30 ml of acetone containing 220 mg of $[Rh(NBD)(PPhMe_2)_3]^+PF_6^-$ and 30 mg of 70% aqueous perchloric acid was stirred under H_2 until 95% of the theoretical amount of H_2 had been absorbed. The product mixture was distilled at 103° and 57 mm to give 7.4 g of *cis*-**5** containing only a trace of $C_6H_5C{\equiv}CCO_2C_2H_5$ and $C_6H_5CH_2CH_2CO_2C_2H_5$ and no *trans*-**5**. The attempted specific reduction with a Lindlar-type catalyst (5% Pd on $BaSO_4$) gave primarily $C_6H_5CH_2CH_2CO_2C_2H_5$.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research (J.A.O.). R.R.S. is indebted to the National Institutes of Health for a predoctoral fellowship.

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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.

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.[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 mmol/h onto the sapphire plate cooled to 10 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 mmol 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 h. 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 h (5 mmol total) and the absorption spectrum revealed no bands from 600 to 200 nm; the scattering background increased to 1.0 OD (optical density) 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 1 h, a very intense band appeared at 312 nm (1.0 OD). Exposure to the tungsten lamp reduced the band to 0.50 OD and the peak shifted to 292 nm. Another experiment was done codepositing sodium atoms with an $Ar/F_2 = 100/1$ sample. After 1 h, a 309-nm absorption (0.50 OD) was observed which became a strong 310-nm band (0.90 OD) after 2 h; this feature is illustrated in Figure 1. After 20 min of tungsten light, the band measured 303 nm (0.50 OD) which is also illustrated in Figure 1, and after 102 min, the absorption was reduced to 0.24 OD 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 3.5 h and a 300 ± 3 nm band (0.31 OD) resulted. Five minutes of W light reduced the band to 0.04 OD at 280 ± 5 nm and 5 more minutes destroyed it completely, as is shown by the spectrum in Figure 1a.

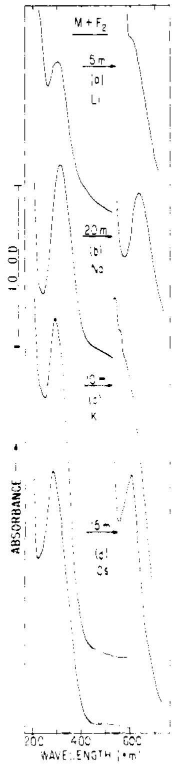

Figure 1. Ultraviolet spectra of the products of alkali metal atom matrix reactions with fluorine in argon. $Ar/F_2 = 100/1$. The spectra displaced to the right were recorded following sample exposure to the tungsten lamp for the given time.

Table I. Absorption Band Maxima (nm) for Products of Alkali Metal Atom Matrix Reactions with Fluorine and Chlorine[a]

	Li^+	Na^+	K^+	Rb^+	Cs^+
F_2^-	300 ± 3	310	294	288	284
Cl_2^-	338	345	343	343	344
Cl_3^-	248	250	247	248	251

[a] Wavelength accuracy is ±1 nm unless otherwise noted. Rubidium data recorded on a Cary 17 spectrophotometer at the University of Virginia and added in proof.

A 1% F_2 sample was treated with potassium atoms for 3.5 h which produced the strong (1.0 OD) 294 ± 1 nm band illustrated in Figure 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 2.5 h and a strong (0.85 OD) band appeared at 284 ± 1 nm. This band is shown in Figure 1 along with the result of 15 min of W lamp photolysis, a 269-nm band with 0.66 OD. A total of 25 min of W light reduced the band to 0.60 OD. 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 mmol of condensed gas produced a 0.4 OD 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 Figure 2 illustrates the spectrum. Two bands were observed, a 248 ± 1 nm band (0.42 OD) on the rising background and a strong band at 338 ± 1 nm (0.66 OD). Four minutes of W lamp operation reduced the 338-nm band to 0.52 OD and left the 248-nm absorption unchanged. These samples appeared clear with a faint yellow color in white light.

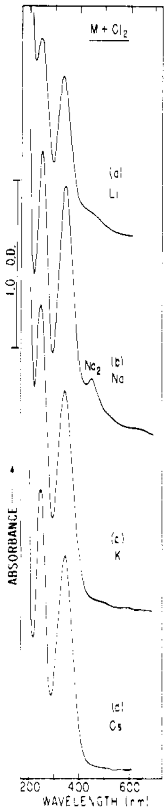

Figure 2. Optical spectra of the products of Li, Na, K, and Cs atom matrix reactions with chlorine in argon, Ar/Cl_2 = 100/1.

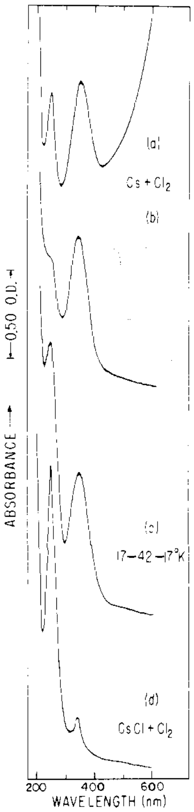

Figure 3. Optical spectra of the products of the matrix reaction of Cs and Cl_2. (a) Ar/Cl_2 = 400/1 and (b) Ar/Cl_2 = 300/1 with less Cs, dashed trace follows 10 min exposure to W lamp. Trace (c) shows the effect of sample warming to allow diffusion. Spectrum (d) illustrates the CsCl and Cl_2 matrix reaction products.

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 Figure 2 shows a very strong 250 ± 1 nm band (1.0 OD), a strong 344 ± 1 nm absorption (0.82 OD) and a weak band at 450 nm. Operation of the W lamp for 20 min destroyed the 450-nm feature, reduced the 344-nm band to 0.57 OD, and left the 250-nm absorption unchanged.

An experiment with potassium and chlorine produced spectrum c of Figure 2 which contained very intense bands at 343 ± 1 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 ± 1 and 250 ± 1 nm in the last trace of Figure 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 Figure 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 Figure 3a and Figure 2d shows that the cesium atom concentration in these experiments is greater than 0.25% but less than 1%. The next reaction, shown in Figure 3b 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 OD), the 344 ± 1 nm band appeared as a strong 0.58 OD absorption, and no other absorption was observed out to 800 nm after 4 h of sample deposition. The dashed trace in Figure 3b shows the effect of 10 min of W lamp irradiation: 344 nm was reduced to 0.53 OD 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 OD absorption while the 344-nm band was essentially unchanged (0.55 OD). 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 of Figure 3 shows a very strong 250 ± 1 nm absorption (1.0 OD) 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 OD.

Discussion

The present optical absorption data, coupled with analogous laser Raman studies, provide a basis for the characterization of several unstable chemical species and contribute 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.

$$M + F_2 \rightarrow M^+F_2^- \rightarrow MF + F \qquad (1)$$

Infrared studies of these 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[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 Figure 2d and Figure 3a,b indicate. At lower reagent concentrations the 250-nm band yield is reduced significantly, 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 2 is "first order" in each reagent. However, the $M^+Cl_3^-$ product of reaction 3 is "second order" in Cl_2 and "first order" 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 2.

$$M + Cl_2 \rightarrow M^+Cl_2^- \rightarrow MCl + Cl \tag{2}$$

$$MCl + Cl_2 \rightarrow M^+Cl_3^- \tag{3}$$

Accordingly, the concentration and sample warming data indicate that the 250-nm band is a secondary reaction product, eq 3, and the 340-nm absorption is due to the primary reaction (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 ± 1 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 wavelength 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 wavelength 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 wavelength side.

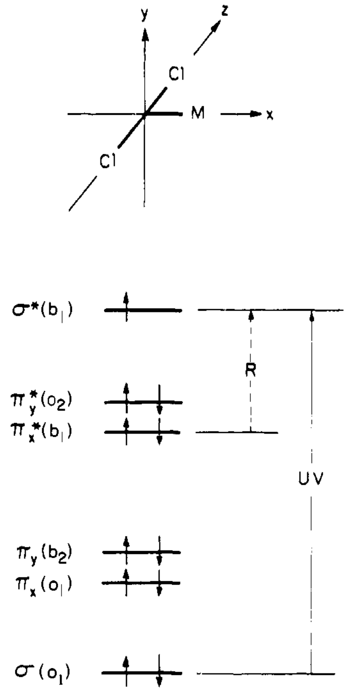

Figure 4. Schematic energy level diagram for the $M^+Cl_2^-$ species assuming C_{2v} symmetry.

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[25a] 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 absorption was parallel to the molecular axis. Hence, assignment of the near-ultraviolet absorption to the $\sigma \rightarrow \sigma^*$ 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 $\pi^* \rightarrow \sigma^*$ 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 $\sigma \rightarrow \sigma^*$ transition depicted in Figure 4. Unfortunately, the very much weaker $\pi^* \rightarrow \sigma^*$ red transitions for these species were not detected.[25b] It is well-known in trihalide ion systems that $\sigma_g \rightarrow \sigma_u^*$ transitions are much more intense than $\pi_g \rightarrow \sigma_u^*$ transitions.[12,26]

The strong 251-nm band observed for Cl_3^- in the $Cs^+Cl_3^-$ species is assigned to the $\sigma_g \rightarrow \sigma_u^*$ transition which has been described in detail for Br_3^- and I_3^-.[12] 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

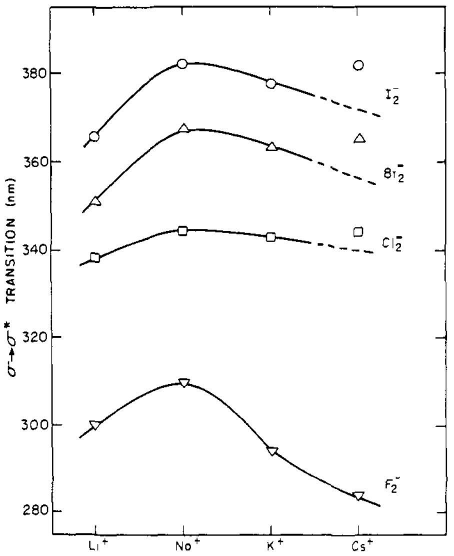

Figure 5. Wavelengths (nm) of the $\sigma \rightarrow \sigma^*$ transitions for the dihalide radical anions displayed for the Li^+, Na^+, K^+, and Cs^+ counterions. The dashed extensions are predicted by the ionic model of polarizable ion pairs.

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 $\sigma \rightarrow \sigma^*$ 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 $\sigma \rightarrow \sigma^*$ 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 $\sigma \rightarrow \sigma^*$ transitions for $M^+F_2^-$ as a function of M^+, which is displayed in Figure 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 O-O 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. The alkali metal effect on the Cl_2^- optical transition is small (Li^+ to Na^+ is approximately 500 cm^{-1}) whereas the shift from Cl_2 to $M^+Cl_2^-$ is very large (approximately 32 000 cm^{-1}). In like fashion, the Raman fundamental of O_2^- shows a small M^+ effect (1094 cm^{-1} for $Na^+O_2^-$ to 1115 cm^{-1} for $Cs^+O_2^-$) whereas the shift from O_2 to $M^+O_2^-$ is approximately 450 cm^{-1}.[30]

Lastly, notice the increasing deviation of the $Cs^+Cl_2^-$, $Cs^+Br_2^-$, and $Cs^+I_2^-$ transitions from the dashed curves in Figure 5. This departure from the ionic model trend will be rationalized in the following paper.[27]

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 eightfold 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 photodecomposition 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.

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

Second, the salt-halogen reaction (3) proceeds readily to give the $M^+Cl_3^-$ species, which is analogous to the solution reaction of chloride ion with chlorine. Reaction 3 requires little or no activation energy since sample warming to 42 K (Figure 3c) 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.

Acknowledgments. This work was supported by the U.S. Energy Research and Development Administration, the University of Virginia, and the Alfred P. Sloan Foundation. The loan of a Model 21 Cryodyne by Cryogenic Technology, Inc. and a Cary 14 spectrophotometer by Professor C. B. Harris, the donation of a fluorine sample by Professor Neil Bartlett, and the hospitality of Professor Leo Brewer are gratefully acknowledged.

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Optical Spectra of the Dibromide and Diiodide Ions in the Matrix-Isolated $M^+Br_2^-$ and $M^+I_2^-$ Species

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Received August 29, 1975

Abstract: The products of argon matrix reactions of alkali metal atoms and bromine and iodine have been studied optically in thin films on a sapphire window at 17 K. The bromine reaction produced a strong band near 360 and a weak band near 640 nm, depending upon the alkali reagent, and the reactions with iodine gave a strong absorption near 380 and a medium intensity absorption near 680 nm. These bands are due to $\sigma \rightarrow \sigma^*$ and $\pi^* \rightarrow \sigma^*$ transitions, respectively, of the dihalide anions in the $M^+X_2^-$ species. The small alkali metal effect on the transition energies is in accord with an ionic model of polarizable ion pairs, with the exception of cesium, which is capable of inner shell bonding and red-shifting the transitions from their expected positions. In addition, a very strong 227 nm absorption in bromine and a strong 254, 286 nm doublet in iodine experiments are attributed to molecular halogen aggregates.

The dibromide and diiodide radical anions were first proposed in 1933 as intermediates in photoreactions involving aqueous solutions of the halide, halogen, and oxalates.[2] Subsequent work of Taube in 1948 on the oxidation of bromide ion in aqueous solution provided mechanistic evidence for an intermediate complex between atomic bromine and bromide ion.[3] Radiolysis of the alkali halide salt[4a] or solutions[4b] and mercury arc photolysis of NaBr and NaI glasses containing oxidizers[5] at low temperatures have provided ESR spectroscopic evidence for the Br_2^- and I_2^- species.

Of particular interest to this work, flash photolysis of Br^- and I^- in aqueous solutions has produced transient absorptions near 350 and 370 nm, which have been attributed to the Br_2^- and I_2^- species, respectively.[6] Pulse radiolysis of aqueous KBr solutions yielded a strong transient absorption at 360 nm which disappeared in 100 μs and a new 270 nm absorption appeared which was stable for 2 min; these absorptions were assigned to Br_2^- and Br_3^-, respectively.[7] In similar studies of aqueous KI, a strong absorption was observed at 380 nm for I_2^-.[8] γ-Irradiation of $NaBr-H_2SO_4$ glasses at 77 K produced 355-nm absorption which was replaced by a 270-nm band upon warming to room temperature, and a like investigation using NaI gave strong I_3^- absorption and a weak new absorption at 380 nm.[9] After x-raying solid KBr at 77 K with impurity ions such as Tl^+ present, the optical spectrum revealed a strong absorption at 385 nm and a weak band at 750 nm which were assigned to the Br_2^- color center.[10] Analogous studies on KI produced a strong 400 nm absorption and a medium-intensity 800-nm band which were attributed to I_2^- and assigned to the ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ and ${}^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ transitions, respectively.[10,11] Flash photolysis studies of dilute KI in ethanol have shown that, in addition to the strong near-ultraviolet I_2^- absorption, there is residual 750-nm absorption which cannot be due to solvated electrons, and accordingly, the red absorption is also associated with I_2^-.[12]

Laser Raman studies of the products of alkali metal atom–iodine matrix reactions found a resonance Raman progression using 647.1-nm excitation with a strong 114-cm^{-1} fundamental and five overtones which was attributed to the diiodide anion in the $M^+I_2^-$ species.[13] The present optical experiments were done to observe the red absorption band which was responsible for the resonance Raman spectrum. Similar laser-excitation studies of the alkali metal-bromine reaction produced Raman fundamentals near 157 cm^{-1} which are believed to be due to Br_2^-.[14] Absorption spectra of these reaction products will help understand the chemistry and identify the product species.

In addition, gas-phase absorption spectra of bromine and iodine vapors[15-17] have shown temperature dependent bands which were assigned to $(Br_2)_2$ and $(I_2)_2$. The present matrix-isolation study observed these bands which supports the dimer assignments. Here follows an optical absorption study of alkali metal bromine and iodine matrix reaction products.

Experimental Section

The vacuum system, cryogenic apparatus, spectrophotometer, and experimental technique were the same as discussed in the previous paper.[18] Bromine (B.D.H. Chemicals, Ltd.) was frozen, outgassed, thawed, refrozen, and evacuated before use. Iodine (Mallinckrodt, reagent) crystals were placed in a Pyrex finger, evacuated, and allowed to reach equilibrium vapor pressure (0.25 mm at 23 °C), in a 2-l. Pyrex bulb; 100 Torr of argon was added giving an