dimer [$(ICl)_2$] in CCl_4 solutions.

In stronger complexes the iodine monochloride absorption becomes broader and more intense. The isotopic splitting is much less pronounced in CS_2–ICl and is absent altogether in benzene–ICl complexes. This is due to the broadening of the band observed for the stronger complexes.

It is obvious from Fig. 1 and Table II that there is a definite correlation between the three parameters of the iodine monochloride absorption band and the strength of the complex formed. This gives a very quick and easy method for classifying complexes of iodine monochloride semi-quantitatively according to their strength.

One of the more interesting results of this study is the fact that there seems to be a definite interaction between iodine monochloride and a number of so-called "purple" solvents. These solvents were listed above in the carbon disulfide group. The changes in the infrared are not completely unexpected, because there is some "blue shift" in the ultraviolet spectra of iodine monochloride dissolved in these solvents. This shift is small, and the heavy absorption of the solvent molecules prevented the detection of the charge-transfer spectrum which probably is present further out in the ultraviolet. The sensitivity of the infrared spectrum of the iodine monochloride to complex formation will provide us with a means of studying these complexes quantitatively.

Justification for the belief that the "carbon tetrachloride-type solvents" are normal solvents with little interaction with the solute is provided by the fact that we can account readily for the differences between the spectrum of ICl in the vapor state and in these solutions by the changed index of refraction. However, the changes observed on going to the stronger complexes are much greater than those expected from this simple index of refraction effect. It is true that this effect may account for some of the intensification observed in carbon disulfide solution, but less than half of this change is predicted; for all other solutions studied, the observed changes are much greater.

The charge-transfer theory[12] predicts changes of this sort, provided the complexed iodine monochloride molecule is located in an unsymmetrical position. According to this theory, stabilization of the complex is provided by resonance between a no-bond structure D····I–Cl and an ionic structure D^+–$(ICl)^-$. The electron transferred to form the latter structure is presumed to go into an antibonding orbital, thus causing the I–Cl stretching frequency to decrease. If we further postulate that this antibonding orbital is more or less strongly localized on the chlorine, we write the resonance structure as $(DI)^+$····Cl^-. Thus, as this structure becomes more important due to stronger interaction, the infrared absorption due to the I–Cl stretching motion will become more intense. From Fig. 1 and Table II, we see that this "charge-transfer" model for these complexes is consistent with the observed spectrum. It is of some interest to attempt a more quantitative check.

In the pure $(D{\cdot}I)^+$····Cl^- structure the separation between the positive and negative charges would be quite large. We can be moderately certain, in fact, that this distance will be greater than for cesium chloride. Using Fig. 3 of the paper by Rice and Klemperer[20] we can estimate that the

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(20) S. A. Rice and W. Klemperer, *J. Chem. Phys.*, **27**, 573 (1957).

force constant of the I–Cl bond in this ionic structure will be less than 0.75 millidyne/Å. On the other hand, the force constant for I–Cl in the vapor is 2.38 md./Å.[21] Thus, the importance of the structure $(DI)^{+}\cdots Cl^{-}$ to a given complex can be measured by how much the force constant has decreased from 2.38. The force constants for the I–Cl^{35} bond are listed as a function of frequency in Table III. If we consider the pyridine–ICl complex, for example, we see that the structure $(PyI)^{+}$–Cl^{-} must be of considerable importance.

TABLE III

FORCE CONSTANTS FOR THE I–Cl^{35} BAND AS A FUNCTION OF FREQUENCY

ν (cm.$^{-1}$)	k (md./Å.)	k/2.27
375	2.27	1.00
361	2.10	0.93
355	2.03	.90
310	1.55	.68
270	1.18	.52

Some verification of these deductions may be furnished by a consideration of the intensity changes. Using a simplified model, we can interpret the increased intensity of the I–Cl vibration in the complex as being due to an additional effective charge, ϵ_a ($\equiv d\mu/dr$) added to the chlorine atom. Thus, the total intensity is proportional to $(\epsilon_0 + \epsilon_a)^2$, where ϵ_0 is the intrinsic effective charge of a normal I–Cl molecule. Table IV lists the values of ϵ_a for some of the typical complexes. We see, for example, that ϵ_a is quite high for the pyridine–ICl complex. Thus, we would say that the intensity of the pyridine–ICl complex is consistent with a structure that is highly ionic.

TABLE IV

EFFECTIVE CHARGES FOR THE ICl BAND IN DIFFERENT COMPLEXES

Donor	$B \times 10^{-3}$ (darks)	$(\epsilon_0 + \epsilon_a)^a$ (d./Å.)	ϵ_a
CCl_4	1.0	2.5	0.0
CS_2	1.4	3.0	0.4
Benzene	1.9	3.5	1.0
PMT	7.7	7.1	4.5
Pyridine	8	7.2	4.7

[a] Calculated from equation 15 of reference 21: $(\epsilon_0 + \epsilon_a) = 1.537 \times 10^{-2}\sqrt{B/0.036465}$ d./Å.

It should be remembered that this interpretation of intensity data is extremely naive. With this in mind, it seems that one can still say that both the intensity data and the force constants are consistent with a resonance structure for the pyridine–ICl complex with a contribution of about 50% from the structure $(PyI)^{+}\cdots Cl^{-}$.

Comparison of the results presented here in Fig. 1 and Tables II–IV with the results obtained in studying the O–H stretching frequency in hydrogen-bonding systems[22,23] reveals striking similarity in the spectral changes observed with increasing interaction in the two systems. The characteristic decrease in frequency and increase in intensity and half-intensity width as the strength of the interaction increases are observed in both systems. Preliminary results in this Laboratory on the changes in the infrared spectrum of ICN complexes indicate that the spectral similarities between hydrogen-bonding systems and other charge-transfer complexes extend to the bending frequencies as well. Of course, the theory[10–12] of charge-transfer complexes includes hydrogen bonding as a special case. However, this is the first experimental verification, to our knowledge, of the similarity between halogen complexes and hydrogen bonds.

Finally, we should consider the question of ionization of the iodine monochloride or of the complexes. The argument outlined above seems to indicate that the Pyridine–ICl complex should ionize quite readily in a solvent of high dielectric constant. It is, in fact, well known that this does occur in dilute solutions in acetonitrile.[24] We were not able to find any evidence of ionization at the concentrations we studied in this work, however. We did not notice any particular difference in the behavior of pyridine–ICl in acetonitrile from the behavior of ICl alone in acetonitrile. The experimental difficulties we have encountered did not permit us to determine absolutely that ionization does, or does not, occur. At present, we do not think that it does to any extent for any of the solutions studied. We expect to continue our experiments on this phase of the work.

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