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Infrared and Raman Spectra of the $M^+F_3^-$ Ion Paris and Their Mixed Chlorine–Fluorine Counterparts in Solid Argon

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The products of the reaction of alkali fluoride and alkali chloride salt molecules with F_2, ClF, and Cl_2 were investigated in argon matrices at 15 K. The reactions of CsF and RbF with F_2 produced a strong infrared band at 550 cm^{-1} and a strong Raman band at 461 cm^{-1}, which are assigned to ν_3 and ν_1, respectively, of the F_3^- anion in the $M^+F_3^-$ ion pair. The observation of mutual exclusion between the infrared and Raman spectra of these species indicates a centrosymmetric anion in the ion pair. Infrared bands were observed for all of the mixed trihalide species. With CsCl and F_2 halogen scrambling was found. The lack of formation of the F_3^- anion with Na^+ shows that the trifluoride species needs a relatively large cation for stability.

Introduction

The trihalide anions, X_3^-, have been of interest to chemists for many years. A large number of studies have been reported on Cl_3^-, Br_3^-, and I_3^-, both in solutions and in crystals.[1,2] The most reactive member of this group, F_3^-, evaded characterization until very recently,[3] in spite of the fact that ClF_2^- was prepared over a decade ago.[4] Interest in these 22-electron species lies with the geometry and the nature and strength of the bonding.

Salt–molecule matrix reactions have recently been used to synthesize trihalide species.[5] The matrix technique provides a means to isolate single cation–anion pairs and to study a specific anion with a range of metal cations and a minimum of solvation effects. Such a study of the Cl_3^- anion and its mixed chlorine–bromine analogues has been reported;[5] an analogous investigation of the F_3^- anion and the mixed chlorine–fluorine species will be described here.

Experimental Section

The cryogenic refrigerators, vacuum systems, and high-temperature ovens have been described previously.[6-8] Cesium fluoride and rubidium fluoride (Alfa Inorganics), potassium fluoride and sodium fluoride (Allied Chemical), cesium chloride (Fisher), and rubidium chloride (Fairmount) were placed in a Knudsen cell and outgassed at, or above, operating temperatures under vacuum for several hours before use. Typical evaporation temperatures for the salts were as follows: CsF, 490 °C; CsCl, 500 °C; RbF, 640 °C; RbCl, 525 °C; KF, 595 °C; NaF, 750 °C; these correspond to about 1 μ vapor pressure for the salt molecule.[9] The rate of the salt deposition was monitored in the infrared experiments by observation of the salt monomer absorption, except in the case of CsCl. Fluorine (Matheson) was used in a stainless steel vacuum line without purification, while Cl_2 (Matheson) and ClF (Ozark Mahoning) were condensed with liquid nitrogen and degassed to remove volatile impurities. The alkali metals used in several experiments were handled in a manner described previously.[10] Argon (Air Products, 99.995%) was used without further purification.

Infrared spectra were recorded after approximtely 24 h of sample deposition, while Raman and optical spectra were recorded after 4-h deposition periods. Infrared spectra were recorded on a Beckman IR-12 infrared spectrophotometer with an accuracy of ± 1 cm^{-1}, and Raman spectra were taken on a Spex Ramalog instrument, using exciting lines from an argon ion laser (Coherent Radiation). Optical spectra were recorded on a Cary 17 visible–ultraviolet spectrometer, generally over the range 200–800 nm.

Results

Infrared Spectra. CsF. Cesium fluoride vapor was codeposited with argon at 15 K for 11 h and bands were observed at 313, 248, and 207 cm^{-1}, which have been assigned to CsF and $(CsF)_2$.[3] In addition a weak band was observed at 595 cm^{-1}.

CsF was deposited in several experiments with samples of $Ar/F_2 = 400/1$. In each study, bands were observed at 313, 248, and 207 cm^{-1}, and a new, very intense band was observed at 550 cm^{-1}. This band was the dominant feature in a number of experiments where the CsF oven temperature was varied over the 480–520 °C range. At the higher oven temperature, a 340-cm^{-1} shoulder appeared on the CsF band and a second, weak band was observed at 595 cm^{-1}, but at the lower oven temperature with a lower CsF concentration, only the 550-cm^{-1} band remained. The 550-cm^{-1} band was stable to 26 min of AH-4 arc photolysis through CsI. When the matrix was warmed to 42 K to allow diffusion and then recooled to 15 K, the 550-cm^{-1} band broadened slightly and remained intense, and the band at 595 cm^{-1} and the 313-cm^{-1} CsF band disappeared. The 595-cm^{-1} band was observed in a number of long CsF experiments with different reagents, and it is probably due to a weak CsF-impurity complex. All of the salt reactions produced a band which has been attributed[3,5] to a complex of the salt molecule with H_2O impurity. These bands, labeled A in the figures, appeared near 470 cm^{-1} for chloride salts and near 350 cm^{-1} for fluoride salts.

CsF was deposited with several samples of $Ar/ClF = 400/1$; new bands were observed at 298 cm^{-1} (0.40), 365 cm^{-1} (0.88), 554 cm^{-1} (0.12), and 566 cm^{-1} (0.75); optical densities are given parenthetically. The 298-cm^{-1} band is probably another matrix site of the very strong 313-cm^{-1} CsF band. CsF was reacted with a sample of $Ar/Cl_2 = 400/1$ and new bands were observed at 213 (1.0), 237 (0.35), and 412 (0.20) cm^{-1}.

CsCl. Cesium chloride vapor was deposited with samples of $Ar/ClF = 300/1$ and $500/1$; new bands were observed at 213 (1.0), 237 (0.12), 268 (0.14), 412 (0.18), and 474 (0.40) cm^{-1}. CsCl was condensed with samples of $Ar/F_2 = 400/1$ and $300/1$; new bands were detected at 312 (0.12), 365 (0.17), 550 (0.10), and 560 (0.21) cm^{-1}; mercury-arc photolysis for 23 min had no effect on the absorption bands. Finally, the CsCl + Cl_2 reaction spectrum[5] is included in Figure 1 for comparison of the spectra from all of the CsF and CsCl reactions with F_2, ClF, and Cl_2. Table I lists the new bands produced in these salt reactions.

RbF. Rubidium fluoride vapor was condensed with argon at 15 K for 14 h. The sharp RbF monomer was observed at 345 cm^{-1} (0% *T*) with a resolved site splitting at 332 cm^{-1} and dimer bands were observed at 266 and 230 cm^{-1}. In addition a band appeared at 614 cm^{-1} (0.07) which is believed to be due to a salt-impurity complex.

When RbF was evaporated at 510 °C and deposited with a sample of $Ar/F_2 = 400/1$, a strong new product band was observed at 550 cm^{-1} along with a weak 614-cm^{-1} band in addition to bands due to RbF and $(RbF)_2$. This band was very intense and sharp, like the product band in the analogous CsF + F_2 experiment. In another experiment at 640 °C oven temperature and consequently higher RbF concentrations, a pronounced 572-cm^{-1} shoulder appeared on the intense 550-cm^{-1} band and the 614-cm^{-1} band was enhanced.

RbF was reacted with one sample of $Ar/ClF = 400/1$. Very intense, sharp product bands were observed at 371 (>1.0) and

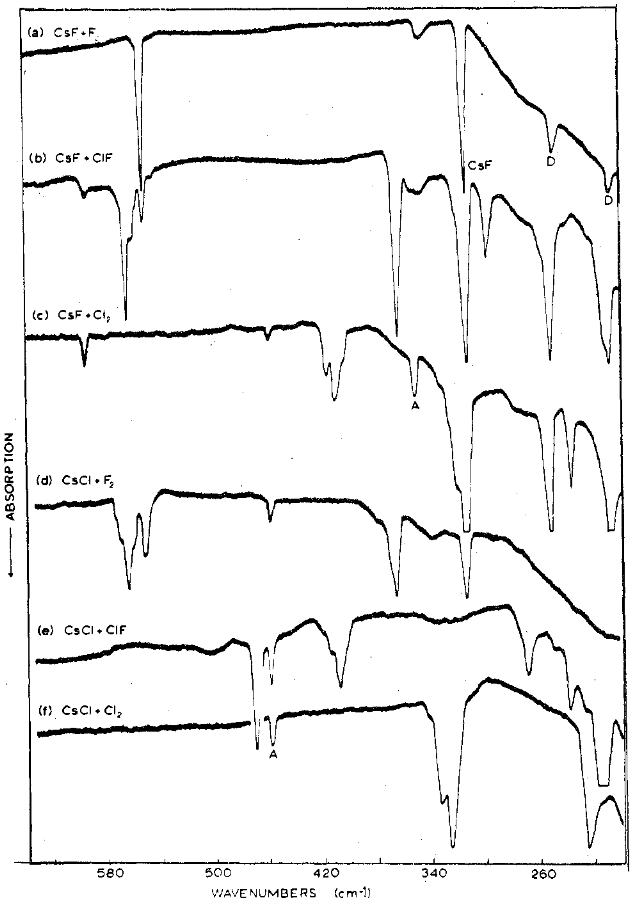

Figure 1. Infrared spectra of cesium salt matrix reaction products for the fluorine–chlorine system in solid argon at 15 K. Traces a, b, and c are for CsF codeposited with F_2, ClF, and Cl_2, respectively, at $Ar/X_2 = 400/1$. Traces d, e, and f are for CsCl codeposited with F_2, ClF, and Cl_2, respectively at $Ar/X_2 = 300/1$.

Table I. New Infrared Absorptions (cm^{-1}) Observed for Alkali Metal Salt–Fluorine–Chlorine Reactions

Reagents	Product absorptions[a]
CsF + F_2	550
CsF + ClF	365, 554, 566
CsF + Cl_2	213, 237, . . ., 412, . . .
CsCl + ClF	213, 237, 268, 412, 474
CsCl + F_2	312, 365, 550, 566
CsCl + Cl_2	225, 327
RbF + F_2	550
RbF + ClF	371, 548, 555, 559, 565
RbF + Cl_2	. . ., 409, . . ., . . .
RbCl + ClF	228, 266, 409, 480
RbCl + F_2	345, 371, 548, 555, 559, 565
KF + F_2	463, 467, 549
NaF + F_2	455, 460, . . .
NaF + ClF	307, . . ., 589
NaCl + ClF	511

[a] Not including MF, $(MF)_2$, MF-impurity complexes, and weak bands (<0.02) which cannot be assigned.

565 (>1.0) cm^{-1}, with the 565-cm^{-1} band split into four components at 565, 559, 555, and 548 cm^{-1}. RbF was deposited in one experiment with a sample of $Ar/Cl_2 = 400/1$, and a single product band was observed at 409 cm^{-1} (0.53).

RbCl. RbCl was deposited with a sample of $Ar/ClF = 400/1$ and new bands were detected at 228, (0.26), 266 (0.05), 409 (0.04), and 480 (0.18) cm^{-1}. Then, RbCl was reacted with a sample of $Ar/F_2 = 400/1$, and product bands were observed at 345 (0.12), 371 (0.22), and 565 (0.22) cm^{-1}, where the 565-cm^{-1} band was split into four components, just as in the RbF + ClF experiment. Sample warming to 30 K and recooling to 15 K had no effect on these absorptions; however, a new doublet appeared at 601, 611 cm^{-1} (0.15 OD). The band positions from the RbF and RbCl salt reactions are listed in Table I.

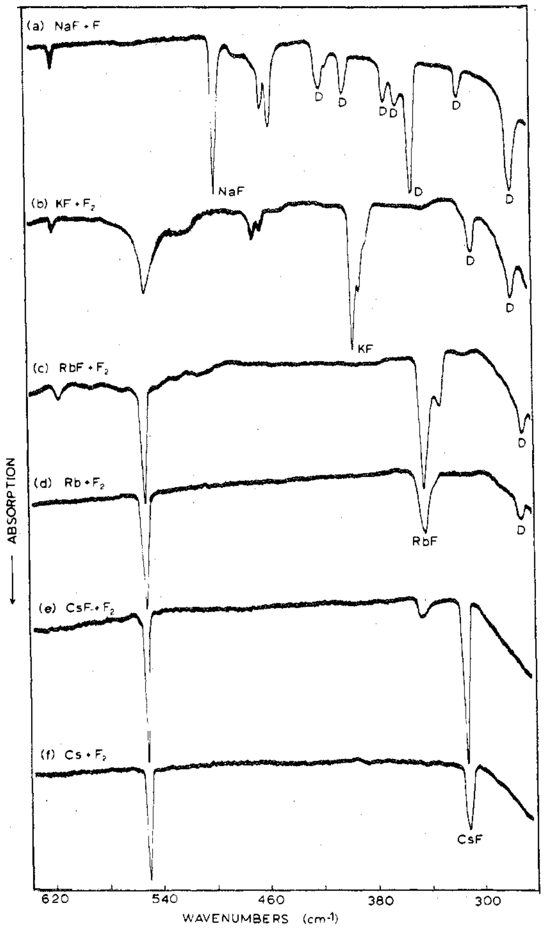

Figure 2. Infrared spectra for alkali fluoride–fluorine matrix reaction products in solid argon at 15 K: (a) NaF + $Ar/F_2 = 100/1$, (b) KF + $Ar/F_2 = 100/1$, (c) RbF + $Ar/F_2 = 400/1$, (d) Rb atoms + $Ar/F_2 = 100/1$, (e) CsF + $Ar/F_2 = 400/1$, and (f) Cs atoms + $Ar/F_2 = 100/1$.

KF. KF was deposited with samples of $Ar/F_2 = 400/1$ and 100/1 for 30 and 20 h, respectively, and new product bands were observed at 467, 549, and 616 cm^{-1}, in addition to bands due to KF and $(KF)_2$ at 396, 306, and 275 cm^{-1}. This 549-cm^{-1} absorption was broader and less intense than its Cs and Rb counterparts. On sample warming to 40 K, the sharp 396-cm^{-1} KF band and the weak 616-cm^{-1} band disappeared, the $(KF)_2$ bands and the 467-cm^{-1} band broadened and increased, and the 549-cm^{-1} absorption broadened and decreased. When KF was deposited at a slightly higher temperature, with a sample of $Ar/F_2 = 100/1$, a similar spectrum was observed with an increase in the 549- and 467-cm^{-1} bands relative to the weak 616-cm^{-1} feature. The 467-cm^{-1} band exhibited a resolved splitting at 463 cm^{-1} and the 549-cm^{-1} band had a 520-cm^{-1} shoulder, which are illustrated in Figure 2(b).

NaF. Two blank experiments were done with NaF in argon using 8- and 20-h deposition periods from a 750 °C Knudsen cell. The spectra were sharper than those of previous workers[11] and more NaF was isolated as the sharp monomer absorption at 495 cm^{-1} along with cyclic dimer at 418 and 370 cm^{-1} and other dimers or aggregates labeled D in Figure 2. Weak impurity complex bands were also observed at 616 and 350 cm^{-1}. NaF was deposited with samples of $Ar/F_2 = 100/1$ and 400/1, and in each case, no product bands were detected near 550 cm^{-1}. The only new product was observed at 455 cm^{-1}

with a 460-cm^{-1} splitting, in addition to absorptions of NaF and $(NaF)_2$, which are illustrated at the top of Figure 2. The NaF monomer and 455 cm^{-1} bands decreased while $(NaF)_x$ increased on sample warming to 35 K and no new bands appeared. NaF was codeposited with ClF in argon for 8 h; the major product bands were observed at 589 cm^{-1} (0.15) and 307 cm^{-1} (0.25); the only spectral features between these absorptions were a NaF–H_2O band at 349 cm^{-1} and a weak $(NaF)_x$ band at 385 cm^{-1} (0.06).

NaCl. Sodium chloride vapor was reacted with one Ar/ClF = 300/1 sample. The product spectrum was dominated by a sharp 511-cm^{-1} band (0.30) with a 496-cm^{-1} shoulder. No bands were observed between the 478-cm^{-1} A band and NaCl at 334 cm^{-1}. The low-frequency region contained 272- and 226-cm^{-1} $(NaCl)_2$ bands[5] and weak (0.02) features at 208, 240, and 255 cm^{-1}.

Alkali Metal Atoms. Matrix reactions of alkali metal atoms with F_2 in argon were reported 2 years ago.[10] In addition to the bands identified in this earlier paper, the reactions of Cs and Rb with F_2 also produced intense, sharp bands at 550 cm^{-1}, identical with bands produced by reaction of alkali fluoride salts with F_2 which are compared in Figure 2. These reaction products were omitted from the figure and discussion in the previous paper due to suspicion of COF_2 impurity, which absorbs in this region, although Ar/F_2 blank experiments showed no 550-cm^{-1} band. The major product of the M + F_2 reaction was the MF salt molecule, so the 550-cm^{-1} bands in the Cs and Rb reactions with F_2 are due to the same species as the 550-cm^{-1} bands formed in the analogous salt reaction. In addition, the reaction of K with F_2 produced a weak, broad feature near 550 cm^{-1}, and the Na + F_2 reaction gave a new band at 454 cm^{-1}, again in agreement with the salt–molecule reactions reported here.

A series of reactions of alkali metal atoms with samples of Ar/ClF has recently been investigated in this laboratory.[12] A number of reaction product bands were observed in these experiments, some of which are relevant to the studies reported here. The reaction of Cs atoms with ClF produced bands, among others, at 566, 412, and 365 cm^{-1}, in each case identical with the reaction products of CsF and CsCl with ClF. Also, a strong band was observed at 313 cm^{-1}, which is due to CsF. Rubidium atoms and ClF produced bands at 565, 479, 410, and 370 cm^{-1}, again analogous to the RbF and RbCl reactions with ClF reported above, in addition to bands due to RbF at 345 cm^{-1} and RbCl at 204 cm^{-1}. The reaction of K atoms with ClF in Ar showed analogous bands at 571 and 486 cm^{-1}, in addition to the strong KF absorption at 395 cm^{-1} and KCl absorption at 246 cm^{-1}. While salt reactions of KF and KCl with ClF were not undertaken, the metal atom reactions provide bands near the Rb and Cs counterparts for the two highest energy bands. The reaction of Na atoms with Ar/ClF yielded new bands at 589 and 511 cm^{-1}, which were also produced by the NaCl and NaF reactions with ClF.

Raman Spectra. CsF. Several experiments were performed with CsF codeposited with samples of Ar/F_2 using different concentrations. In each case, two Raman bands were observed at 461 and 389 cm^{-1} using excitation with the blue argon ion laser lines. These bands varied considerably relative to each other with different concentrations. At high dilution of either the salt or the gas sample, the 461-cm^{-1} band dominated, while the 389-cm^{-1} band increased in relative intensity at high concentrations. Warming the matrix to 40 K to allow diffusion and then recooling to 14 K diminished the intensity of the 389-cm^{-1} band, while the 461-cm^{-1} band remained intense. Cesium fluoride vapor was condensed with argon in a blank experiment and no Raman signals were observed; this sample contained a relatively high concentration of CsF as judged from the salt film left after evaporating the argon matrix. CsF was then deposited with samples of Ar/Cl_2 = 200/1, and in the best experiments, a weak band was observed near 411 cm^{-1} using 488.0-nm excitation. No other bands were observed in these experiments with any of the available laser lines. CsF was reacted with a sample of Ar/ClF = 200/1, and no bands were detected, although oven temperatures were varied over a considerable range.

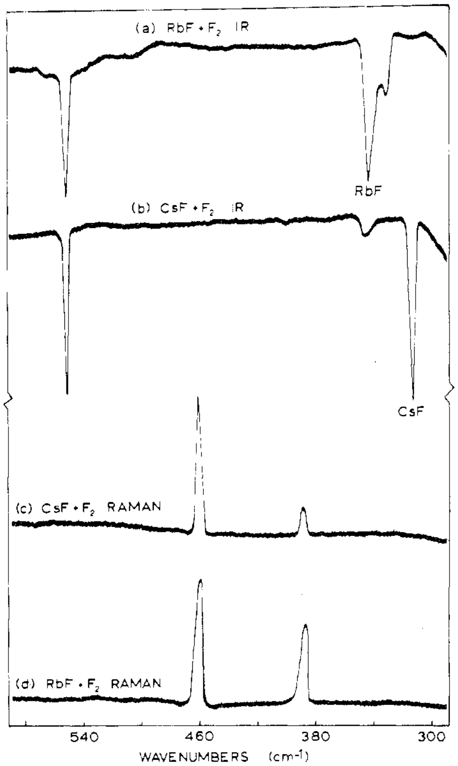

Figure 3. Comparison of infrared absorption and Raman scattering spectra for CsF and RbF matrix reaction products with F_2: traces a and b, infrared, Ar/F_2 = 400/1; traces c and d, Raman, Ar/F_2 = 100/1.

CsCl. Cesium chloride was deposited with a sample of Ar/ClF in several experiments, and in each case, the only detectable signal was near 410 cm^{-1}. This band was weak, but reproducible, like the 411-cm^{-1} band from the CsF + Ar/Cl_2 experiment.

RbF. Rubidium fluoride was deposited with samples of Ar/F_2 in several experiments, and the spectra resembled those obtained by the reaction of CsF with Ar/F_2. A strong Raman band was observed near 460 cm^{-1}, and a weaker band near 390 cm^{-1}. These two bands showed the same concentration and diffusion dependence as the 461- and 389-cm^{-1} bands in the analogous CsF experiments. Infrared and Raman spectra of the product of RbF and CsF reactions with F_2 are contrasted in Figure 3.

Ultraviolet Spectra. CsF. Several experiments were done in which CsF was codeposited with a sample of Ar/F_2. In each case, the spectrum increased sharply at 200 nm, but no band maximum was observed before the short-wavelength limit of the instrument was reached. The sharp rise in the background was not detected in blank experiments of Ar/F_2 or Ar + CsF. When CsF was codeposited with a sample of Ar/ClF = 100/1, the spectrum showed a similar rise in background at the spectrometer limit, but no band maximum was reached. In addition, a weak broad band was observed near 260 nm, which is due to ClF as it was present in a blank experiment involving only Ar/ClF. Finally, CsF was deposited in one experiment with a sample of Ar/Cl_2 = 100, and the spectrum of the reaction mixture showed, in addition to the Cl_2 band at 325 nm,[13] a strong band superimposed on the sample background, centered near 249 nm. This absorption required both CsF and Cl_2 and grew steadily with deposition of the reactants.

CsCl. CsCl was deposited in one experiment with a sample of Ar/ClF = 100, and the spectrum of this reaction mixture showed a single band, located at 249 nm, with the same behavior and intensity at the band produced through the reaction of CsF with Cl_2. Deposition of CsCl with a sample of Ar/F_2 showed a very steeply rising background in the region near 200 nm, but again no band maximum was resolved.

Discussion

Trifluoride. The reaction of an alkali fluoride salt molecule with F_2 is expected to produce the $M^+F_3^-$ ion pair, reaction 1, based on a thermodynamic cycle used to predict the stability

$$CsF + F_2 \rightarrow Cs^+F_3^- \tag{1}$$

of other ion pairs.[14] In the preliminary communication of this work,[3] bands produced in the reaction of CsF with F_2, at 550 cm^{-1} in the infrared experiment and at 461 cm^{-1} in the Raman experiment, were assigned to the F_3^- anion. The strong, sharp 550-cm^{-1} band dominates the infrared spectrum as does the 461-cm^{-1} counterpart band in the Raman spectrum. The reactions of RbF and KF with F_2 produced a band at 550 cm^{-1} in each case. The lack of shift of the 550-cm^{-1} band with the different cations Cs^+ through K^+ indicates that the vibration is a fluorine motion, and the assignment to ν_3 of F_3^- in the $M^+F_3^-$ species is indicated.

Reactions of alkali metal atoms with Ar/F_2 produced the same 550-cm^{-1} infrared absorptions as did the above salt reactions, in addition to other product bands. The reaction of Cs atoms, for example, with F_2 produced $Cs^+F_2^-$, some of which decomposed to CsF + F. CsF was observed in the spectrum, and it can react with F_2 to form $Cs^+F_3^-$. This secondary reaction has been observed in Na + Cl_2 studies, where $Na^+Cl_2^-$ and $Na^+Cl_3^-$ were detected.[5,15] The observation of the 550-cm^{-1} band in Cs, Rb, and K experiments with F_2 supports the assignment to the F_3^- anion, in agreement with the salt–molecule reactions.

The Raman spectrum of the CsF + F_2 reaction products showed an intense band at 461 cm^{-1} and a weaker band near 389 cm^{-1}; the 461-cm^{-1} band persisted at high dilution and was stable on diffusion, while the 389-cm^{-1} band was less stable and favored at high concentrations. This ties the 461-cm^{-1} band to the 550-cm^{-1} infrared band, with the assignment of the 461-cm^{-1} band to ν_1 of F_3^-, and suggests that the 389-cm^{-1} band is due to a higher salt complex. The reaction of RbF and F_2 in Raman experiments shows no shift of the 461-cm^{-1} band with a different cation, indicating a pure fluorine vibration. All of the evidence supports assignment of the 550-cm^{-1} infrared band and the 461-cm^{-1} Raman band to the same species, F_3^- in the $M^+F_3^-$ complex.

It can be readily seen in Figure 3 that mutual exclusion holds for the F_3^- anion. ν_1 was not observed in the infrared spectrum and ν_3 was not observed in the Raman. This requires a center of symmetry in the molecule. While mutual exclusion applies only within the limits of detectability, the evidence indicates a linear centrosymmetric $D_{\infty h}$ geometry for F_3^-. This is in agreement with the geometry found for the HCl_2^- and HBr_2^- anions[14,16] formed through the salt–molecule reactions and is different from the geometry observed for the Cl_3^- anion.[5] The polarizability of the anion probably determines the degree to which the cation may distort the anion away from the $D_{\infty h}$ geometry, and the greater polarizability of Cl_3^- allows for distortion to $C_{\infty v}$ or C_{2v} geometry.

Reactions of CsF and RbF with F_2 gave very strong, sharp infrared and Raman bands, indicative of a well-defined species. The reaction of KF with F_2 gave a weaker, broad band at 550 cm^{-1}, while the reaction of NaF with F_2 did not yield a band near 550 cm^{-1}, but rather two bands were observed at 455 and 460 cm^{-1}. This indicates that the smaller K^+ cation is less able to stabilize a well-defined F_3^- anion and that Na^+ cannot stabilize F_3^- at all. The 455, 460 cm^{-1} bands in the NaF + F_2 studies are probably due to a $Na^+F^- \cdots F_2$ complex, in which a well-defined F_3^- ion was not formed, and the vibrational motion may be a $F^- \leftrightarrow F_2$ stretching mode. The weak 467-cm^{-} feature in KF + F_2 experiments increased on sample warming while KF monomer disappeared and the 549-cm^{-} $K^+F_3^-$ band broadened and decreased. This absorption could be due to an analogous $K^+F^- \cdots F_2$ complex which is more stable than $K^+F_3^-$ on sample warming. In solution and solid trihalide anion studies, the larger cations were more effective for stabilizing the linear symmetric anions,[1] so the above alkali trifluoride trend is expected. In addition, CsF catalyzes oxidative fluorination reactions, but NaF does not.[17] If the catalytic intermediate is F_3^-, this provides further evidence for the stabilizing role of the larger Cs^+ cation.

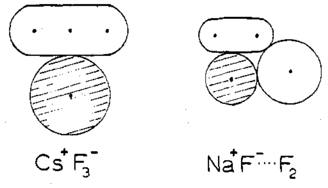

Figure 4. Sketch of the $Cs^+F_3^-$ and $Na^+F^- \cdots F_2$ species drawn to scale showing the importance of alkali cation size for stabilizing the trifluoride ion.

The $Cs^+F_3^-$ complex probably has a "T-shaped" structure with a linear F_3^- unit centered over the Cs^+ ion. This structure is sketched in Figure 4 to scale. The F–F distance in F_3^- was estimated to be 1.55 Å from the distance in F_2 and the I_3^-/I_2 ratio.[18] A possible structure for $Na^+F^- \cdots F_2$ is shown for comparison. Clearly the large alkali cations are necessary to stabilize F_3^-.

Mixed Chlorine–Fluorine Trihalides. Observation of the possible mixed chlorine–fluorine trihalides provides further information about these systems. Experiments with bromine–chlorine species[5] showed that end-on addition was the only reaction path, although the relative stabilities of Cl^- and F^- might allow rearrangement.

The reaction of CsF with Cl_2 produced an infrared absorption at 412 cm^{-1}, which can be assigned to a predominantly chlorine–fluorine vibration in $(ClClF)^-$, while the RbF + Cl_2 pair formed an analogous band at 409 cm^{-1}. Reaction of CsCl with ClF could give two different products, $(ClClF)^-$ discussed above and $(ClFCl)^-$, depending on which end of ClF adds the chloride. The CsCl + ClF system produced a new band at 412 cm^{-1}, identical with the case of the CsF + Cl_2 reaction, which requires the $(ClClF)^-$ assignment, and two additional new bands at 474 and 268 cm^{-1}. The latter two bands are tentatively assigned to the stretching modes of $(ClFCl)^-$, which, from these data, cannot have a center of symmetry.

The reaction of CsF with ClF yielded strong new bands at 566 and 365 cm^{-1}, as shown in Figure 1(b), and the RbF, ClF combination gave very strong absorptions at 371 and 565 cm^{-1} with the latter resolved into four components which could be due to isotopic and site splittings; however, the NaF + ClF reaction produced a strong upper band at 589 cm^{-1} and a new lower band at 307 cm^{-1} without product absorption in between. The lack of a sodium counterpart to the 365-cm^{-1} band in cesium experiments indicates that the 365- and 566-cm^{-1} absorptions are due to different species. The 566-cm^{-1} band is assigned to the anticipated major product $Cs^+(FClF)^-$. In the solid compound,[4] ν_3 has been observed at 636 cm^{-1}, so the 566-cm^{-1} value for the ion pair in solid argon is reasonable. The sharp 365-cm^{-1} absorption is tentatively assigned to the Cl–F stretching mode of the $(ClFF)^-$ anion. This species was formed only with Cs^+ and Rb^+ counterions, which parallels the $M^+F_3^-$ case.

Table II. Infrared Absorptions (cm^{-1}) Assigned to $M^+X_3^-$ Species Derived from F_2, ClF, and Cl_2 in Solid Argon at 15 K

	Cs^+	Rb^+	K^+	Na^+
$(F_3)^-$	550	550	549	
$(FClF)^-$	566	565	571[a]	589
$(ClFF)^-$ [c]	365	371		
$(ClFCl)^-$ [c]	474	480	486[a]	511
$(ClClF)^-$	412	409		
$(Cl_3)^-$	327[b]	340[b]	345[b]	375[b]

[a] Reference 12. [b] Reference 5. [c] Tentative identifications.

The reaction of CsCl with F_2 gave nearly an identical spectrum as the reaction of CsF with ClF. The most interesting observation is the new band at 312 cm^{-1} which must be due to CsF. This provides direct evidence that exchange reaction 2 occurs and, therefore, observation of the F_3^- anion

$$\mathrm{CsCl} + \mathrm{F_2} \rightarrow \underset{(\mathrm{Cs^+})}{(\mathrm{Cl{-}F{-}F})^-} \rightarrow \underset{(\mathrm{Cs^+})}{(\mathrm{F{-}Cl{-}F})^-} \rightarrow \mathrm{CsF} + \mathrm{ClF} \qquad (2)$$

at 550 cm^{-1} in this experiment is anticipated. The reactions of RbF with ClF and RbCl with F_2 yielded virtually identical spectra; the formation of RbF was noted at 345 cm^{-1} in the RbCl + F_2 experiment. A similar exchange reaction has been proposed for CsI + Cl_2 in gas-phase molecular beam reactions.[19]

Alkali metal reactions with ClF add complementary information, since these reactions also produce the MCl and MF salt molecules, which may react with ClF to form the trihalide anions. To this end, the reactions of Rb and Cs atoms with ClF gave some of the same product bands as the salt–molecule reactions, in addition to bands assigned to the M^+ClF^- species.[12] With K^+, the $FClF^-$ anion was observed at 572 cm^{-1}, the $ClFCl^-$ anion was observed at 498 cm^{-1}, and the region of the $ClClF^-$ anion was obscured by the KF absorption. With Na^+, bands were observed at 598 and 511 cm^{-1}, which are appropriate for the $FClF^-$ and $ClFCl^-$ anions. In each case, the anion frequency varied slightly with the cation, and each of two possible mixed combinations was observed, again supporting the formation of a unique trihalide anion. The $M^+X_3^-$ assignments are collected in Table II.[20]

The mixed complexes are probably asymmetric variations on the "T-shaped" structure noted in Figure 4 for $Cs^+F_3^-$. The $(F{-}Cl{-}F)^-$ unit may be linear symmetric, but the $(Cl{-}F{-}Cl)^-$ species appears to be distorted or bent, from the observation of two infrared bands.

The Raman spectra obtained for these systems were weak, and the only well-defined band was observed at 411 cm^{-1} for both the CsF + Cl_2 and CsCl + ClF reactions. This matches the infrared absorption for the $(ClClF)^-$ anion and supports this assignment to an intraionic vibration. The region between 200 and 300 cm^{-1} was very difficult to scan due to a sharply rising background near the exciting line.

Optical experiments were done for the Cs reactions, and bands were observed in only two experiments, namely, the reaction of CsF with Cl_2 and CsCl with ClF. Since both pairs of reagents can produce $Cs^+(ClClF)^-$, the 249-nm band in each case is assigned to the $(ClClF)^-$ anion. The Cl_3^- anion has been observed at 250 nm,[13] and the shift is very slight to the $(ClClF)^-$ anion. The remaining mixed species are expected to absorb at higher energies, and although no bands were detected, the strongly increased baseline near 200 nm in these experiments suggested strong absorption below 200 nm. It is likely that the ClF_2^- and F_3^- species absorb just below 200 nm, which could not be resolved from the sample background in these experiments.

Conclusions

Salt–molecule reactions involving alkali fluoride salts and F_2 have produced sharp, intense bands at 550 cm^{-1} in the infrared and 461 cm^{-1} in the Raman spectrum, which have been assigned to the F_3^- anion with the larger cations. The spectra indicate that mutual exclusion holds and that a center of symmetry is preserved in F_3^-. Further experiments with both fluoride and chloride salts and F_2, ClF, and Cl_2 have yielded a number of bands for the mixed chlorine–fluorine trihalide species, $(ClClF)^-$, $(ClFCl)^-$, $(ClFF)^-$, and $(FClF)^-$. Their observation from two synthetic routes supports assignment to a unique trihalide species, rather than a perturbed salt molecule, and provides further evidence that the F_3^- anion should be stable. The difficulty of forming the F_3^- anion with K^+ and the failure to form the F_3^- anion with Na^+ indicate that this species is sufficiently unstable to require a large adjacent cation for stabilization in an argon matrix.

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Registry No. $Cs^+(F_3)^-$, 62625-09-6; $Cs^+(FClF)^-$, 15321-03-6; $Cs^+(ClFF)^-$, 62625-08-5; $Cs^+(ClFCl)^-$, 62625-07-4; $Cs^+(ClClF)^-$, 62625-06-3; $Rb^+(F_3)^-$, 62625-05-2; $Rb^+(FClF)^-$, 62625-04-1; $Rb^+(ClFF)^-$, 62625-03-0; $Rb^+(ClFCl)^-$, 62625-02-9; $Rb^+(ClClF)^-$, 62625-00-7; $K^+(F_3)^-$, 62625-01-8; $Na^+(FClF)^-$, 62624-99-1; $Na^+(ClFCl)^-$, 62624-98-0; Cl_2, 7782-50-5; F_2, 7782-41-4; ClF, 7790-89-8; CsF, 13400-13-0; CsCl, 7647-17-8; RbF, 13446-74-7; RbCl, 7791-11-9; KF, 7789-23-3; NaF, 7681-49-4; NaCl, 7647-14-5.

References and Notes

(1) W. Gabes and D. J. Stufkens, *Spectrochim. Acta, Part A*, **30**, 1835 (1974).
(2) J. C. Evans and G. Y.-S. Lo, *J. Chem. Phys.*, **44**, 3638 (1966).
(3) B. S. Ault and L. Andrews, *J. Am. Chem. Soc.*, **98**, 1591 (1976).
(4) K. O. Christe and J. P. Guertin, *Inorg. Chem.* **4**, 905, 1785 (1965); K. O. Christe, W. Sawodny, and J. P. Guertin, *ibid.*, **6**, 1159 (1967).
(5) B. S. Ault and L. Andrews. *J. Chem. Phys.*, **64**, 4853 (1976).
(6) L. Andrews, *J. Chem. Phys.*, **48**, 972 (1968); **54**, 4935 (1971).
(7) D. A. Hatzenbuhler and L. Andrews, *J. Chem. Phys.*, **56**, 3398 (1972).
(8) L. Andrews, *J. Chem. Phys.*, **63**, 4465 (1975).
(9) "Handbook of Chemistry and Physics" 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970.
(10) W. F. Howard, Jr., and L. Andrews, *Inorg. Chem.*, **14**, 409 (1975).
(11) Z. K. Ismail, R. H. Hauge, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **35**, 3201 (1973).
(12) E. S. Prochaska, B. S. Ault, and L. Andrews, *Inorg. Chem.*, previous paper in this issue.
(13) L. Andrews, *J. Am. Chem. Soc.*, **98**, 2147, 2152 (1976).
(14) B. S. Ault and L. Andrews, *J. Chem. Phys.*, **62**, 2466 (1975).
(15) W. F. Howard, Jr., and L. Andrews, *Inorg, Chem.*, **14**, 767 (1975).
(16) B. S. Ault and L. Andrews, *J. Chem. Phys.*, **64**, 1986 (1976).
(17) F. A. Hohorst and J. M. Shreeve, *J. Am. Chem. Soc.*, **89**, 1809 (1967); P. G. Thompson, *ibid.* **89**, 1811 (1967).
(18) J. Runisnk, S. Swen-Walstra, and T. Migchelsen, *Acta Crystallogr., Sect. B*, **28**, 1331 (1972).
(19) D. L. King and D. R. Herschbach, *Faraday Discuss. Chem. Soc.*, **No. 55**, 331 (1973).
(20) Several bands below 310 cm^{-1} have not been assigned. Since the region below CsF monomer at 313 cm^{-1} includes $(CsF)_2$ and possibly other aggregates, the confidence level for identifying bands in this lower region is not good enough to justify assignments.