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Lester Andrews

August 21, 1975

DISCLAIMER

OPTICAL SPECTRA OF THE DIFLUORIDE, DICHLORIDE AND TRICHLORIDE IONS
IN THE MATRIX-ISOLATED $M^+F_2^-$, $M^+Cl_2^-$, and $M^+Cl_3^-$ SPECIES

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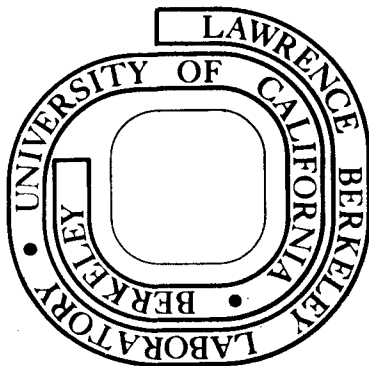
ABSTRACT

Alkali metal atoms were codeposited with fluorine and chlorine at
high dilution in argon on a sapphire plate cooled to 17 K.   Ultraviolet
spectra contained strong absorptions near 300 nm for $M^+F_2^-$ and 340 nm for
$M^+Cl_2^-$ which are assigned to the $\sigma \rightarrow \sigma^*$ transition of the dihalide anion.
This transition for Cl_2^- occurs at half of the energy known for Cl_2.
The alkali metal effect on the absorption spectra is consistent with an
ionic model of polarizable ion pairs.   In addition, the strong ultraviolet
band of the trichloride anion was observed at 250 nm with the metal-chlorine
reactions and with the matrix reaction of CsCl and Cl_2.

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INTRODUCTION

Very recently Howard and Andrews reported the observation of Raman signals near 460 cm^{-1} from argon-fluorine matrix samples codeposited with alkali atoms which were assigned to the intraionic F_2^- vibration in the $M^+F_2^-$ species.[1,2] The first evidence for the difluoride radical anion came from ESR spectra of irradiated fluoride salts at 77 K.[3] Subsequent work confirmed the ESR spectrum of F_2^- in solid LiF and recorded a strong optical band at 348 nm which was assigned to the $^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ transition of the F_2^- center.[4] Hence, optical spectroscopic observation of F_2^- using the same reactions as the Raman experiments would provide support for this chemical preparation of the unstable species F_2^-.

On the other hand, the dichloride radical anion has been more widely studied. Cl_2^- has been observed in irradiated chloride salts at 77 K by ESR and optical spectroscopy,[5] in irradiated 77 K glasses by optical[6] and Raman methods[7] and as a transient species in aqueous chloride solutions by flash photolysis[8] and pulse radiolysis.[9] Laser-Raman studies of matrix samples prepared by codepositing chlorine with alkali atoms yielded strong resonance Raman progressions in the Cl_2^- vibration.[10,11] The dependence of resonance Raman spectra of Cl_2^- upon the wavelength of the exciting line required a near ultraviolet optical band for the $M^+Cl_2^-$ species which was one of the goals of this study.

Even though optical spectra of the more stable triiodide and tribromide ions have been studied extensively,[12] the limited spectral data on the less stable trichloride ion has not been well characterized. Aqueous solutions of Cl_2 and Cl^- exhibited broad absorptions near 230 nm which have been attributed to Cl_3^-.[13,14] Upon warming irradiated NaCl-

H_2SO_4 glasses, the Cl_2^- absorption decayed and a band assigned to Cl_3^- appeared at 230 nm.[6] The $M^+Cl_3^-$ species is produced as a secondary reaction product in the matrix reactions of alkali metal atoms with chlorine,[11] which has been confirmed by the matrix reaction of MCl salt molecules with chlorine.[15] The optical spectrum of the trichloride ion in the $M^+Cl_3^-$ species will also be presented in the following study.

EXPERIMENTAL SECTION

The vacuum vessel used for optical matrix-isolation studies was similar to that previously described for infrared work[16] except for quartz optical windows and a Model 21 Cryodyne (Cryogenic Technology, Inc.) closed-cycle helium refrigerator for the sapphire cold window which was mounted with indium gaskets to a copper block. A Cary 14 recording spectrophotometer with a modified sample compartment was used to obtain spectra from 800 to 200 nm.

Fluorine (Matheson) was slowly passed through a coil immersed in liquid oxygen. The stainless steel vacuum manifold and sample can were thoroughly passivated with F_2 before use. Chlorine (Matheson) was condensed at 77 K and outgassed. Argon (Liquid Carbonic, 99.997%) matrix samples were prepared and deposited at the rate of 2 mM/hr onto the sapphire plate cooled to 10 K or 17 K. The higher temperature gave more transparent, less scattering matrices.

Lithium metal (Fisher Scientific Co.), sodium metal (J. T. Baker Chemical Co.), potassium metal (Baker and Adamson, Allied Chemical Co.) and a lithium metal-cesium chloride (Orion Chemical Co.) mixture were loaded into a stainless steel Knudsen cell as described previously[17] and heated to operating temperature in the apparatus behind a sliding

door. Metal atom deposition temperatures for Li, Na, K and Cs atoms
were 425, 230, 160 and 290°C, respectively. Cesium chloride vapor was
also deposited from a 425°C Knudsen cell in several experiments.

Approximately 2 mM of matrix sample were deposited on the cold
sapphire plate, the absorption spectrum was recorded, and alkali metal
vapor was codeposited with the gas mixture for 1-4 hr. Absorption
spectra were recorded during sample deposition to monitor the reaction.
In order to eliminate absorption due to metal aggregate species, the
matrix reactions were done with excess halogen. Samples containing
alkali metal atoms and F_2 were clear and colorless in the center
whereas matrices containing M and Cl_2 were a clear, faint yellow. After
recording final spectra, selected samples were exposed to the tungsten
lamp near-infrared source of the Cary 14 and/or warmed to higher
temperatures to allow diffusion of trapped species then recooled and
additional spectra were recorded. The standard Cary 14 tungsten lamp
(General Electric, 100 W, pyrex envelope) operates at about 3000 K. At
300 nm the lamp output is approximately 1% of its maximum at 900 nm, about
8% of maximum at 350 nm, and 80% of maximum at 700 nm.

RESULTS

Optical absorption studies of the products of alkali metal atom
matrix reactions with fluorine and chlorine will be described in turn.

Fluorine

A sample of fluorine in argon (Ar/F_2 = 50/1) was deposited for 3 hr
(5mM total) and the absorption spectrum revealed no bands from 600 to

200 nm; the scattering background increased to 1.0 O.D. at 200 nm.
The very weak optical absorption of molecular fluorine at 285 nm[18]
was not detected in these experiments.

When sodium atoms were codeposited with the Ar/F_2 = 50/1 sample
for one hour, a very intense band appeared at 312 nm (1.0 O.D.).
Exposure to the tungsten lamp reduced the band to 0.50 O.D. and the
peak shifted to 292 nm. Another experiment was done codepositing sodium
atoms with an Ar/F_2 = 100/1 sample. After 1 hr, a 309 nm absorption
(0.50 O.D.) was observed which became a strong 310 nm band (0.90 O.D.)
after 2 hr; this feature is illustrated in Fig. 1. After 20 min of
tungsten light, the band measured 303 nm (0.50 O.D.) which is also
illustrated in Fig. 1, and after 102 min, the absorption was reduced to
0.24 O.D. at 293 nm. It should be noted that the alkali metal-fluorine
samples were clear and colorless in the sample center, as the lack
of visible absorption indicates.

Lithium atoms were codeposited with an Ar/F_2 = 100/1 sample for
3½ hr and a 300±3 nm band (0.31 O.D.) resulted. Five min of W light
reduced the band to 0.04 O.D. at 280±5 nm and 5 more min destroyed it
completely, as is shown by the spectrum in Fig. 1(a).

A 1% F_2 sample was reacted with potassium atoms for 3½ hr which
reduced the strong (1.0 O.D.) 294±1 nm band illustrated in Fig. 1. After
10 min of exposure to the W lamp, the band was reduced to a weak broad
shoulder on the steep sample background.

Finally, cesium atoms were codeposited with an Ar/F_2 = 100/1 sample
for 2½ hr and a strong (0.85 O.D.) band appeared at 284±1 nm. This

band is shown in Fig. 1 along with the result of 15 min of W lamp

photolysis, a 269 nm band with 0.66 O.D.. A total of 25 m of W light

reduced the band to 0.60 O.D.. Warming the sample successively to 32,

37 and 42 K merely broadened the band with little effect on its intensity

or position.

The absorption band maxima are listed in Table I for the alkali

metal-fluorine reactions.

Chlorine

A blank experiment was run using a chlorine-argon sample with

Ar/Cl_2 = 100/1; 9 mM of condensed gas produced a 0.4 O.D. absorption

at 327±2 nm which is in good agreement with the gas phase band maximum,

325 nm, for Cl_2.[19]

Two experiments were run with lithium and chlorine; the top trace

of Fig. 2 illustrates the spectrum. Two bands were observed, a 248±1 nm

band (0.42 O.D.) on the rising background and a strong band at 338.4±0.5 nm

(0.66 O.D.). Four min of W lamp operation reduced the 338 nm band to

0.52 O.D. and left the 248 nm absorption unchanged. These samples

appeared clear with a faint yellow color in white light.

Several sodium experiments were performed with Ar/Cl_2 = 100/1

samples searching for the optimum sodium concentration. With excess

sodium, a strong feature was observed at 450 nm which is believed to

be due to Na_2 which absorbs strongly at 460-480 nm in the gas phase.[20]

Spectrum (b) in Fig. 2 shows a very strong 250±1 nm band (1.0 O.D.), a

strong 344.5±0.3 nm absorption (.82 O.D.) and a weak band at 450 nm.

Operation of the W lamp for 20 m destroyed the 450 nm feature, reduced the 344 nm band to 0.57 O.D. and left the 250 nm absorption unchanged.

An experiment with potassium and chlorine produced spectrum (c) of Fig. 2 which contained very intense bands at 343.0±0.3 and 247±1 nm. The latter increased on sample warming to 37 K and the former decreased upon exposure to the W lamp.

Cesium atoms at 297±2°C were codeposited with a 1% chlorine sample in argon for 40 min and the very strong bands shown at 344.0±0.3 and 250±1 nm in the last trace of Fig. 2 were produced. In order to gain chemical information on the identity of these two absorptions, two additional cesium experiments were conducted. First, using a reduced cesium source temperature (294±1°C) and a reduced chlorine concentration (Ar/Cl_2 = 400/1), the top spectrum in Fig. 3 shows the two bands at 249±1 and 351±1 nm, slightly shifted due to the steep red absorption of excess cesium in the sample which was royal blue in appearance. Comparison of Fig. 3 (a) and Fig. 2 (d) shows that the cesium atom concentration in these experiments is greater than 0.25% but less than 1%. The next reaction, shown in Fig. 3 (b) used a lower cesium source temperature (288±2°C) and Ar/Cl_2 = 300/1. The 250 nm band was observed as a shoulder (0.08 O.D.), the 344.0±0.3 nm band appeared as a strong 0.58 O.D. absorption, and no other absorption was observed out to 800 nm after 4 hr of sample desposition. The dashed trace in Fig. 3 (b) shows the effect of 10 min of W lamp irradiation: 344 nm was reduced to 0.53 O.D. while 250 nm was unchanged. Upon sample warming to 42 K and recooling to 17 K, the 250 nm shoulder increased to

a partially resolved 0.46 O.D. absorption while the 344 nm band was

essentially unchanged (0.55 O.D.). The absorptions from alkali

metal-chlorine studies are collected in Table I.

Finally, suspecting that the 250 nm band in cesium-chlorine

experiments was due to a secondary reaction product of CsCl and Cl_2,

cesium chloride vapor was evaporated from a Knudsen cell and codeposited

with an Ar/Cl_2 = 200/1 sample. The last trace in Fig. 3 shows a very

strong 250.7±0.3 nm absorption (1.0 O.D.) and a weak 340 nm band; the

latter weak absorption appeared after the Knudsen cell was warm, but

before the shutter was opened, and it was bleached by the W lamp which

had no effect on the strong 250 nm absorption. Sample warming to 37 K

increased the 250 nm band to 1.7 O.D.

DISCUSSION

The present optical absorption data, coupled with analogous laser

Raman studies, provides a basis for the characterization of several

unstable chemical species which contributes to understanding bonding

and electronic structure in ionic molecules.

Identification of New Species

A single intense new absorption band was observed near 300 nm

following the reaction of alkali atoms and fluorine. Analogous laser

Raman studies produced a single new Raman band near 460 cm^{-1} which

exhibited small alkali metal shifts. Comparison of Raman spectra of

sodium reactions with F_2, mixed F_2 and Cl_2, and Cl_2 samples showed, by

the absence of new features in the mixed experiment, that the new signal was due to an intermediate in the primary reaction 1.   Infrared studies of these

$$M \;+\; F_2 \longrightarrow M^+F_2^- \longrightarrow MF \;+\; F \tag{1}$$
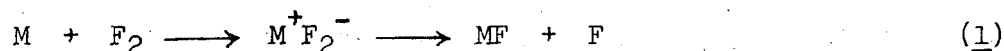
reactions yielded strong metal fluoride monomer and dimer bands, and in several cases, tentative assignments to the $M^+ \leftrightarrow F_2^-$ stretching mode of the intermediate species.[2]
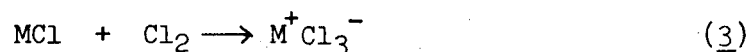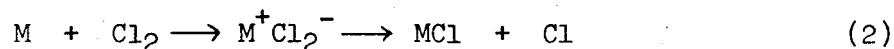
Since alkali metal fluoride molecules produce weak continuous absorptions below 200 nm,[21] it is reasonable to assign the strong absorptions between 284 and 310 nm depending on M^+ to the difluoride molecular anion in the $M^+F_2^-$ species.   This is in accord with the observation of a strong 348 nm band for F_2^- in irradiated LiF at 77 K.[4]

Although it is difficult to discriminate between the long wavelength tail of an absorption and the scattering background of the matrix, the F_2^- absorption observed here appears to tail up to the visible region of the spectrum such that preresonance enhancement of Raman signals with 488 nm excitation might be possible.   This helps explain the observation of reasonably strong F_2^- Raman signals from samples[1,2] which probably contained a relatively low concentration of trapped $M^+F_2^-$.

Now, considering the alkali metal-chlorine reactions, two optical bands were observed, one near 250 nm and the other near 340 nm, depending upon the alkali cation.   The relative intensities of these bands were strongly dependent on the concentrations of M and Cl_2 as comparison of the spectra of Fig. 2(d) and Fig. 3(a,b) indicate.   At lower reagent concentrations the 250 nm band yield is reduced signficantly, relative to the 340 nm band.

The intermediate dichloride radical anion and the metal chloride

are both primary reaction products whose yields depend upon the concentration

of each reagent, i.e. reaction $\underline{2}$ is "first order" in each reagent. However,

the $M^+Cl_2^-$ product of reaction $\underline{3}$ is "second order" in Cl_2 and "first order"

$$M \ + \ Cl_2 \longrightarrow M^+Cl_2^- \longrightarrow MCl \ + \ Cl \qquad\qquad (\underline{2})$$

$$MCl \ + \ Cl_2 \longrightarrow M^+Cl_3^- \qquad\qquad (\underline{3})$$

in M making the yield of the secondary species $M^+Cl_3^-$ a higher order reaction

which is more sensitive to Cl_2 concentration than the products of reaction

$\underline{2}$. Accordingly, the concentration and sample warming data indicate that

the 250 nm band is a secondary reaction product, $\underline{3}$, and the 340 nm

absorption is due to the primary reaction $\underline{2}$. Although alkali chlorides

are known to produce weak continuous absorption in the ultraviolet, a

recent matrix isolation study of several orders of magnitude more

NaCl than formed in the present matrix reactions produced no absorption

spectra.[22] Hence, the two bands observed here are due to diatomic and

triatomic anions which are very strong absorbers.

In order to confirm that the 250 nm band is due to the secondary

product $M^+Cl_3^-$ species, the direct matrix reaction of CsCl vapor and

Cl_2 was carried out, and it produced a very strong 250.7 ± 0.3 nm band

in agreement with the feature produced by the cesium-chlorine reaction.

The strong absorption between 338 and 344 nm, depending upon

alkali metal, is due to Cl_2^- in the $M^+Cl_2^-$ species. This observation is

in agreement with Cl_2^- bands in solid KCl at 365 nm,[5] aqueous solution

at 340 nm[8,9] and alkali chloride-borate or H_2SO_4 glasses at 335 nm.[6,7]

The resonance Raman spectra using blue laser excitation produced

very strong Cl_2^- fundamentals between 264 and 225 cm^{-1} depending upon M^+ and overtone progressions out to 8ν which exhibited resolved chlorine isotopic splittings consistent with a molecule containing two equivalent chlorine atoms.[11] The faint yellow sample color and the long wave length tail of the absorption bands show that the Cl_2^- absorption reaches weakly into the blue visible region which is in accord with the observation of resonance Raman spectra of Cl_2^- with argon ion laser lines. It was also noted that decreasing the exciting wave length from 514.5 to 457.9 nm produced a marked enhancement in the resonance Raman spectrum of $Cs^+Cl_2^-$ as the laser excitation approached the absorption band maximum from the long wave length side.

Band Assignments

In order to understand the spin resonance spectra of V-centers in alkali chloride salts, the electronic structure of the Cl_2^- ion has been considered.[23,24] Absorptions have been predicted in the violet and red regions.

Figure 4 shows a schematic energy level diagram from the $M^+Cl_2^-$ species assuming C_{2v} symmetry since the chlorine isotopic splittings in the resonance Raman overtones suggest equivalent chlorine atoms.[10,11] Only the symmetry designation will change if the molecule has only a plane of symmetry. The π_x and π_x^* orbitals which point toward the metal have been placed lower in energy than their π_y counterparts in accord with recent theoretical calculations[25] on $Li^+O_2^-$. The ultraviolet and red absorptions are indicated. Delbecq, et. al.[5] observed a very

weak 750 nm band in addition to the strong 365 nm absorption of Cl_2^- in the KCl lattice. These workers concluded, from absorption and bleaching effects on the 365 nm band with polarized light, that the transition moment giving rise to the 365 nm abosrption was parallel to the molecular axis. Hence, the assignment of the near ultraviolet absorption of the $\sigma \to \sigma^*$ transition between the $^2\Sigma_u^+$ ground and $^2\Sigma_g^+$ excited states of Cl_2^- follows. The very weak band is due to a $\pi^* \to \sigma^*$ transition between the $^2\Sigma_u^+$ and $^2\pi_g$ states.

The near ultraviolet bands for $M^+F_2^-$ and $M^+Cl_2^-$ are assigned to the $\sigma \to \sigma^*$ transition depicted in Fig. 4. Unfortunately, the very much weaker $\pi^* \to \sigma^*$ red transitions for these species were not detected. It is well-known in trihalide ion systems that $\sigma_g \to \sigma_u^*$ transitions are much more intense than $\pi_g \to \sigma_u^*$ transitions.[12,26]

The strong 251 nm band observed for Cl_3^- in the $Cs^+Cl_3^-$ species is assigned to the $\sigma_g \to \sigma_u^*$ transition which has been described in detail for Br_3^- and I_3^-.[12] Preliminary salt reaction experiments were done with CsBr, Br_2, and CsI, I_2 and strong absorptions due to $Cs^+Br_3^-$ and $Cs^+I_3^-$ were observed at 268 and 273 nm, respectively,[27] which are in accord with the solution work.[12] The trend in $Cs^+X_3^-$ absorptions from 251 to 268 to 273 nm is also consistent with halogen spectra.[26] The strong 251 nm Cl_3^- band observed here is also supportive of the 230 nm aqueous solution assignments;[13,14] however, the absence of absorption near 320 nm following exposure to the W lamp indicates that most of the long wavelength absorption in the aqueous solution studies was due to unreacted Cl_2 in solution, which is, of course, in equilibrium with Cl_3^-.

Bonding

It is of interest to compare transitions for the halogen molecule and the dihalide molecular ion for the effect of the extra electron. Since the $\sigma \to \sigma^*$ transition for F_2 has not been determined, our comparison is limited to this transition energy for Cl_2 and Cl_2^-. For Cl_2, the upper states $^1\Sigma_u^+$ and $^3\Sigma_u^+$ with energies of 63,975 and 58,454 cm^{-1} correspond to the $\sigma \to \sigma^*$ transition[28] giving an average value of 61,215 cm^{-1} which compares with 29,400 cm^{-1} (340 nm average) for Cl_2^- in $M^+Cl_2^-$. This red shift is expected for the anion as extra electron-electron repulsions and the presence of an extra electron to be attracted by the nuclei lead to an increase in the valence electron-nuclear distances and a corresponding increase (algebraic) in the electronic energy of the system. A similar red shift from neutral to anion has been observed for C_2 (230 nm) and C_2^- in $M^+C_2^-$ (500 nm).[29]

Note also the trend in $\sigma \to \sigma^*$ transitions for $M^+F_2^-$ as a function of M^+, which is displayed in Fig. 5 for the four X_2^- species. The wavelength increases (energy decreases) Li^+ to Na^+ then decreases to K^+ and to Cs^+. This trend can be taken as a measure of the ionicity in the $M^+F_2^-$ species as a function of the M^+ ion polarizability. Ionic model calculations on $M^+O_2^-$ and Raman spectra of O_2^- in these species show that $Na^+O_2^-$ is the most ionic as measured by the lowest 0-0 vibrational frequency owing to the largest antibonding electron density.[30] As the polarizability of M^+ increases, the induced dipole moment on M^+ increases and withdraws some anion electron density and slightly shifts the spectrum back in the direction of the neutral molecule.

Notice, however, that, as for Raman spectra of O_2 and $M^+O_2^-$, the alkali metal effect on electronic spectra of Cl_2^- is small (Li to Na^+ is approximately 500 cm^{-1}) whereas the shift from Cl_2 to Cl_2^- is very large (approximately 32,000 cm^{-1}).

Lastly, notice the increasing red shift for the $Cs^+X_2^-$ species for Cl, Br and I from the curve in Fig. 5. This departure from the ionic model trend will be explained in the following paper[27] in terms of inner shell (5p) bonding with cesium.[31]

Matrix Reaction Chemistry

The present results reflect on the stability of the intermediate species formed. First, the $M^+F_2^-$ species all decomposed when exposed to the tungsten lamp even though the lamp output was very low in the F_2^- absorption band. By comparison the $Na^+F_2^-$ species was halved by a 22±2 min exposure whereas the $Na^+Cl_2^-$ band intensity was reduced to 70% by a like exposure; however, the lamp was eight-fold more intense in the $Na^+Cl_2^-$ absorption band. These observations indicate that the $M^+F_2^-$ species is considerably more photolytically unstable than the $M^+Cl_2^-$ compounds. It is suggested that photo-decomposition of the $M^+F_2^-$ and $M^+Cl_2^-$ species produces the final alkali halide products of reactions 1 and 2. Of the four $M^+F_2^-$ species studied, the Cs^+ compound was the most stable with a tungsten lamp exposure half-life of 50 min. Half-lives of the $M^+F_2^-$ and M^+Cl_2 band intensities are contrasted in Table II. As might be expected, the stability increases with increasing atomic weight of the alkali atom and the halogen for F_2 and Cl_2.

Second, the salt-halogen reaction $\underline{3}$ proceeds readily to give the $M^+Cl_3^-$ species, which is analogous to the solution reaction of chloride ion with chlorine. Reaction $\underline{3}$ requires little or no activation energy since sample warming to 42 K (Fig. 3(c)) to allow limited diffusion of trapped species produced marked growth of the $Cs^+Cl_3^-$ absorption.

Finally, if the secondary reaction of CsF with F_2 produced a $Cs^+F_3^-$ species, its absorption was not detected here due to coincidence with the strong $Cs^+F_2^-$ absorption, or appearance below the steeply rising sample background at 220 nm.

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Table I

Absorption Band Maxima (nm) for Products of Alkali Metal Atom
Matrix Reactions with Fluorine and Chlorine

	Li^+	Na^+	K^+	Cs^+
F_2^-	300±3	310±1	294±1	284±1
Cl_2^-	338.4±0.5	344.5±0.3	343.0±0.3	344.0±0.3
Cl_3^-	248±1	250.0±0.5	247.0±0.5	250.5±0.5

Table II

Half-lives (min) of the $M^+F_2^-$ and $M^+Cl_2^-$ Absorption Intensities
When Exposed to the Infrared Source Tungsten Lamp of the Cary 14

	Li^+	Na^+	Cs^+
F_2^-	2	20,24	50
Cl_2^-	11	38	77

FIGURE CAPTIONS

Fig. 1.   Ultraviolet spectra of the products of alkali metal atom matrix

reactions with fluorine in argon, $Ar/F_2 = 100/1$.   The spectra

displaced to the right were recorded following sample exposure

to the tungsten lamp for the given time.

Fig. 2.   Optical spectra of the products of Li, Na, K, and Cs atom matrix

reactions with chlorine in argon, $Ar/Cl_2 = 100/1$.

Fig. 3.   Optical spectra of the products of the matrix reaction of Cs and Cl_2.

(a) $Ar/Cl_2 = 400/1$ and (b) $Ar/Cl_2 = 300/1$ with less Cs, dashed trace

follows 10 min exposure to W lamp.   Trace (c) shows the effect of

sample warming to allow diffusion.   Spectrum (d) illustrates the

CsCl and Cl_2 matrix reaction products.

Fig. 4.   Schematic energy level diagram for the $M^+Cl_2^-$ species assuming C_{2v}

symmetry.

Fig. 5.   Wavelengths (nm) of the $\sigma \rightarrow \sigma^*$ transitions for the dihalide radical

anions displayed for the Li^+, Na^+, K^+, and Cs^+ counterions.

Figure 1

Figure 2

ABSORBANCE ⟶

0.50 O.D.

(a)

Cs + Cl₂

(b)

(c)

17-42-17°K

(d)

CsCl + Cl₂

WAVELENGTH (nm)
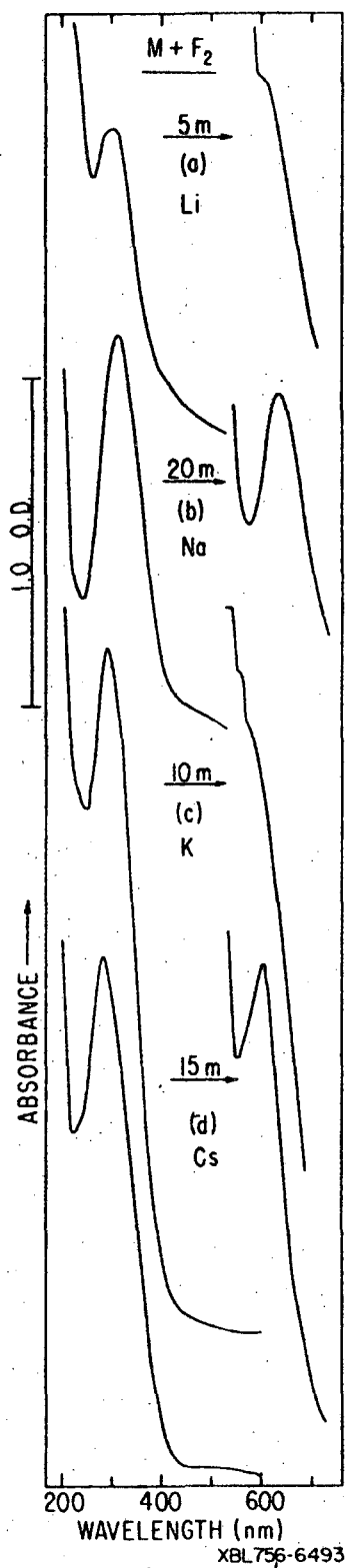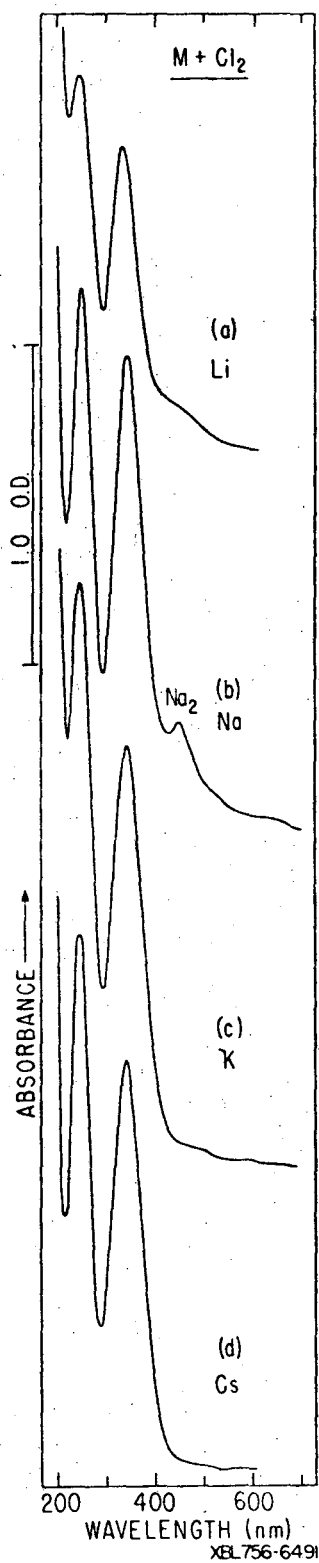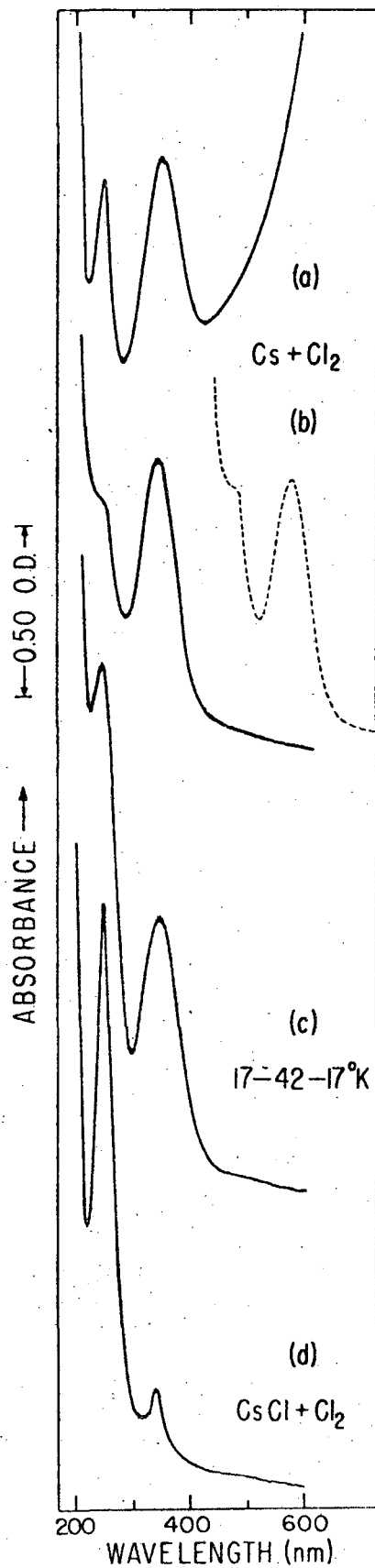
XBL 755-6303

Figure 3

XBL 756-6597

Figure 4

Figure 5

XBL756-6595