

Infrared, Raman, and Ultraviolet Spectra of M^+ClF^- Species in Solid Argon

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The alkali metal-chlorine monofluoride matrix reaction products were examined by infrared, Raman, and ultraviolet matrix techniques. Strong bands near 340 cm^{-1} in both the infrared and Raman spectra are assigned to the intraionic ($Cl\leftrightarrow F$)⁻ mode and strong metal-dependent infrared absorptions are attributed to the interionic $M^+\leftrightarrow(ClF)^-$ mode. Intense ultraviolet absorptions near 290 and 250 nm are assigned to M^+ClF^- and $M^+Cl_2F^-$, respectively.

Introduction

The products of reactions between alkali metal atoms and chlorine and fluorine molecules have been studied using infrared, Raman,^{1,2} and ultraviolet³ matrix isolation spectroscopy, where the $M^+X_2^-$ intermediate in reaction 1 was of particular



interest. The spectra were appropriate for a halogen species with an extra antibonding electron, decreasing the bond order by half. This was reflected in the intraionic vibrational frequency, which was about half that of the neutral parent, and in a decrease in the energy of the $\sigma \rightarrow \sigma^*$ electronic transition.

The corresponding mixed-halogen species, M^+ClF^- , are expected to be electronically related in a similar way to the neutral ClF molecule and to both the Cl_2^- and F_2^- species. The mixed-halogen system was studied using infrared, Raman, and ultraviolet techniques, and these results are the subject of this paper.

Experimental Section

The vacuum systems, cryogenic refrigerators, and spectrometers have been described previously.⁴⁻⁶ Stainless steel vacuum apparatus was well passivated with ClF or ClF_3 before all experiments involving ClF. Chlorine monofluoride (Ozark Mahoning) was purified by freeze-pump-thaw cycles, followed by distillation from an *n*-pentane slush bath (-130°C) with a vapor pressure of about 2.5 in. Chunks of Na (J. T. Baker, lump) and K (Baker and Adamson, lump) were placed in stainless steel Knudsen cells and outgassed to operating temperatures of 230 and 160 $^\circ\text{C}$, respectively, before use. Rubidium and cesium were prepared by heating liquid lithium (Fisher) with RbCl (Fairmount Chemical Co.) or CsCl (Fisher) in a Knudsen cell to about 295 $^\circ\text{C}$ to initiate reaction.

Chlorine monofluoride samples were prepared by diluting ClF gas with Ar (Air Products, 99.995%) matrix gas, used without purification, in ratios of $M/R = 100/1$ for Raman and ultraviolet experiments and $M/R = 300/1$ for infrared experiments. Samples were prepared in 2- or 3-L stainless steel cans. Infrared samples were deposited onto a 15-K CsI window for 1 h at 1.6 mmol/h before metal codeposition was begun for about 20 h. Raman samples were deposited on a 12-K copper wedge at 2.5 mmol/h with metal codeposition starting after 1 h. Ultraviolet samples were deposited on a 15-K sapphire window at a rate of 1.5 mmol/h with metal codeposition starting after 1 hour and continuing for about 4 h. Selected samples were photolyzed with an AH-4 (General Electric) medium-pressure mercury arc.

Results

Observations from reactions of ClF with alkali metals will be described for the infrared, Raman, and ultraviolet experiments in turn.

Infrared Spectra. Ar/ClF = 300/1 samples were codeposited with alkali metal atoms for about 20 h, and infrared spectra were recorded during and after deposition in the region 200 to about 1200 cm^{-1} . Parent ClF bands were observed as reported previously.⁷ Figure 1 contrasts spectra for sodium, potassium, rubidium, and cesium experiments; two new bands were observed with potassium at 289 and 350 cm^{-1} , with rubidium at 241 and 340 cm^{-1} , and with cesium at 224 and

Table I. Infrared Absorptions (cm^{-1}) Observed for Alkali Metal Matrix Reactions with Chlorine Monofluoride

Identification	M			
	Na	K	Rb	Cs
MF ^a	491	395	332, 345	295, 313
(MF) ₂ ^a	349, 427	279, 309	229, 269	207, 245
MCl ^b	334	246	204	
(MCl) ₂ ^b	225, 271			
$M^+ClF_2^-$ ^c	589	571, ...	564, 370	567, 363
$M^+Cl_2F^-$ ^c	511	486	479, 410	..., 410
M^+ClF^-		289, 350	241, 340	224, 336
Other	367, 374 306, 407	337, 372	278, 345	265, 635

^a References 8 and 9. ^b Reference 11. ^c Reference 10.

336 cm^{-1} which are labeled X in Figure 1. The sodium experiment produced a new 374, 367 cm^{-1} doublet and a 306- cm^{-1} band. In addition, absorptions corresponding to salt monomer and dimer^{8,9} and secondary reaction product mixed chlorine and fluorine trihalide anions¹⁰ were observed and are identified in Table I.

Raman Spectra. After about 4 h of sample deposition, Raman spectra were recorded using argon ion laser excitation. Product bands were observed with ClF and potassium at 349 cm^{-1} , with rubidium at 340 cm^{-1} , and with cesium at 338 cm^{-1} shifted from the exciting line, which are labeled X in Figure 2. No new bands were observed in the Raman experiment with sodium. Bands corresponding to Cl_2 , $M^+Cl_2^-$, ClF, and ClF_3 impurity were also observed in the Raman spectra. The product bands exhibited varying intensities with different laser exciting lines at 488.0, 476.5, and 457.9 nm. In each experiment, the emission region (19 000–11 000 cm^{-1} absolute) was scanned, but no emissions attributable to new reaction products were observed.

Ultraviolet Spectra. UV spectra were taken before, during, and after the 4-h deposition period. Bands appeared at 288 and 244 nm with potassium, both of which decreased in intensity after 5 min of photolysis with a medium-pressure mercury-arc lamp. After thermal cycling to 40 K and re-cooling to 15 K the 288-nm band was reduced, but the 244-nm band was increased in intensity. With rubidium, bands were produced at 290 and 249 nm. With cesium, bands were observed at 292 and 253 nm with moderate metal concentration. The 292-nm band was slightly more intense. After 5 min of photolysis, the 292-nm band had decreased in intensity and remained about the same after thermal cycling to 40 K. The 253-nm band was little changed by photolysis but grew with warming. In an experiment with lighter metal concentration, a band was observed at 289 nm, with a slight shoulder near 250 nm. After thermal cycling to 40 K and then to 45 K, a band grew in at 255 nm, while the 286-nm band lost intensity. Spectra from the two cesium experiments are illustrated in Figure 3. In experiments with sodium, a single weak band was observed at 328 nm which was unchanged by 10 min of photolysis but grew slightly after warm-up. This band is due to molecular chlorine.³

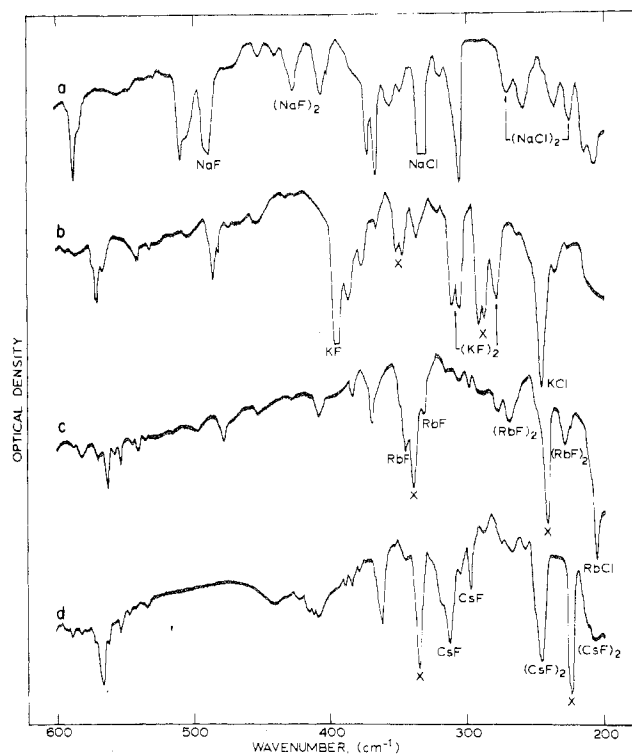


Figure 1. Infrared spectra from 200 to 600 cm^{-1} for alkali metal atom matrix reactions with $\text{Ar}/\text{ClF} = 300/1$ samples: (a) Na, (b) K, (c) Rb, and (d) Cs.

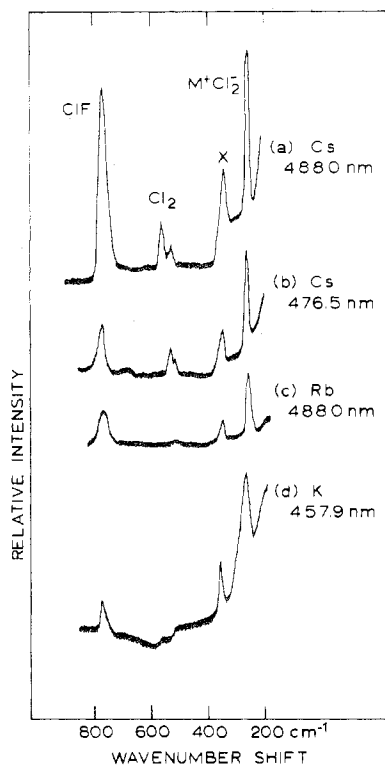


Figure 2. Raman spectra for heavy alkali metal atom matrix reaction products with $\text{Ar}/\text{ClF} = 100/1$ samples: (a) Cs, 488.0-nm excitation, (b) Cs, 476.5-nm excitation, (c) Rb, 488.0-nm excitation, and (d) K, 457.9-nm excitation.

Discussion

Infrared spectra of alkali metal-ClF matrix reaction products exhibited alkali fluoride monomers and dimers^{8,9} and mixed trihalide species.¹⁰ In addition new bands observed at 350 cm^{-1} with K, 340 cm^{-1} with Rb, and 336 cm^{-1} with Cs

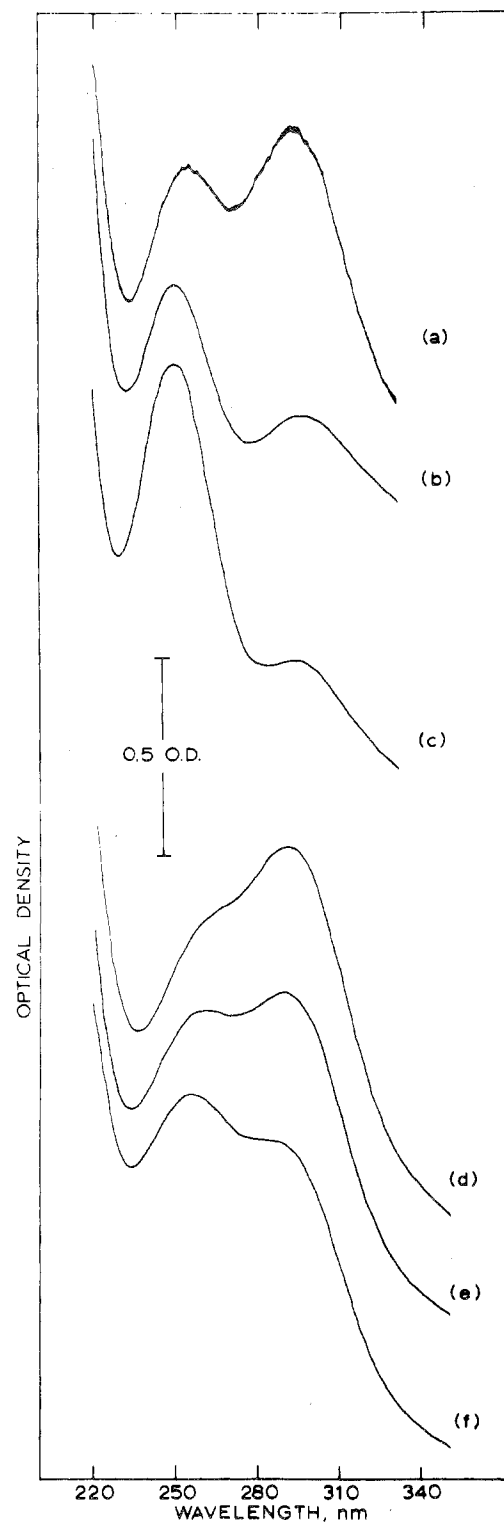


Figure 3. Ultraviolet spectra for cesium-ClF matrix reaction products (a) at higher Cs concentration, (b) after 5 min of photolysis, and (c) after thermal cycles to 40 and 45 K; (d) at lower Cs concentrations, (e) after thermal cycle to 40 K, and (f) after thermal cycle to 45 K.

are appropriate for the intraionic $(\text{Cl}-\text{F})^-$ mode in the M^+ClF^- species as they fall midway between the F_2^- and Cl_2^- frequencies^{1,2} and at about half of the ClF fundamental at 770 cm^{-1} , which is expected for the addition of one more anti-bonding electron.

Raman spectra confirm the intraionic mode assignments with the observation of new signals at 349 cm^{-1} with K, 340 cm^{-1} with Rb, and 338 cm^{-1} with Cs, in excellent agreement with the infrared results. This mode is expected to be the most

intense Raman band in the product species.

Strong infrared absorptions at 289 cm^{-1} with K, 241 cm^{-1} with Rb, and 224 cm^{-1} with Cs are assigned to the interionic $M^+\leftrightarrow(ClF)^-$ mode. Perhaps the best model for this interionic mode is the B_{3u} mode of the cyclic salt dimer. This absorption appears at 306 cm^{-1} for $(KF)_2$, 266 cm^{-1} for $(RbF)_2$ and 248 cm^{-1} for $(CsF)_2$,⁹ and 193 cm^{-1} for $(KCl)_2$.⁸ The interionic $M^+\leftrightarrow(ClF)^-$ modes fall just below the $(MF)_2$ modes and considerably above the $(MCl)_2$ vibration, which suggests that the alkali cation may be more strongly bound to the more electronegative fluorine in the M^+ClF^- species.

Several bands in the infrared spectra are assigned to alkali trihalide species. These ion pairs are formed by the secondary reactions 2 and 3, which are discussed in the following paper.¹⁰



Similar reactions have been used to synthesize $M^+Cl_3^-$ species.¹¹ It is interesting to note that the fluoride secondary reaction 3 gave relatively more product yield with the heavier alkali metals, whereas with sodium both reactions 2 and 3 were comparable.

The two ultraviolet absorptions near 250 and 290 nm are attributed to products of the $M + ClF$ reactions. Again, comparing the corresponding Cl_2 and F_2 reactions, the band at 292 nm with cesium falls between those for F_2^- at 284 nm and Cl_2^- at 344 nm, also formed by reaction with cesium.³ Similar bands are observed with ClF and rubidium at 290 nm and with potassium at 288 nm. These bands are attributed to the $\sigma \rightarrow \sigma^*$ transition for the ClF^- species similar to the F_2^- and Cl_2^- observations.³ The bands observed at 244 nm with potassium, 249 nm with rubidium, and 253 nm with cesium can be assigned to secondary reaction product $M^+Cl_2F^-$, which has been observed for the salt reaction between MCl and ClF and for the $M^+Cl_3^-$ species at 250 nm.³

These assignments are supported by the appearance of the spectra under conditions of different metal concentration, photolysis, and thermal cycling, as shown in Figure 3. Trace a illustrates the final spectrum in an experiment with a higher cesium concentration. The M^+ClF^- band is the larger, but the $M^+Cl_2F^-$ band is significant. Trace b shows the spectrum after 5 min of photolysis; the M^+ClF^- band decreased considerably in intensity, but the $M^+Cl_2F^-$ band remained about the same. After subsequent thermal cycling of the sample to 40 K and then to 45 K, trace c shows that the M^+ClF^- band has further decreased and the $M^+Cl_2F^-$ band has increased considerably. The relative instability of the 292-nm band is consistent with assignment to the intermediate M^+ClF^- species, while the more stable secondary reaction product is expected to form following warming to allow diffusion of reagents within the matrix.

Trace d of Figure 3 shows the final spectrum in an experiment with a lower cesium concentration. In contrast to trace a, the M^+ClF^- intermediate is favored and less of the secondary product is formed. However, after thermal cycles to 40 K (trace e) and 45 K (trace f), the M^+ClF^- intermediate

is decreased and $M^+Cl_2F^-$ is increased.

Several infrared experiments were done with both lithium metal isotopes, and Raman, infrared, and ultraviolet experiments were done with sodium metal. New bands were observed in the infrared with sodium at 374 and 367 cm^{-1} , which might be due to Na^+ClF^- . However, there was no band assignable to the $(Cl\leftrightarrow F)^-$ mode in the Raman spectrum and no evidence of the Na^+ClF^- species in ultraviolet experiments. The $374, 367\text{ cm}^{-1}$ doublet is possibly due to the $Na^+Cl_3^-$ species,¹¹ arising from Cl_2 impurity, and the strong 306-cm^{-1} band in the sodium experiment is likely due to $Na^+F\cdots FCl$.¹⁰ No bands were found for Li^+ClF^- species in the lithium experiments. For both lithium isotopic reactions, only salt monomer and dimer bands were observed in the infrared spectrum.

The absence of substantial amounts of intermediate M^+ClF^- species in the lighter metal reactions is consistent with the trend of increasing stability of the species with larger cations. In every case, the cesium reactions produced the best yield of the intermediate as indicated by relative intensities of bands. This trend in stability is also consistent with the results for $M^+Cl_2^-$ and $M^+F_2^-$ species. It is, however, noteworthy that a new ClF^- hole center has been observed by ESR in mixed KCl-KF crystals at 77 K following x irradiation,¹² which indicates that the ClF^- ion is physically stable.

Conclusions

The alkali metal-ClF matrix reaction produced large yields of alkali fluoride and chloride monomers and dimers, alkali trihalide species, and for the heavier alkali metals, a stable M^+ClF^- species was trapped and identified by infrared, Raman, and ultraviolet spectra. Strong bands near 340 cm^{-1} in both infrared and Raman spectra are assigned to the intraionic $(Cl-F)^-$ mode and strong metal-dependent infrared absorptions are due to the interionic $M^+\leftrightarrow(ClF)^-$ mode. Intense ultraviolet bands near 290 and 250 nm are assigned to M^+ClF^- and $M^+Cl_2F^-$, respectively.

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Registry No. K^+ClF^- , 62682-74-0; Rb^+ClF^- , 62682-75-1; Cs^+ClF^- , 62682-73-9; ClF, 7790-89-8; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2.

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