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# Photochemical reactions of CIF and BrF with hydrogen in solid argon. Infrared spectra of mixed hydracid dimers

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Argon diluted samples of  $H_2$  and ClF were codeposited at 10 K, and no reaction was observed. Photolysis produced a sharp 2834.5, 2832.5 cm<sup>-1</sup> doublet, in agreement with (HF) (HCl) dimer from HF and HCl codeposition experiments. Irradiation at 14–16 K markedly increased the mixed dimer and produced weak monomer and dimer bands of HCl and HF, mixed trimer absorptions, and a sharp band at 3857.9 cm<sup>-1</sup> for the Cl--HF radical complex. In similar experiments with HD, two mixed dimers, (HF) (DCl) and (HCl) (DF), were formed; likewise, photolyzing D<sub>2</sub> with ClF produced two mixed dimers of the form (DF) (DCl) and (DCl) (DF). In the H<sub>2</sub> and BrF system, photolysis produced a sharp absorption at 3814.6 cm<sup>-1</sup>, in agreement with (HBr) (HF) dimer from HBr and HF codeposition experiments, and a new 3830.5 cm<sup>-1</sup> band due to the Br--HF radical complex. In a parallel study with HD, two mixed dimers, (HBr) (DF) and (DBr) (HF), were observed while only one mixed dimer, (DBr) (DF), was formed by BrF and D<sub>2</sub>. In complementary experiments with H<sub>2</sub> and Cl<sub>2</sub>, (HCl)<sub>2</sub> was observed at 2818.1 and 2816.2 cm<sup>-1</sup>.

# INTRODUCTION

Due to the importance of hydrogen bonding in determining the physical properties of a vast array of chemical systems, dimers and larger aggregates of hydracids, especially HF, serve as key prototypes in the investigation of this bonding phenomenon. Mixed hydracid dimers are of particular interest owing to the relative stabilities of different isomeric arrangements. Only one gas phase study has been performed on a mixed hydracid dimer; molecular beam electric resonance found only the (HF) (HCl) complex,<sup>1</sup> which is in agreement with theoretical calculations for the more stable arrangement. Since hydracids undergo extensive self-association even in the gas phase, the matrix isolation technique in conjunction with infrared spectroscopy has proven extremely valuable in examining the structure and bonding of small hydracid clusters. Several studies using these techniques have obtained detailed vibrational and librational spectra of hydracid clusters  $(HX)_n$  (X = F,<sup>3-5</sup> Cl, and Br<sup>6,7</sup>) formed by depositing HX diluted in a rare gas. However, matrix investigations of mixed hydracid polymers have included only the HCl-HBr and HCl-HI dimers and trimers.<sup>6,7</sup>

The purpose of this Fourier-transform infrared (FTIR) study is to expand our understanding of mixed hydracid clusters by characterizing the dimers and trimers of HF with HCl and HBr. Using the techniques recently developed for the matrix infrared study of the  $H_2$  and  $F_2$  reaction,<sup>8</sup> the  $H_2$  and ClF (BrF) matrix system was examined over a range of concentration and photolysis conditions as a source of mixed hydracid clusters. The major photolysis products at 10 K are dimers, and photolyzing at 14–16 K also yields trimers. In addition, new product absorptions are assigned to the Cl-HF and Br-HF radical complexes. The dimer and trimer assignments were confirmed by performing HF and HCl or HBr codeposition experiments. Here follows a detailed FTIR study of the  $H_2$  reaction with ClF and BrF in solid argon.

# **EXPERIMENTAL**

The vacuum and cryogenic apparatus and FTIR spectroscopic techniques have been described in detail in earlier reports.<sup>9,10</sup> Most of the infrared spectra were recorded on a Nicolet 7199 Fourier-transform infrared spectrometer at 1.0 cm<sup>-1</sup> resolution in the region 4000–400 cm<sup>-1</sup> and at 2.0 cm<sup>-1</sup> resolution in the region 425–125 cm<sup>-1</sup>. A single beam spectrum of the CsI window at 10 K was recorded and ratioed as a background for each single beam spectrum in the codeposition experiments and for the spectrum following deposition in the photolysis studies. All spectra recorded after photolysis used the spectrum following deposition as background. For several HF and HCl codeposition experiments, a Perkin–Elmer 983 spectrophotometer was used to record spectra over the 4000–180 cm<sup>-1</sup> range; the frequency accuracy of band locations is + 0.2 cm<sup>-1</sup>.

For the photolysis experiments, BrF was prepared by equilibrating  $Br_2$  (Mallinckrodt) with  $F_2$  (Matheson) at low pressures in a passivated stainless steel vacuum system. Chlorine monofluoride (Ozark–Mahoning) was purified by evacuation at 77 K to remove volatile impurities. The BrF and ClF samples were diluted from 50/1 to 200/1 mol ratios with argon (Air Products) while the  $H_2$  (Matheson) dilutions ranged from 100/1 to 200/1 mol ratios. Isotope effects were examined by using HD (MSD Isotopes) and  $D_2$  (Air Products) in place of  $H_2$ .

The appropriate samples were codeposited at rates of 2– 3 mmol/h onto the cold window at 10 K until approximately 30 mmol of each sample was deposited. After completing deposition, an infrared spectrum was recorded. The matrix was photolyzed for 30–60 min by the full light of a highpressure mercury arc (Illumination Industries, Inc., BH-6-1, 1000 W) passed through a water filter. After another spectrum was taken, the resulting matrix was warmed to 14–16 K, photolyzed for an additional 30–60 min, and recooled to 10–11 K; a final spectrum was recorded.

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For the codeposition experiments, hydrogen fluoride (Matheson), deuterium chloride (MSD Isotopes), and hydrogen bromide (Matheson) were condensed at 77 K and evacuated to remove any volatile impurities. DF was prepared from the elements. The hydracids were diluted between 75/1 and 400/1 mol ratios with argon in order to examine concentration effects. Reagent samples were codeposited on the CsI window at approximately 10 total mmol/h for 6 h. The samples following deposition were annealed to 20–22 K for 10 min and then recooled to 10 K. Spectra were recorded before and after sample preparation and annealing. Blank samples were prepared and annealed for each reagent separately.

# RESULTS

Matrix isolation experiments of CIF and BrF with the different isotopes of hydrogen will be described in turn. In addition, the HF/DF codeposition experiments with HCl, DCl, and HBr will be discussed.

#### H<sub>2</sub>+CIF

Four experiments were performed with  $H_2$  and ClF in solid argon. Figure 1(a) shows the product region of the spectrum taken after codepositing  $Ar/H_2 = 100/1$  and Ar/ClF = 200/1 samples. Sharp weak HF absorptions were observed at 3962 and 3953 cm<sup>-1</sup> along with a weak water (labeled W)<sup>11</sup> band at 3756 cm<sup>-1</sup>, and a strong ClF doublet at 767 and 760 cm<sup>-1</sup>;<sup>12</sup> the absence of HCl bands indicates that no reaction occurred during deposition. Photolysis for 1 h produced new absorptions, which are shown in Fig. 1(b) as the difference in the absorbance between the spectrum after photolysis and the spectrum before photolysis of the deposited sample [Fig. 1(a)]. Sharp, new D' (for mixed dimer) bands appeared; these included 3897.3 cm<sup>-1</sup>, a 3:1 relative

intensity chlorine isotopic doublet at 2834.5 and 2832.5  $cm^{-1}$ , and sharp new site split bands at 3930 and 3928  $cm^{-1}$ . It should be noted that the 3897  $\text{cm}^{-1}$  band is partly due to the HF--ClF complex, which will be discussed in detail in a later paper.<sup>13</sup> In addition, a new absorption (labeled  $\mathbf{R}$ ) was observed at 3857.9  $cm^{-1}$ , and the HF monomer isotopic bands grew slightly while new HCl monomer isotopic bands appeared at 2889, 2887  $\text{cm}^{-1}$  and at 2869, 2867  $\text{cm}^{-1}$ . Secondary reaction products common to CIF photochemistry were observed at 1445 and 1442  $\text{cm}^{-1}$  (ClO<sub>2</sub>),<sup>14</sup> at 688 and  $677 \text{ cm}^{-1}$  (ClF<sub>3</sub>), and at 573 and 566 cm<sup>-1</sup> (ClF<sub>2</sub>).<sup>12</sup> Irradiating the matrix at 14 K for 1 additional h and recooling to 11 K also produced considerable changes. The D' and R absorptions as well as the HF and HCl monomer bands more than doubled in intensity. New absorptions at 3826, 2817 (labeled D), and  $3702 \text{ cm}^{-1}$  (labeled T) have been previously assigned to (HF)<sub>2</sub>, (HCl)<sub>2</sub>, and (HF)<sub>3</sub>, respectively.<sup>4,6</sup> Sharp new bands appeared at 3742, 3685, 2792, and 2775  $\text{cm}^{-1}$  (labeled T') and at 3795 cm<sup>-1</sup> (labeled R'); the latter is due to the F(HF)<sub>2</sub> complex.<sup>13</sup> In sharp contrast, the 3930 and 3928 cm<sup>-1</sup> bands were destroyed during the 14 K photolysis. The other experiments using H<sub>2</sub> and ClF had a similar growth and decay pattern for the product bands. FTIR scans in the far IR region revealed no new bands above the noise level.

#### HD+CIF

Two studies were performed with HD and ClF, and the product band positions are listed in Table I. Figure 1(c) displays the product region of the difference spectrum after a 1 h photolysis at 10 K of the matrix formed by codepositing Ar/HD = 100/1 and Ar/ClF = 200/1 samples. One major difference was observed between the H<sub>2</sub> and HD photo-



FIG. 1. (a) FTIR spectrum in the 4000–1900 cm<sup>-1</sup> region for Ar/isotopic molecular hydrogen = 100/1 mixture and Ar/CIF = 200/1 mixture codeposited at 10 K; (b) spectrum of H<sub>2</sub> and CIF samples after 1 h photolysis; (c) spectrum of HD and CIF samples after photolysis; (d) spectrum of D<sub>2</sub> and CIF samples after photolysis. The arrows denote chlorine isotopic splitting in the H–Cl or D–Cl stretching vibration.

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TABLE I. Absorptions  $(cm^{-1})$  of hydrogen bonded complexes produced by the photochemical reaction of molecular hydrogen and CIF or by association of HF and HCl on codeposition.

| $H_2 + ClF$          | HD + ClF       | $D_2 + ClF$      | Identification                       |
|----------------------|----------------|------------------|--------------------------------------|
| 3897.3               |                |                  | D' = (HF)(HCl)                       |
| 3857.9               | 3857.9         |                  | R = Cl-HF                            |
|                      | 2830.3         | 2830.3           | R = CI - DF                          |
| 3836,2822            |                |                  | $N_2(HF)(HCl)$                       |
|                      | 3837,2044      |                  | $N_2(HF)(DCl)$                       |
|                      |                | 2811,2043        | $N_2(DF)(DCl)$                       |
| 3795                 | 2789           | 2789             | $R' = F(HF)_2$                       |
| 3742,2775            |                |                  | $T' = (\text{HCl})(\text{HF})_2$     |
|                      | 3742,2777      |                  | T'                                   |
|                      | 2767           | 2718             |                                      |
| 3739                 |                | 2746             | $Cl(HF)_2$                           |
| 3685,2792            |                |                  | $T' = (\mathrm{HCl})_2(\mathrm{HF})$ |
|                      | 3684,2794      |                  | T'                                   |
|                      |                | 2705             | T'                                   |
| 2834.5,2832,5*       |                |                  | D' = (HF)(HCl)                       |
|                      | 2052.2,2049.3* |                  | D' = (HF)(DCl)                       |
|                      |                | 2051.5,2048.6*   | D' = (DF)(DCl)                       |
|                      | 2807.2         |                  | $D' = (\mathrm{HCl})(\mathrm{DF})$   |
|                      |                | 2806.5           | D' = (DCl)(DF)                       |
| 149,264 <sup>5</sup> |                |                  | D' = (HF)(HCl)                       |
|                      |                | 287 <sup>6</sup> | $D' = (\mathrm{DCl})(\mathrm{DF})$   |
|                      | 281°           |                  | $D' = (\mathrm{HCl})(\mathrm{DF})$   |
|                      |                | 203 <sup>6</sup> | D' = (DF)(DCl)                       |
|                      | 202°           |                  | $D' = (\mathrm{HF})(\mathrm{DCl})$   |

\* Chlorine isotopic doublets,

<sup>b</sup>Bands observed from codeposition of appropriate acids.

chemistry. In the HD experiments, two distinctly different D' species were created instead of the one formed in the  $H_2$  study.

#### D<sub>2</sub>+CIF

Three experiments with  $D_2$  produced bands very similar to the HD study, and the results are listed in Table I. Figure 1(d) presents the product region of the difference spectrum after a 1 h photolysis at 10 K of the matrix formed by depositing  $Ar/D_2 = 100/1$  with Ar/CIF = 200/1.

#### BrF+H<sub>2</sub>

Nine experiments were performed using H<sub>2</sub> and equilibrium BrF in solid argon. In the spectrum taken after codepositing  $Ar/H_2 = 100/1$  and equilibrated  $Ar/Br_2/F_2 = 50/1/$ 1, sharp HF monomer absorptions were observed at 3962, 3953, and 3919 cm<sup>-1</sup> as well as N<sub>2</sub>--HF, (HF)<sub>2</sub>, and (HF)<sub>3</sub> bands at 2881, 3826, and 3702  $\text{cm}^{-1}$ , respectively.<sup>4,15</sup> Several absorptions assigned to HF complexes<sup>13</sup> with F<sub>2</sub>, BrF, and  $Br_2$  from the equilibrium mixture were seen at 3915 (F<sub>2</sub>), 3857, 3845 (BrF), 3851, and 3841 cm<sup>-1</sup> (Br<sub>2</sub>). In addition, strong absorptions at 661, 659 and 596, 594  $cm^{-1}$  were due to BrF and BrF<sub>3</sub>,<sup>12</sup> respectively. Photolysis for 30 min produced sharp D' bands at 3814.6 and 2543.0 cm<sup>-1</sup>, R at 3830.5 cm<sup>-1</sup>, and a  $Br_2F_2$  doublet<sup>12</sup> at 555, 553 cm<sup>-1</sup>. It should be noted that this **R** absorption was also produced by photolyzing  $F_2$  with HBr in a separate experiment. Photolyzing at 14 K increased the intensity of these product bands. The other experiments using H<sub>2</sub> and BrF mixtures exhibited similar growth patterns.

# $HD(D_2) + BrF$

Parallel BrF studies were conducted with HD and  $D_2$ , and the results of these experiments are listed in Table II. In contrast to the ClF studies with HD and  $D_2$ , only one configuration of the D' species, (ABr)(AF) (A = H or D), was produced photochemically in the BrF system. The D' absorptions were observed at 3812.6, 2799.7, and 2542.3 cm<sup>-1</sup> for HD and at 2798.3 and 1827.8 cm<sup>-1</sup> for D<sub>2</sub>. For both HD and D<sub>2</sub>, a new **R** absorption appeared at 2811.3 cm<sup>-1</sup>.

#### HF+HCI

Numerous codeposition experiments in the mid- and far IR were conducted over a wide range of concentrations for HF and HCl as well as their deuterium counterparts. The results are presented along with CIF and H<sub>2</sub> photochemical results in Table I. In the HF and Cl codeposition experiments, strong monomer, dimer, and trimer absorptions of HF and HCl were present as well as weak bands due to nitrogen complexes with HF and HCl.<sup>3-7</sup> In addition to very strong D' and T' product bands, new product bands arising from the small nitrogen impurity were observed at 3835.2 and 2822.3 cm<sup>-1</sup>. In the far IR region, new medium intensity 264 and 149 cm<sup>-1</sup> absorptions in the HF + HCl system exhibited the same growth pattern as the D' bands in the mid-IR experiments. Likewise, new far IR bands in the HF plus HCl and DCl system and in the HCl plus HF and DF system correlate with appropriate mid-IR bands and are listed in Table I.

| $H_2 + BrF$   | HD + BrF         | $D_2 + BrF$   | Identification             |
|---------------|------------------|---------------|----------------------------|
| 3830.5        | 3830.5           |               | R = BrHF                   |
|               | 2811.3           | 2811.3        | R = Br-DF                  |
| 3814.6,2543.0 |                  |               | D' = (HBr)(HF)             |
|               | 3812.6           |               | D' = (DBr)(HF)             |
|               | 2799.7,2542.3    |               | D' = (HBr)(DF)             |
|               |                  | 2798.3,1827.8 | D' = (DBr)(DF)             |
| 3746,2499     |                  |               | $T' = (HBr)(HF)_2$         |
|               | 2749,2742        |               | T'                         |
| 3674          |                  |               | $T' = (HBr)_2(HF)$         |
|               | 2699             |               | $T' = (HBr)_2(DF)$         |
| 365ª          |                  |               | $T' = (HBr)(HF)_2$         |
|               | 294 <sup>b</sup> |               | T'                         |
| 320ª          |                  |               | $T' = (HBr)_{a}(HF)$       |
|               | 267 <sup>b</sup> |               | T'                         |
| 286ª          |                  |               | $\hat{D}' = (HBr)(HF)$     |
|               | 222p             |               | $\mathcal{D}' = (HBr)(HF)$ |

TABLE II. Absorptions  $(cm^{-1})$  of hydrogen bonded complexes produced by the photochemical reaction of molecular hydrogen and BrF or by association of HF and HBr on codeposition.

<sup>a</sup> From codeposition of HF and HBr mixtures.

<sup>b</sup> From codeposition of DF and HBr mixtures.

#### HF+HBr

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A similar codeposition study was performed with HBr and HF samples. The product band positions are listed in Table II along with the BrF and  $H_2$  results. Figure 2(a) shows the product region in the mid-IR of the spectrum after depositing Ar/HF = 200/1 and Ar/HBr = 100/1 samples. In addition to the absorptions seen previously in HF and HBr deposition experiments  $[D = (HF)_2 \text{ or } (HBr)_2;$  $T = (HF)_3 \text{ or } (HBr)_3]$  a very strong, sharp absorption (labeled D') was observed at 3814.5 cm<sup>-1</sup> while a considerably weaker D' band appeared at 2543.0 cm<sup>-1</sup>. Three other prod-



FIG. 2. FTIR spectra of hydrogen bromide-hydrogen fluoride sample in the 4000-3600 and 2600-2400 cm<sup>-1</sup> regions. (a) After codeposition of 32 mmol of Ar/HBr = 100/1 and 7 mmol of Ar/HF = 200/1 at 10 K for 6h; (b) after warming to 20 K and recooling to 10 K.

uct absorptions (labeled T') were seen at 3746, 3674, and 2449 cm<sup>-1</sup>. Warming the matrix to 20 K for 10 min produced considerable changes in the product band intensities which are shown in Fig. 2(b). The D' bands decreased slightly while the T' absorptions increased by over a factor of 2. Figure 3 is representative of the product region in the far infrared. The absorption at 286 cm<sup>-1</sup> as well as the bands at 365 and 320 cm<sup>-1</sup> had the same growth patterns as the D' and T' bands, respectively.

# $H_2 + Cl_2$

The  $H_2 + Cl_2$  photochemical reaction was examined in eight experiments using the techniques and conditions developed in the  $H_2 + F_2$  photolysis work.<sup>8</sup> Sharp weak HCl absorptions at 2888.0 and 2885.8 cm<sup>-1</sup> were observed in each spectrum taken after deposition. Photolysis of these samples increased the HCl monomer absorptions and produced a weak doublet at 2818.1 and 2816.2 cm<sup>-1</sup> (A > 0.05), which has been previously assigned to the  $H_b$  –Cl mode of (HCl)<sub>2</sub>.<sup>6</sup> No evidence (A < 0.002) was found for the weaker H<sub>a</sub>-Cl mode at 2855.5 cm<sup>-1</sup>. Photolyzing at 13-15 K produced weak absorptions at 2786.7 and 2785.7  $\text{cm}^{-1}$ , which are due to (HCl)<sub>3</sub>.<sup>6</sup> Six additional experiments were carried out with HD and  $D_2$ ; the principal photolysis products were the 2040.6, 2037.7  $cm^{-1}$  doublet with HD and the 2039.2, 2036.3 cm<sup>-1</sup> doublet with D<sub>2</sub>. These absorptions are due to  $D_b$ -Cl mode of (HCl)(DCl) and (DCl)<sub>2</sub>, respectively. No evidence was found here for the  $H_b$ -Cl mode in the other mixed dimer  $(D_a-Cl)(H_b-Cl)$ . As in the (HF)(DF)case,<sup>8</sup> the deuterium bonded form (HCl)(DCl) is probably more stable and thus formed preferentially in the (HD)(Cl<sub>2</sub>) photolysis experiments.



FIG. 3. FTIR spectra of hydrogen bromide-hydrogen fluoride samples in the 425-125 cm<sup>-1</sup> region. (a) After codeposition of 31 mmol of Ar/HBr = 75/1 and 25 mmol of Ar/HF = 300/1 at 10 K for 8 h; (b) after warming to 20 K and recooling to 10 K.

#### DISCUSSION

A model is proposed for the  $Ar/H_2/ClF$  and  $Ar/H_2/$ BrF systems, which is consistent with the photochemical observations. Identification of the mixed dimers and trimers as well as other photochemical intermediate species will be made.

#### Sample model

In the present experiments,  $Ar/H_2$  and Ar/XF (X = Cl or Br) samples were codeposited relatively slowly at 10 K. The deposited sample is expected to contain isolated H<sub>2</sub> and XF monomers and a major fraction of  $(H_2)(XF)$  heterodimers with smaller amounts of heterotrimers  $(H_2)_2(XF)$ and  $(H_2)(XF)_2$ . The presence of a small amount of HF impurity in the XF sample will also give heteromultimers containing HF. This heterodimer model is supported by similar  $(CH_4)(F_2)$  and  $(H_2)(F_2)$  experiments where the principal photolysis products were CH<sub>3</sub>F--HF and HF--HF, respectively.<sup>8,16</sup> The major photolysis products in the molecular hydrogen and ClF experiments were strong, sharp D' bands at 3897.3 cm<sup>-1</sup> and a doublet at 2834.5 and 2832.5 cm<sup>-1</sup>  $(H_2 + ClF)$ ; 2807.2 cm<sup>-1</sup> and a doublet at 2052.2 and 2049.3 cm<sup>-1</sup> (HD + ClF); and 2806.5 cm<sup>-1</sup> and a doublet at 2051.5 and 2048.6 cm<sup>-1</sup> ( $D_2$  + ClF). The sharp doublets are chlorine isotopic splittings for H-Cl or D-Cl stretching vibrations. Minor photolysis products included HF, DF, HCl, and DCl as well as sharp, weak R bands at 3857.9 and  $2830.3 \text{ cm}^{-1}$ . The principal photolytic products in the molecular hydrogen and BrF studies were sharp D' absorptions at 3814.6 and 2543.0 cm<sup>-1</sup> (H<sub>2</sub> + BrF); 3812.6, 2799.7, and 2542.3 cm<sup>-1</sup> (HD + BrF); and 2798.3 cm<sup>-1</sup> (D<sub>2</sub> + BrF). Minor R photolysis products were observed at 3830.5 and  $2811.3 \text{ cm}^{-1}$ . The relative intensities of the hydracid monomers, mixed dimers, and higher aggregates were substantially different from the codeposition experiments. Identification of these absorptions will now be considered.

#### Dimers

The strongest photolysis product bands in each experiment (labeled D' in Figures) are in agreement with the results from the corresponding codeposition experiments, and their assignments to the  $H_b$ -X and  $D_b$ -X (X = Cl or F) stretching modes of the hydrogen bonded position in the isotopic dimers <u>1-9</u> is substantiated.



In the HF and HCl codeposition experiments, mid- and far infrared absorptions provide evidence for only the 1 ar-

rangement, which is in agreement with molecular beam studies.<sup>1</sup> The far infrared absorptions marked D' exhibited the same growth pattern as the strong, mid-IR D' dimer absorptions produced by codeposition. The 264  $cm^{-1}$  absorption and the weaker  $149 \text{ cm}^{-1}$  band are assigned to the librational or bending modes of  $H_h$ -Cl and  $H_a$ -F, respectively, in (HF) (HCl). These frequencies for the librational modes of (HF)(HCl) are quite reasonable when compared to the corresponding librational modes of  $(HF)_2$  (189  $(cm^{-1})^8$  and  $(HCl)_2$  (232 cm<sup>-1</sup>).<sup>17</sup> The  $v_{lb}$  mode (264)  $cm^{-1}$ ) of (HF) (HCl) dimer is substantially higher than the  $v_{lb}$  mode (232 cm<sup>-1</sup>) of (HCl)<sub>2</sub> dimer. Since H<sub>a</sub>-F is a smaller base than  $H_a$ -Cl, the orientation of  $H_b$ -Cl to  $H_a$ -F is more critical which limits the librational motion of the H<sub>b</sub>-Cl. In addition, the  $v_{la}$  mode (149 cm<sup>-1</sup>) of (HF)(HCl) is considerably lower than the  $v_{la}$  mode (189 cm<sup>-1</sup>) of (HF)<sub>2</sub>. The H<sub>b</sub>-Cl submolecule weakens the H<sub>a</sub>-F mode more than the  $H_b$ -F mode because HCl forms a stronger hydrogen bond to HF than HF does.

The observation of two product bands between 200 and  $300 \text{ cm}^{-1}$  for the DF + DCl system requires that two different dimer structures are formed and trapped. Four absorptions are assigned based on isotopic shifts and growth patterns to the  $D_{h}-X$  (X = F or Cl) librational motion for mixed dimers 2-5. The  $v_{lb}$  mode of (DCl)(DF) is 6 cm<sup>-1</sup> higher than  $v_{lb}$  of (HCl)(DF) while  $v_{lb}$  of (DF)(DCl) is only 1 cm<sup>-1</sup> higher than  $v_{lb}$  of (HF) (DCl). Since the librational amplitude of the deuterated bases are smaller than their hydrogen counterparts, the complexes with deuterated bases are less flexible, which allows these complexes to form a slightly more rigid hydrogen bond. The H/D ratio of the  $v_{lb}$  mode for (HCl)<sub>2</sub> is 1.24 which is slightly less than the H/ D ratio of 1.30 for (HF) (HCl). The H/D ratio for this librational mode increases as the size of the base decreases. Since the librational motion of D is more restricted than H, D is less influenced by size of the base than H. The relatively small 6 cm<sup>-1</sup> shift for the  $D_{h}$ -F librational modes for dimers 3 and 5 indicates that the HCl-DF coupling is considerably less than the DF-DF coupling which produces an 18-19  $cm^{-1}$  shift between (HF)(DF) and (DF)<sub>2</sub>.<sup>8</sup>

Likewise in the HBr and HF codeposition experiments, the far infrared band marked D' in Fig. 3 exhibited the same growth pattern as the strong, sharp D' absorption in the mid-IR. The 286 cm<sup>-1</sup> absorption is assigned to the H<sub>b</sub>-F librational mode in (HBr) (HF); a similar 222 cm<sup>-1</sup> band is due to the D<sub>b</sub>-F librational mode in the deuterium substituted (HBr) (DF) species. The H/D ratio for this mixed dimer is 1.29 which is slightly smaller than the H/D ratio of 1.33 for (HF)<sub>2</sub>. This observation again illustrates the inverse relationship between the H/D ratio of  $v_{lb}$  and the size of the base.

In the mid-IR, the photolysis experiments with ClF and BrF and HD are of particular interest. Photolyses of ClF with HD produced a strong absorption at 2807.2 cm<sup>-1</sup> and a sharp 3:1 relative intensity doublet at 2052.2, 2049.3 cm<sup>-1</sup>; these absorptions were also observed in the appropriate codeposition experiments. The sharp 2807.2 cm<sup>-1</sup> band is clearly due to the  $D_b$ -F stretching mode of a dimer based on the observation<sup>4</sup> of (DF)<sub>2</sub> at 2803.5 cm<sup>-1</sup>, and the 2052.2, 2049.3 cm<sup>-1</sup> chlorine isotopic doublet is due to the  $D_h$ -Cl stretching mode of a dimer complex owing to proximity to  $(DCl)_2$  absorption<sup>6</sup> at 2039.2 cm<sup>-1</sup>. The production of only these two strong absorptions from the (HD)(ClF) photochemical reaction in the matrix cage verifies that only (HCl)(DF) and (HF)(DCl) dimer arrangements are formed. The formation of only these two mixed dimers, therefore, demonstrates the greater stability of D than H in the hydrogen bonding role.<sup>8,18</sup> Similarly, photolysis of HD and BrF produced two sharp absorptions at 3812.6 and 2799.7 cm<sup>-1</sup>. The 3812.6 cm<sup>-1</sup> band is assigned to the  $H_b$ -F mode of (DBr)(HF) while the 2799.7 cm<sup>-1</sup> band is clearly due to the  $D_b$ -F mode of (HBr)(DF). The (DBr)(HF) species is unique; this mixed dimer is only the second observed case of the hydrogen bond being formed by H when a D was available. The first case is (DF)(HF) which was formed in low yield by photolyzing HD and F2.8 The population ratio of (DBr)(HF) to (HBr)(DF) was near 1/1, which is considerably higher than the (DF)(HF)/(HF)(DF) population ratio (1/17). This observation shows that hydrogen fluoride, regardless of deuteration, forms a much stronger hydrogen bond than hydrogen bromide.

It is of interest that any hydracid dimer products of the  $H_2 + ClF$  (BrF) reactions are trapped in the photolysis experiments, since the matrix cage must remove at least 119 kcal/mol of reaction exothermicity (based on bond energies) plus the dimerization energy for the mixed dimers to be stabilized. This observation attests to the rapid quenching ability of the solid argon matrix.

#### Trimers

The sharp product absorptions labeled T' were favored relative to the D' bands at slightly higher temperatures in both the photolysis (14–16 K) and codeposition (20–22 K) experiments. In the photolysis studies, the T' bands were stronger in the experiments containing more hydracid monomer. Clearly, the T' bands cannot be due to the same species as the D' band; T' absorptions must involve more HX than the mixed dimers. Due to the close proximity of these new product bands to the (HX)<sub>3</sub> (X = F, Cl, and Br),<sup>6,8</sup> absorptions, cyclic mixed trimer assignments are made for the T' bands, based on relative hydracid concentrations.

#### **CI---HF and Br---HF radicals**

For the past two decades, attempts to identify and characterize hydrogen dihalide radicals, XHX, have proven unsuccessful for the most part, since the controversy over (ClHCl) radical has been settled in favor of (ClHCl)<sup>-</sup> anion.<sup>19-21</sup> Nevertheless, infrared evidence has been obtained for a weakly bound Cl--HF complex formed by photolyzing HCl with  $F_2$ ,<sup>22</sup> and for the more weakly bound Cl--HCl radical complex isotopic doublet at 2836.4 and 2834.5 cm<sup>-1</sup>.<sup>13</sup> The minor product **R** absorption in the H<sub>2</sub> and ClF photolysis study at 3857.9 cm<sup>-1</sup> is due to the same Cl--HF complex, which is in agreement with the previous work after frequency calibration. The Cl--HF complex was formed by F atom abstraction of hydrogen from HCl in the previous work and by H atom escaping the matrix cage during the  $H_2$  and ClF photochemical reaction in the present work. The deuterium counterpart for this radical was observed here at 2830.2 cm<sup>-1</sup>, and this HF/DF ratio (1.363) is characteristic of a H–F fundamental vibration in a weak complex. In the photolysis experiments containing large amounts of Cl--HF radical and HF impurity, a new absorption (labeled **R**') at 3739 cm<sup>-1</sup> is assigned to the Cl--(HF)<sub>2</sub> complex. The **R**' bands have the same growth pattern as the 3795 cm<sup>-1</sup> band which has been recently assigned to the F--(HF)<sub>2</sub> radical.<sup>13</sup>

In addition to the Cl--HF complex, the band at 3830.5 cm<sup>-1</sup> (labeled **R**) in the H<sub>2</sub> and BrF photolysis experiments is due to the analogous Br--HF complex. This radical had the same growth pattern as the Cl--HF radical, the **R** band did not appear until the first photolysis, and it grew by more than a factor of 3 during later photolyses at 14–16 K. The 3830.5 cm<sup>-1</sup> absorption was also produced in this laboratory by photolyzing F<sub>2</sub> with HBr. The deuterium counterpart was seen at 2811.3 cm<sup>-1</sup>, and its DF/HF ratio is the same as the chlorine radical counterpart. Comparison of the 3858 and 3830 cm<sup>-1</sup> HF fundamentals shows that a bromine atom interacts more strongly with HF than a chlorine atom, which is expected owing to the higher polarizability of atomic bromine.

# N<sub>2</sub>-HF-HCI

Two absorptions at 3836 and 2822 cm<sup>-1</sup> were observed in the HF and HCl codeposition experiments. The bands were not seen in the HF or HCl blank experiments nor in the  $H_2 + ClF$  photolysis experiments. These bands have the same growth pattern as the  $N_2$ -(HF)<sub>2</sub> band at 3788 cm<sup>-1</sup>, which arose from nitrogen impurity in the samples. The 3836 and 2822 cm<sup>-1</sup> absorptions are assigned to the  $H_a$ -F and the H<sub>b</sub>-Cl modes of N<sub>2</sub>-HF--HCl, respectively. These absorptions are red shifted from the corresponding band at 3897 and 2834  $\text{cm}^{-1}$  or the (HF)(HCl) dimer due to the hydrogen bonding interactions betwen  $N_2$  and (HF)(HCl) dimer. It is readily seen that the effect of  $N_2$  on the  $H_a$ -F mode is greater than the effect on the  $H_b$ -Cl mode. Similar arguments can be made for two additional N<sub>2</sub> complexes containing isotopic hydrogen fluoride and hydrogen chloride.

#### Bonding trends and comparisons

The configurations of the more stable mixed hydracid dimers (all H) are (HF)(HCl), (HCl)(HBr), (HBr)(HCl), and (HBr)(HF). While the lack of a definite bonding trend is surprising, this series of mixed dimers clearly illustrates the complexity of the hydrogen bonding phenomenon. Nonetheless, the (HF)(HCl) and (HBr)(HF) dimers do provide information about the relative basicity of these hydracids. Since the H<sub>b</sub>-Cl mode is 2834 cm<sup>-1</sup> for (HF)(HCl), 2818 cm<sup>-1</sup> for (HCl)<sub>2</sub>, and 2801 cm<sup>-1</sup> for (HBr)(HCl), the base strength is HBr > HCl > HF when HCl is serving as the proton donor. This trend is also repeated with the D<sub>b</sub>-F modes in dimers (HF)(DF), (HCl)(DF), and (HBr)(DF) with HF (2809 cm<sup>-1</sup>), HCl (2807 cm<sup>-1</sup>), and HBr (2800 cm<sup>-1</sup>). In sharp contrast, *ab initio* molecular orbital calculations<sup>2</sup> using a 4-31G basis set were not sensitive enough to correctly predict this relative basicity trend. However, this theoretical study did predict that the (HF)(HCl) arrangement was more stable than (HCl)(HF), which is in agreement with matrix infrared and molecular beam electric resonance investigations.<sup>1</sup> Similarly, based on the  $H_b$ -F mode for (HF)<sub>2</sub> at 3826 cm<sup>-1</sup> and for (HBr)(HF) at  $3815 \text{ cm}^{-1}$ , HBr is a slightly better electron donor than HF when HF is the acceptor. Another interesting trend involves the effect of base deuteration on the D' bands for three mixed dimers. For the (HBr)(HF), (HCl)(DF), and (HF)(DCl) mixed dimers, the  $H_b$ -F or  $D_{h}$ -X absorptions are red shifted by 0.7-2.0 cm<sup>-1</sup> when the base (submolecule a) is deuterated. Since the librational amplitudes of the deuterated bases are smaller than their hydrogen counterparts, the complexes with deuterated bases are slightly more rigid, which allows these complexes to form a

slightly stronger hydrogen bond. A final trend was observed for the absorptions of both HF/HCl and HF/HBr mixed trimers. The HX mode of  $(HX)_2(HY)$  is blue shifted from its corresponding  $(HX)_3$  mode while the HY mode of  $(HX)_2$  (HY) is red shifted from its corredponding  $(HY)_3$ mode.

#### CONCLUSIONS

H<sub>2</sub> and ClF (BrF) at high dilutions in argon were condensed on a 10 K substrate without reaction. Photolysis to initiate the reaction between ClF and H<sub>2</sub> produced major sharp infrared absorptions at  $3897.3 \text{ cm}^{-1}$  and an isotopic doublet at 2834.5 and 2832.5 cm<sup>-1</sup>, while photolysis of  $H_2$ and BrF samples gave a band at  $3814.6 \text{ cm}^{-1}$ . These absorptions are in agreement with the bands produced in the correponding codeposition experiments and assigned to (HF)(HCl) and (HBr)(HF) heterodimers, respectively. The results support the model that a major fraction of the H<sub>2</sub> and ClF (BrF) in this study is trapped as  $H_2$ --ClF(BrF) pairs. The matrix must dissipate at least 119 kcal/mol of reaction exothermicity plus dimerization energy for the mixed dimers to be stabilized. The photolysis of CIF with HD produced only two mixed dimers, (HF)(DCl) and (HCl)(DF). These dimers clearly illustrate the added stability of forming the hydrogen bond with deuterium instead of hydrogen. Photolyzing HD with BrF also produced two mixed dimers, (HBr)(DF) and (DBr)(HF). However, hydrogen fluoride hydrogen bonds to the hydrogen bromide regardless of the deuterium position indicating that the greater basicity of hydrogen bomide dictates that the fluoride will be the acid. Preferential trapping of the more stable mixed dimers indicates that sampling of the potential surface is essentially under thermodynamic control in these experiments.

Photolyzing ClF (BrF) with molecular hydrogen at 14– 16 K produced several weaker bands, which are in agreement with absorptions assigned to cyclic trimers in the appropriate codeposition experiments based on sample concentration and annealing behavior. The lack of substantial photochemical yield at 10 K of these absorptions clearly demonstrates that the bands are not due to a dimer species. The photochemical production of the hydracid monomers can be rationalized by two distinctly different ways. First, a hydracid may escape the matrix cage during the photochemical reaction. Second, some ClF (BrF) is trapped without  $H_2$  in the matrix cage, and the halogen atoms which are produced during photolysis can diffuse and react with  $H_2$  at 12 K and with hydracid monomers at 12–16 K. Some of the former are trapped as hydracid monomer while some of the latter are trapped as Cl--HF and Br--HF. This work provides evidence that atomic bromine is a stronger base than atomic chlorine.

Photolysis of  $H_2$  and ClF (BrF) in a solid argon matrix at 10 K provides a unique way to form a large quantity of mixed dimers without higher aggregates. Photolyzing at 14– 16 K provides a method for stepwise association of hydracid to form successive generations of cyclic mixed trimers and higher aggregates which can be identified from their matrix infrared spectra. These studies demonstrate that molecular hydrogen can be used successfully as a reagent in argon matrix photochemical reactions up to 16 K.

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