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Matrix Reactions of Fluorine with Chlorine, Bromine, and Iodine. Infrared Detection of the XF_2, X_2F_2, and X_2F Species

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Infrared and laser-Raman matrix isolation studies have been done on the $X_2 + F_2$ systems, where X = Cl, Br, or I. Mercury arc photolysis produced the new species XF_2, X_2F, and X_2F_2, as well as some of the normally unfavored members of the series XF_n (n = 1, 3, 5). The symmetric, T-shaped XXF_2 species is the dominant product in all three infrared studies. Other species were identified based on photolysis, concentration, and temperature cycling behavior of new infrared absorptions.

Introduction

The usual reaction between molecular fluorine and another halogen molecule X_2 follows the stoichiometry shown in reaction 1, where products with $n = 1$ or 3 are favored with Cl_2,

$$X_2 + nF_2 \rightarrow 2XF_n \tag{1}$$

$n = 3$ or 5 with Br_2, and $n = 5$ with I_2. Matrix isolation is a method by which intermediates in this reaction may be trapped for spectroscopic observation. Also, photolysis induced reaction products from X_2, F_2, and XF_n may be observed in a matrix. Of particular interest are unfavored XF_n species, as well as the new species XF_2, X_2F, and X_2F_2.

Mamantov and co-workers[2] have studied the ClF_2 species, produced by photolysis of isolated ClF_3 or of codeposited ClF + F_2. Recently, Prochaska and Andrews,[3] reexamined the ClF_2 radical, for which the most favorable synthetic route was photolysis of ClF and F_2 in a nitrogen matrix. Mamantov and co-workers[4] have also reported spectra of chlorine–fluorine mixed species produced by photolysis of isolated chlorine and fluorine and have proposed assignments to vibrations of Cl_2F_2, Cl_2F_3, and Cl_2F. The migration of photolytically produced fluorine atoms in matrices was established as a crucial step in the formation of these new mixed halogen species.

This paper reports a study of the reaction of fluorine with each of the molecular halogens, chlorine, bromine, and iodine, upon photolysis in solid matrices. Some experiments using BrF_3 as precursor are also reported, as well as some using equilibrium mixtures of Br_2, F_2, BrF, and BrF_3.

Experimental Section

The closed cycle refrigerators and vacuum systems for infrared[5a] and Raman[5b] experiments at Virginia have been described previously. The stainless steel vacuum apparatus was thoroughly passivated with fluorine prior to sample preparation. Infrared samples were deposited on a CsI cold window, and spectra were recorded on a Beckman IR-12 spectrophotometer from 200 to 800 cm^{-1}. Photolysis was done using a General Electric BH-6 high-pressure mercury arc, focused by a quartz lens system mounted on a 10-cm water filter cell (220–1000 nm) plus a Pyrex plate (290–1000 nm). Raman samples were deposited on an OFHC tilted block, and laser-Raman spectra were recorded on a Spex Ramalog instrument (500 μ slits), using the 488.0- and 514.5-nm lines of a Coherent Radiation Model 52 argon ion laser. Laser lines were used with a dielectric spike filter for recording spectra and were unfiltered for photolysis of Raman samples.

Chlorine (Matheson) samples were purified by freeze–pump–thaw cycles at liquid nitrogen temperature. $^{37}Cl_2$ was prepared by oxidizing $Rb^{37}Cl$ in concentrated HNO_3 and purified by condensing with Drierite. Bromine (Mallinckrodt) vapor over liquid was purified by freeze–pump–thaw cycles in a glass finger at liquid nitrogen temperature. Iodine (Mallinckrodt) crystals were outgassed by pumping while being held at liquid nitrogen temperature in the finger of a glass bulb. Iodine samples were prepared by putting the appropriate amount of argon over the solid in the bulb at room temperature (vapor pressure = 0.25 Torr). Fluorine (Matheson) was expanded through a "U" tube immersed in liquid N_2 before sample preparation to remove condensable impurities. Argon (Air Products, 99.998%) was used directly as the matrix gas.

Because of the variation in reactivity between fluorine and the three heavy halogens, different methods of sample deposition were used. Some samples were prepared with both halogens premixed in the same sample can. This was satisfactory for $Cl_2 + F_2$ samples, as only a moderate amount of ClF was formed by gas-phase reaction. However, for bromine and fluorine samples, an equilibrium mixture of BrF, BrF_3, and BrF_5 with the halogens was actually deposited from a single can and with iodine and fluorine a thorough conversion to IF_5 occurred with premixing. This type of experiment will later be referred to as a "premixed" experiment. To avoid prior reaction, bromine or iodine samples were prepared in separate cans from the fluorine, and the halogen and fluorine were mixed in the sample deposition line, about 10 cm above the cold window. These experiments will later be referred to as "separate can" experiments. In addition, some samples were prepared in completely separate vacuum manifolds and deposited through separate tubes. These will later be referred to as "separate manifold" experiments.

Matrix-isolation experiments at Tennessee utilized a Cryodyne Model 350 closed cycle helium refrigerator and experimental techniques previously described.[2,4] Temperatures were monitored and controlled to within ±1 K utilizing a Cryogenic Technology Inc. digital electronic temperature controller in conjunction with a gold–chromel thermocouple and resistance heater. Matrix mixtures were prepared in a stainless steel vacuum line well-passivated with chlorine trifluoride (Matheson, 98.0%). Research grade argon (Matheson, 99.9995%) was utilized as the matrix gas. Purified fluorine (99.99%, obtained from W. N. Hubbard, Argonne National Laboratory) was used without further purification. Reagent grade bromine (Fisher) was purified by passing the vapors over the liquid through a tube containing molecular sieve utilizing vacuum transfer techniques. Bromine trifluoride (Matheson, 98.0%) was purified by transfer from a lecture bottle under vacuum by pumping into a trap held at ~−20 °C. Matrix samples were photolyzed by BH-6 mercury arc, with an 11-cm water-filled quartz cell (220–1000 nm), with the addition of a Corning CS-7-54 glass filter (280–420 nm) for more limited photolysis. Microwave discharge experiments at Tennessee used a Raytheon Microtherm Model CMD-10 microwave generator to supply a maximum of 125 W at 2450 MHz. The microwave energy was directed through an Evenson type cavity to generate discharge in a 0.5-in. o.d. Lucalox tube using a gas flow rate of about 1.0 cm^3/min. Infrared spectra were recorded under low resolution on a Perkin-Elmer Model 337 infrared spectrophotometer and at high resolution using a Digilab Model FTS-20 Fourier transform infrared spectrometer.

Results

Infrared. $Cl_2 + F_2$. All experiments with chlorine and fluorine were done with premixed samples, and ClF was the major gas-phase reaction product observed in the spectrum of the condensed samples. In the first experiment, an $Ar/F_2/Cl_2 = 100/1/1$ sample was deposited for 22 h and photolyzed for 10 min with 220–1000 nm light; a very strong band system appeared at 636 cm^{-1} (completely absorbing), a sharp doublet was observed at 559.0, 551.0 cm^{-1} (absorbance = A = 0.29 and 0.09), a partially resolved triplet was found at 464, 462, 459 cm^{-1} (A = 0.10, 0.07, 0.01), and a new band appeared at 270 cm^{-1} (A = 0.06). Additional photolysis for 25 min reduced these bands to approximately half of their first observed intensities.

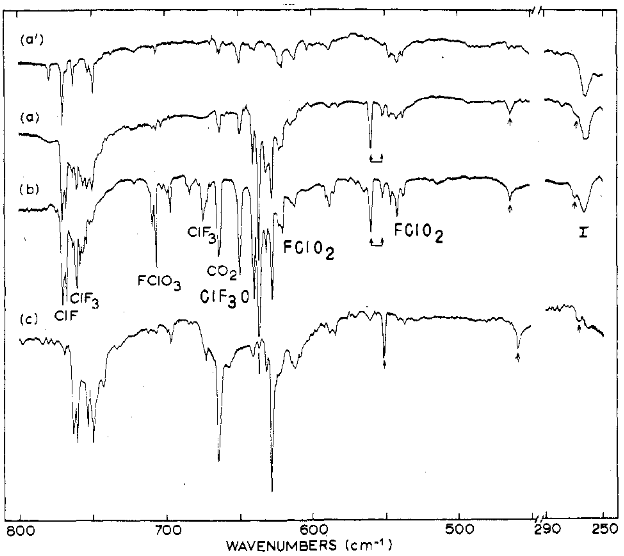


Figure 1. Infrared spectra of premixed chlorine and fluorine samples: (a') $Ar/F_2/Cl_2 = 400/1/4$, 61 mmol deposited, before photolysis; (a) previous sample after 55 min of Hg arc photolysis with the water and Pyrex plate filters; (b) $Ar/F_2/Cl_2 = 400/4/1$, 60 mmol deposited, after 51 min of Hg arc photolysis, same filters; (c) $Ar/F_2/{}^{37}Cl_2 = 250/2.5/1$, 46 mmol of deposited, after 21 min of Hg arc photolysis, same filters.

Two additional experiments were performed using samples with one reagent concentration reduced a factor of 4 relative to the above higher yield study. The spectrum of an $Ar/F_2/Cl_2 = 400/1/4$ sample after deposition is shown in Figure 1a'. Following 55 min of photolysis with 290–1000 nm light, a strong new doublet was observed at 636 cm^{-1} ($A = 0.54$), 627 cm^{-1} ($A = 0.16$) with weaker site splittings at 640 and 631 cm^{-1}, another doublet was observed at 559 cm^{-1} ($A = 0.10$), 551 cm^{-1} ($A = 0.03$), and weaker bands were produced at 464 cm^{-1} ($A = 0.03$) and 270 cm^{-1} which are shown in Figure 1a.

The next sample, $Ar/F_2/Cl_2 = 400/4/1$, with excess fluorine, gave the spectrum in Figure 1b after photolysis; the 636, 627 cm^{-1} doublet ($A = 0.72, 0.22$) was increased while the other three absorptions, 559 cm^{-1} ($A = 0.10$), 464 cm^{-1} ($A = 0.03$), and 270 cm^{-1} remained the same as in the above excess chlorine sample, and in addition, ClF *and* ClF_3[7] were produced by photolysis. The $FClO_3$ and $FClO_2$ impurities,[8] present throughout this study, were more intense in Figure 1b. Also, another chlorine-isotopic doublet at 649, 640 cm^{-1} present before photolysis in all experiments, and enhanced in the excess fluorine run, is due to ClF_3O.[8] The broad 260-cm^{-1} band is due to an impurity often observed in fluorine experiments.

Thermal cycles of these samples into the 32–38 K range decreased the above new bands by approximately half and weak new bands appeared at 454 and 305 cm^{-1}.

The chlorine-37 sample, $Ar/F_2/{}^{37}Cl_2 = 400/2.5/1$, gave the lower multiplet components at 627 ($A = 0.90$), 551 ($A = 0.11$), and 459 cm^{-1} ($A = 0.05$) which indicates that these absorptions are due to chlorine-37 vibrations. A weak shoulder was observed at 268 cm^{-1}. A thermal cycle decreased these bands while a sharp feature at 571 cm^{-1} due to ${}^{37}ClF_2$[2,3] and weak 450- and 300-cm^{-1} bands appeared.

Two further experiments were done on the chlorine–fluorine system using different fluorine atom sources. A study with $Ar/ClF/Cl_2 = 200/1/1$ produced only ClF_3, $FClO_2$, and $FClO_3$ upon photolysis. Another experiment with a sample of $Ar/OF_2/Cl_2 = 200/1/1$ yielded only small amounts of ClF, ClF_3, and again $FClO_2$ and $FClO_3$.[8]

$Br_2 + F_2$. Experiments were run using BrF_3 in argon, equilibrium mixtures of BrF, BrF_3, and Br_2 in argon, alone and codeposited with F_2 in argon, and Br_2 in argon and F_2 in argon deposited from separate manifolds. Microwave discharge experiments were done with samples of Ar/Br_2 and Ar/F_2 mixed before and during discharge. Bands assignable to BrF and BrF_3 monomers and BrF_3 dimer were observed, and several BrF_5 absorptions were seen as well.[7,9] New bands that appeared on photolysis and warmup and during microwave discharge will be described in more detail.

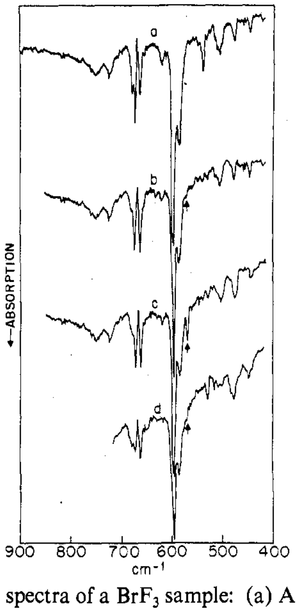


Figure 2. Infrared spectra of a BrF_3 sample: (a) $Ar/BrF_3 = 2000/1$, 17 mmol deposited; (b) after 25 min of Hg arc photolysis with the quartz–water and Corning CS-7-54 glass filters; (c) after a thermal cycle to 25 K; (d) after a thermal cycle to 33 K.

Several experiments with Ar/BrF_3 (M/R = 2000 and 1000) samples were done at Tennessee to optimize the yield of a new doublet at 567, 569 cm^{-1}. This feature was observed after 10 min of photolysis with the quartz–water filter and enhanced by a thermal cycle to 25 K. The yield was maximized by subsequent photolysis for 25 min using the quartz–water plus Corning filters, followed by a thermal cycle to 25 K, as shown in Figure 2. Subsequent thermal cycling to 36 K destroyed the band completely. A small band was observed at 527 cm^{-1} in these experiments, that was enhanced by photolysis and thermal cycling. This band was not destroyed even by warming to 36 K. A similar experiment was done by co-condensing an equilibrium mixture of Br_2, BrF, and BrF_3 in argon at M/R = 50 with F_2 in argon at M/R = 170 using 8.5 mmol of each mixture. After 40 min of photolysis with the quartz–water plus Corning filter combination, new doublets at 554, 556 and 561, 563 cm^{-1} were observed, plus a very small feature at 567, 569 cm^{-1} on the side of the large BrF_3 monomer and dimer bands. Thermal cycling to 25 K caused the 555-cm^{-1} doublet to increase significantly, while the 562-cm^{-1} doublet decreased with loss of resolution. The 569-cm^{-1} feature had increased slightly. The 527-cm^{-1} band was observed on deposition and was unaffected by photolysis but grew considerably on warmup.

Similar experiments were done at Virginia on two chemical systems. Two experiments were done in which bromine and fluorine were premixed and allowed to react such that a mixture of Br_2, BrF, BrF_3, and some F_2 was actually deposited. With excess F_2 ($Ar/Br_2/F_2 = 200/1/2$, 58 mmol deposited), large amounts of BrF at 660.0, 661.5 cm^{-1}, BrF_3 monomer and dimer, and some BrF_5 were observed. Ten minutes of photolysis with the quartz–water and Pyrex filters resulted in good yields of new bands at 554.1, 556.1 cm^{-1}, with a smaller pair at 562.0, 564.0 cm^{-1}. A thermal cycle to 26 K caused a small decrease in both these bands, and a new doublet at 568.0, 570.2 cm^{-1} appeared. Thirty minutes more photolysis and a thermal

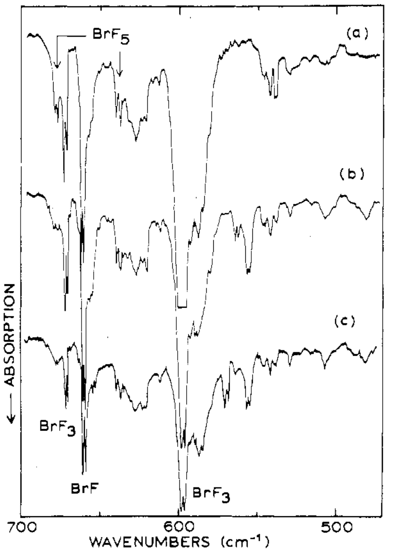


Figure 3. Infrared spectra of a premixed bromine and fluorine experiment: (a) $Ar/F_2/Br_2$ = 200/1/1, 53 mmol deposited; (b) after 40 min of Hg arc photolysis with the quartz–water and Pyrex plate filters; (c) after a thermal cycle to 28 K.

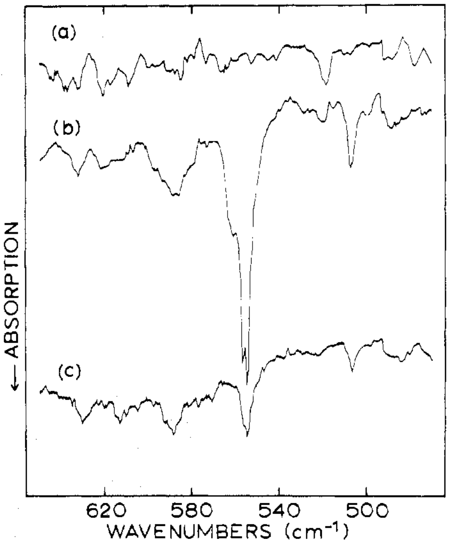


Figure 4. Infrared spectra of a separate manifold bromine and fluorine experiment: (a) Ar/Br_2 = 100/1, 34 mmol, and Ar/F_2 = 100/1, 43 mmol deposited; (b) after 40 min of Hg arc photolysis with the quartz–water and Pyrex plate filters; (c) after a thermal cycle to 27 K.

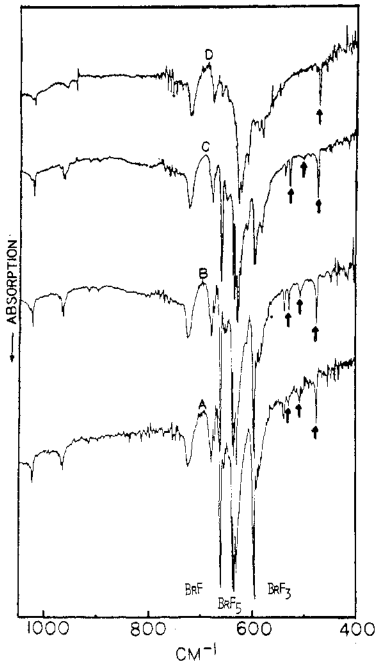


Figure 5. Infrared spectra of a premixed bromine and fluorine discharge experiment: (A) $Ar/F_2/Br_2$ = 425/2.5/1 deposited during microwave discharge; (B) after a thermal cycle to 25 K; (C) after a thermal cycle to 30 K; (D) after a thermal cycle to 40 K.

cycle regenerated the 555-cm^{-1} band, but both the higher frequency bands lost intensity and resolution. A band at 529 cm^{-1} grew slightly on warmups. A similar experiment with equal initial bromine and fluorine ($Ar/F_2/Br_2$ = 200/1/1, 53 mmol deposited) gave a reduced yield of the mixed halogen species, which is illustrated in Figure 3. Ten minutes of photolysis with the quartz–water and Pyrex filter produced both the 554.1-, 556.1-cm^{-1} and 562.0-, 564.0-cm^{-1} doublets. The less dominant BrF_3 bands show clearly that none of the 569-cm^{-1} feature is present after photolysis. A thermal cycle to 28 K causes a decrease in both bands, with loss of resolution on the higher doublet. The 568.0-, 570.2-cm^{-1} feature grows in clearly with good yield (absorbance = 0.13). A band at about 538 cm^{-1} was decreased considerably by photolysis, but no photolysis or temperature effect was observed for a small band at 529 cm^{-1}.

Two further experiments simultaneously codeposited Ar/Br_2 and Ar/F_2 samples from separate vacuum lines. With excess F_2 (Ar/F_2 = 50/1, 46 mmol; Ar/Br_2 = 200/1, 46 mmol), no bands are observed on initial deposition. Ten minutes of photolysis with the quartz–water and Pyrex combination produced numerous bands assignable to BrF_3 dimer, plus small amounts of BrF_3 and BrF_5 monomers. In addition, a full scale band was observed centered at 555 cm^{-1}, and a smaller feature at 560.0 cm^{-1} was seen, with a shoulder at about 562 cm^{-1}. A band at 507 cm^{-1} was considerably sharper than the BrF_3 dimer feature observed in the premixed experiments and is relatively larger than other BrF_3 dimer bands in this experiment. A very weak band was observed at 529 cm^{-1}. Thirty minutes more photolysis produced growth in the 507-, 529-, and 555-cm^{-1} features, as well as the BrF_3 dimer bands. The 560-cm^{-1} feature lost intensity and resolution, and a very small feature appeared at 570 cm^{-1}. A subsequent thermal cycle to 26 K resulted in a slight increase in the 507-cm^{-1} band, little change in the 529- and 560-cm^{-1} features, and a decrease in both the 555-cm^{-1} and in the tiny 570-cm^{-1} feature. A similar experiment with equal bromine and fluorine concentrations (Ar/Br_2 = 100/1, 34 mmol; Ar/F_2 = 100/1, 43 mmol) gave analogous results and is shown in Figure 4. Nothing was observed on initial deposition, but 40 min of photolysis with the quartz–water plus Pyrex assembly produced the 507-cm^{-1} feature, a strong 555.0-, 557.0-cm^{-1} doublet with a 561-cm^{-1} shoulder and very small BrF_3 dimer bands. A thermal cycle to 27 K caused all features to lose intensity, and the 555-cm^{-1} feature lost resolution and most of the shoulder, as is shown in Figure 4.

Further experiments were done at Tennessee with bromine and fluorine samples passed through a microwave discharge. A blank experiment with 10 mmol of $Ar/F_2/Br_2$ = 425/2.5/1 deposited without discharge produced only features assignable to BrF and BrF_5. Discharge of a similar premixed sample resulted in the appearance of bands assignable to BrF_3 monomer, as well as BrF and BrF_5. New features observed at 475, 507, and 527 cm^{-1} are shown in Figure 5. A thermal cycle to 25 K caused an increase in the 507- and 527-cm^{-1} bands, while the 475-cm^{-1} band remains unchanged. Further cycling to 30 K resulted in a further increase in the 527-cm^{-1} band, and the loss of the 507-cm^{-1} band. Warming to 40 K

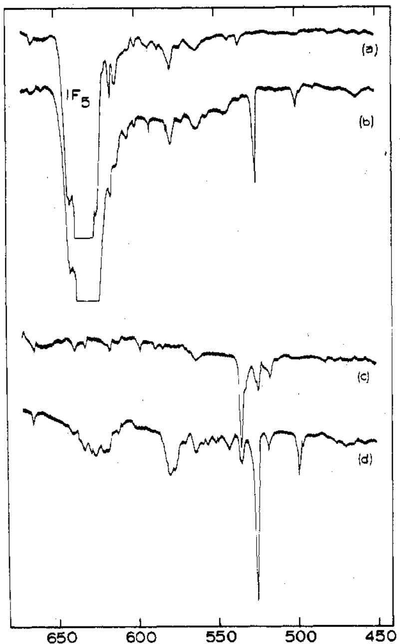


Figure 6. Infrared spectra of separate can and separate manifold iodine and fluorine experiments: (a) $Ar/F_2 = 100$, 11.6 mmol, and $Ar/I_2 = 200$, 7.5 mmol deposited from separate cans; (b) after 30 min of Hg arc photolysis with the quartz–water and Pyrex plate filters, plus 15 min with the quartz–water filter only; (c) $Ar/F_2 = 100$, 10.4 mmol, and $Ar/I_2 = 200$, 7.9 mmol deposited from separate manifolds; (d) after 15 min of Hg arc photolysis with the quartz–water and Pyrex plate filters, plus 20 min with the quartz–water filter only.

caused the loss of the 527-cm^{-1} band as well, but the 475-cm^{-1} feature remained virtually unchanged even on warming to 50 K.

In a similar experiment, Br_2 and F_2 samples were mixed just prior to discharge ($Ar/Br_2 = 160/1$, 26 mmol; $Ar/F_2 = 80/1$, 13 mmol). The 507- and 527-cm^{-1} bands were observed in good yield. The 527-cm^{-1} band is stable on thermal cycling as high as 30 K, while the 507-cm^{-1} band is decreased by warming to 25 K and further on warming to 30 K.

Another experiment was run, mixing the two reactants within the discharge ($Ar/Br_2 = 170/1$, 8 mmol; $Ar/F_2 = 85/1$, 8 mmol). The 527-cm^{-1} band was observed, but was quite small, and was stable on warming to as high as 30 K, but was gone after warming to 35 K. A band at 570 cm^{-1} appeared on warming to 25 K, increased on warming to 30 K, and was gone after a cycle to 35 K. A similar experiment with more dilute samples produced the 570-cm^{-1} band following a thermal cycle.

$I_2 + F_2$. Iodine and fluorine react very readily in the gas phase and spectra from premixed experiments showed strong bands at 704, 634, 370, and 317 cm^{-1} due to IF_5.[10] No new bands were produced by photolysis. Spectra from separate can experiments, which allow a short reaction time in the deposition line before the sample reaches the cold surface, also showed a good yield of IF_5 and weak bands at 578 and 535 cm^{-1}, which are shown in Figure 6a. Trace (b) illustrates the spectrum after photolysis with the quartz–water and Pyrex filters which produced new bands at 499 and 526 cm^{-1}, while the weak band at 535 cm^{-1} was destroyed. A subsequent photolysis with the quartz–water filter had little effect. A thermal cycle to ~35 K caused both bands to grow a small amount, but no other new bands appeared.

Two experiments were done using completely separate deposition lines allowing almost no gas-phase reaction. An experiment with excess fluorine, $Ar/F_2 = 100/1$ and $Ar/I_2 = 200/1$, is shown in scans (c) and (d) of Figure 6 before and after photolysis with quartz–water and Pyrex filters. Before photolysis, weak bands at 516 and 524 cm^{-1} and a strong band at 535 cm^{-1} (absorbance = A = 0.22) were observed. After photolysis, a new band appeared at 499 cm^{-1} (A = 0.048), a strong band grew in at 526 cm^{-1} (A = 0.98), and the 535-cm^{-1} band lost intensity. Broad bands centered at 577 and 624 cm^{-1} grew in as well. Further photolysis with the quartz–water filter only produced some growth in the 499-cm^{-1} band, further reduction of the 535-cm^{-1} band, and slight reduction of the 526-cm^{-1} band. A thermal cycle had little effect on this sample.

Another separate manifold experiment, with equal iodine and fluorine concentrations ($Ar/I_2 = 200/1$, 813 mmol; $Ar/F_2 = 200/1$, 17 mmol) showed virtually the same spectrum as Figure 6c before photolysis. Pyrex–water filtered photolysis produced the 499- and 526-cm^{-1} bands, but this time, with lower fluorine concentration, the 535-cm^{-1} band grew slightly, rather than decreasing, as it did with excess fluorine. Further quartz–water filtered photolysis again produced growth of the 499-cm^{-1} band, slight growth of the 526-cm^{-1} band, and reduction of the 535-cm^{-1} band.

$Cl_2 + Br_2$. Two separate can experiments were done with chlorine and bromine, since these elements react to give BrCl in the gas phase. The first, using 1% samples, produced a weak, broad band at 427 cm^{-1} after Pyrex- and water-filtered photolysis. The second experiment with $Ar/Cl_2 = Ar/Br_2 = 50/1$ samples produced a stronger 427-cm^{-1} absorption (A = 0.08) after water-filtered photolysis.

Raman. Raman experiments were done for the three fluorine–halogen systems. Premixed and separate manifold experiments were run with chlorine and fluorine, with total M/R for each halogen of 50 and 100. Initial scans showed signals corresponding to Cl_2, ClF, and F_2 at 562, 760, and 892 cm^{-1} shifted from the laser line.[9] Laser photolysis produced a weak signal at 528 cm^{-1} due to ClF_3[11] on the low-frequency side of the Cl_2 band and a weaker band approximately coinciding with the ClF band near 760 cm^{-1}. Otherwise, no new features were observed.

Bromine and fluorine experiments did produce new scattered light signals on laser photolysis. A typical experiment is illustrated in Figure 7 using $Ar/F_2 = 25/1$ and $Ar/Br_2 = 25/1$ samples. The first scan (a) shows a strong signal at 296 cm^{-1} [12] and a weak F_2 signal and a broad feature which is actually two weak signals at about 603 and 638 cm^{-1}. Twenty-five minutes of 488.0-nm laser photolysis, scan (b), caused definite growth in the 603-cm^{-1} band, and a new band grew in at 675 cm^{-1}, while the 638-cm^{-1} band was lost. A thermal cycle to about 29 K, scan (c), caused further growth in the 675-cm^{-1} band but a reduction in the 603-cm^{-1} band. Further laser photolysis for 15 min, scan (d), regenerated the 603-cm^{-1} band, with little further effect on the 675-cm^{-1} band. Similar behavior was observed for a premixed experiment ($Ar/F_2/Br_2 = 100/2/1$), except that the 675-cm^{-1} band was favored slightly with the excess F_2. Another premixed experiment ($Ar/F_2/Br_2 = 50/1/1$) again showed the 603-cm^{-1} band in better yield. Interestingly, the two photolysis-product bands showed up in the initial scan in the experiment where 514.5-nm laser light was used. Further separate manifold experiments using $Ar/F_2/Br_2 = 50/1/1$ samples produced only very weak bands in the 600–700-cm^{-1} region.

Laser Raman experiments with iodine and fluorine produced no new signals. Initial spectra showed a weak F_2 band, and strong resonance Raman spectra of isolated I_2.[12] Prolonged photolysis only decreased these signals while resonance Raman bands due to aggregated I_2 appeared. All experiments were done with separate manifolds, using Ar/F_2 and Ar/I_2 as low as 25/1.

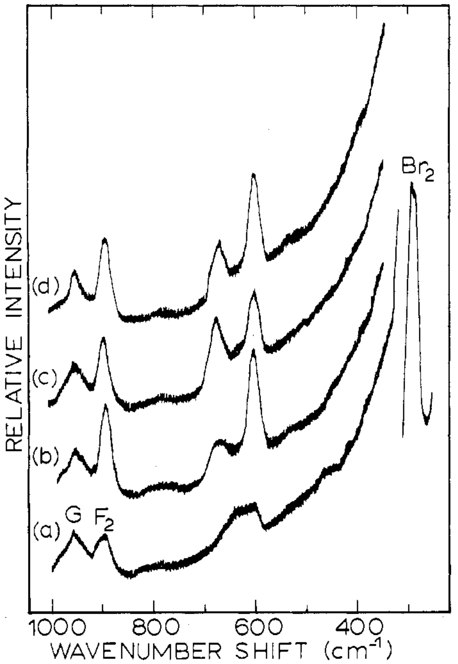


Figure 7. Raman spectra of a separate manifold bromine and fluorine experiment: (a) $Ar/F_2 = 25/1$, 13.7 mmol, and $Ar/Br_2 = 25/1$, 13.5 mmol deposited; (b) after 25 min of unfiltered 488.0-nm laser photolysis 470 mW at sample; (c) after a thermal cycle to 29 K; (d) after 15 min more unfiltered laser photolysis. Scans were taken at 50 cm^{-1}/min, 500-μ slits, range = 1×10^{-9} A, dielectric spike filter (Br_2 peak, range = 3×10^{-9} A); G = grating ghost.

Discussion

Absorptions assigned to new photolysis product species for each chemical system will be discussed in turn.

Chlorine and Fluorine. The four infrared absorptions in these chlorine–fluorine experiments were observed and assigned previously by Mamantov et al.[4] The present reexamination done at Virginia suggests an alternate assignment for three of these bands.

The 627-, 636-cm^{-1} Doublet. The 627-, 636-cm^{-1} absorptions were the most intense new product feature. The 3/1 relative intensities of these two bands clearly indicate that they are the ^{35}Cl, ^{37}Cl isotopic components of a single chlorine atom vibration. The isotope splitting of 9 cm^{-1} is larger than that of isolated ClF, 7 cm^{-1}. Such a large, distinct isotope splitting is characteristic of a nearly linear F–Cl–F antisymmetric vibration containing a single chlorine atom, as proposed earlier.[4] This band was also favored by an abundance of molecular fluorine, indicating that it probably involves more than one fluorine atom. The evidence supports assignment of this feature to the antisymmetric stretch of the F–Cl–F unit in a symmetric, T-shaped $ClClF_2$ species. The location of this absorption slightly below the corresponding vibration of matrix-isolated ClF_3 at 683 cm^{-1} in argon[7] is consistent with this assignment, which is in agreement with the previous work.[4]

The 559-, 464-, and 270-cm^{-1} Absorptions. The 464- and 270-cm^{-1} features were previously observed in very concentrated samples ($Ar/F_2/Cl_2 = 400/10/1$) and assigned[4] to another stretch and a bend of the Cl_2F_2 molecule, and the 559-cm^{-1} band was attributed to Cl_2F_3. The 559-cm^{-1} absorption was observed when the 636-cm^{-1} feature was intense, and it exhibited a large Cl isotope splitting, 559 to 551 cm^{-1}, so assignment to a derivative of the Cl_2F_2 molecule was proposed.[4] There is, however, an alternate assignment that can be made for these three bands which is consistent with the earlier information and with these more recent observations.

Table I. Observed and Calculated Isotopic Frequencies (cm^{-1}), Vibrational Potential Function, and Potential Energy Distribution for Cl_2F

Isotope	Assignment	Obsd	Calcd[a]
35-35-19	ν_1	559.0	560.1
	ν_2	464.0	465.4
	ν_3	270.0	271.2
37-37-37	ν_1	551.0	549.9
	ν_2	459.0	457.6
	ν_3	268.0	266.7

	Potential energy distribution[b]		
Potential function	ν_1	ν_2	ν_3
$F_{Cl-F} = 2.12$ mdyn/Å	71.9[c]	30.3	1.3
$F_{Cl-Cl} = 2.77$ mdyn/Å	50.1	51.0	2.4
$F_{Cl-Cl-F} = 0.95$ (mdyn Å)/rad^2	0.0	4.3	95.7
$F_{Cl-Cl,\ Cl-F} = 0.44$ mdyn/Å	−22.0	14.4	0.6

[a] Average difference between calculated and observed frequencies is 1.2 cm^{-1}. [b] For 35-35-19 isotope. [c] Interpretation: ν_1 is 71.9% Cl–F bond stretching in character.

One important point must be made with respect to the dependence of the 559-cm^{-1} band on fluorine concentration. The previous work showed that this feature was favored by an abundance of fluorine atoms, based on relative growth after photolysis with wavelengths that favor F_2 dissociation. The recent data indicate, however, that these bands are favored *relative* to the 627-, 636-cm^{-1} features in experiments with lower total fluorine concentration. The earlier experiments used a many (10–20)-fold excess of F_2, while the recent ones employed only a fourfold F_2 excess and also a fourfold Cl_2 excess. This latter observation does not support assignment of these absorptions to a fluorine addition product of Cl_2F_2. A species that would be favored by both efficient fluorine atom production and low total fluorine concentration is one containing a single fluorine atom, specifically Cl_2F.

The 464- and 270-cm^{-1} absorptions appear to be associated with the 559-cm^{-1} absorption on changing the F_2/Cl_2 ratio in the sample. It is reasonable to consider these lower two bands for assignment to the Cl–Cl stretching mode and the bending mode of Cl–Cl–F, respectively. In the most productive experiment, the 464-cm^{-1} feature contained partially resolved components at 462 and 459 cm^{-1} with the appropriate relative intensities for a vibration of two chlorine atoms. The 559-cm^{-1} band is assigned to the Cl–F stretching mode of Cl_2F; the chlorine isotopic intensities show that one chlorine atom participates in this vibration.

Force constant calculations were done for the Cl–Cl–F radical with these assignments using the Schachtschneider program FADJ and the assumed bent structure (150°) with Cl–Cl and Cl–F distances of 2.2 and 1.8 Å, respectively. Bond lengths for the diatomic molecules are 1.99 and 1.63 Å, respectively.[9] A satisfactory agreement was obtained between calculated and observed frequencies (average difference = 1.2 cm^{-1}); a substantial Cl–Cl, Cl–F stretch–stretch interaction force constant was required to fit the isotopic data which are listed in Table I along with the force constants. It can be seen from the potential energy distribution that the two bond stretching modes are extensively mixed; however, the 559-cm^{-1} band is more Cl–F stretch and the 464-cm^{-1} band is predominantly Cl–Cl stretch in character. This vibrational analysis is supportive of the Cl_2F assignment, but it cannot be considered to confirm the observation of Cl_2F.

If this identification of the Cl_2F free radical is correct, another interesting 21-electron species is available for bonding considerations. The two stretching fundamentals of Cl_2F, 559 and 464 cm^{-1}, are near the stretching modes[3] of ClF_2 at 578 and 500 cm^{-1}. Comparison between the two modes for Cl_2F with the Cl_2 and ClF fundamentals at 549 and 770 cm^{-1} in solid argon,[6,13] and the force constants in Table I with values for ClF (4.29 mdyn/Å)[6] and Cl_2 (3.10 mdyn/Å),[13] suggests that Cl_2F contains a weak Cl–F bond and a Cl_2 bond only slightly weaker than diatomic Cl_2. This is reminiscent of the F···ClO and Cl···ClO molecules and the bonding in F···ClCl can be rationalized by the simple p–π^* bonding model used for these species.[6,14] However, in the F···ClCl case, a three-electron F(2p)–$Cl_2(\pi^*)$ bond is involved which affects the Cl–Cl bond by increasing antibonding electron density, opposite to the case in F···ClO. Finally, a simple molecular orbital model for X_3 systems using valence s and p orbitals gives three more bonding than antibonding electrons which also predicts one "single" bond and one "half" bond for F···ClCl.

The failure to produce $ClClF_2$ and ClClF with the alternate but less prolific fluorine atom sources, ClF and OF_2, may shed some light on a possible mechanism by which these species are formed. This observation suggests that the mechanism is not only simple addition of fluorine atoms to molecular chlorine but that chlorine molecule–fluorine molecule van der Waals dimers may play an important role. $ClClF_2$ could be formed directly upon photolysis of Cl_2···F_2 van der Waals dimers and Cl_2F could result when one fluorine escapes this cage. Of course, direct fluorine addition to Cl_2 can form Cl_2F as well.

Bromine and Fluorine. The infrared experiments on the Br_2 + F_2 system were the most interesting and fruitful in terms of new species observed. The moderate gas-phase reactivity of the reagents made the contrast between premixed and separate experiments particularly illuminating and informative.

The 554-, 556-cm^{-1} Doublet. The 554-, 556-cm^{-1} doublet exhibited a distinct bromine isotope splitting characteristic of a vibration involving a single Br atom. The bromine isotopic splitting for BrF is 1.5 cm^{-1} for the 661-cm^{-1} fundamental in solid argon, whereas the splitting on the 554–556-cm^{-1} doublet is 2.0 cm^{-1}, a good bit larger. This suggests an antisymmetric stretch of an approximately linear F–Br–F unit. The fact that this band is strongly favored in experiments where Br_2 is the bromine source leads to the conclusion that the species contains two Br atoms. Finally, the increased yield with excess F_2 suggests that the molecule probably contains more than one F atom. These observations lead to the assignment of this band to the symmetric T-shaped $BrBrF_2$ molecule. The 555-cm^{-1} band was the major product species in these studies, as was the analogous Cl_2F_2 molecule in chlorine–fluorine experiments. This species is probably produced largely from the photoreaction of Br_2–F_2 van der Waals dimers trapped in the matrix, although the reaction of two successive fluorine atoms with Br_2 is also expected. It is noteworthy that the antisymmetric F–Br–F mode in Br–BrF_2, 555 cm^{-1}, is slightly reduced from that of F–BrF_2, 597 cm^{-1}.

The 568-, 570-cm^{-1} Doublet. The 568-, 570-cm^{-1} band exhibits the same distinct splitting characteristic of a nearly linear F–Br–F antisymmetric vibration. The fact that this feature grows dramatically on warming shows that it is produced by the diffusion and reaction of F atoms. The species may be formed during photolysis as well but destroyed at roughly the same rate. This behavior was observed less dramatically with the ClF_2 radical.[2,3] The 569-cm^{-1} band is only observed in experiments where precursor molecules with a single Br atom are present, BrF and BrF_3, indicating that it probably contains only one Br atom. Further, it is not especially favored in experiments where excess fluorine is present in which case the single Br species BrF_3 would be the preferred product. This evidence leads to the assignment of this feature to the BrF_2 radical.

Although the formation and behavior of this species are comparable to that of ClF_2, it is noteworthy that a comparison of the ClF and BrF frequencies, and the ClF_3 and BrF_3 ν_4 modes, predicts BrF_2 in the low 500-cm^{-1} region, where bands are observed at 507 and 527 cm^{-1}. Still, the parallel photolytic behavior and the bromine isotopic splitting point to assignment of the 569-cm^{-1} band to ν_3 of BrF_2.

The isotopic fundamentals 570.2 and 568.0 cm^{-1}, respectively, for $^{79}BrF_2$ and $^{81}BrF_2$ can be used to calculate a lower limit to the F–Br–F valence angle. This value, 152 ± 8°, is in good agreement with the 136 ± 4° lower limit[3] for ClF_2 and it strongly suggests that the 21-electron BrF_2 free radical is obtusely bent.

The 507-cm^{-1} Band. The band at 507 cm^{-1} falls in a region with a broad unstructured BrF_3 dimer band[7] that is observed in experiments where this compound is present. However, the band is much sharper in experiments where bromine and fluorine are deposited separately, and its intensity is large relative to other BrF_3 dimer bands in these experiments. This leads to the conclusion that a new, photolysis-product species is responsible for this sharp feature. The fact that this feature is most prominent in experiments with Br_2 parent indicates again a species containing two Br atoms. Further, it is favored over BrF_3 dimer in an experiment with low F_2 concentration, indicating that it contains fewer F atoms. These observations justify the tentative assignment of this feature to the asymmetric Br_2F species formed by reaction of one F atom with Br_2. Unfortunately, no bromine isotopic splitting was resolved on this absorption; however, the splitting is only 1.0 cm^{-1} for a simple Br–F mode in this region, which would be difficult to resolve for a weak absorption.

The observation of the 507-cm^{-1} band in discharge experiments is consistent with the Br_2F assignment. It is not expected in the blank experiment, since only the known reaction products BrF_n (n = 1, 3, 5) would be formed without any photolysis after deposition, and the premixed sample would be expected to react such that little Br_2 would be available anyway. The good yield obtained with reactants mixed just prior to discharge is consistent with the deposition of intact bromine molecules and fluorine atoms.

The 527-cm^{-1} Band. The band at 527 cm^{-1} is of interest as it was observed in both photolysis and discharge experiments. It is present in scans of premixed samples *prior to photolysis* but was not observed in the blank discharge experiment, although no BrF_3 was observed either. It seems to be favored by excess fluorine and by thermal cycling but is lost on thermal cycling above 35 K. The 527-cm^{-1} absorption observed before photolysis is most likely due to $(BrF_3)_2$, as assigned previously.[7] This species could be formed by warming a sample containing Br_2 and excess fluorine atoms since the Br_2 unit need not separate in the dimer. However, its disappearance on warming above 35 K in discharge experiments suggests that a more reactive species might contribute to the 527-cm^{-1} absorption. A possibility is BrF_4 which is expected to increase on diffusion and reaction of F atoms to a point. BrF_4 should be more stable than ClF_4 (which has been detected by ESR[15] and studied via computer experiments[16]) as shown by the comparison of ClF_5 and BrF_5.

Others. The small band at 538 cm^{-1} is noticeable by virtue of its photolysis behavior. This feature has been observed in other work with mixed Br–F compounds, where it was attributed to an impurity, obviously photosensitive. This assignment is acceptable, insofar as its behavior is not particularly compatible with any of the other assigned new bands. The 475-cm^{-1} band observed in discharge experiments may possibly be due to higher polymers of BrF_3, based in particular on its stability to relatively high thermal cycling to 50 K.

The doublet observed at 561, 563 cm^{-1} has not been assigned to a new species; it is probably due to a site splitting of the 554-, 556-cm^{-1} Br_2F_2 feature. The intensity of the smaller band decreases slightly more than the 554-, 556-cm^{-1} feature on warming, and the resolution of the doublet is lost. This is reasonable behavior for a less stable matrix site.

Iodine and Fluorine. Premixed iodine and fluorine samples revealed a good yield of IF_5 on decomposition, and no new products were formed on photolysis. Even separate can experiments, which provide a short reaction time in the spray on line, produced a large amount of IF_5, indicating that this is the strongly favored product. The matrix isolation experiments, that allow a brief reaction time even just at the matrix surface, provide a situation in which IF or IF_3 could be observed as intermediates in the formation of IF_5.

The 535-cm^{-1} Band. The 535-cm^{-1} band was present before photolysis in both separate can and separate manifold experiments, with larger yields in the latter case. The band was observed to decrease significantly on photolysis when an initial twofold excess of fluorine over iodine was present. However, with a lower fluorine concentration, the band increased on initial quartz, water, and Pyrex photolysis, though further photolysis did decrease it. The species, then, is favored by a lower fluorine concentration and can be both formed and destroyed by photolysis. A species that could form and be trapped during deposition is IF_3, and the observed photolysis behavior can be readily rationalized for this assignment. In solid IF_3 the corresponding band occurs[17] at 480 cm^{-1}. We have, however, observed[18] a frequency shift of similar magnitude for the ν_4 band of solid ClF_3.

Photolysis of a sample containing an excess of fluorine would result in conversion of IF_3 to IF_5, by addition of fluorine atoms. Indeed, a broad band in the region of IF_5 absorption is seen to grow in on photolysis in the separate manifold experiments (Figure 6d). Growth of IF_3 on photolysis with less F_2 could arise from fluorine reaction with IF or I atoms liberated in the initial fluorine–iodine reaction during sample condensation. Finally, assignment of the 535-cm^{-1} band to IF_3 is in reasonable correlation with ClF_3 at 683 cm^{-1} and BrF_3 at 597 cm^{-1} in argon matrices.[7]

The 526-cm^{-1} Band. The 526-cm^{-1} band is by far the dominant absorption produced by photolysis in the iodine–fluorine experiments. This new species is expected to contain two iodine atoms, as it is probably formed from isolated I_2 in the matrix. It probably contains more than one fluorine atom, since the best yields are obtained in excess-fluorine experiments. The straightforward assignment for this band is to the symmetric IIF_2 species. This assignment is in good agreement with those for Cl_2F_2 at 636 cm^{-1} and Br_2F_2 at 555 cm^{-1}, which were the major products in their respective experiments.

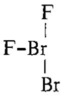
The 499-cm^{-1} Band. This species is present in considerably lower yields in all experiments, as might be expected for a species with either fewer or more fluorine atoms than the dominant species. The position of this band makes reasonable a tentative assignment to I_2F, following Cl_2F at 559 cm^{-1} and Br_2F at 507 cm^{-1}. However, the continued growth of this band on successive photolyses, and the fact that it is favored relative to the 526-cm^{-1} band in the excess-fluorine separate manifold experiment, means that assignment to a higher fluorine species such as I_2F_3 or I_2F_4 cannot be ruled out. Higher fluorine species are expected to be more stable in experiments with iodine, as compared to chlorine or bromine.

Others. The broad, weak feature centered at about 624 cm^{-1} is slightly lower than the strong IF_5 absorption, and it is reasonably assigned to this molecule. The small feature at 578 cm^{-1} is present both before and after photolysis in separate can experiments and only after photolysis in separate manifold experiments. This feature and a weak band at 518 cm^{-1} present throughout the separate manifold experiments are probably due to more stable species which cannot be identified without additional information.

Bromine and Chlorine. The only new infrared absorption produced by photolysis of Br_2–Cl_2 samples appeared at 427 cm^{-1}. This feature was not observed in a previous study involving discharged mixtures of Br_2 and Cl_2 which suggested the Br–$BrCl_2$ identification for a band near 325 cm^{-1}.[19] The BrCl fundamental has been observed at 430 ± 2 cm^{-1} in Raman studies;[13] this suggests that the present 427-cm^{-1} band is due to bromine monochloride monomer and perhaps the dimer, $(BrCl)_2$. The earlier Br–$BrCl_2$ assignment appears reasonable relative to BrCl at 430 cm^{-1} considering the present XXF_2 species as compared to the XF diatomics. It is interesting to note that the failure to form $BrBrCl_2$ by photolysis indicates its instability relative to 2BrCl or $(BrCl)_2$; however, the XXF_2 species are produced by photolysis which shows that the symmetric XXF_2 molecule is more stable than the $(XF)_2$ dimer species.

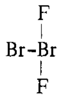
Raman Spectra. Most of the assignments made from the infrared work to single modes of polyatomic species are based on relative band intensity and concentration behavior. Supporting evidence could, in principle, be obtained from Raman spectra, but, unfortunately, the Raman observations were not helpful in this regard. Bromine and fluorine experiments were the only ones that showed new photolysis product signals, which came at 603 and 675 cm^{-1}. Neither of these bands correspond to signals observed in the infrared, which is not surprising, since Raman and infrared intensities often vary indirectly.

The 603-cm^{-1} Raman signal is below the equatorial Br–F stretching mode[7] of BrF_3 at 672 cm^{-1} and the 603-cm^{-1} band could be due to the equatorial mode of an asymmetric species (I). Infrared data were obtained for the symmetric species (II) and not the asymmetric species; however, the symmetric isomer is probably the stronger infrared absorber. It is also possible for ultraviolet photolysis to favor the production of one isomer and visible laser photolysis to favor the other. Isomerization could also occur by a dimer exchange mechanism.[7] The Raman observation suggests that an asymmetric Br_2F_2 species is also formed, but it does not provide a definitive identification.



$\mathrm{F{-}Br(F){-}Br}$

I



$\mathrm{Br{-}Br(F)(F)}$

II

Although the 675-cm^{-1} band is markedly similar to the equatorial Br–F mode of BrF_3, absence of the stronger axial Br–F mode for BrF_3 at 547 cm^{-1} rules out BrF_3 monomer for the present Raman band. However, this band increased on sample warming which suggests a dimer that presumably contains two Br_2F_2 species, but this is not a definitive identification.

Conclusions

Matrix samples containing fluorine and chlorine, bromine, or iodine were photolyzed and infrared absorptions were produced for new interhalogen species. The major absorption in each study was assigned to the symmetric XXF_2 molecule, analogous to XF_3. Three infrared bands have been attributed to each of the $^{35}Cl_2F$ and $^{37}Cl_2F$ isotopic species. A sharp 568.0-, 570.2-cm^{-1} doublet was assigned to the BrF_2 free radical. A new band produced by the matrix cocondensation reaction of I_2 and F_2 was assigned to IF_3 which was converted to IF_5 by photolysis in samples with excess fluorine. A summary of vibrational modes for interhalogen molecules in solid argon is given in Table II. The production of these species on photolysis is indicative of mechanisms involving fluorine atom migration through the matrix and the photoreaction of van der Waals dimers. The matrix allows new

Table II. Vibrational Modes (cm^{-1}) for Interhalogen Molecules in Solid Argon

Mode	Cl–F species		Br–F species		I–F species	
X–F str	Cl–F	770	Br–F	661	I–F	603[a]
Antisym X–F	ClF_2	578[b]	BrF_2	569		
Eq X–F	ClF_3	754[c]	BrF_3	672[c]		
Ax, antisym X–F	ClF_3	683	BrF_3	597	IF_3	535
Ax, antisym X–F	Cl_2F_2	636	Br_2F_2	555	I_2F_2	526
X–F′ str	ClF_5	722[d]	BrF_5	681	IF_5	704
Antisym X–F	ClF_5	726	BrF_5	636	IF_5	634
X–F str	Cl_2F	559	(Br_2F	507)	(I_2F	499)
X–X str	Cl_2F	464				
X–X–F bend	Cl_2F	270				

[a] Deduced from electronic spectra.[9] [b] References 2 and 3. [c] Reference 7. [d] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

intermediate interhalogen species to be produced and trapped for spectroscopic study.

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Registry No. ClF, 7790-89-8; ClF_3, 7790-91-2; Cl_2F_2, 37621-12-8; ClF_5, 13637-63-3; Cl_2F, 65516-29-2; BrF, 13863-59-7; BrF_2, 64973-51-9; BrF_3, 7787-71-5; Br_2F_2, 65414-56-4; BrF_5, 7789-30-2; Br_2F, 64973-52-0; IF_3, 22520-96-3; I_2F_2, 65414-57-5; IF_5, 7783-66-6; I_2F, 58751-33-0; F_2, 7782-41-4; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2.

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Preparation and Photoelectrolytic Behavior of the Systems WO_{3-x} and $WO_{3-x}F_x$

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A convenient method of preparing compounds in the system $WO_{3-x}F_x$ is described and the photoelectrolytic behavior of WO_{3-x} and $WO_{3-x}F_x$ anodes has been investigated. It was found that the substitution of small amounts of fluorine for oxygen in WO_3 does not affect adversely its photoelectrolytic behavior. Moreover, substituted fluorine increases the stability of electrodes of WO_3 when used for the photoelectrolysis of water.

Introduction

There has been considerable interest recently in the search for stable electrode materials for use in photoelectrolysis. This process is one in which water is decomposed into hydrogen and oxygen when a suitable semiconductor, placed in an electrochemical cell, is illuminated with energy greater than the band gap, creating electron-hole pairs.[1] Under appropriate conditions, these electron-hole pairs can be separated and used as oxidizing and reducing species.[2]

The requirements of such a stable electrode material are indeed stringent. The material must be chemically inert and should have a band gap that utilizes an optimum of the solar spectrum (~1.6 eV). In addition, the semiconductor must be conducting and when placed in an electrolyte it should have sufficient band bending to separate the photogenerated electron-hole pairs. The position of bands relative to the electrochemical scale must be such that oxidation of O^{2-}/O_2 and reduction of H^+/H_2 can take place.

The degree of band bending and the position of the bands can be controlled to some degree by varying the pH of the electrolyte used in the cell and by the application of an external bias. It is known that the conductivity of such materials can be altered by chemical substitution or doping procedures. Therefore, the properties which are most difficult to control and, thus, more critical are the magnitude of the band gap and the material's chemical stability.

To date, the only materials which have been used successfully have been broad-band oxides.[3-6] These oxides were made conductive by removing small amounts of oxygen. Since there is some question as to the long-term stability of these defect structures in a highly oxidizing environment,[7] it was of interest to compare the relative stability of defect oxides to those of oxyfluorides.

The use of WO_3 as a stable electrode in photoelectrolysis has been reported by several investigators. Butler et al.[8] have indicated that WO_3 is an n-type semiconductor with a band gap of 2.7 eV. Experiments performed with single crystals in a 1.0 M sodium acetate solution showed spontaneous photocurrent (i.e., no applied bias) with no decay in photocurrent or visible deterioration of the electrode surface even after passage of approximately 75 C/cm^2. They indicated that an appreciable applied bias was necessary before photodecomposition of water was observed. Hodes et al.[9] found similar results with polycrystalline films of WO_3 prepared by either

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