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Infrared spectra of OC–HX hydrogen-bonded complexes in solid argon

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The hydrogen-bonded complexes OC–HX (X = F, Cl, Br) has been prepared by condensing Ar/HX and Ar/CO reagent mixtures at 12 K. FTIR spectra of the complexes are characterized by strong H–X absorptions (v_s) displaced below the isolated HX fundamental, strong C–O absorptions displaced above the isolated CO fundamental, and sharp degenerate librational modes (v_l) in the far infrared. Observation of a single degenerate v_l mode indicates linear structures for the complexes. The displacements Δv_s and Δv_{CO} for the complexes decrease in magnitude in the series HF > HCl > HBr in direct relationship with the trend in hydrogen bonding strength for the hydrohalic acids.

INTRODUCTION

Weakly bound molecular dimers have been characterized recently by radiofrequency and microwave spectra. The OCO--HF and OC--HF complexes are of particular interest owing to hydrogen bonding to oxygen in the former and carbon in the latter case, and the different 1.91 and 2.12 Å internuclear hydrogen bond distances, respectively.[1,2] The matrix infrared spectrum provides complementary information on bonding and structure in the complex by comparing submolecule modes in the complex with molecular spectra and by symmetry imposed splitting of vibrational modes in the complex. The FTIR matrix spectrum of OCO--HF exhibited a v_s(HF) mode at 3871 cm^{-1}, 83 cm^{-1} below the isolated HF value, and a sharp single v_l (HF) librational mode at 313 cm^{-1} supporting the linear geometry of the complex.[3] The analogous OC--HF, OC--HCl, and OC--HBr complexes have been prepared for FTIR matrix isolation study in order to learn more about molecule–molecule interactions from the vibrational spectra of the weakly bound dimers.

EXPERIMENTAL

The vacuum and cryogenic systems and techniques used in the present matrix isolation experiments have been described previously.[4] Details of the FTIR spectroscopy have also been reported in this journal[3]; spectra were obtained at 1.0 cm^{-1} resolution from 400 to 4000 cm^{-1} and at 2.0 cm^{-1} from 125 to 425 cm^{-1}; wave number accuracy is ±0.3 and ±0.5 cm^{-1}, respectively. Hydrogen and deuterium fluoride were prepared by reacting the elements (Matheson) at low pressure in a well-passivated stainless steel vacuum system. Carbon monoxide and hydrogen chloride (Matheson) were used as received; hydrogen bromide (Matheson) was condensed to evacuate H$_2$ and evaporated at − 78 °C to hold any less volatile contaminants; DCl (Merck and Co.) was exchanged for a week in a vacuum manifold heated to about 50 °C and fresh DCl was used for the experiments.

RESULTS

HF + CO

A group of experiments was conducted with Ar/HF = Ar/CO = 300/1 samples co-deposited at 12 K. The HF blank contained the strong 3962.3, 3953.8 cm^{-1} monomer doublet, weaker HF-related species at 3919, 3881, and 3826 cm^{-1}, and HF dimer at 3702 cm^{-1} in the HF stretching region[5] and at 446, 402, and 263 cm^{-1} in the far-IR. The CO blank exhibited a strong completely absorbing CO monomer fundamental at 2138 cm^{-1} and a trace of water at 3756 and 1624 cm^{-1}; an early scan revealed the sharp CO fundamental at 2138.3 cm^{-1} and a weak sharp 2149.1 cm^{-1} band. The 2149.1 cm^{-1} band maintained constant relative intensity with H$_2$O impurity absorptions, which supports its earlier assignment to the OC--H$_2$O complex.[6] After simultaneous co-condensation of the HF and CO reagents over an 18 h period, the FTIR spectrum revealed very strong, sharp new 3789.3 and 2162.4 cm^{-1} product absorptions and weaker bands at 3772, 3646, and 2171 cm^{-1}. This sample was temperature cycled 12–24–12 K; the strong 3789.3 and 2162.4 cm^{-1} bands increased slightly, the sharp product absorptions at 3772.5, 3645.7, and 2170.5 cm^{-1} increased fourfold, sharp new bands appeared at 3697.5, 3586.4, 2160.5, and 2178.7 cm^{-1}, and broad higher polymer absorptions were observed in the 3000–3400 cm^{-1} region. A similar sample was prepared for examination in the far-IR; the spectrum revealed a single sharp product band at 389.6 cm^{-1}.

Another experiment was done co-depositing separate Ar/HF = Ar/CO = 600/1 samples at 12 K for 9 h. The major bands were the HF doublet at 3962.3, 3953.7 cm^{-1}, the sharp 3789.3 cm^{-1} product (A =absorbance units = 0.28, FWHM = 2.2 cm^{-1}, labeled v_s), water vibration-rotation bands[7] at 3776.0, 3756.4, 3723.5, 3711.0, 3669.6, and 3653.3 cm^{-1} (labeled W) and H$_2$O–HF complex[8] (labeled W^c) at 3554.6 cm^{-1}, which are illustrated in Fig. 1(a); a sharp 2162.4 cm^{-1} product band (A = 0.10, FWHM = 1.0 cm^{-1}) is not illustrated. The sample was temperature cycled 12–20–12 K over a 5 min period, and the HF monomer band at 3962.3 cm^{-1} decreased (A = 0.61 to 0.59) slightly while the 3789.3 cm^{-1} product increased 80%, a weak HF dimer band appeared at 3702 cm^{-1} and weak new bands appeared at 3771.7 cm^{-1} (A = 0.03) and 3645.7 (A = 0.034), as shown in Fig. 1(b); the 3756 cm^{-1} water band decreased by 15% and the 3554 cm^{-1} H$_2$O--HF band increased by 50%. Weak new bands also appeared at 2168.4–2170.5 and 2160.5 cm^{-1} (A = 0.004) around the 2162.4 cm^{-1} product which increased by 80%. The
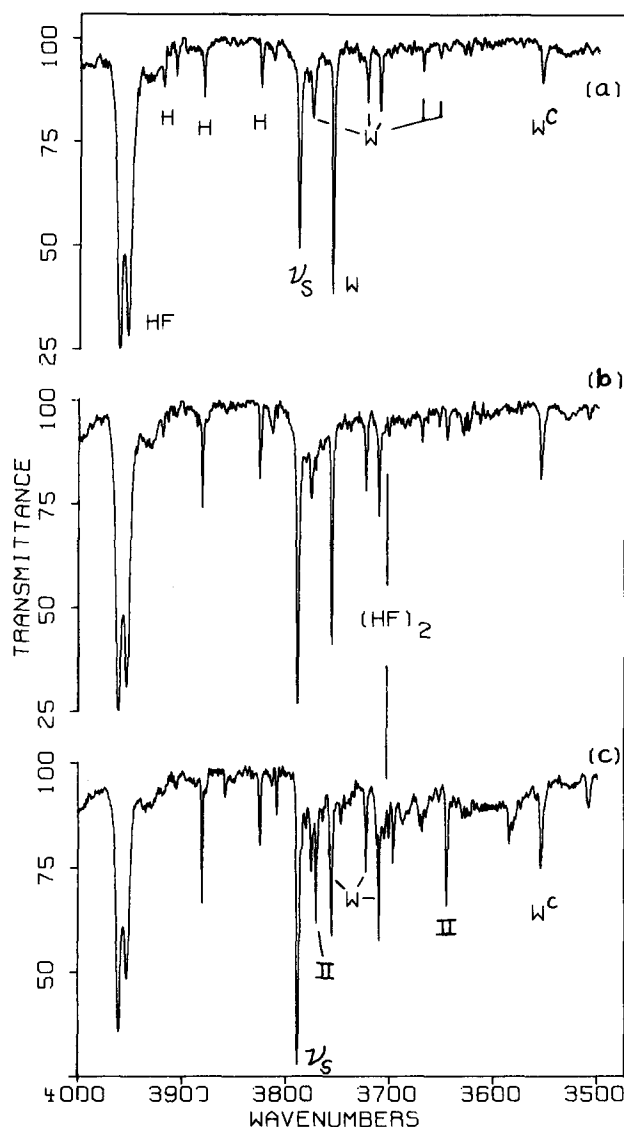
FIG. 1. The FTIR spectrum in the 3500–4000 cm^{-1} region for Ar/HF = Ar/CO = 600/1 samples codeposited at 12 K is shown in trace (a). The effect of temperature cycling the sample 12–20–12 K is illustrated in scan (b), and spectrum (c) shows the effect of a 12–22–12 K cycle. HF monomer is so labeled, H denotes HF related species present in the HF sample, W identifies water absorptions, and W^c denotes the H$_2$O--HF complex. The ν_s band is assigned to complex I, identified in the text; complex II bands are so designated.

sample was then warmed 12–22–12 K over a 10 min period, and the 3962 cm^{-1} HF band decreased (to A = 0.41), the 3789.3 cm^{-1} product increased less than 10%, the 3702 cm^{-1} HF dimer band doubled, the 3771.7 and 3645.7 cm^{-1} bands increased a factor of 5, and the 3554 cm^{-1} H$_2$O--HF band increased another 20%, as is illustrated in Fig. 1(c). The sharp 2162.4 cm^{-1} band was unchanged within 10% and the 2160.5 cm^{-1} shoulder increased (to A = 0.03), the 2170.5 cm^{-1} band increased (to A = 0.02) and a new 2178.7 cm^{-1} band appeared (A = 0.01). Additional bands at 3697, 3586, 3508, 3697, 3433, and 3403 cm^{-1} were produced on this warming cycle. The 3776.0, 3723.5, and 3711.0 cm^{-1} water vibration-rotation bands increased slightly

and the 3756.4 cm^{-1} band decreased on temperature cycling consistent with changes in nuclear spin isomers, since the spectra recorded immediately after the thermal cycle are characteristic of the nuclear spin distribution of the higher temperature.[9] The 3723.5 cm^{-1} "water" band was substantially stronger with CO present, which suggests that some of this absorption might be due to a OC--H$_2$O complex. A further 12–24–12 K cycle had little effect on the spectrum.

Two experiments were done with water added in the ratio Ar/H$_2$O = 3600/1; in the first experiment, a sample of Ar/CO/H$_2$O = 3600/6/1 was codeposited with an Ar/HF = 600/1 sample for 20 h. The water bands given above were, of course, substantially stronger, and the 2149.1 cm^{-1} OC–H$_2$O band and 3554.6 cm^{-1} H$_2$O–HF absorption were increased approximately tenfold. The new product bands were observed at 3789.1 and 2162.4 cm^{-1} with approximately the same absorbances as in the Fig. 1 experiment. Thermal cycling the sample to 19 K for 10 min and then to 22 K for 10 min had a similar effect to that described above. The 3789.1 cm^{-1} band increased then decreased while new bands were produced at 3771.8, 3645.8, and 2170.5 cm^{-1} with approximately the same absorbances given above and weak new bands appeared at 3697.5, 3586.5, 2160.5, and 2178.7 cm^{-1}. Finally, bands at 3508 and 3457 cm^{-1} increased substantially on sample warming and were more intense than in the previous experiment, and the weak 3433 and 3403 cm^{-1} bands were observed as before. In the second experiment, Ar/H$_2$O = 3600/1 and Ar/HF = 600/1 samples were codeposited for 20 h; the water bands and H$_2$O--HF complex band[8] were observed as in the previous experiment without any of the product bands from the CO doped experiments. Spectra recorded after 9 h of sample condensation in the 3600/1 experiments provide an approximate measure of the water impurity concentration in Fig. 1 as Ar/H$_2$O ≈ 10 000/1; however, most of the water impurity in these experiments probably desorbs from the walls of the vacuum vessel in the first 1–2 h so the actual H$_2$O impurity concentration varies somewhat during the deposition period.

Figure 2 illustrates spectra of samples prepared by co-depositing HF/DF mixtures with CO. For the first experiment Ar/HF, DF = Ar/CO = 600 /1 samples (15 mmol each) were condensed for 9 h; in addition to the HF doublet at 3962.6, 3953.7 cm^{-1}, the strong sharp DF monomer band was observed at 2895.7 cm^{-1}. New product bands were observed at 3789.4 (A = 0.18, FWHM = 2.0 cm^{-1}) and 2781.2 cm^{-1} (A = 0.39, FWHM = 1.8 cm^{-1}) (labeled ν_s) and 2163.4 cm^{-1} (A = 0.18, FWHM = 1.0 cm^{-1}) (labeled ν_{CO}) with a 2162.4 cm^{-1} shoulder (A = 0.07). The far infrared spectrum of a different sample prepared by condensing Ar/HF, DF = Ar/CO = 300/1 samples (36 mmol each) for 20 h revealed sharp bands at 389.5 (A = 0.17, FWHM = 5.3) and 305.0 cm^{-1} (A = 0.31, FWHM = 3.5 cm^{-1}) (labeled ν_t). Sample warming to 22 K again produced the sharp new 3772.5 and 3645.7 cm^{-1} bands, and deuterium counterparts at 2769.6 and 2686.4 cm^{-1}. In the far-IR, the 389.5 cm^{-1} band absorbance increased threefold and
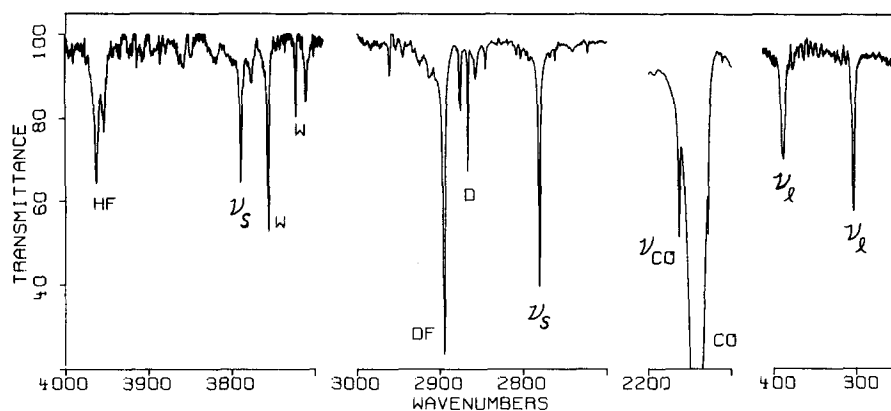
FIG. 2. FTIR spectra of samples prepared by condensing Ar/HF, DF = Ar/CO = 600/1 mixtures at 12 K in the mid-IR and Ar/HF, DF = Ar/CO = 300/1 mixtures in the far-IR. (DF/HF ≈ 3/1). W denotes water absorptions and D identifies DF related species from the sample.

split into a sharp 390.4–388.6 cm^{-1} doublet, and the 305.0 cm^{-1} band tripled without showing any changes in band contour.

HCl + CO

A series of experiments was done with Ar/HCl = Ar/CO = 200/1 samples codeposited at 12, 15, and 20 K. When the gas mixtures were deposited at 20 K, strong product bands were observed at 2815.7, 2813.7, 2810.1, 2803.2, and 2154.2 cm^{-1} with a strong 2152.8 cm^{-1} shoulder, and a weaker band was observed at 2791 cm^{-1}. These bands correspond closely to those assigned to CO-(HCl)$_x$ species by Hallam *et al.*[10] Far-infrared examination of a similar sample revealed a strong, sharp 247.1 cm^{-1} band (labeled ν_l) and a weaker 232 cm^{-1} absorption, which are illustrated in Fig. 3(a); the latter band has been assigned to (HCl)$_2$ by Katz *et al.*[11] Three experiments were done on the

Beckman IR-12 using a 15 K substrate to correlate the 240 and 2800 cm^{-1} regions in the same experiment. Increasing the HCl concentration favored the 232 cm^{-1} band relative to the 247 cm^{-1} band and the 2803 cm^{-1} band relative to the 2815 cm^{-1} band, and decreasing the HCl concentration to half of the CO concentration produced only the 2815.7, 2813.7 cm^{-1} doublet in the 2800 cm^{-1} region and both of the 247 and 232 cm^{-1} bands in the far-IR.

The spectrum from a sample prepared by co-depositing 12 mmol of an Ar/CO = 500/1 sample with 4 mmol of Ar/HCl = 100/1 at 12 K over a 6 h period is shown in Fig. 3(a). Sharp HCl monomer[12] bands were observed at 2888.0 and 2853.3 cm^{-1}, a sharp product band was observed at 2815.1 cm^{-1} with a 2813.3 cm^{-1} shoulder (labeled ν_s), a new relatively sharp band appeared at 2664.3 cm^{-1} (labeled W^c), which was absent in experiments with very little water contamination, and
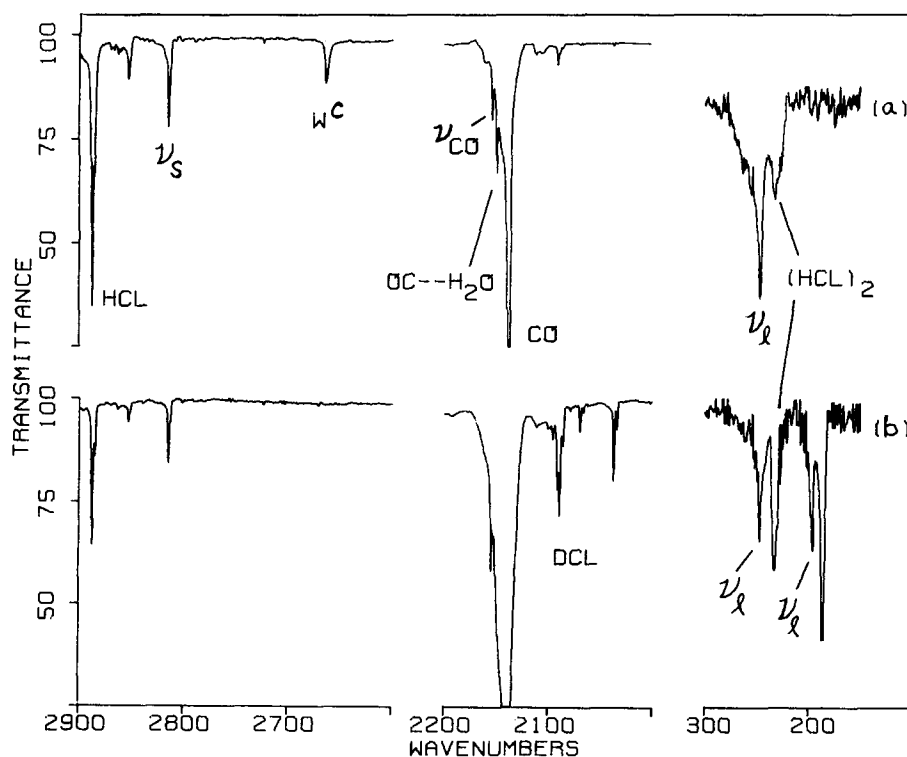

FIG. 3. Infrared spectra of hydrogen chloride–carbon monoxide samples. (a) mid-IR, Ar/HCl/CO ≈ 700/2/1 deposited at 12 K; far-IR, Ar.HCl/CO ≈ 600/2/1 deposited at 20 K. (b) mid-IR, Ar/HCl, DCl/CO ≈ 600/1.5/1 deposited at 12 K, DCl/HCl ≈ 1/1; far-IR, Ar/HCl, DCl/CO ≈ 600/2/1 deposited at 20 K, DCl/HCl ≈ 3/2. W^c denotes H$_2$O--HCl complex.
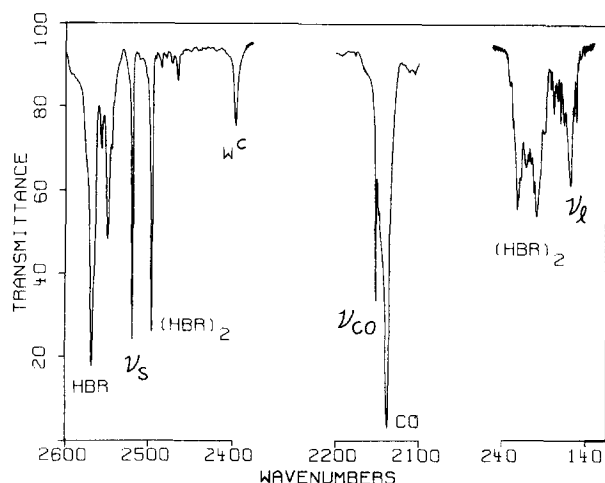
FIG. 4. Infrared spectra of hydrogen bromide—carbon monoxide samples. mid-IR, Ar/HBr/CO = 600/1/1 deposited at 12 K; far-IR, Ar/HBr/Co = 400/2/1 deposited at 20 K. W^c denotes H_2O--HBr complex.

sharp 2154.3 and 2149.3 cm^{-1} bands (labeled ν_{CO} and OC--H_2O) were observed on the side of the strong CO absorption at 2138.3 cm^{-1}.

Infrared spectra from experiments using DCl/HCl reagent mixtures are illustrated in Fig. 3(b). The HCl monomer bands and the ν_s product band were observed at 2888.0, 2853.3, and 2815.2, DCl counterpart bands were observed at 2089.6 and 2069.8 cm^{-1}, the ν_s counterpart at 2037.6 cm^{-1} exhibited a resolved splitting at 2034.5 cm^{-1}, and a sharp new band was observed at 2154.2 cm^{-1} in a final sample with (HCl + DCl)/CO ≈ 1/1 deposited at 12 K. The far-IR revealed the 247.1 and 232 cm^{-1} bands, observed in HCl experiments, and new 196.3 and 187 cm^{-1} bands due to the DCl reagent from a final sample with (HCl + DCl)/CO ≈ 2/1 deposited at 20 K.
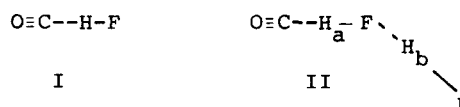
HBr + CO

Four experiments were done with hydrogen bromide and carbon monoxide and the results are summarized in Fig. 4. A 10 mmol sample of Ar/HBr = 400/1 was deposited at 12 K for 6 h and the HBr monomer bands were observed at 2568.4 and 2549.6 cm^{-1}, HBr dimer[12] was observed at 2496.5 cm^{-1}, and a new band appeared at 2395.4 cm^{-1}. Another experiment was done with Ar/CO/HBr = 600/1/1 concentrations and sharp 2520.1 cm^{-1} (ν_s) and 2152.4 cm^{-1} (ν_{CO}) product bands appeared in the spectrum. In the far-IR, a 20 mmol sample of Ar/HBr = 100/1 deposited at 20 K revealed new bands at 221 and 198 cm^{-1}; codeposition of a similar HBr sample with CO diluted in argon (300/1) gave the sharp, new product band at 158.3 cm^{-1} (labeled ν_l) and the 221 and 198 cm^{-1} bands [labeled (HBr)$_2$].

DISCUSSION

The hydrogen-bonded complexes will be identified from their infrared spectra; the structure of the complexes and bonding trends will be considered.

Identification

The major product absorptions of the CO and HF cocondensation reaction at 3789.3 and 2162.4 cm^{-1} increased substantially in concert on 12–20–12 K sample warming to allow controlled diffusion and reaction of HF in the cold matrix; they increased less than 10% on a 12–22–12 K cycle, which markedly increased 3771.7, 3645.9, and 2170.5 cm^{-1} bands. The major product bands are assigned to the hydrogen bonded complex I, and the 3771.7, 3645.9, and 2170.5 cm^{-1}

$$O\equiv C--H-F \qquad\qquad O\equiv C--H_a- F_{\diagdown}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad {}^{\diagup}H_b$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad {}_{\diagdown}F$$
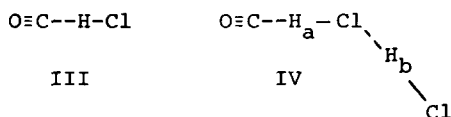$$\quad I \qquad\qquad\qquad\qquad\qquad II$$

absorptions favored at higher HF concentration and on sample warming are identified with complex II, where the OC--HF arrangement is taken from the microwave study.[2] The weak 3697.5, 3586.4, 2160.5, and 2178.7 cm^{-1} bands produced on sample warming in 600/1 experiments were sixfold stronger on warming in 300/1 experiments, which associates these bands with higher aggregate $(OC)_x(HF)_y$ species. The enriched water experiment did not change the intensities of the above absorptions which shows conclusively that these absorptions are not due to H_2O-containing species, although the weak bands at 3508 and 3457 cm^{-1} might be due to ternary complexes. Owing to their proximity to the 3953.7 cm^{-1} HF fundamental and their HF/DF ratios, 3789.3/2781.2 = 1.3625, 3771.7/2769.6 = 1.3618, 3645.9/2686.4 = 1.3572, which are near the HF/DF monomer fundamental ratio (1.3654), the 3789.3, 3771.7, and 3645.9 cm^{-1} absorptions are clearly due to H-F stretching vibrations. The 3789.3 cm^{-1} absorption is assigned to ν_s, the H-F stretching mode, in complex I. The 2162.4 cm^{-1} absorption above the C–O fundamental at 2138.3 cm^{-1} shows a small shift to 2163.4 cm^{-1} in DF experiments which shows that this CO species is associated with hydrogen fluoride. The 2162.4 cm^{-1} FTIR measurement disagrees slightly with a 2159 cm^{-1} measurement for CO perturbed by HF in argon presumably owing to calibration of the grating instrument.[13] The 1.0 cm^{-1} greater $\Delta\nu_{CO}$ for the DF complex in the present experiments indicates a very slightly stronger hydrogen bond for DF owing to the smaller DF librational amplitude. The 2162.4 cm^{-1} absorption is assigned to the ν_{CO} mode in complex I.

The sharp 389.5 cm^{-1} band is assigned to the librational mode ν_l of H–F in complex I. The HF/DF ratio 389.5/305.0 = 1.277 is relatively low, which indicates a relatively large amplitude anharmonic motion that might be expected for a linear complex. The observation of a single sharp ν_l mode characterizes a degenerate vibration and demonstrates that complex I is linear, in agreement with microwave studies.[2] The 1.8 cm^{-1} splitting on the 389.5 cm^{-1} band after sample warming and the lack of a splitting on the 305.0 cm^{-1} band is probably a consequence of matrix site asymmetry and the larger librational amplitude of HF in complex I as compared to DF.

The effect of the H_b–F molecule in II is to support a

slightly stronger OC--H_a hydrogen bond owing to the fluoride ion affinity of H_b-F. This increases the displacement of the H_a-F and O≡C fundamentals from complex I H-F and C-O values and indicates assignment of the 3771.7 and 2170.5 cm^{-1} bands to these modes in II. The H_b-F fundamental in II is likewise expected to fall below its value in HF dimer owing to the proton affinity of CO, which weakens the H_b-F bond. The 3645.9 cm^{-1} band is accordingly assigned to the H_b-F fundamental in II. This mode of $(HF)_2$ was observed at 3702 cm^{-1} in solid argon and at 3720 cm^{-1} in gas-phase vibrational predissociation studies.[14] No ν_l modes were observed for II presumably owing to lower yield and a less well-defined structure.

The 2815.2 cm^{-1} product in the more dilute HCl experiments with CO deposited at 12 K to minimize diffusion and aggregation of HCl is assigned to ν_s of III. This assignment is supported by the HCl/DCl ratio 2815.2/2037.6 =1.382 which is in excellent agreement with the isolated monomer $R(0)$ ration 2888.0/2089.6 =1.382 and Q-branch ratio 2865.7/2076.0 =1.3804.[9] The 2154.3 cm^{-1} band is assigned to ν_{CO} in III, in agreement with earlier work[7]:

$$O≡C--H-Cl \qquad O≡C--H_a-Cl$$

III   IV H_b Cl

The sharp 247.1 cm^{-1} band is assigned to the degenerate ν_l mode in the linear complex III. The HCl/DCl ratio 247.1/196.3 =1.259 is low for III, even lower than the analogous ratio for I, indicating a large amplitude anharmonic motion consistent with the linear structure.

The 2803 and 2791 cm^{-1} bands observed in the more concentrated HCl experiments with CO deposited at 20 K are appropriate for the H_a-Cl and H_b-Cl modes in IV, respectively. The ν_{CO} mode in IV is probably not intense enough to be resolved from the strong 2154.3 cm^{-1} band in the present experiments. The weaker 2157.2 cm^{-1} shoulder in the CO studies of Barnes et al.[10] is probably due to complex IV.

Following the above pattern for OC--HX complexes, the sharp 2520.1 and 2152.4 cm^{-1} product bands in HBr experiments with CO are assigned to the ν_s and ν_{CO} modes in V. The sharp degenerate 158.3 cm^{-1} absorption is assigned to the ν_l mode for this linear complex:

$$O≡C--H-Br \qquad H_a-Cl$$

V   VI H_b Cl

The 232 cm^{-1} band in HCl experiments is in exact agreement with a previous assignment to $(HCl)_2$; however, the $(DCl)_2$ counterpart band at 187 cm^{-1} is slightly different from the previous 173 cm^{-1} observation[8] and the absence of a strong central component for a (HCl)(DCl) dimer in the present experiments is noteworthy. The present observations are consistent with assignment of the 232 cm^{-1} band to the ν_l mode of H_b-Cl in a bent dimer species VI. In like fashion, the 221 and 198 cm^{-1}

bands in HBr experiments are probably due to analogous motions in a bent $(HBr)_2$ species.

The present observation of the 2664 cm^{-1} band in HCl experiments is consistent with its assignment to ν_s of the H_2O--HCl complex. This complex has been identified by broad 2638 and 2540 cm^{-1} bands in solid nitrogen.[15] The analogous 2395 cm^{-1} band in HBr experiments, assigned to the ν_s mode in the H_2O--HBr complex, is also somewhat above a broad 2310 cm^{-1} band in similar nitrogen matrix studies.[16] The nitrogen matrix clearly interacts more strongly with a partially ionic species than the argon matrix, as has been discussed for the H_3N--HF complex.[17]

Bonding trends

The displacement of ν_s below the nonrotating monomer value[12] decreases in the complexes I, III, and V, $\Delta\nu_s$ =165, 51, and 39 cm^{-1}, respectively, and demonstrates that the heavier hydrogen halide forms the weaker hydrogen bond. The shift of ν_{CO} above the isolated CO value for the complexes, $\Delta\nu_{CO}$ =24, 16, and 14 cm^{-1}, respectively, also decreases in the same order demonstrating that the weakest hydrogen bond has the least perturbation on ν_{CO}. The OC--H_2O complex also fits this trend with $\Delta\nu_{CO}$ =11 cm^{-1} for the weaker hydrogen bond expected for the weaker acid H_2O.

A number of workers have observed displacements in ν_{CO} to higher energies with CO adsorbed on zeolites[18] or complexed to metal halide ligands in argon matrices.[13,19,20] The CO fundamental has been correlated with the strength of the electric field near the cation proposed to bind the CO molecule. In general the ν_{CO} fundamental in OC--$M^{n+}(F^-)_n$ complexes increases in the ranges from 2172–2184 cm^{-1} for $n=1$, 2160–2205 cm^{-1} for $n=2$, and 2185–2212 cm^{-1} for $n=3$ depending upon the metal ion ionic radius.[20] These observations are rationalized by electron density removal from the 5σ orbital of CO by the positive metal ion. Ab initio calculations have shown that the 5σ CO orbital is weakly antibonding and located primarily on the carbon atom.[21] Accordingly, removal of electron density from the 5σ orbital leads to an increase in bond strength and C-O stretching frequency. Complete ionization raises the fundamental from 2143 cm^{-1} for CO(g) to 2184 cm^{-1} for CO$^+$(g).[22]

The present hydrogen-bonded complexes I, III, and V with ν_{CO} at 2162, 2154, and 2152 cm^{-1}, respectively, involve a smaller amount of electron density transfer from the 5σ CO orbital to the σ^* HX orbital, which of course, also has the effect of reducing the HX fundamental from the isolated HX values. A comparison between the OC--Li-F and OC--H-F complexes is of interest. The former[20] exhibits a $\Delta\nu_{CO}$ of 47 cm^{-1}, substantially higher than $\Delta\nu_{CO}$ of 24 cm^{-1} for complex I, as expected from the higher ionicity of LiF. The ν_{Li-F} is reduced 27 cm^{-1} in the complex which is, however, not as large a fractional reduction as the $\Delta\nu_{H-F}$ in complex I; the larger lithium ion apparently can accommodate more electron density from the CO 5σ orbital without adversely affecting the Li-F bond.

The OC--HF complex has a hydrogen bond of strength intermediate between the weaker CO_2--HF and the stronger HCN--HF complexes as determined by matrix ν_s and ν_l values for each complex.[3,23] The ν_s values are 3871, 3789, and 3626 cm^{-1} and the ν_l values are 313, 389, and 586 cm^{-1} in the group of complexes, respectively, with increasing hydrogen bonding strengths.

CONCLUSIONS

Co-condensation of Ar/CO and Ar/HX mixtures (X = F, Cl, Br) at 12 K produces the OC--HX hydrogen bonded complexes. FTIR spectra of the complexes show decreasing displace nents of the complex C–O and H–X fundamentals *above* isolated CO and *below* isolated HX values as the hydrogen bonding becomes weaker in the above series. Observation of a single sharp degenerate librational fundamental with a relatively small HX/DX ratio indicates a linear structure and a relatively large amplitude, anharmonic librational motion for the HX ligand in the complexes. The FTIR spectrum of the $O{\equiv}C$--H_a–F--H_b–F complex reveals a slightly higher C–O fundamental and a slightly lower H_a–F fundamental than the 1 : 1 complex and a slightly lower H_b–F fundamental than $(HF)_2$, which are consistent with simple bonding considerations.

Note added in proof. A close examination of gas-phase HF infrared spectra [D. F. Smith, J. Mol. Spectrosc. 3, 473 (1959); P. Van Huong and M. Couzi, J. Chim. Phys. 66, 1309 (1969)] provides strong evidence for the hydrogen-bonded H–F fundamental in $(HF)_2$ near 3860 cm^{-1} and not at 3720 cm^{-1} as assigned in Ref. 14. This suggests that the two strongest argon matrix bands in this region for the HF system at 3826 and 3702 cm^{-1}, are due respectively, to $(HF)_2$ and open $(HF)_3$, and that the 3771. 7 and 3645. 7 cm^{-1} bands of species II should be assigned, respectively, to the H_b–F and H_a–F stretching modes. The H_a–F stretching mode in II should be lower in frequency due to the additive effects of hydrogen bonding $O{\equiv}C$ and H_b–F at opposite ends of H_a–F.

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