JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office.

VOLUME 89, NUMBER 15 JULY 19, 1967

Physical and Inorganic Chemistry

The Raman Spectra of Some Iodine, Bromine, and Iodine Monochloride Charge-Transfer Complexes in Solution[1]

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Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland. *Received November 21, 1966*

Abstract: The Raman spectra of iodine, bromine, and iodine monochloride have been studied in various solutions in the region below 400 cm^{-1} by means of a Raman spectrophotometer equipped with a 50 mw He–Ne laser. Quite satisfactory Raman spectra of these colored solutions were obtained, but for some bromine and iodine chloride complexes chemical reactions occurred. The observed Raman frequencies for the halogens or the interhalogen were considerably lower than the corresponding gas values, and the data have been interpreted on the basis of charge-transfer interaction. Some very strong donor–halogen interactions were observed, in which the stretching force constant of the halogens was reduced to approximately half the gas value. A Raman band at 163 cm^{-1} in the pyridine–iodine system was interpreted as the N–I stretching mode; otherwise no Raman bands were observed which can with certainty be assigned to the stretching of the donor–halogen charge-transfer bond.

Although a large amount of work has dealt with the infrared spectra of various charge-transfer complexes, these studies have mostly been concerned with perturbations in the donor spectrum on complex formation.[3] However, in line with earlier work by Collin and D'Or,[4,5] Person, *et al.*, several years ago focused attention on features in the acceptor spectra. In a series of papers[6–9] they studied changes in the I—Cl, Br—Br, and I—C≡N stretching vibrations when these acceptors were complexed with various donors. Invariably, the halogen stretching band was displaced to lower frequencies on complex formation relative to the gas value, and an increased intensity was observed.

Further infrared work was done by Plyler and Mulliken,[10] who studied the iodine complexes with benzene and pyridine and by Yada, Tanaka, and Nagakura,[11] who reported infrared data for the trimethylamine–iodine crystals. Recently Ginn and Wood[12] published far-infrared spectra of pyridine with iodine, iodine chloride, and iodine bromide and assigned bands in the region 160–120 cm^{-1} to the intermolecular vibrations.

Essentially, these low vibrations should be well fitted for study by means of Raman technique for the following reasons. (1) The halogen-stretching frequency is Raman active even in the uncomplexed molecule. (2) The sample is contained in a glass or quartz cell, and no corrosion or etching problems arise. (3) The whole spectral region can be covered in one run, using the same cell.

However, the obvious reason why Raman technique has not been extensively used for such studies is the

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[1] This work has been supported in part by NATO Research Grant No. 214.

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[3] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p 94.

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

[5] L. D'Or, R. Alewaeters, and J. Collin, *Rec. Trav. Chim.*, **75**, 862 (1956).

[6] W. B. Person, R. E. Humphrey, W. A. Deskin, and A. I. Popov, *J. Am. Chem. Soc.*, **80**, 2049 (1958).

[7] W. B. Person, R. E. Erickson, and R. E. Buckles, *J. Chem. Phys.*, **27**, 1211 (1957).

[8] W. B. Person, R. E. Humphrey, and A. I. Popov, *J. Am. Chem. Soc.*, **81**, 273 (1959).

[9] W. B. Person, R. E. Erickson, and R. E. Buckles, *ibid.*, **82**, 29 (1960).

[10] E. Plyler and R. S. Mulliken, *ibid.*, **81**, 823 (1959).

[11] H. Yada, J. Tanaka, and S. Nagakura, *J. Mol. Spectry.*, **9**, 461 (1962).

[12] S. G. W. Ginn and J. L. Wood, *Trans. Faraday Soc.*, **62**, 777 (1966).

strong visible absorption bands of the halogens and the interhalogens preventing completely the use of the 4358- or the 5460-A Hg lines for excitation. Thus, this field has been restricted to the relatively few Raman laboratories employing excitation in the red or infrared regions, *e.g.*, by using rubidium or helium as sources. The Raman spectra of the halogens and the interhalogens have for many years been studied by Stammreich and co-workers. They have reported[13] the frequencies of the halogens in the gas and in carbon tetrachloride with great accuracy and discussed the Raman spectra under high resolution of some halogens and interhalogens in different solutions.[14] They were able to verify some of the earlier infrared work[4-9] regarding the stretching frequencies. However, the number of systems they studied was limited by the large effort which went into every exposure. Moreover, their solvents were generally fairly weak bases which did not interact strongly with the halogens.

The commercially developed recording Raman spectrophotometers with laser source offer great advantages in their simplicity of operation and the speed with which the spectra can be recorded. The present work was done in order to determine if the 6328-A He-Ne laser line would be suitable for Raman excitation of these colored substances. It will be shown that with the high sensitivity of the present commercial Raman laser spectrometers the spectra of the halogen complexes were in some cases recorded quite easily. In other instances it was necessary to keep the halogen and the donor concentrations within quite narrow limits. Generally, the Raman spectra were no more difficult to record than the corresponding infrared spectra. Thus Raman technique should be of considerable importance in the study of these species.

The present study was restricted by various factors, which will be discussed in the Experimental Section. They were related to the temporary setup of the Raman facilities and limited the investigation considerably. Future workers in this field, who work with their own instruments, should be able to expand these studies greatly.

Experimental Section

General. The laser Raman spectrophotometers used were the prototype instruments belonging to the manufacturers, displayed in connection with the Spring Raman Institute, held at the University of Maryland in May 1966. Since the instruments were available to the author for a very limited time only, it was necessary to concentrate on the qualitative Raman spectra of the halogen complexes. No serious attempts were made to study the intensity changes of the Raman bands in the free acceptors and the complexes. Such data would have required the use of internal intensity standards, accurate concentrations, and a temperature control device around the Raman cell; moreover, the complex formation constants should be known beforehand, *e.g.*, from ultraviolet absorption data.

The donor molecules studied were mostly standard laboratory chemicals from the shelves and they were not systematically collected with this study in mind. Otherwise it would have been desirable to make a more thorough study of groups of related donor molecules.

The Raman spectrophotometers were situated in an exhibit hall, with no ventilation hood or chemical laboratory facilities. Because of these difficult experimental conditions the concentrations of the donors and the acceptors listed in Tables I-III are only semiquantitative.

Some preliminary efforts were made to record the Raman spectra of the present halogen solutions with the Perkin-Elmer Model LR-1 laser Raman spectrophotometer equipped with a 6 mw He-Ne laser. The 2-ml wedge-shaped sample cell was used, but no satisfactory Raman spectra were obtained. Therefore, the data reported in this paper were all obtained with the more sensitive Cary 81 laser Raman spectrophotometer.

The depolarization ratio of the observed Raman bands were generally not determined although these data can be fairly easily obtained with the laser instruments. It was expected, however, that the halogen stretching modes would be totally symmetric and give rise to polarized Raman lines in these complexes. Semiquantitative polarization measurements of the bands at 205 and 167 cm^{-1} in the benzene and pyridine complexes with iodine, respectively, indicated polarized bands in both cases.

Exciting Frequencies and Raman Intensities. The acceptor molecules iodine, bromine, iodine chloride, iodine bromide, and bromine chloride all have broad electronic absorption bands in the region 4000-5500 A when dissolved in inert solvents. Therefore, in order to record the Raman spectra of these compounds, exciting frequencies outside this region, *viz.*, in the ultraviolet or the visible-infrared region must be employed. Since the halogens or interhalogens in solution exhibit strong ultraviolet absorption bands from charge-transfer or contact-charge-transfer interaction with the solvent, only the long-wavelength Raman excitation is feasible. Accordingly, Stammreich, *et al.*,[14] used the He lines (5876 and 6678 A) and the Rb resonance doublet (7800 and 7948 A) in their studies of the halogens. Since iodine, bromine, iodine bromide, iodine chloride, and bromine chloride have very broad bands, they absorb considerably even around 8000 A. Therefore dilute solutions, fast spectrographs, and long exposure times were used[14] to record these Raman spectra with the 7800-A Rb line.

Because the halogens have a much higher absorption at 6300 A than at 7800 A, it was by no means certain that successful Raman spectra could be obtained with a He-Ne gas laser. We found, however, that in dilute (for Raman spectroscopy) solutions of 0.1-0.5 *M* reasonably good spectra were obtained of bromine and iodine chloride in carbon tetrachloride. No Raman spectrum of iodine can be measured in this solvent because of the very strong solvent band at 218 cm^{-1}. However, hardly any Raman signal was detected of the solvent bands in a 0.2 *M* iodine solution in carbon tetrachloride. Thus, the 5200-A band of iodine in inert solvents prevents the use of the 6328-A exciting line. In chloroform, however, in which the iodine absorption is situated around 5050 A, a Raman band at 208 cm^{-1} was observed.

The geometry of the small, capillary Raman cell used for these recordings seemed very favorable, since the laser beam only passed once axially through the cell and the Raman radiation from a large solid angle entered the monochromator. Undoubtedly, the combination of the high-powered 50-mw laser, the fast monochromator, and the capillary cell offered great advantages for these strongly colored solutions.

When the halogens interact more strongly with the solvent, the solutions change color to brown or even to light yellow. The blue shift of the visible halogen absorption band which is observed in these cases will greatly reduce the absorbed Raman irradiation and therefore enhance the Raman signal. It is well known that the blue shift generally increases with stronger halogen-solvent interaction. Iodine gives a weak, an intermediate, and a strong interaction with benzene, dimethyl sulfoxide, and triethylamine, respectively, and the blue shifts are approximately 18, 74, and 106 $m\mu$. For the corresponding bromine complexes the blue shifts are smaller; for the iodine chloride complexes they are larger than for iodine. It was found that the 6328-A He-Ne laser frequency was very well suited for exciting the Raman spectra of the yellow solutions. However, a large excess of donor (as a solvent or as a solute in an inert solvent) relative to the halogen is required in most cases to keep the concentration of uncomplexed halogen as low as possible.

To compare the efficiency of the He-Ne laser excitation with conventional sources, two strongly interacting systems, pyridine-I_2 and diethyl sulfide-I_2, were irradiated with the green Hg line (5461 A) using a Jarrel-Ash grating spectrograph and photographic registration. Solutions containing 0.1 *M* iodine in the pure donors had negligible concentrations of free halogen, but no traces of any Raman lines were detected after 2 hr of exposure. Therefore, the green Hg line was very efficiently absorbed even by these light yellow solutions.

In another experiment, a 0.2 *M* iodine solution in benzene was irradiated with a Rb lamp (7800 A) for 15 hr, using the Raman

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(13) See H. Stammreich, *Spectrochim. Acta*, 8, 41 (1956).

(14) H. Stammreich, R. Forneris, and Y. Tavares, *ibid.*, 17, 1173 (1961).

instrument[15] with a radiofrequency source.[16] However, the resulting Raman spectrum was no better than that obtained with the Cary 81 laser instrument in 0.5 hr. The halogen solution is undoubtedly more transparent to the 7800-A Rb line than the 6328-A He–Ne laser line. On the other hand, the high-intensity ratio between the sources, the fourth power dependence of the Raman intensities on the exciting frequency, and perhaps an increased resonance Raman effect achieved with the laser source made the laser excitation favorable.

Considering the large experimental effort that goes into every Raman exposure with the present Rb source, a rough estimate of the spent time would indicate a factor of at least 1:100 in favor of the commercial laser spectrometer. Moreover, a large part of the Raman spectra reported in the present study could not have been obtained by conventional means because of chemical instabilities.

Chemicals. The chemicals used were all from commercial sources. Iodine was sublimed with calcium oxide and resublimed under nitrogen atmosphere. Bromine was Mallinckrodt reagent grade, used without further purification, and iodine chloride was purified by fractional crystallization.

All the solvents were spectroscopic grade if available, and they were generally used without further purifications. However, dimethyl sulfoxide, tetramethylene sulfoxide, and pyridine were dried with barium oxide and fractionated over barium oxide in a Rotaband column. Triethylamine and cyclohexylamine were treated with potassium hydroxide and distilled.

The solid donors were of the highest available purity and they were used without further purifications.

Instrumental. The Raman spectra were recorded with the aid of a Cary 81 Raman spectrophotometer equipped with the 50-mw Spectra Physics Model 125 He–Ne laser using the 6328-A radiation. Most of the spectra were recorded only in the 50–450-cm^{-1} region, but in a few cases the complete Raman spectra below 3000 cm^{-1} were obtained.

The solutions were contained in a silica capillary tube[17] sealed in one end of approximately 0.7 mm i.d. 5 cm long, and containing approximately 20 μl. The Raman cells were filled by a fine capillary pipet and "sealed" with a drop of glycerol. This liquid was also employed between the capillary cell and the spectrometer lens to assure good optical contact. Most of the Raman spectra were recorded using slit widths of 5–10 cm^{-1}. However, for many of the iodine solutions, larger slits were employed, in some cases 20 cm^{-1}. Because of the low concentrations of halogens in all the solutions, fairly high gain settings were necessary. The scanning speed was 1 cm^{-1} sec for most of the runs, covering the region 0–450 cm^{-1} in 8 min. The short recording time was a great advantage for some of the unstable systems. However, the noise level was somewhat higher than desirable and made the detection of very weak bands difficult. The Raman spectra of the pure (or dissolved) donors, recorded for comparison, were obtained with smaller slits and much lower gain settings. Because of background radiation probably caused by fluorescing impurities, most of the spectra were recorded with the maximum setting of the zero suppression.

Procedure. The solutions were made up by a rough weighing of the halogens into 5-ml volumetric flasks with subsequent dilution.

(a) **Iodine.** Whenever the donor was a liquid at room temperature, iodine was dissolved directly into the donor. A suitable iodine concentration was dependent upon several factors: the complex formation constant, the blue shift of the iodine visible band, eventual chemical reactions, and the solubility of iodine.

In weak bases like chloroform, aromatic compounds, and the nitriles low iodine concentrations of approximately 0.05 *M* were suitable. Higher concentrations of 0.1–0.2 *M* were used in the stronger bases when the solutions absorbed less. However, in some cases, when the appearance of a very strong band around 114 cm^{-1}, assigned to the triiodide ion, suggested reactions, *e.g.*, in the sulfoxide,[18] lower iodine concentrations were employed. The solids were dissolved in benzene, chloroform, or acetonitrile, sometimes to saturation. Some of the strong donors were dissolved in chloroform as well as in acetonitrile to study the effect of varying the dielectric constants.

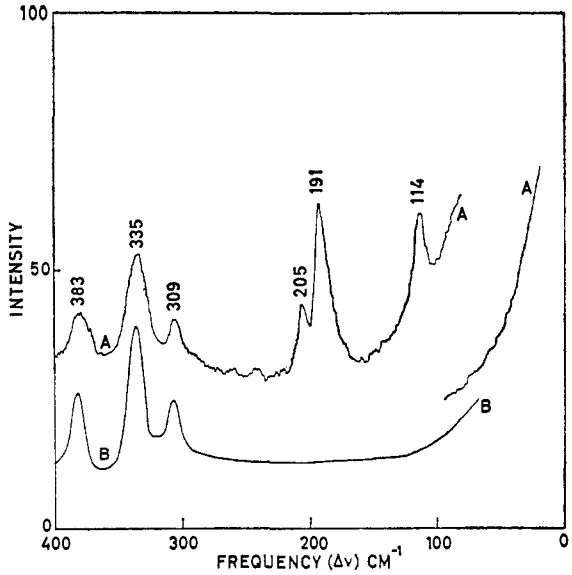

Figure 1. Raman spectra of 0.15 *M* iodine and 1.0 *M* dimethyl sulfoxide in benzene (A) and 1.0 *M* dimethyl sulfoxide in benzene (B). In this and the following figures, the curves B have been recorded with lower gain settings than the curves A.

No severe cases of irreversible reactions were encountered in the case of iodine. When reactions were expected, the recordings were repeated to determine eventual spectral changes with time.

(b) **Bromine.** Bromine has a much higher solubility than iodine in most solvents and the absorption of the 6328-A line is less prominent. Thus, it would appear that the bromine complexes would be easier to study and that fairly high halogen concentrations could be employed. However, it was found that bromine was so reactive that oxidation and substitution reactions easily occurred in the mixed solutions. These reactions were in several cases accompanied by precipitations or violent fumes; in less obvious instances by new Raman bands, assigned to various new species, caused by the reactions. Dilution experiments indicated that these new species were formed by irreversible reactions and not by complex formation.

The tendency for reactions was diminished by reducing the concentration of bromine to below 0.5 *M* and by dissolving the donor in a suitable solvent. However, since bromine is a weak acceptor, low donor concentrations will complex only a small fraction of the bromine, except for very strong donors. All the donors which were studied with iodine were tried with bromine, but only the systems listed in Table II gave reproducible data.

(c) **Iodine Chloride.** This acceptor is very soluble in most solvents. Since it is quite reactive, many of the same problems were encountered as for the bromine systems: precipitation, fumes, and spectral changes with time. The reactions were greatly diminished by keeping the iodine chloride as well as the donor concentrations low. The systems listed in Table III gave reproducible Raman spectra under the conditions listed. The entire process of mixing the solutions and recording the spectra was completed in 15 min.

(d) **Solvents.** An inert solvent like heptane or carbon tetrachloride might have been chosen to dissolve these complexes. However, they have strong Raman bands in the low-frequency region and were therefore not suitable. Instead, benzene was preferred for most of the recordings since it has no significant Raman band below 400 cm^{-1}, and it has good solvent properties for the halogens and the donors. Although benzene interacts with the halogens it did not interfere significantly with the strong complexes. In other cases, acetonitrile, which has a strong Raman band around 380 cm^{-1}, was chosen as a very polar solvent.

Results

Acceptor Spectra. The Raman spectrum of an intermediately strong complex, dimethyl sulfoxide and iodine dissolved in benzene, is plotted in Figure 1 for the region below 400 cm^{-1}. It appears that a number of Raman bands are observed in this region. The bands which

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(15) R. T. Bailey and E. R. Lippincott, *Spectrochim. Acta*, 21, 389 (1965).

(16) F. X. Powell, O. Fletcher, and E. R. Lippincott, *Rev. Sci. Instr.*, 34, 36 (1963).

(17) Bulletin 281, Applied Physics Corp., Monrovia, Calif.

(18) E. Augdahl and P. Klaboe, *Acta Chem. Scand.*, 18, 18 (1964).

Table I. Raman Bands of Various Donor–Iodine Charge-Transfer Complexes

Donor	Donor concn, *M*	I_2 concn, *M*	Solvent	Observed bands,[a] cm^{-1}	K_c, l./mole (temp, °C)	$-\Delta H°$, kcal/mole	% of I_2 complexed
		Gaseous		213[b]			
π Donors							
Benzene		0.1	None	205	0.15 (25)[c]	1.3[c]	60
Toluene		0.1	None	204	0.16 (25)[c]	1.8[c]	60
o-Xylene		0.1	None	202	0.27 (25)[c]	2.0[c]	70
n Donors							
Acetonitrile		0.1	None	112, 207	0.42[d]	1.9[d]	90
Benzonitrile		0.1	None	205	0.8 (20)[e]		90
Benzaldehyde		0.1	None	114, 204	0.6 (28)[f]		85
Acetone		0.1	None	114, 202	0.28 (30)[g]	3.7[h]	80
Ethanol		0.1	None	114, 202	0.45 (20)[i]	2.1[i]	90
Dimethylnitrosamine		0.15	None	198			
N,N-Dimethylacetamide		0.15	None	114, 196	6.9 (25)[j]	4.0[j]	>95
Methyl acetate	1.0	0.15	C_6H_6	114, 198, 208 165			
Dimethyl sulfoxide	1.0	0.15	C_6H_6	114, 191, 205	11.2 (25)[k]	3.7[k]	90
Dimethyl sulfoxide		0.1	None	114, 189			>95
Tetramethylene sulfoxide	1.0	0.15	C_6H_6	114, 190, 205	18.8 (30)[l]	4.1[l]	90
sym-Trioxane	0.8	0.15	C_6H_6	114, 188, 205			
Pyridine N-oxide	0.8	0.15	CH_3CN	112, 185, 207	77.9 (23)[m]	5.85[m]	>95
Thioacetamide	Satd	0.10	CH_3CN	112, 178,	12000 (17)[n]	8.2[n]	>99
Triethylamine	1.0	0.05	C_6H_6	114, 205	6460 (20)[o]	12.0[o]	>99
Cyclohexylamine	1.0	0.05	C_6H_6	114, 170			
Pyridine		0.15	None	114, 167	290 (16.7)[p]	7.8[p]	>99
Dipropyl sulfide		0.15	None	165			
sym-Trithiane	Satd	0.05	CH_3CN	112, 159, 207			
Ethylene trithiocarbonate	1.0	0.15	C_6H_6	114, 158, 205	45 (25)[q]	8.5[q]	
Thiourea	Satd	0.10	C_6H_6	114, 157	8500 (20)[n]	9.6[n]	>99
Thiourea	Satd	0.10	CH_3CN	112, 144			>99
p-Dithiane	0.5	0.15	C_6H_6	157	77 (25)[r]	6.2[r]	>95
p-Dithiane	0.5	0.15	CH_3CN	112, 145			>95
Acetylthiourea	Satd	0.15	CH_3CN	112, 156			
Ethylenethiourea	Satd	0.10	C_6H_6	114, 141			
Ethylenethiourea	Satd	0.10	CH_3CN	112, 137			

[a] Raman bands which are not present in the components. [b] Value from band spectra. [c] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74,** 4500 (1952). [d] W. B. Person, W. C. Golton, and A. I. Popov, *ibid.*, **85**, 891 (1963). [e] P. Klaboe, *ibid.*, **84**, 3458 (1962). [f] E. Augdahl and P. Klaboe, *Acta Chem. Scand.*, **16,** 1637 (1962). [g] H. Yamada and K. Kozima, *J. Am. Chem. Soc.*, **82,** 1543 (1960). [h] S. N. Bhat and C. N. R. Rao, *ibid.*, **88,** 3216 (1966). [i] P. A. D. de Maine, *J. Chem. Phys.*, **26,** 1192 (1957). [j] R. S. Drago, R. L. Carlson, N. J. Rose, and D. A. Wenz, *J. Am. Chem. Soc.*, **83,** 3572 (1961). [k] Reference 29. [l] J. Grundnes and P. Klaboe, *Trans. Faraday Soc.*, **60,** 1991 (1964). [m] Reference 24. [n] Reference 23. [o] Reference 22. [p] C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76,** 3868 (1954). [q] K. R. Bhaskar, S. N. Bhat, A. S. N. Murthy, and C. N. R. Rao, *Trans. Faraday Soc.*, **62,** 788 (1966). [r] Reference 21.

are situated between 300 and 400 cm^{-1} belong to dimethyl sulfoxide[19] dissolved in benzene (curve B), but those at 114, 191, and 205 cm^{-1} are characteristic for the mixed solutions. When iodine is dissolved in the pure dimethyl sulfoxide, only two bands appear, at 189 and 114 cm^{-1}. If this spectrum is rescanned 1 hr later, the 189-cm^{-1} band has nearly vanished and the 114-cm^{-1} band has become very strong and broad. In Figure 2 the spectrum of iodine dissolved in dipropyl sulfide is plotted (curve A). The strong, broad Raman band at 165 cm^{-1} is not present in the pure donor spectrum (curve B). The Raman bands which were observed for the mixed donor–iodine solutions and are *not* present in the pure donor or solvent spectra are listed in Table I. It appears that two or even three new Raman bands were frequently observed below 400 cm^{-1}. The fairly high noise level which could not be avoided in some of the mixed solutions may cover other very weak bands. On the other hand, some small peaks which appeared, *e.g.*, at 242 and 263 cm^{-1} in Figure 1, were merely background noise.

The Raman spectra of two bromine complexes are presented in Figures 3 and 4. A broad band at 302 cm^{-1} appeared in the benzene–Br_2 solution (Figure 3) and seemed to have a shoulder at the high-frequency

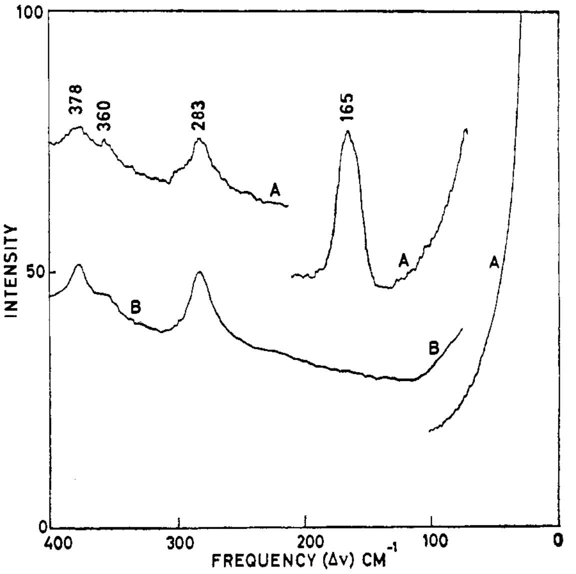

Figure 2. Raman spectra of 0.15 *M* iodine in dipropyl sulfide (A) and dipropyl sulfide (B).

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(19) A. K. Horrocks and F. A. Cotton, *Spectrochim. Acta*, 17, 134 (1961).

Table II. Raman Bands of Various Donor–Bromine Charge-Transfer Complexes

Donor	Donor concn, M	Br_2 concn, M	Solvent	Observed bands,[a] cm^{-1}	K_c, l./mole (temp, °C)	% of Br_2[b] complexed
		Gaseous		317		
π Donors						
Benzene		0.5	None	302, 309	0.10 (25)[c]	50
Toluene		0.5	None	300, 309	0.14 (25)[c]	50
o-Xylene		0.5	None	299, 309	0.23 (25)[c]	60
n Donors						
Acetonitrile		0.5	None	202, 250, 308		
Benzonitrile		0.5	None	198, 307	0.2 (20)[d]	60
Benzaldehyde		0.5	None	303		50
Ethanol		0.3	None	299		60
Acetone		0.4	None	198, 299		40
Dimethylnitrosamine		0.2	None	162, 292		...
Dimethyl sulfoxide	1.0	0.1	C_6H_6	164, 288, 311		70
Tetramethylene sulfoxide	1.0	0.1	C_6H_6	163, 287, 311		70
Pyridine	1.0	0.2	C_6H_6	281, 302		>90
Dipropyl sulfide	1.0	0.2		280		...
Thiourea	Satd	0.1	CH_3CN	278, 308		>90
p-Dithiane	1.0	0.2	C_6H_6	278		>90
Ethylenethiourea	Satd	0.1	CH_3CN	276, 308		>90

[a] Raman bands which are not present in the components. [b] In the cases of unknown K_c, it has been assumed: $K_c(Br_2 \text{ complex}) = {}^1/_5K_c$ (I_2 complex). [c] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950). [d] P. Klaboe, *ibid.*, **84**, 3458 (1962).

side. However, the bromine solutions had to be scanned fast because of instability, and the Raman bands generally seemed broad for these systems. The experimental uncertainties were larger than for the iodine solutions. In the pyridine–Br_2 system dissolved in benzene (Figure 4), two distinct Raman bands were observed at 302 and 281 cm^{-1}. The Raman bands for 16 different donor–Br_2 solutions, which are not present in the donor or the solvent spectra, are listed in Table II. Several other donors were tried with bromine, but they did not give reproducible data.

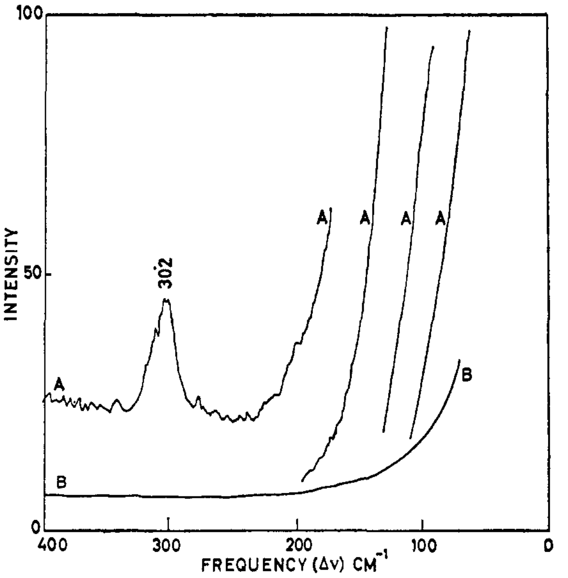

Figure 3. Raman spectra of 0.5 *M* bromine in benzene (A) and benzene (B).

Three representative examples of the Raman spectra of iodine chloride complexes are presented in Figures 5–7, while the observed Raman bands for the successful runs are collected in Table III. It is seen that often three or four new Raman bands appeared when iodine chloride was added to the solution. In addition to the donors listed in Table III, about 10 others were tried with iodine chloride but fast reactions occurred. Many of the iodine chloride systems listed could only be studied at low halogen (below 0.1 *M*) and donor (below 1 *M*) concentrations.

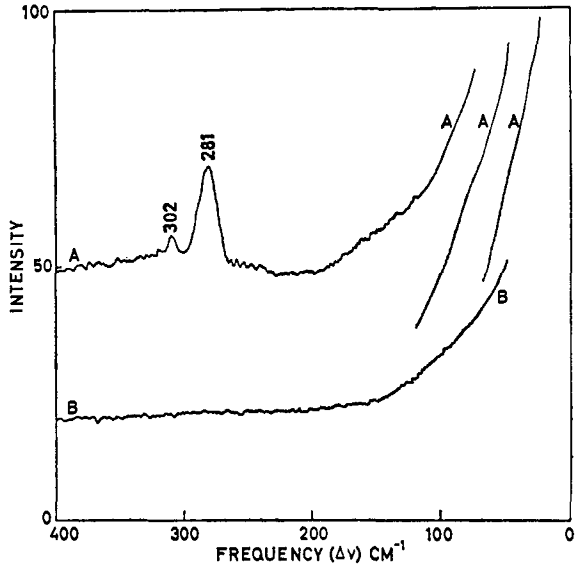

Figure 4. Raman spectra of 0.2 *M* bromine and 1.0 *M* pyridine in benzene (A) and 1.0 *M* pyridine in benzene (B).

Donor Spectra. It is well known from various infrared studies[3] that the donor vibrational spectrum is also perturbed when the donors interact with the halogens. These spectral changes can be of various kinds: (1) an appearance of new bands in the complex allowed by symmetry considerations, (2) an intensity variation of certain donor bands, and (3) a displacement of some vibrational bands usually accompanied by intensity variations. The latter effect has been extensively studied in halogen complexes, *e.g.*, with the oxo compounds.[20]

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(20) I. Lindqvist, "Inorganic Adduct Molecules of Oxo-compounds," Springer-Verlag, Berlin, 1963.

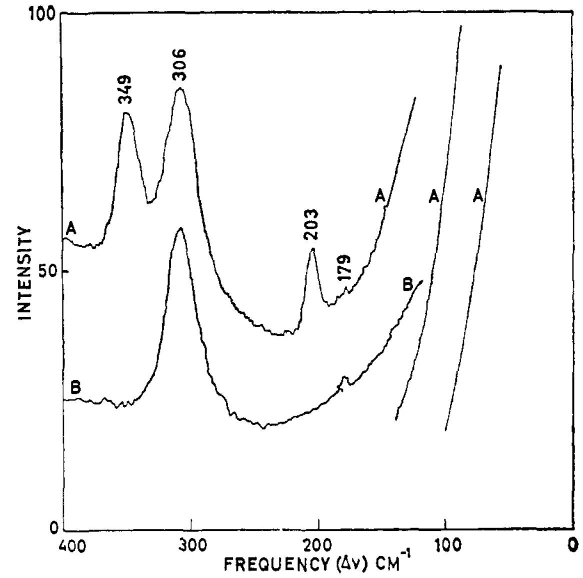

Figure 5. Raman spectra of 1.0 *M* iodine chloride and 1.0 *M* methyl acetate in benzene (A) and 1.0 *M* methyl acetate in benzene (B).

Table III. Raman Bands of Various Donor–Iodine Chloride Charge-Transfer Complexes

Donor	Donor concn, *M*	ICl concn,[a] *M*	Solvent	Observed bands,[b] cm^{-1}
		Gas		381.5[c]
Solvents				
Carbon tetrachloride		0.2	None	270, 376
Dichloromethane		0.2	None	264, 361
π Donors				
Benzene		0.2	None	204, 261, 355
Toluene		0.2	None	203, 259, 353
o-Xylene		0.2	None	200, 254, 350
n Donors				
Methyl acetate	1.0	0.1	C_6H_6	203, 351
Acetonitrile		0.1	None	207, 268, 313, 347
Benzonitrile		0.1	None	207, 268, 344
Acetone	1.0	0.1	C_6H_6	202, 341, 393
Methanol		0.1	None	204, 268, 325, 340
Dimethylnitrosamine	1.0	0.1	C_6H_6	201, 266, 234
N,N-Dimethylacetamide	1.0	0.1	C_6H_6	202, 228, 326
Dimethyl sulfoxide	1.0	0.1	C_6H_6	204, 321
Tetramethylene sulfoxide	1.0	0.1	C_6H_6	114, 147, 316
sym-Trioxane	1.0	0.1	C_6H_6	204, 268, 314
Pyridine	1.0	0.15	C_6H_6	202, 285
Pyridine		0.2	None	163, 268, 277
sym-Trithiane	Satd	0.05	C_6H_6	203, 274
p-Dithiane	0.5	0.1	C_6H_6	189, 205, 274
p-Dithiane	0.5	0.1	CH_3CN	208, 269, 304, 362
Ethylenethiourea	Satd	0.05	C_6H_6	206, 262, 362
Ethylenethiourea	Satd	0.05	CH_3CN	204, 254, 347

[a] More than 95% of the ICl should be complexed for all systems with π donors and n donors. [b] Raman bands which are not present in the components. [c] Reference 31.

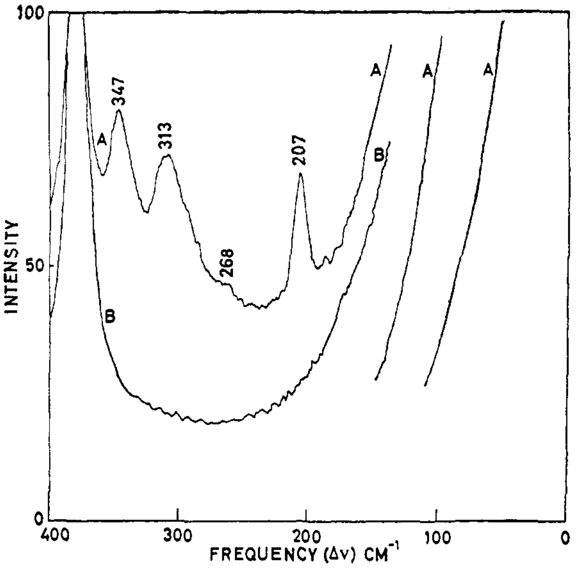

Figure 6. Raman spectra of 0.1 *M* iodine chloride in acetonitrile (A) and acetonitrile (B).

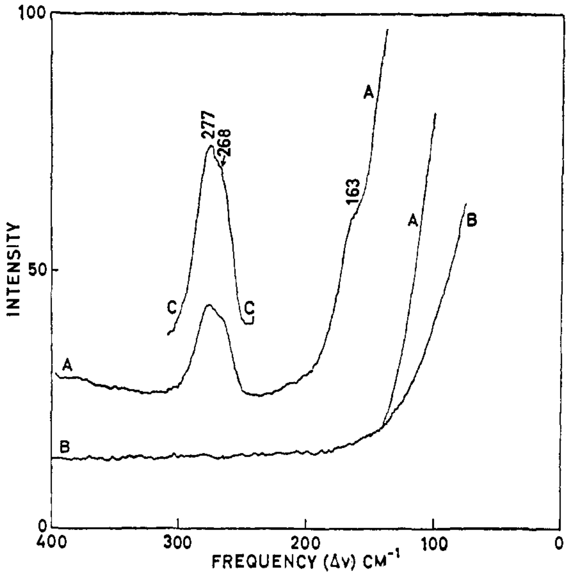

Figure 7. Raman spectra of 0.2 *M* iodinechlor ide in pyridine (A) and pyridine (B).

We wanted to investigate if equivalent changes in the donor spectrum could be detected with the present Raman technique and the three following bases were studied with iodine: dimethyl sulfoxide, diethyl sulfide, and pyridine N-oxide. They all form medium to strong complexes with iodine. In the two oxo compounds a perturbation of the Raman bands connected with the S=O and the N=O stretching modes is expected. The two liquids were studied in the pure state, the solid pyridine N-oxide was dissolved in chloroform, and the spectra were recorded in the entire region 50–3000 cm^{-1}. However, no higher iodine concentration than 0.5 *M* could be added or the amount of uncomplexed iodine would absorb most of the exciting radiation. Therefore, only a small fraction of the donor molecules would be engaged in complex formation to iodine, and no spectral changes could be detected with certainty. We believe that with excitation with a laser in the 8000–9000-A region, having a sufficiently high intensity, perturbations in the donor spectrum can be studied, since much higher halogen concentrations would be feasible.

In another recording a 1 *M* solution of *p*-dithiane in carbon tetrachloride was recorded and iodine chloride was added in a 0.4 *M* concentration. Since this complex is presumably of the 1:1 type like the iodine system,[21] the C_{2h} symmetry of the donor should break down and new Raman bands become active. Because of the mutual exclusion of the infrared and Raman bands in this molecule, some of the infrared-active bands should become Raman active and *vice versa*. Two new Raman bands appeared at 800 and 485 cm^{-1}, but they did not correspond to any infrared frequencies and were probably caused by reaction products. Neither did addition of iodine chloride to *p*-dithiane cause any significant changes in the infrared spectrum.

Discussion

The ability of the halogens or interhalogens to form complexes with organic bases is well known and has been extensively studied.[3] The effect can be very weak as in the case of nonpolar halogens in inert solvents like heptane or carbon tetrachloride. Weak van der Waals effects and quadrupole and induced dipole effects are probably the main contributors to these very weak interactions. In a polar acceptor like iodine chloride as well as in polar donors, the permanent dipole moments will interact mutually as well as with induced dipole moments and quadrupole moments. The resulting interaction should therefore be stronger than for the unpolar components.

The interactions, measured by the quantities $-\Delta F°$ or $-\Delta H°$, for the charge-transfer complexes of the n,σ type, can be of orders of magnitude higher than for the more unspecific interactions mentioned. The halogens act as Lewis acids through the σ bonds, and because they have easily polarizable electron clouds they are "soft" and interact with "soft" bases. In the n,σ complexes the intermolecular bond is localized to the lone-pair electron orbitals, and the intermolecular distances can be quite small, indicating a strong interaction.

Formation constants of the order of 1–10,000 l./mole at 20° and enthalpies of formation of the order of -10 kcal/mole are reported for triethylamine,[22] thiourea,[23] amine oxides,[24] and triphenylarsine[25] complexes with I_2.

The interactions observed in the iodine complexes with aromatic donors or olefins are of the π,σ type, and enthalpies of formation around 1–3 kcal/mole are reported.[3] Even if much less quantitative work has been done on iodine chloride and bromine as acceptors compared to iodine, it is well known that the order of acid strength is $ICl > I_2 > Br_2$. The formation constants (K_c) for ICl, I_2, and Br_2 complexed to the same donor may roughly be of the order 25:5:1.

Since we have worked with strong and moderately strong n,σ complexes for some years, the main purpose of the present work was to obtain Raman spectra of these. Stammreich, *et al.*,[14] on the other hand, studied weaker interactions, with the exception of the pyridine–I_2 and the pyridine–ICl systems. The strong complexes should offer the following advantages: (a) with high formation constants a lower concentration of donor is required to complex most of the acceptor, (b) large blue shifts of the halogen visible absorption bands should greatly diminish the absorption of the 6328-A line, (c) the complex bond should be fairly strong and the intermolecular stretching mode easier to observe since the Raman band should be farther from the exciting line. However, it was found that in the strongly interacting systems, various species, different from the molecular complex, may be formed. There is undoubtedly a large tendency for ionization in such systems, caused by a complete transfer of the donor electron to form halide ions. In a recent paper Toyoda and Person[26] suggest that because of the high value obtained for the dipole moment of the triethylamine–I_2 complex in dioxane solution, the species are present as ion pairs, involving the I_3^- ion. Kobinata and Nagakura[27] on the other hand observed lower values for the dipole moments in other amine–iodine systems, indicating that the real molecular complexes were present. The present results can be interpreted along the same lines, since no Raman band was observed for the triethylamine–iodine system, except the 114-cm^{-1} band to be assigned to the I_3^- ion. For the cyclohexylamine–iodine system, however, a Raman band was observed at 170 cm^{-1} in addition to the 114-cm^{-1} band.

It appears from Table I that in practically every spectrum a Raman band was observed around 114 cm^{-1}. In this region we might expect Raman bands characteristic for the donor–I_2 intermolecular stretching mode.[11,12] However, the constancy of this band strongly points out that it belongs to a species formed from iodine and is independent of the specific basicity of the donor. In agreement with Stammreich[14] we assign this band to the I_3^- ion. It is well known that this species is often formed in iodine solutions and is characterized by the strong ultraviolet absorption bands at 2950 and 2630 A.[28] The I_3^- ion is clearly present, *e.g.*, in the dimethyl sulfoxide–I_2 solution (Figure 1) as previously reported from ultraviolet measurements,[29] and its formation is photocatalyzed and is accelerated by moisture and certain impurities in the solutions. The Raman-active 114-cm^{-1} band is accordingly the symmetric stretching mode in I_3^-, and the infrared-active asymmetric stretching mode is assigned[12] to a band in the 133–140-cm^{-1} region. If the I_3^- ion is situated in an asymmetric environment as the result of complex formation, the asymmetric stretching mode might become Raman active. For the very strongest donors (the thiourea derivatives) Raman bands were observed in the region 130–140 cm^{-1}, assigned to the I–I stretching mode, but it cannot be completely ruled out that the band is caused by I_3^- ions. With very few exceptions the 114-cm^{-1} band increased in intensity with time, indicating an increased amount of the I_3^- ions being formed.

It appears from Table I that when iodine was dissolved directly into the base, only one Raman band was observed in the region 210–140 cm^{-1}. If the donor–I_2 complex was studied in a solvent, however, an additional Raman band around 205 cm^{-1} was frequently

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Table IV. The Halide–Halide Stretching Frequencies, Force Constants, and Force-Constant Variations for Various I_2, Br_2, and ICl Complexes

		Iodine			Bromine			Iodine chloride		
	Solvent	ν_{I-I}, cm^{-1}	k_{I-I},[a] mdynes/A	$\Delta k/k$	ν_{Br-Br}, cm^{-1}	k_{Br-Br},[a] mdynes/A	$\Delta k/k$	ν_{I-Cl}, cm^{-1}	k_{I-Cl},[a] mdynes/A	$\Delta k/k$
Gas		213	1.695		317	2.366		381.5	2.358	
π Donors										
Benzene	None	205	1.57	0.07	302	2.15	0.09	355	2.04	0.13
Toluene	None	204	1.55	0.08	300	2.12	0.10	353	2.01	0.14
o-Xylene	None	202	1.53	0.10	299	2.10	0.11	350	2.00	0.15
n Donors										
Acetonitrile	None	207	1.60	0.06	308	2.23	0.06	347	1.95	0.18
Benzonitrile	None	205	1.57	0.07	307	2.22	0.06	344	1.91	0.19
Benzaldehyde	None	204	1.56	0.08	303	2.16	0.09			
Acetone	None	202	1.53	0.10	299	2.10	0.11	341	1.88	0.20
Ethanol	None	202	1.53	0.10	299	2.10	0.11	340	1.87	0.21
Dimethylnitrosamine	None	198	1.47	0.14	292	2.01	0.15	334	1.80	0.24
N,N-Dimethylacetamide	None	196	1.44	0.15				326	1.72	0.27
Methyl acetate	C_6H_6	193	1.39	0.18				351	1.99	0.16
Dimethyl sulfoxide	C_6H_6	191	1.36	0.19	288	1.95	0.18	321	1.66	0.29
Dimethyl sulfoxide	None	189	1.33	0.21						
Tetramethylene sulfoxide	C_6H_6	190	1.35	0.20	287	1.94	0.18	316	1.61	0.32
sym-Trioxane	C_6H_6	188	1.32	0.22				314	1.59	0.32
Pyridine N-oxide	CH_3CN	185	1.28	0.25						
Thioacetamide	CH_3CN	178	1.18	0.30						
Triethylamine	C_6H_6									
Cyclohexylamine	C_6H_6	170	1.08	0.36						
Pyridine	None	167	1.04	0.39	281	1.86	0.21	277	1.24	0.47
Dipropyl sulfide	None	165	1.02	0.40	280	1.85	0.22			
sym-Trithiane	CH_3CN	159	0.94	0.44				274	1.21	0.49
Ethylene trithiocarbonate	C_6H_6	158	0.93	0.45						
Thiourea	C_6H_6	157	0.92	0.46						
Thiourea	CH_3CN	144	0.78	0.54	278	1.82	0.23			
p-Dithiane	C_6H_6	157	0.92	0.46	278	1.82	0.23	269	1.17	0.50
p-Dithiane	CH_3CN	145	0.79	0.54						
Acetylthiourea	CH_3CN	156	0.91	0.46						
Ethylenethiourea	C_6H_6	141	0.74	0.56				262	1.11	0.53
Ethylenethiourea	CH_3CN	137	0.70	0.59	276	1.79	0.24	254	1.04	0.56

[a] $k = 4\pi^2C^2\nu^2/N\mu$; μ is equal to $2/m_I$, $2/m_{Br}$, and $(1/m_I) + (1/m_{Cl})$ for I_2, Br_2, and ICl, respectively.

observed. The assignment of these bands seems fairly straightforward. They are attributed to the I–I stretching modes in the donor–I_2 complex and eventually in the weak solvent–I_2 complex, respectively. The I–I stretching modes are listed in Table IV, and the frequencies agree quite well with the earlier Raman[14] and infrared[10,12] data in the few cases of overlapping investigations.

The percentage of added iodine which is complexed to the donor is calculated to a first approximation and listed in Table I. It is seen that for all but the weakest donors more than 90% of the iodine should be complexed. The remaining iodine should be complexed to the solvent or, in the case of no solvent, it may exist as "free" iodine. Since the band around 205 cm^{-1} has been observed in several solutions where practically all the iodine should be complexed to the donor, it seems probable that the calculated percentages are too high. It is not surprising if the formation constants listed in the literature are not applicable to these very concentrated solutions which deviate considerably from ideality.

For the weakly interacting donor–I_2 systems listed at the top of Table I the obvious question arises: where is the Raman band for the "free" I–I stretching mode which should be detectable in these cases? Although these iodine species are supposedly not complexed to specific donor molecules, they are effected by the dielectric medium and by van der Waals and quadrupole effects. Their stretching frequencies might be intermediate between the gas value at 213 and 205 cm^{-1} in, *e.g.*, benzene. No Raman bands were detected with certainty in this region. However, in these particular Raman spectra the spectral resolution was poor and the background noise high because of the strong absorption of the exciting frequency. Thus, the free I–I stretching frequency may be covered as a shoulder on the high-frequency side of the observed bands or it may be hidden by background noise.

From Table II it follows that the Raman bands observed for the bromine complexes fall into rather irregular patterns. Because bromine can react with many of the organic bases or oxidize them, the interpretations of these spectral data should be made with extreme caution even for the systems which apparently gave reproducible spectra. The percentage of complexed bromine has been estimated from the few reported formation constants, or more often from the very crude assumption that the formation constant for a Br_2 complex is $^1/_5$ of the formation constant for the corresponding I_2 complex. In the weak bromine interactions with the aromatic donors, approximately 50% of the bromine should be complexed and 50% free. Two Raman bands were observed for these solutions, the stronger situated around 300 cm^{-1} and the weaker at 309 cm^{-1}. They are attributed to the Br–Br stretching mode of the complexed and the free bromine, respectively; the latter should be inactive in the infrared.

When bromine was dissolved directly in an n donor, only one Raman band was observed in the region around 300 cm^{-1}. Since these bands were quite broad, a free Br–Br stretching band might have been hidden. For the stronger bromine complexes studied in solution, two Raman bands frequently appeared in this region. They are assigned to the Br–Br stretching modes in the donor–Br_2 complex (Table IV) and the solvent–Br_2 complex, respectively.

The assigned bands seem consistent with earlier work.[7,12] Among the extra Raman bands observed in these solutions, the 162-cm^{-1} band, which has been assigned to the Raman-active symmetric stretching in the Br_3^- ion,[30] was observed for dimethylnitrosamine and for the two sulfoxides. Since very few strong bromine complexes have been studied by Raman or infrared technique, the present results should be of interest, indicating the considerable perturbations of the Br–Br stretching mode even for this weak acceptor.

A large number of Raman bands were frequently observed for the ICl solutions. Some of these bands are undoubtedly caused by species different from the donor, solvent, or iodine chloride. It appears from Table III that a Raman band was frequently observed around 205 cm^{-1}, and the constant position suggests that it is caused by a species independent of the complex. A band was observed around this frequency for the weaker donor–I_2 complexes (Table I). Since it is well known that iodine chloride can form iodine in solutions, the bands around 205 cm^{-1} may tentatively be attributed to species of I_2 complexes being formed. Another band which appears in many solutions is situated around 264 cm^{-1}, which might be the symmetric stretching mode of the ICl_2^- ion,[30] formed by ionization of the complex in solution.

Although the assignments of the I–Cl stretching band in the complex can be subject to considerable uncertainty, the frequencies listed in Table IV appear in agreement with the earlier infrared[6,9,11] and Raman work.[14] Moreover, the data seem consistent with the relative basicities of the donors. The assignment of the 277-cm^{-1} band in the pyridine–ICl complex to the I–Cl stretching mode corresponds well with the data for other strongly interacting systems, and the possible assignment of this band as caused by ICl_2^- ions[14] seems unlikely.

The formation constants for the ICl complexes are generally quite large, and practically the entire amount of iodine chloride present in the solutions should be complexed to the donors. This is in agreement with the spectral data since there are no indications of I–Cl stretching modes of iodine chloride molecules which are free or complexed to the solvents. Iodine chloride absorbs less of the 6328-A radiation than the other halogens studied, and the Raman spectra could be recorded in carbon tetrachloride and in dichloromethane solutions. It is seen that in the former solvent the I–Cl stretching mode was found at 376 cm^{-1} which is very close to the reported gas value[31] at 381.5 cm^{-1}, in agreement with the very weak interaction in this "inert" solvent.

According to Mulliken[32] the electron donated to the halogen should enter a nonbonding orbital in the halogen molecule, weakening the bond. Thus, the halogen stretching frequency should diminish, and the interhalogen distance should increase on complex formation. The latter effect has been verified by the X-ray crystallographic work on numerous solid halogen complexes by Hassel and co-workers.[33] The halogen stretching force constants in the present molecules were estimated by the simple, diatomic Hook's law approximation from the assigned frequencies in Table IV. This approach should be quite good for the weaker complexes where the donor–halogen interaction is low. For the stronger complexes, however, the intermolecular distance becomes smaller, and the donor–halogen stretching frequency and force constant increase. Obviously, for such complexes the donor atom and the two halogen atoms should be treated as a three-body problem, because the intermolecular frequency and the halogen frequency can be thoroughly mixed. However, the intermolecular frequencies for these complexes are generally not known, but the present treatment should give the variations of the halogen force constants to a first approximation. The calculated force constants k and the ratio $\Delta k/k$, relative to the gas value, are listed in Table IV for all the systems reported. It appears that for the stronger complexes the force constants for I–Cl and I–I are reduced to half the gas value; for Br–Br the reduction is smaller. Generally the order of increasing $\Delta k/k$ coincides with increasing K_c and $-\Delta H°$.

Friedrich and Person[34] have proposed a semiempirical relationship between $\Delta k/k$ and the weight of the dative structure wave function in the complex. It would be very desirable to test these ideas with the data obtained for the various halogen complexes. The weights of the dative and no-bond structures can be estimated from various molecular and spectral parameters for the donor, acceptor, and complex, but generally includes rather uncertain estimates[3] of the overlap integral S. More workers will probably focus their attention on these relationships when the infrared and Raman spectra of the halogen and the intermolecular stretching modes for more complexes become available.

For some of the stronger donor–acceptor systems, the Raman spectra were recorded in two solvents of different dielectric constants. It was observed that in each case the halogen stretching mode had a lower value in the more polar medium. As an example thiourea complexed to iodine had a stretching mode observed at 157 cm^{-1} in benzene, but at 144 cm^{-1} in acetonitrile. The data are too few to draw any general conclusions from this apparent trend, but they indicate a stronger donor–acceptor interaction in polar solvents. A polar solvent should favor the charge-separated dative structure with a larger contribution of this structure in the ground state. We have previously reported stronger interaction for the triphenylarsine–iodine complex[25] in dichloromethane than in carbon tetrachloride. The recent far-infrared data of Ginn and Wood[12] and the dipole moment measurements reported by Kobinata and Nagakura[27] have also been interpreted in this way.

We had hoped to observe Raman bands which might be attributed to the donor–halogen intermolecular

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stretching mode. The values for the intermolecular force constant should be of very great interest and could be correlated with the intermolecular distances as obtained from X-ray work on the crystals. Moreover, the intermolecular force constant might be even more characteristic for the "strength" of the complex than the thermodynamic functions $\Delta F°$ and $\Delta H°$ in solution, since solvation effects can give large contributions to these functions.

A few infrared bands which were assigned to the N–halogen stretching mode in pyridine complexes with iodine, iodine chloride, or iodine bromide in solution have been reported.[12] Thus, for iodine and iodine chloride dissolved in excess pyridine, bands were observed[12] at 120 and 160 cm^{-1}, respectively. When the pyridine–ICl complex was studied in benzene solution the corresponding band was observed[12] at 147 cm^{-1}. It appears from Figure 7 and Table III that a Raman band was observed around 163 cm^{-1} for iodine chloride dissolved in pyridine, but we observed no corresponding band for the pyridine–ICl system in benzene. The 163-cm^{-1} Raman band supports the earlier infrared data reported for this system[12] and the interpretation as an intermolecular mode seems reasonable. It was highly unexpected that we did not observe corresponding bands in the other iodine, bromine, or iodine chloride systems. Since iodine chloride gave the strongest complexes, these intermolecular stretching modes should have higher frequencies and be easier to observe in Raman than for the iodine and bromine complexes. The fairly strong background scattering near the exciting line prevented observation of Raman bands below 100 cm^{-1} in the present solutions, but in the region 100–200 cm^{-1} eventual bands should have been observed. From the present data it might be concluded that the intermolecular stretching modes are fairly weak in the Raman effect.

However, it would be worth trying to get the Raman spectra of the solid complexes, since the present instrument in many cases gave very good spectra of crystalline powders or pellets. The intermolecular mode might show up in the solid, if the data are interpreted with care because of the lattice modes. As an example we observed the Raman spectra of solid $\mathrm{I{-}C{\equiv}C{-}C{\equiv}N}$ and observed a strong Raman band at 79 cm^{-1} which might tentatively be assigned[35] to the $\mathrm{N\cdots I}$ intermolecular mode in the long chains[36] which probably are held together by charge-transfer forces.

More work studying the solids and the solutions simultaneously by infrared and Raman techniques would be of interest. With the many commercial far-infrared spectrophotometers and interferometers and the laser Raman spectrophotometers now available, considerably more work will probably be done along these lines.

Acknowledgments. The author is grateful to Professor Ellis R. Lippincott for the invitation to work in his laboratory. The Raman spectra were recorded on the prototype of the Cary 81 laser spectrophotometer through the courtesy of the Applied Physics Corporation. A research grant from NATO awarded through the Royal Norwegian Council for Scientific and Industrial Research is gratefully acknowledged.

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