Volume 7
Number 9
September 3, 1968

Inorganic Chemistry

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Infrared Spectra of Chlorine–Bromine Polyhalogens by Matrix Isolation

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Received May 10, 1968

The infrared spectra of several new chlorine–bromine compounds have been obtained. The compounds were produced by passing a mixture of inert gas (Ar, Kr, or Xe), chlorine, and bromine through a microwave discharge and then condensing upon a cesium iodide window maintained at 20°K. Analysis of the spectra has shown that several T-shaped molecules (analogous to ClF_3) possessing either the Cl–Br–Cl or the Cl–Br–Br linear unit have been formed. The most definitely identified species is $BrBrCl_2$. The bond force constants derived are estimated to be slightly larger than those for the corresponding ions, in accordance with comparisons of ClF_3 to ClF_2^- and of the Cl_3 radical to Cl_3^-.

Mixed chlorine–bromine interhalogen ions are known, $ClBrCl^-$ [1,2] and $ClBrBr^-$,[3] but the only neutral compound yet discovered is BrCl. In particular, there seems to be no evidence for the existence of any of the possible T-shaped molecules (like ClF_3), $BrCl_3$, Br_2Cl_2, or Br_3Cl. Neither has there been comment in the literature concerning the free radicals ClBrCl and ClBrBr. The recent discovery of Cl_3[4] through matrix techniques has led us to attempt the preparation of these molecules coupled with infrared spectroscopic detection and diagnosis. Assignments of our spectra and force constant calculations further correlate the bonding of these electron-excess molecules.

Experimental Section

Mixtures of an inert gas, chlorine, and bromine were passed through a microwave discharge and then condensed upon a cesium iodide window maintained at 20°K, using apparatus and methods like those described earlier.[4,5] In some experiments, the sample was prepared by simultaneously depositing two mixtures, one of inert gas and Cl_2 and the other of inert gas and Br_2, only one of which was passed through the glow discharge. Diffusion experiments (to 45°K) were conducted as usual. Deposition rates were always close to 2.8 mmol/hr. Infrared spectra were recorded (4000–200 cm^{-1}) with a Perkin-Elmer 225 grating infrared spectrophotometer; frequency accuracy was ± 0.2 cm^{-1} and spectral slit widths were as noted in the figures.

The xenon, krypton, and chlorine were all Matheson research grade gases and were used without further purification. The bromine (J. T. Baker Chemical Co.) was degassed using a chloroform slush (−63.5°), and then a middle cut was taken while it was distilled at −17.5° (*o*-dichlorobenzene slush). The argon (Linde, 99.99%) was passed through a glass coil immersed in liquid oxygen before use.

Results

Experiments were conducted using argon, krypton, and xenon matrices. Molecular species were segregated through their dependence upon the Cl_2/Br_2 ratio, upon which halogen (or both) was passed through the discharge, and upon spectral changes caused by diffusion. Despite the usual small matrix shifts, molecular absorbers in the different matrices were related through their absorption frequencies and similar isotopic splittings.

Argon Matrix.—Four experiments were conducted using argon; Table I summarizes the observed bands and their optical densities. The most interesting spectral region in these experiments was 335–315 cm^{-1} and the spectra recorded in expt 1 and 2 are shown in Figure 1. Seven bands were obtained in expt 1, two of which were not present in expt 2, in which Br_2 was not passed through the discharge. These two features at 332.2 and 330.2 cm^{-1} are called B. Of the remaining five bands, the one at 327.7 cm^{-1} shows distinctly less loss during diffusion; it is called C. The four features at 325.6, 323.8, 321.6, and 319.4 cm^{-1} retain reasonably constant relative intensities in expt 1 and 2 during diffusion; they are called D. Experiment 2 showed one band, at 290 cm^{-1}, not observed in expt 1. This band, called E, disappeared on diffusion at 43°K.

Experiment 3 shows that none of the features, B, C, D, or E, appears if chlorine is not discharged. Chlorine atoms are needed, apparently. Experiment 4 shows that B is not obtained in excess bromine.

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[1] J. C. Evans and G. Y.-S. Lo, *J. Chem. Phys.*, **44**, 4356 (1966).

[2] W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, and R. Forneris, *ibid.*, **35**, 908 (1961).

[3] J. C. Evans and G. Y.-S. Lo, *ibid.*, **45**, 1069 (1966).

[4] L. Y. Nelson and G. C. Pimentel, *ibid.*, **47**, 3671 (1967).

[5] L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.*, **6**, 1758 (1967).

TABLE I
INFRARED SPECTRA OF DISCHARGED CHLORINE AND BROMINE IN ARGON AT 20°K[a]

		Expt no.			
		1	2	3	4
		Matrix compn, Ar:Cl_2:Br_2			
ν, cm^{-1}	Identity	200*:2*:1*	75*:1*:0 + 50:0:1	50*:0:1* + 75:1:0	200*:1*:3*
332.2	B	0.04 (0.005)	...	...	...
330.2	B	0.08 (0.01)	...	...	...
327.7	C	0.03 (0.02)	0.02 (0.02)	...	0.02
325.6	D	0.08 (0.05)	0.09 (0.06)	...	0.03
323.8	D	0.14 (0.08)	0.18 (0.11)	...	0.06
321.6	D	0.07 (0.04)	0.11 (0.07)	...	0.03
319.4	D	0.01 (0.005)	0.05 (0.03)	...	0.01
310	Br_2	0.15 (0.17)	0.05 (0.05)	0.05	0.02
290	E	...	0.05 (0.01)	...	...

[a] Asterisk indicates gas passed through discharge; parenthetical optical densities follow diffusion.

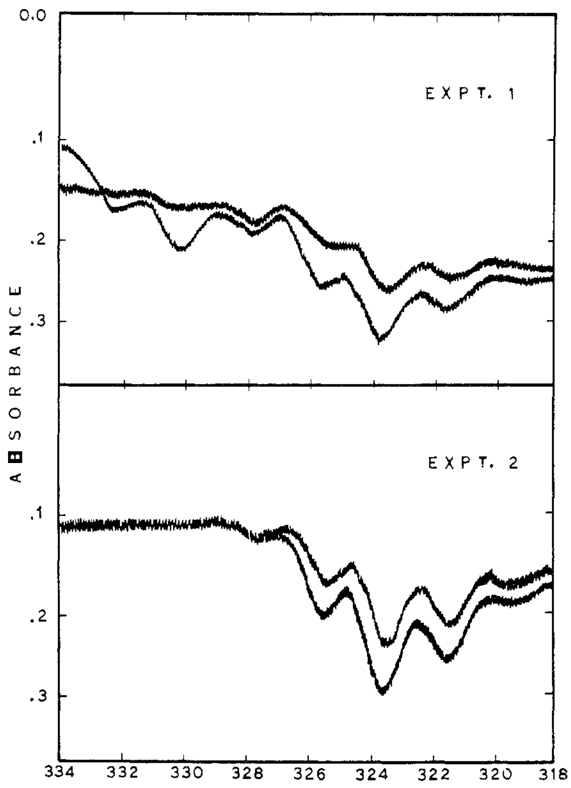


Figure 1.—Infrared spectra of discharged chlorine and bromine in argon at 20°K: expt 1, Ar* + Cl_2* + Br_2* (200:2:1), spectral slit width 1.0 cm^{-1}; expt 2, (Ar + Cl_2*) + (Ar + Br_2), spectral slit width 0.9 cm^{-1}. Upper spectrum in each case was recorded after warming to 43°K and recooling to 20°K.

TABLE II
INFRARED SPECTRA OF DISCHARGED CHLORINE AND BROMINE IN KRYPTON AT 20°K[a]

		Expt no.	
		5	6
		Matrix compn, Kr:Cl_2:Br_2	
ν, cm^{-1}	Identity	200*:1*:3*	100*:1*:1*
374.6	Cl_3	...	0.14
373.0	Cl_3	...	0.13
368.0	Cl_3	...	0.10
366.3	Cl_3	...	0.07
364.3	A	...	0.07
362.5	A	...	0.07
326.1	B	...	0.14
324.0	B	...	0.22
321.8	C	...	0.16
319.6	D	0.05	0.32
317.7	D	0.06	0.3
315.8	D	0.04	0.44
(313)	D	0.02	0.34
289.5	E	0.08	0.05
286.0	E	0.04	0.04
238	G	...	0.12[b]

[a] Asterisk indicates gas passed through discharge. [b] This band disappeared upon standing at 20°K for 7 hr exposed to an ir spectrometer source but without diffusion.

Krypton Matrix.—Table II summarizes the results of two krypton matrix experiments. In expt 5, two prominent absorptions appear at 320 and 290 cm^{-1}; these, respectively, only a few reciprocal centimeters above the frequencies of the argon matrix species D and E. Under high resolution, the 320-cm^{-1} band reveals four features with spacing quite similar to those of D, and we presume they are the same molecule in the krypton environment.

Experiment 6 differs in that there is no longer a large excess of bromine. The spectrum is more complex, as shown in Figure 2. The B, C, D, and E features are all observed, the first three at very high intensity. There is also absorption near 370 cm^{-1} which, under high resolution, proves to include the most intense absorptions of Cl_3 as reported by Nelson and Pimentel[4] and, in addition, a doublet not observed in the Cl_3 studies nor in the present argon matrix work. This doublet, at 364.3 and 362.5 cm^{-1}, is called species A. Finally, a new absorption appeared at 232 cm^{-1}, species G, which displayed unique behavior by disappearing while continuously under irradiation for 7 hr by the globar source of the spectrometer but without significant temperature rise.

In one other krypton matrix experiment, Kr:Br_2 = 75:1 (passed through the discharge), no absorption was observed except a small feature attributable to C (optical density, 0.02).

Thus the krypton matrix experiments confirm the existence of species B, C, D, and E, proving none of these is an argon-containing molecule, and they add two new molecules to our roster, A and G. The experiments show, further, that excess bromine favors E over both D and C and it prevents the formation of Cl_3, A, or G.

Xenon Matrix.—Experiments 7 and 8 differ in the relative amounts of the two halogens. With excess bromine, a set of not quite resolvable features was observed in the region of the E bands. These are shown in Figure 3 and the deduced frequencies are listed in Table III. In excess chlorine (expt 8), these bands were not observed but, instead, strong features of $XeCl_2$ were observed.[5] Also, the spectrum included four bands not observed either in argon or in krypton: a new doublet at 263.4 and 258.3 cm^{-1} (species F) and three features at 646, 579, and 296 cm^{-1} (H_1, H_2, and H_3). It is not possible to conclude whether B, C, and D were present in expt 8 because of $XeCl_2$ interference. They did not appear, however, in expt 7 in which

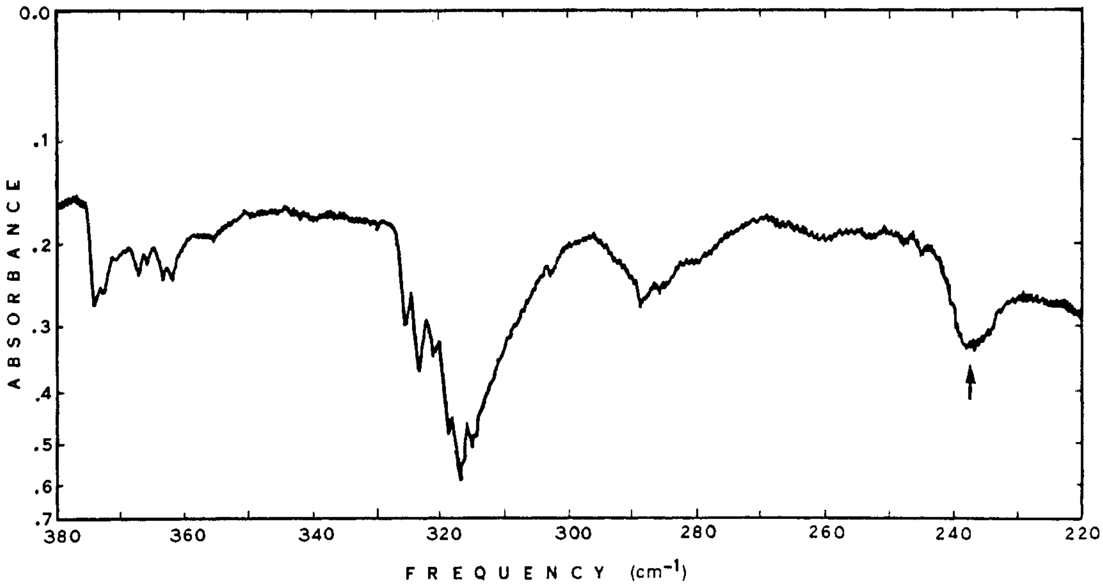


Figure 2.—Infrared spectrum of discharged chlorine and bromine in krypton at 20°K: expt 6, Kr* + Cl_2* + Br_2* (100:1:1), spectral slit width 1.2 cm^{-1}. Arrow shows band (G) which disappeared during prolonged irradiation with globar source.

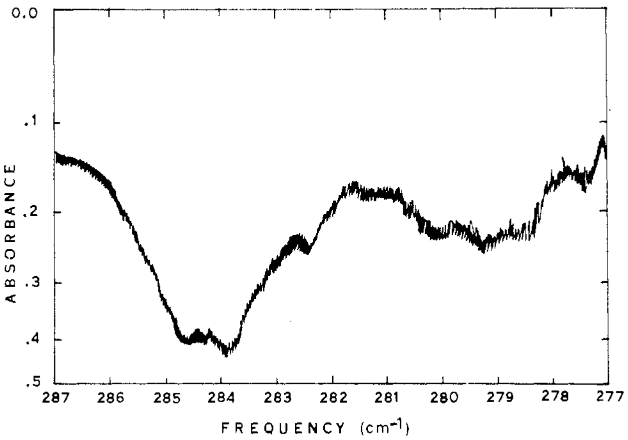


Figure 3.—Infrared spectrum of discharged chlorine and bromine in xenon at 20°K: expt 7, Xe* + Cl_2* + Br* (200:1:3), spectral slit width 0.42 cm^{-1}.

TABLE III

INFRARED SPECTRA OF DISCHARGED CHLORINE AND BROMINE IN XENON AT 20°K[a]

		Expt no.	
		7	8
		Matrix compn, Xe:Cl_2:Br_2	
ν, cm^{-1}	Identity	200*:1* 3*	120*:3*:1*
646	H_1	0.03	0.19
579	H_2	...	0.09
(370.5)	A	...	0.03
313	$XeCl_2$	0.09	0.25
311	$XeCl_2$	0.07	0.20
296	H_3	...	0.05
284.6	E	0.28	...
283.8	E	0.30	...
282.4	E	0.13	...
280.2	E	0.10	...
279.3	E	0.12	...
278.4	E	0.10	...
263.4	F	...	0.17
258.3	F	...	0.09

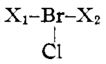
[a] Asterisk indicates gas passed through discharge.

$XeCl_2$ interference was much smaller. This is in accord with the krypton matrix result in which excess bromine caused a diminution of these features (expt 5).

Summary.—Table IV contrasts the observations in the three matrices. Two features, F and G, were each observed in only one matrix and hence could conceivably be inert gas compounds. Of the remaining species, C is probably an impurity. E is favored by excess Br_2 while A, B, and D are diminished in excess Br_2. Species D requires that Cl_2 be discharged and B requires that both Cl_2 and Br_2 be discharged.

Discussion

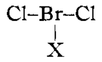
Assignment.—Assignment of possible structures to these molecular absorbers is aided by consideration of the frequency region and the isotopic shifts. The diatomic BrCl absorbs at 440 cm^{-1}. A T-shaped molecule



$$\underset{\mathrm{Cl}}{X_1\text{–}\underset{|}{\mathrm{Br}}\text{–}X_2}$$

would retain an absorption near 400 cm^{-1}, since the Br–Cl force constant is little affected in this molecular structure. Its isotopic shifts would be for the chlorine isotopic (35 to 37) change 0.9812 and for bromine isotopic change (79 to 81) 0.9961. The A features are in the appropriate spectral region and their frequencies are in the ratio 0.995. The ^{37}Cl counterpart would not be observed because of low intensity. Hence A can be assigned either to BrCl itself or to the T-shaped molecule shown above.

Either a linear symmetric ClBrCl radical or a T-shaped Cl–Br–Cl



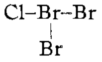
$$\underset{\mathrm{X}}{\mathrm{Cl\text{–}\underset{|}{Br}\text{–}Cl}}$$

molecule would display an asymmetric Cl–Br–Cl stretching frequency characterized by isotopic shifts appropriate to two chlorine atoms moving together

Table IV
Summary of Observed Br–Cl Bands

	Ar	Kr	Xe	Remarks
A	Not obsd	364.3, 362.1	(370.5)	Not obsd in excess Br_2
B	332.2, 330.2	326.1, 324.0	Not obsd	Not obsd in excess Br_2 and not obsd unless both Br_2 and Cl_2 discharged
C	327.7	321.8	Not obsd	Not present in Ar expt 3; present in a Kr expt with only Br_2; probably an impurity
D	325.6, 323.8, 321.6, 319.4	319.6, 317.7, 315.8, 313	Not obsd $XeCl_2$ interference	Not obtained in Ar unless Cl_2 discharged
E	290	289.5, 286.0	284.6, 283.8, 282.4, 280.2, 279.3, 278.4	Diminished in excess Cl_2
F	Not obsd	Not obsd	263.4, 258.3	Favored in excess Cl_2; appeared only in Xe
G	Not obsd	238	Not obsd	Lost under ir irradiation without warming

against the countermovement of the bromine atom. The D bands display an appropriate isotopic splitting pattern, as shown in Table V. These calculations are based on the assumption that the highest frequency component, 325.6 cm^{-1}, is due to the ^{35}Cl–^{79}Br–^{35}Cl isotopic species. Both frequency pattern and relative intensities clearly indicate D is probably due to a linear Cl–Br–Cl unit. This structure is consistent with the observation that D is obtained only when Cl_2 is discharged and is diminished if there is insufficient chlorine present. Since D is obtained without discharge of Br_2 (expt 2), it is probably due to the T-shaped molecule



$$\mathrm{Cl{-}\underset{\underset{\displaystyle Br}{|}}{Br}{-}Br}$$

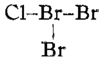
Table V
Observed and Calculated Frequencies for $BrCl_2$[a]

	Frequency, cm^{-1}	
Species	Calcd	Obsd (Ar matrix)
35–79–35	(325.6)	325.6
35–79–37	323.3	323.8
35–81–35	323.7	
37–79–37	320.9	321.6
35–81–37	321.4	
37–81–37	319.0	319.4

[a] $k_r - k_{rr} = 1.157$ mdyn/Å.

The B doublet displays an isotopic ratio of 0.994, again close to that expected for a Cl–Br–Cl unit, either associated with a bromine isotopic substitution (79 → 81) (0.9942) or a single chlorine substitution (35 → 37) (0.9927). The other isotopic components would be weaker or they would be overlapped by the C and D bands. If the assignment of D is correct (to $BrBrCl_2$), then B is probably due to $BrCl_3$. In fact, the A bands appear when the B bands are quite intense (as in expt 6) and they can be assigned as the axial Br–Cl stretch of molecule B.

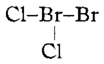
The most intense E features in xenon (284.6 and 283.8 cm^{-1}) show an isotopic ratio of 0.997 which, like the A frequency ratio, is close to that expected for ^{81}BrCl/^{79}BrCl. However, the frequency is lower than that of gaseous BrCl by a factor 1.55, implying the force constant is lower by a factor of 2.4. This suggests a linear Cl–Br–Br unit, in which chlorine vibrates essentially against a single bromine mass and there is a second skeletal motion, a Br–Br stretching mode, below the frequency range studied. With this interpretation, there should be weaker ^{37}Cl counterparts which would be too weak to observe in the krypton experiment. They should be detected, however, at the higher intensity seen in the xenon experiment. Indeed, the two absorptions at 279.3 and 278.4 cm^{-1} are nicely accounted for in this way (see Table III). Despite the fact that E appeared in expt 2 in which Br_2 was not discharged, we suggest that E is due to



$$\mathrm{Cl{-}\underset{\underset{\displaystyle Br}{|}}{Br}{-}Br}$$

as is appropriate to the loss of E in excess chlorine (see expt 1). The remaining E features, at 282.4 and 280.2 cm^{-1}, could be due to the axial Br–Br stretch, since gaseous Br_2 absorbs at 310 cm^{-1} and the splitting is appropriate to that expected for diatomic bromine isotopic shifts.

The F features show an isotopic ratio 0.980, again appropriate to a diatomic Br–Cl shift. This also could be due to a Cl–Br–Br unit, and, if E is correctly assigned, then F would be



$$\mathrm{Cl{-}\underset{\underset{\displaystyle Cl}{|}}{Br}{-}Br}$$

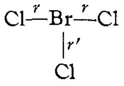
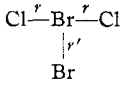
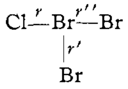
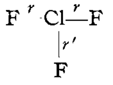
This assignment is appropriate to the need for excess Cl_2. (Since F is observed only in xenon, the possibility that it is due to Cl–Xe–Br must be considered. However, the observed isotopic shift is not readily explained thereby.)

There is no isotopic information about G. Its transient behavior suggests it might be a free radical, or, since it was observed only in krypton, conceivably it could be a krypton compound. We feel the possibilities Br_3 and ClClBr are more likely.

Force Constants.—The preferred assignments are listed in Table VI. These conclusions permit the estimation of some force constants, also shown in Table VI. Of these, the most well-defined is that of D, $BrBrCl_2$. The value of $k_r - k_{rr}$ obtained, 1.16 mdyn/Å, is about 0.44 times the force constant of BrCl itself. This is between the ratio that is observed for Cl_3 relative to Cl_2, $(k_r - k_{rr})/k_{\mathrm{Cl_2}} = 0.3$[4] and the ratio

TABLE VI

FORCE CONSTANTS OF THE POLYHALOGENS

Species	Assigned structure	Force constants, mdyn/Å	Ref
A and B	 $\mathrm{Cl}\overset{r}{\text{—}}\underset{\substack{\mid r' \\ \mathrm{Cl}}}{\mathrm{Br}}\overset{r}{\text{—}}\mathrm{Cl}$	$k_r - k_{rr} \cong 1.16$ $k_{r'} \cong 1.90$	*a*
D	 $\mathrm{Cl}\overset{r}{\text{—}}\underset{\substack{\mid r' \\ \mathrm{Br}}}{\mathrm{Br}}\overset{r}{\text{—}}\mathrm{Cl}$	$k_r - k_{rr} \cong 1.16$	*a*
$BrCl_2^-$	$\mathrm{Cl—Br—Cl^-}$	$k_r - k_{rr} = 0.55$	*b*
E	 $\mathrm{Cl}\overset{r}{\text{—}}\underset{\substack{\mid r' \\ \mathrm{Br}}}{\mathrm{Br}}\overset{r''}{\text{—}}\mathrm{Br}$	$k_r \cong 1.25$ (assuming $k_{r''} \cong 1.0$ and $k_{rr''} \cong 0.30$) $k_{r'} \cong 1.88$	*a*
Br_2Cl^-	$\mathrm{Cl}\overset{r}{\text{—}}\mathrm{Br}\overset{r''}{\text{—}}\mathrm{Br^-}$	$k_r = 1.0$, $k_{r''} = 0.90$, $k_{rr''} = 0.4$	*c*
Cl_3	$\mathrm{Cl—Cl—Cl}$	$k_r - k_{rr} = 0.97$	*d*
Cl_3^-	$\mathrm{Cl—Cl—Cl^-}$	$k_r - k_{rr} = 0.41$	*e*
ClF_3	 $\mathrm{F}\overset{r}{\text{—}}\underset{\substack{\mid r' \\ \mathrm{F}}}{\mathrm{Cl}}\overset{r}{\text{—}}\mathrm{F}$	$k_r \cong 2.90$, $k_{rr} \cong 0.23$, $k_{r'} \cong 3.52$	*f*
ClF_2^-	$\mathrm{F—Cl—F^-}$	$k_r = 2.35$ $k_{rr} = 0.17$	*g*

[a] Present work. [b] Reference 1. [c] Reference 3. [d] Reference 4. [e] J. C. Evans and G. Y-S. Lo, *J. Chem. Phys.*, **44,** 3638 (1966). [f] H. H. Claassen, B. Weinstock, and J. G. Malm, *ibid.*, **28,** 285 (1958); H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *ibid.*, **42,** 1229 (1965). [g] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, **6,** 1159 (1967).

observed for the triatomic part of ClF_3 compared to ClF, $(k_r - k_{rr})/k_{\mathrm{ClF}} \cong 0.6$.[6,7]

Perhaps more interesting is the comparison to the $ClBrCl^-$ ion. Analogous to those of Cl_3 radical and the Cl_3^- ion, the force constant of ClBrCl ($f_r - f_{rr}$ = 1.16 mdyn/Å) is higher than that of $ClBrCl^-$ ($f_r - f_{rr}$ = 0.55 mdyn/Å). Considering the ClF_2^- ion and the ClF_3 molecule, we now have three opportunities for comparison of a linear trihalogen unit in a neutral and in an ionic molecule. These are also compiled in Table VI and they show that the negative charge on the trihalide ions weakens the bond somewhat, as discussed in ref 4.

Conclusions

Owing to the large number of possible bromine–halogen compounds, the molecular identifications proposed are not certain. The identification of the ClBrCl unit, either in the ClBrCl radical or a T-shaped molecule, is quite definite. Despite the tentativity in the other assignments, they are reasonable and they provide the first information about the possible existence of these polyhalogens. The evidence obtained indicates their structures and potential functions may prove to be consistent with those of the already known analogs. In particular, the bonding in an X_1–X_2–X_3 radical or in the linear three-center portion of a corresponding T-shaped molecule may be stronger than that of the analogous negatively charged ion X_1–X_2–X_3^-.

Acknowledgments.—We gratefully acknowledge research support from the Office of Naval Research.

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(6) H. H. Claassen, B. Weinstock, and J. G. Malm, *J. Chem. Phys.*, **28**, 285 (1958).

(7) H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *ibid.*, **42**, 1229 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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An Infrared and Raman Spectral Study of Aqueous Mercury(II) Nitrate Solutions[1]

BY A. R. DAVIS AND D. E. IRISH

Received November 9, 1967

Infrared and Raman spectroscopy have been used to study aqueous solutions of mercury(II) nitrate as well as a mixture of $Hg(NO_3)_2 \cdot H_2O$ and KNO_3. An intensity analysis of the *ca.* 720- and 740-cm^{-1} bands is consistent with the presence of $HgNO_3^+$ and $Hg(NO_3)_2$. The polarization of the 1284-cm^{-1} Raman band is presented as evidence that the nitrate ion is acting as a monodentate ligand. A vibrational assignment for the dinitratomercury(II) species, in terms of the D_{2h} point group, is described.

Introduction

The Raman spectrum of saturated mercury(II) nitrate has been observed to be more complex than that of the alkali metal nitrates.[2] Although the increased complexity suggests that the nitrate ion is considerably perturbed by the mercury(II) ion, the absence of an Hg–O stretch vibration supports the conclusion that there is little or no covalent interaction between the ions.

Formation constants for the species $HgNO_3^+$ and $Hg(NO_3)_2$ have been calculated from emf measurements.[3,4] For nitrate ion–mercury ion concentration ratios much higher than any used in this work the existence of a very weak complex ion, $Hg(NO_3)_4^{2-}$, was

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(1) Presented in part at the Seventh National Meeting, Society for Applied Spectroscopy, Chicago, Ill., May 13–17, 1968.

(2) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

(3) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964 p 174.

(4) G. Infeldt and L. G. Sillén, *Svensk Kem. Tidskr.*, **58**, 104 (1946).