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Lester Andrews

August 1975

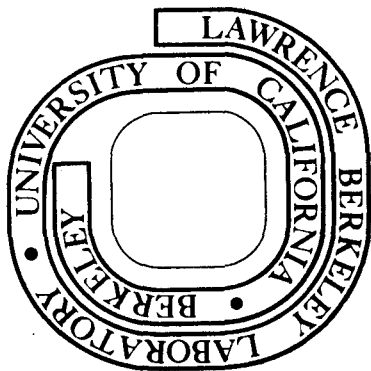
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OPTICAL SPECTRA OF THE DIBROMIDE AND DIIODIDE IONS IN THE
MATRIX-ISOLATED $M^+Br_2^-$ and $M^+I_2^-$ SPECIES

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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.

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INTRODUCTION

The dibromide and diiodide radical anions were first proposed in 1933 as intermediates in photo reactions involving aqueous solutions of the halide, halogen, and oxalates.¹ 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.² Radiolysis of the alkali halide salt³ or solutions⁴ and mercury arc photolysis of NaBr and NaI glasses containing oxidizers⁵ at low temperatures have provided E.S.R. 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 μsec 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 Gamma 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 vapors¹⁵⁻¹⁷ have shown temperature dependent bands which were assigned to $(Br_2)_2$ and $(I_2)_2$. The present matrix-isolation study observed these bands and confirmed 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 approximate Ar/ I_2 ratio of 400/1. Argon-bromine samples were prepared using standard techniques. In addition to alkali metal matrix reactions, cesium bromide

(Orion Chemical Co., Reagent) vapor at 440°C was codeposited with an argon-bromine sample and cesium iodide (Harshaw Chemical Co., Optical) vapor at 438°C was also reacted with iodine in argon matrices. The salts were heated under vacuum above these temperatures before use.

RESULTS

Alkali metal atom matrix reactions with bromine and iodine have produced new absorptions which will be presented for each halogen.

Bromine

Two optical spectra of an argon-bromine sample ($\text{Ar}/\text{Br}_2 = 200/1$) are shown at the top of Fig. 1. A very strong, sharp absorption was observed at 227 ± 1 nm along with the strong bromine absorption at 415 nm with a 480 nm shoulder, the latter in excellent agreement with the gas phase spectrum.¹⁵ The bottom spectrum for an $\text{Ar}/\text{Br}_2 = 600/1$ sample shows that the 227 nm band is concentration-dependent. The 227/415 band intensity ratio of 5/1 in the 200/1 sample is reduced to 1/1 at 600/1.

Lithium atoms were deposited with an argon-bromine sample for 2.5 hrs and the resulting spectrum is shown in Fig. 2(a). The dominant new feature in the spectrum appeared at 351 ± 1 nm (1.2 O.D. = optical density) with a 420 nm shoulder due to unreacted bromine. Additional new bands were observed at 262 ± 1 nm (0.4 O.D.) and 635 ± 1 nm (0.08 O.D.). A 5 min operation of the Cary 14 tungsten lamp to photolyse the sample reduce the 351 nm band to 0.8 O.D. and the 635 nm absorption to 0.05 O.D.

Sodium experiments were done with several bromine samples. The spectrum from the best $\text{Ar}/\text{Br}_2 = 200/1$ experiment contained a very strong new band at 367.5 ± 0.5 nm (1.4 O.D.) and weaker absorptions at 450 (0.15 O.D.), 635 (0.10 O.D.), and 264 (0.20 O.D.). After exposing the sample to the tungsten lamp for 10 min

the spectrum shown in Fig. 2(b) revealed a reduction in the 367 nm band, 635 nm was replaced by a weaker 665 nm band (0.06), 264 nm was unchanged and 450 nm was destroyed. The 635 nm band was due to aggregated sodium, as revealed by a number of experiments with excess sodium, and the sharp 450 nm band is attributed to Na_2 owing to its proximity to the gas-phase bands.¹⁹

The third trace in Fig. 2 shows the potassium-bromine reaction where no interference is present from metal absorptions. A very strong band appeared at 363.3 ± 0.5 nm (1.2 O.D.) and a weak band was found at 660 ± 1 nm (0.07 O.D.). A 10 min W lamp exposure reduced both bands to half of their initial intensities.

The absorption spectrum of cesium-bromine reaction products is illustrated in Fig. 2(d). The very strong band at 365.1 ± 0.5 nm (1.1 O.D.) the weak 660 ± 1 nm feature (0.05 O.D.) were reduced by 20% upon a 10 min exposure to the W lamp. The absorption peaks for the products of alkali metal-bromine reactions are listed in Table I.

Finally, cesium bromide vapor was desposited with an $\text{Ar}/\text{Br}_2 = 200/1$ sample for 3 hr. A very strong new absorption was observed at 268 nm.

Iodine

Several blank experiments were run with argon iodine samples and spectra were recorded between 750 and 200 nm. The first trace in Fig. 3 shows the spectrum of an $\text{Ar}/\text{I}_2 \approx 400/1$ sample. In addition to the dominant iodine band at 520 nm, a strong doublet appeared at 254 and 286 ± 2 nm and a weak feature was observed at 670 nm. When the iodine concentration was reduced to $\text{Ar}/\text{I}_2 \approx 800/1$, the intensity of the ultraviolet doublet was markedly reduced relative to the visible iodine band as Fig. 3(b) illustrates. Further sample dilution to $\text{Ar}/\text{I}_2 \approx 2000/1$ reduced the ultraviolet absorptions

to weak shoulders while the visible band remained prominent in Fig. 3(c). Finally, warming this sample to 40 K to allow limited diffusion of the trapped iodine and recooling to 17 K produced marked growth of the ultra-violet bands at 254 and 286 nm as the last spectrum in Fig. 3 shows.

Lithium atoms were codeposited with an $\text{Ar}/\text{I}_2 \approx 400/1$ sample for 2 hrs; the absorption spectrum is shown in Fig. 4(a). A very strong new band was observed at 365.8 ± 0.3 nm (1.5 O.D.) along with a strong band at 675.3 ± 0.3 nm (0.45 O.D.). These bands grew with a 3/1 relative intensity during reagent deposition and decreased with the same relative intensity following 10, 30, and 50 min exposures to the tungsten lamp.

Three sodium-iodine reactions were examined spectroscopically; an early scan in the first experiment using $\text{Ar}/\text{I}_2 \approx 400/1$ is shown in Fig. 4(b). New product bands appeared at 382.0 ± 0.3 and 695 ± 2 nm along with the iodine precursor absorption at 522 nm and the Na_2 shoulder at 450 nm. Another experiment using excess iodine ($\text{Ar}/\text{I}_2 \approx 250/1$) produced the red band at 693 ± 2 nm (0.28 O.D.) and the violet band at 382 ± 1 nm (0.73 O.D.); exposure to the tungsten lamp for 20 min halved these absorptions. The final experiment using insufficient iodine ($\text{Ar}/\text{I}_2 \approx 800/1$) produced the product bands at 385 and 695 nm (0.45 and 0.15 O.D., respectively) along with a strong Na_2 absorption at 450 nm.

Potassium atoms were reacted with an $\text{Ar}/\text{I}_2 \approx 400/1$ sample. Figure 4(c) shows the new product bands at 377.3 ± 0.3 nm and 685.8 ± 0.5 nm (0.91 and 0.28 O.D., respectively). In order to establish a relationship between the two product bands, successive spectra from this experiment are shown in Fig. 5. The first scan (a) after 26 min of K atom deposition with I_2 sample, shows the red band (0.08 O.D.) and the violet band (0.28 O.D.) appearing in the spectrum.

Scan (b) recorded after 49 min of reaction shows 0.23 and 0.74 O.D. bands and scan (c) taken after a 120 min period illustrates the final bands with 0.40 and 1.3 O.D. The last trace in Fig. 5 shows the effect of 10 min of exposure to the W lamp. The bands were reduced markedly and shifted slightly to 375 nm (0.44 O.D.) and 690 nm (0.15 O.D.). Ten more min of tungsten photolysis reduced the absorptions a little more to 0.38 and 0.12 O.D., respectively.

The experiment with cesium employed a slightly higher iodine concentration ($\text{Ar}/\text{I}_2 \approx 320/1$) to minimize the possibility of excess cesium. After 138 min of reaction, new product bands were observed at 686.0 ± 0.5 and 381.7 ± 0.3 nm with 0.20 and 0.64 O.D., respectively, which is shown in Fig. 4(d). A 17 min exposure to W light reduced these bands only 20% to 0.16 and 0.50 O.D., respectively.

The final reactions were done with CsI and I_2 using dilute samples to minimize the ultraviolet iodine doublet. In the first experiment using $\text{Ar}/\text{I}_2 \approx 800/1$, a new band appeared at 366 nm (0.35 O.D.) when the CsI sample was warm ($370\text{--}380^\circ\text{C}$) but before the sliding door to the Knudsen cell was opened. After opening the door and depositing CsI for 2 hrs, the 366 nm band continued to grow (0.87 O.D.) and a strong absorption appeared at 273 nm (0.86 O.D.). The tungsten lamp (5 min) reduced the 366 nm band to 0.47 O.D. while the 273 nm absorption was reduced to 0.70 O.D. Sample warming to 37 K and recooling increased the 273 nm band to 1.0 O.D. while the 366 nm band was unchanged. The sample was faint pink in color, as caused by unreacted I_2 in the sample. Warming the sample to 50 K changed it to mustard yellow. The CsI sample was outgassed under vacuum for 4 hrs

at 380°C and another experiment was run using an Ar/I₂ ≈ 2000/1 sample. Again, the 366 nm band appeared after the CsI was hot, but before the shutter was opened, and the strong 273 nm band was observed to grow as before.

DISCUSSION

The present observations provide information on bromine and iodine dimers, the dibromide and diiodide radical anions and bonding interactions between cation and anion in ionic molecules.

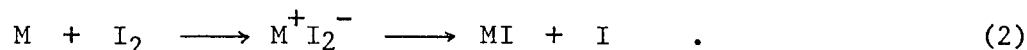
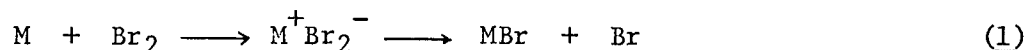
Bromine and Iodine Dimers

Figure 1 shows a strong absorption at 227 nm whose intensity relative to the bromine absorption at 415 nm, is favored at the higher bromine concentration. From the matrix data, this band can be assigned to (Br₂)₂. This observation adds support to the assignment of a broad, temperature dependent 210 nm band to (Br₂)₂ in the gas phase.¹⁵

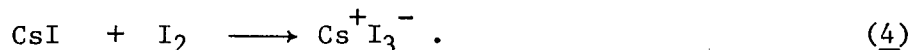
In the iodine spectrum the very weak 670 nm band is due to the X→A absorption of I₂ which has been observed very weakly at approximately 660-690 nm in the gas phase.²⁰ The I₂ absorption at 270 nm in the gas phase is so very weak that it must be obscured by the ultraviolet doublet. The concentration dependence and growth of the ultraviolet doublet shown in Fig. 3 indicate that both of these bands are due to iodine dimeric species presumably of different structural arrangements. Lastly, the broad temperature dependent band at 245 or 265 nm assigned by two groups^{16,17} to (I₂)₂ is in agreement with the 254 and 286 nm argon matrix assignments to iodine dimeric species.

Dibromide and Diiodide Anions

The strong ultraviolet absorptions near 360 and 380 nm depending upon the alkali reagent can be assigned to Br_2^- and I_2^- , respectively, in the M^+Br_2^- and M^+I_2^- species for the following reasons: (a) the bands follow the pattern established in the previous paper for M^+F_2^- and M^+Cl_2^- , (b) the absorptions agree with the pulse radiolysis and flash-photolysis assignments to the transient Br_2^- and I_2^- species in aqueous solution,^{6,7,8} and (c) the strong bands are due to primary reaction products of 1 and 2 since alkali atoms were required for their formation and the bands were not produced with the CsBr and CsI reagents.



The secondary reactions were studied for the CsBr and CsI salts, reactions 3 and 4



The strong bands produced in these experiments at 268 and 273 nm are due, respectively, to the products of reactions 3 and 4. The bands at 262 and 264 nm in Fig. 2 (a and b) are, respectively, due to Li^+Br_3^- and Na^+Br_3^- .

Ultraviolet absorptions due to alkali bromides and iodides are very weak,²¹ and the quantities of these salts produced and studied here do not make an appreciable contribution to the absorption spectrum.

The red absorptions near 640 nm in four different alkali metal bromine reactions maintain a constant relative intensity with the strong 360 nm absorptions; the intensity ratios 360 nm/640 nm were $(18 \pm 3)/1$ for the four

reactions studied. The bands are both photobleached by W light at the same rate. Likewise the red bands near 680 nm in four alkali-iodine studies maintain a constant intensity ratio within 10% with the strong 380 nm absorptions; the intensity ratios 380 nm/680 nm were 3/1 for the four alkali metal species. The two alkali-iodine product bands were destroyed at the same rate by the W lamp. These data indicate that the red and violet bands in each halogen reaction are due to the same species. In fact the W photolysis data links the red and violet $M^+I_2^-$ bands since an order of magnitude more W lamp out-put is available in the red as compared to the violet, more of the $M^+I_2^-$ photolysis is affected by absorption in the red band, but since the red and violet bands belong to the same molecular species, they decrease at the same rate.

In the X-ray studies of solid KBr and KI, near-infrared bands at 750 and 800 nm have been assigned to Br_2^- and I_2^- , respectively.^{10,11} These latter bands must correspond to the red 640 and 680 nm absorptions of the matrix-isolated $M^+Br_2^-$ and $M^+I_2^-$ species.

The smaller band just below 300 nm common to Cl_2^- , Br_2^- , and I_2^- in the flash photolysis studies⁶ was not observed in this work. These weak absorptions are not likely caused by the dihalide anions; however, OH radical absorbs weakly just below 300 nm,⁸ and this species could be responsible for the weak ultraviolet bands observed in the flash photolysis work.

Band Assignments

The strong ultraviolet bands at 360 and 380 nm for Br_2^- and I_2^- continue in the series of 300 and 340 nm established by F_2^- and Cl_2^- . Accordingly, these absorptions are assigned to the $\sigma \rightarrow \sigma^*$ valence electron transition in each dihalide anion in the corresponding $M^+X_2^-$ species.

The red bands are assigned to one of the $\pi^* \rightarrow \sigma^*$ transitions. As the schematic energy level diagram in Fig. 4 of the previous paper indicates, the presence of an intimately bonded M^+ removes the degeneracy of the π and π^* orbitals with presumably the lower energy π orbital in the MX_2 plane. The 640 and 680 nm absorptions for Br_2^- and I_2^- probably arise from the $\pi_x^* \rightarrow \sigma^*$ transition. First, the $\sigma \rightarrow \sigma^*$ energy for $Na^+I_2^-$ is 75 kcal/mole and the red absorption requires 42 kcal/mole which appears to be too much energy for promotion of an electron from the uppermost π^* orbital. Second, the π_x^* orbital is of the proper symmetry to interact with the 5p orbitals of the cesium atom which produces an inflection in the trend of X_2^- transition energies as a function of M^+ which will be discussed in the next section.

The intensity of the $\pi^* \rightarrow \sigma^*$ transition increases relative to the strong $\sigma \rightarrow \sigma^*$ transition intensity with increasing atomic weight in the matrix-isolated $M^+X_2^-$ species, as was found for the X_2^- color centers.¹⁰ This trend may be due to a mixing of the $^2\Sigma_g^+$ and $^2\Pi_g$ electronic states due to increased spin-orbit coupling. A similar trend has been noted for the $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions of Br_3^- and I_3^- in solution.²²

Bonding

As was pointed out in the previous paper,¹⁸ the $\sigma \rightarrow \sigma^*$ energy for Cl_2^- is about half that for Cl_2 . Likewise, these energies for Br_2^- and I_2^- are approximately 28,000 and 26,300 cm^{-1} , respectively, and 54,200 and 49,800 cm^{-1} for Br_2 and I_2 .²³ Again, the anion electron raises the energies of the valence orbitals as compared to the neutral halogen molecule. The same effect is noted for the $\pi^* \rightarrow \sigma^*$ transition on Br_2 (415 nm) as compared to Br_2^- (640 nm) and I_2 (520 nm) as compared to I_2^- (680 nm).

The effect of M^+ on the X_2^- transition energies is also of interest. Figure 5 of the previous paper displays the trend of $\sigma \rightarrow \sigma^*$ wavelength increasing (energy decreasing) Li^+ to Na^+ then decreasing to K^+ and on to Cs^+ for the $M^+F_2^-$ species. This trend is consistent with the ionic model of polarizable ion pairs²⁴ with the maximum ionic character and lowest $\sigma \rightarrow \sigma^*$ energy for $Na^+F_2^-$. The trend holds for Cl_2^- , Br_2^- , and I_2^- with the exception of Cs^+ whose effect becomes more pronounced with increasing halogen size. The somewhat anomalous effect of Cs^+ can be explained by inner shell bonding of the 5p orbitals of cesium with the halogen valence orbitals.²⁵ The (n-1)p orbitals of cesium are enough higher in energy to interact slightly with the valence X_2^- orbitals and this interaction is stronger with the larger halogen. The interaction forces the $\sigma(a_1)$ orbital to higher energy more than the $\sigma^*(b_1)$ orbital causing a red shift in the $\sigma \rightarrow \sigma^*$ transition energy. The same effect is noted for the $\pi_x^*(b_1)$ orbital which is also forced higher in energy more than $\sigma^*(b_1)$ giving again a red shift from the trend in $\pi^* \rightarrow \sigma^*$ energies expected from the ionic model. The $\pi_y^*(a_2)$ orbital is not of the proper symmetry to interact with the cesium 5p orbitals and its energy would not be affected by inner shell bonding in C_{2v} symmetry. The observation of the cesium inflection in the trend of $\pi^* \rightarrow \sigma^*$ energies supports a C_{2v} geometry for $M^+X_2^-$ and the $\pi_x^*(b_1) \rightarrow \sigma^*$ assignment of the red band for Br_2^- and I_2^- .

Finally, there is a red shift for each Br_2^- and I_2^- transition, and the Cl_2^- and F_2^- transitions,¹⁸ on going from the argon matrix-isolated $M^+X_2^-$ species to the X_2^- color center in the solid alkali halide lattice.¹⁰ The largest difference was found for the $\sigma \rightarrow \sigma^*$ transition of F_2^- . These differences

in dihalide radical anion spectra must be attributed to the different types and symmetries of the immediate X_2^- ion environments in the two cases. It may also be possible that charge transfer to the halogen molecule in the $M^+X_2^-$ species is not quite as complete as for the X_2^- color center, owing to the induced dipole moment on the intimately involved M^+ ion in the $M^+X_2^-$ species.

Matrix Reaction Chemistry

Although the tungsten lamp photolysis data is not as quantitatively accurate for $M^+Br_2^-$ and $M^+I_2^-$ as compared to the lighter species due to overlapping Br_2 absorption and a steeply rising background, a general statement can be made. The two heavier $M^+X_2^-$ species photodecompose more readily than $M^+Cl_2^-$; however, they are clearly more stable than $M^+F_2^-$. Again, the Cs^+ compounds appear to be the most stable.

It is of considerable interest that the $M^+X_2^-$ intermediates are trapped in the matrix reaction experiments. In earlier crossed-molecular beam work, evidence has been presented for an electron transfer mechanism forming $M^+ \cdots X_2^-$, which decomposed readily to give the final products of reactions 1 and 2. The role of the X_2^- ion in these reactions has been described by Herschbach.²⁶

Finally, the salt-molecule reactions 3 and 4 proceed readily under the conditions of these experiments. In fact these products increase on sample warming which indicates that reactions 3 and 4 have very little activation energy. This is in accord with the observation of a collision-complex in the crossed-molecular beam reaction of CsI and Cl_2 which persisted for many vibrational periods and then decomposed to give $CsCl$ and ICl .²⁷

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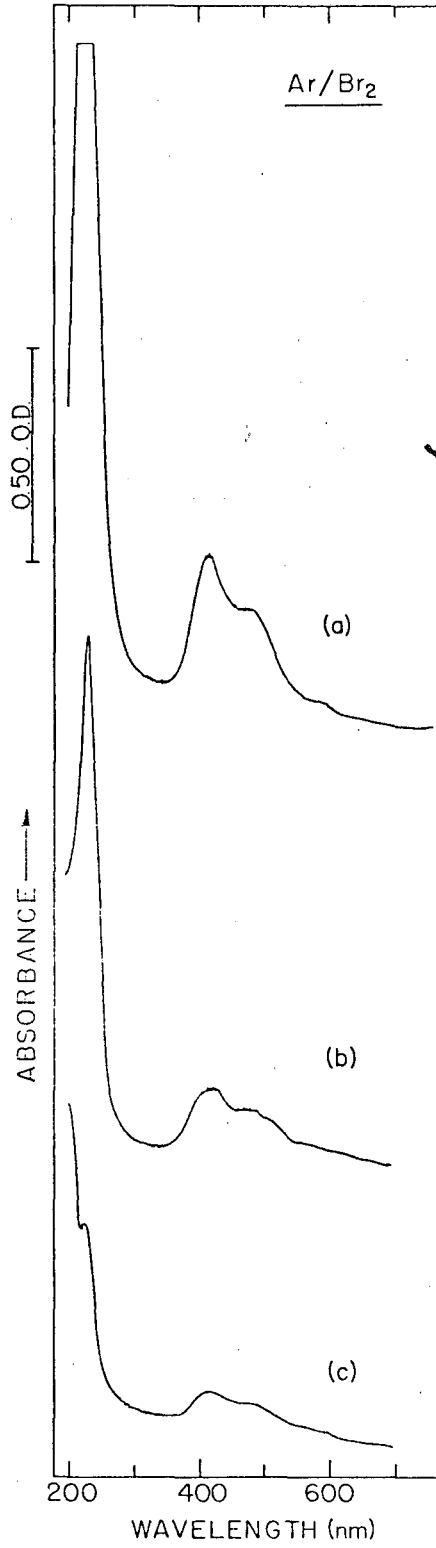
Table I

Absorption band maxima (nm) for the $M^+Br_2^-$ and $M^+I_2^-$ species

	<u>Li⁺</u>	<u>Na⁺</u>	<u>K⁺</u>	<u>Cs⁺</u>
Br ₂ ⁻	351±1	367.5±0.5	363.3±0.5	365.1±0.5
	635±1	665±1	660±1	660±1
I ₂ ⁻	365.8±0.3	382.0±0.3	377.3±0.3	381.7±0.2
	675.3±0.3	695±2	685.8±0.3	686.0±0.3

FIGURE CAPTIONS

- Fig. 1. Visible and ultraviolet spectra of bromine in solid argon at 17 K.
(a) Ar/Br₂ = 200/1, later scan, and (b) earlier scan. (c) Ar/Br₂ = 600/1.
- Fig. 2. Optical spectra in the 300-700 nm region for the products of alkali metal atom matrix reactions with bromine, Ar/Br₂ = 200/1.
(a) Li, (b) Na, (c) K, and (d) Cs.
- Fig. 3. Visible and ultraviolet spectra of iodine in solid argon at 17 K.
(a) Ar/I₂ ≈ 400/1, (b) Ar/I₂ ≈ 800/1, (c) Ar/I₂ ≈ 2000/1, and
(d) after warming the Ar/I₂ ≈ 2000/1 sample to 40 K and recooling to 17 K.
- Fig. 4. Optical spectra in the 300-800 nm region for the alkali metal atom-iodine matrix reaction product, Ar/I₂ ≈ 400/1.
(a) Li, (b) Na, (c) K, and (d) Cs.
- Fig. 5. Optical spectra for the K + I₂ matrix reaction at successive stages in the codeposition period. (a) 26 min, (b) 49 min, (c) 120 min, final, and (d) after 10 min exposure to tungsten lamp.



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Figure 1

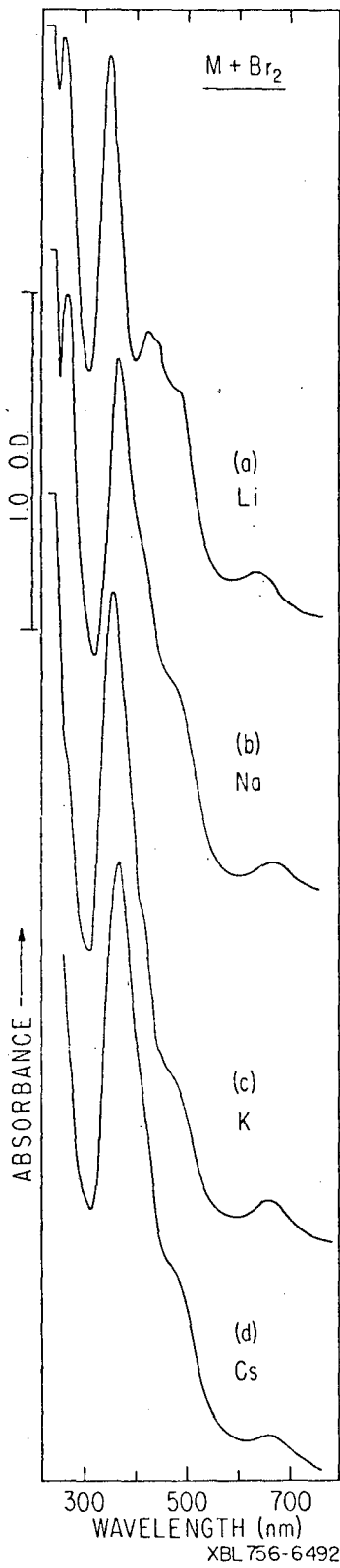
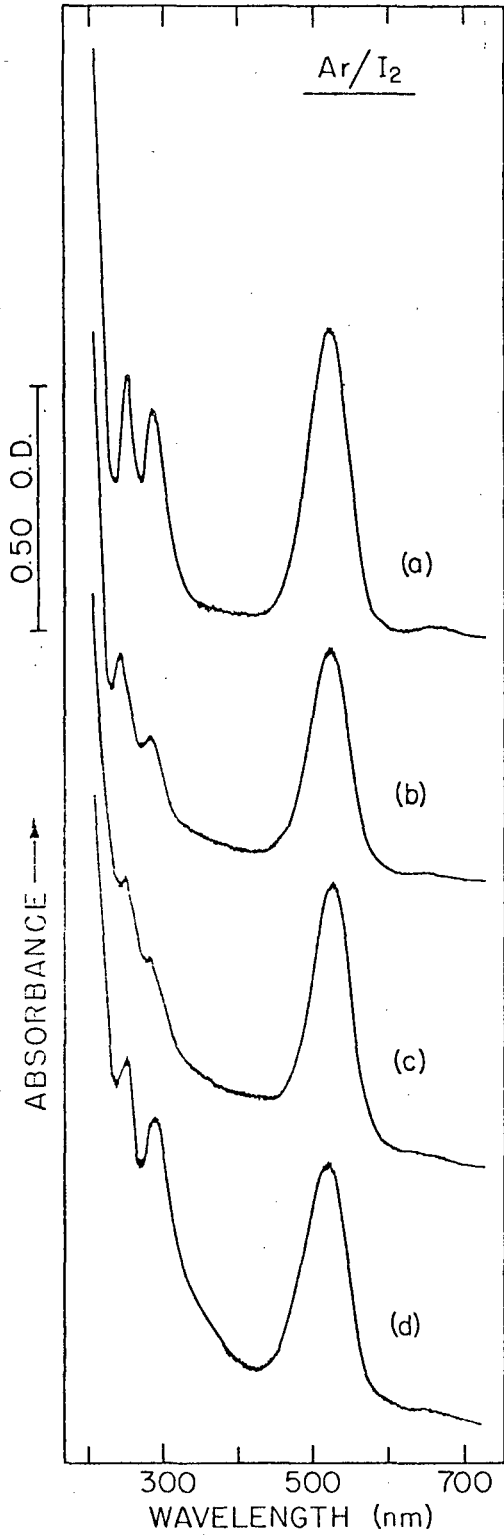
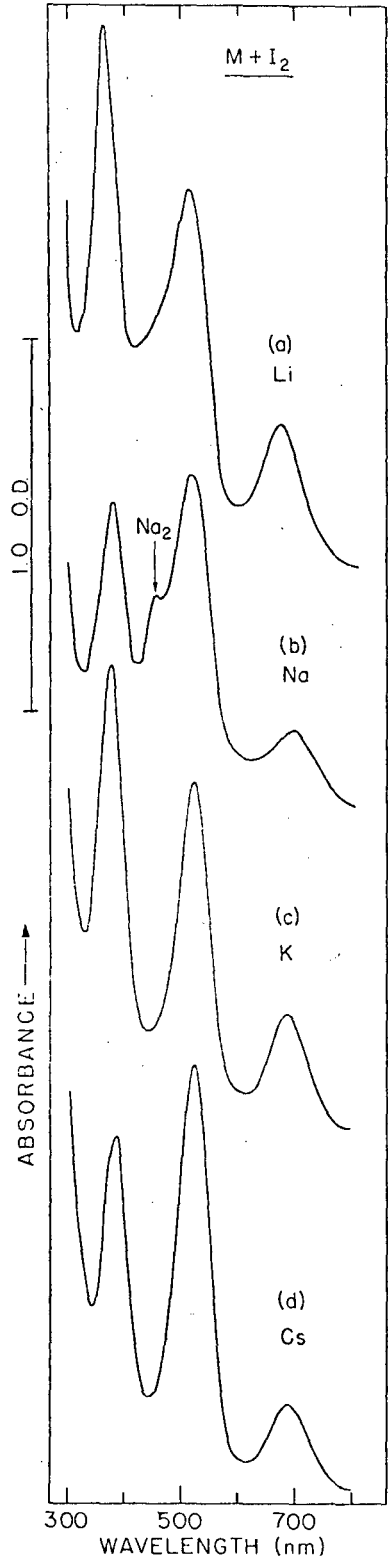


Figure 2



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Figure 3



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Figure 4

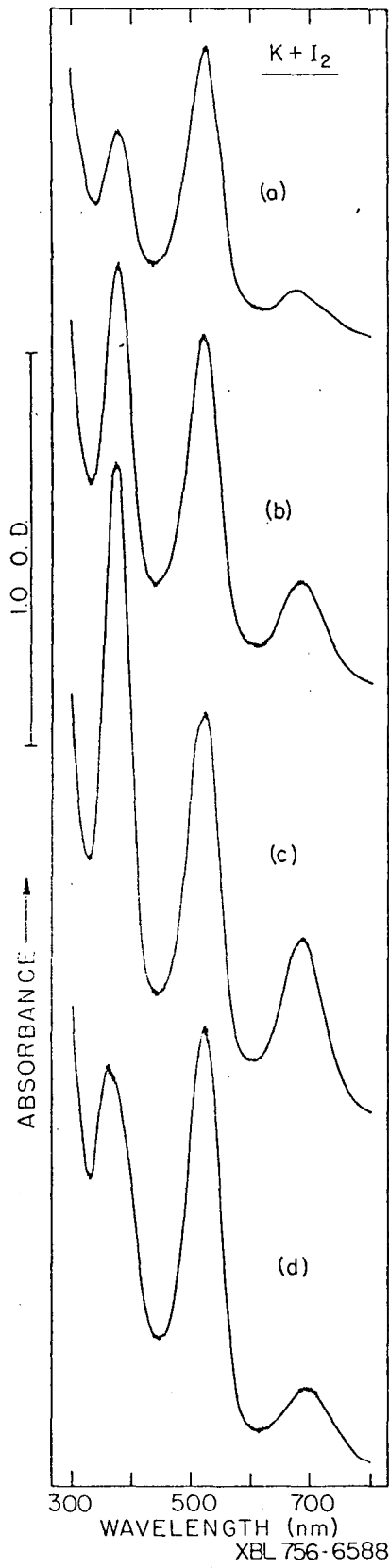


Figure 5

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