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Infrared spectrum of the CO₂-HCl complex in solid argon at 12 K

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Co-condensation of CO₂ and HCl in excess argon at 12 K produced the CO₂-HCl hydrogen-bonded complex. Small shifts in the ν_1 and ν_3 modes, the low ν_1 fundamental, and a very weak infrared Fermi doublet indicate a weakly bound complex. The more strongly bound CO₂-HF and C¹⁸O₂-HF complexes gave more intense infrared Fermi doublets. The infrared intensity ratio ν_3/ν_1 is 200/1 for the CO₂-HF complex demonstrating that the HF ligand induces finite electrical asymmetry in the CO₂ submolecule.

INTRODUCTION

The weakly bound CO₂-HF and CO₂-HCl molecular complexes have been examined recently in molecular beams to record radio frequency and microwave spectra.^{1,2} These weakly bound complexes are linear, and induced dipole moments of 0.59 and 0.45 D, respectively, have been determined from the spectra. The CO₂-HF complex has been prepared by condensing argon diluted samples of each reagent at 12 K, and the Fourier-transform infrared spectrum of the complex³ exhibited a strong H-F submolecule stretching fundamental ν_1 , a sharp degenerate H-F librational mode ν_2 , and perturbed infrared active CO₂ submolecule modes ν_3 and ν_2 , respectively, 10 cm⁻¹ above and 7 cm⁻¹ below CO₂ values. We report here a re-examination of the ν_1 and $2\nu_2$ Fermi-resonance doublet region for the CO₂ submolecule in the CO₂-HF complex as a function of HF concentration and a series of similar FTIR studies for the CO₂-HCl complex aimed particularly at characterizing the ν_1 submolecule mode in the complexes.

EXPERIMENTAL

The vacuum, cryogenic, and spectroscopic techniques have been described previously.^{3,4} Hydrogen chloride (Matheson) was allowed to passivate a stainless steel vacuum system heated to 50 °C overnight. Deuterium chloride (Merck, Sharpe, and Dohme) was exchanged with the heated system repeatedly over a two week period, and fresh DCl was equilibrated with the vacuum

system at room temperature before use; 50%–70% deuterium enrichments were obtained in this manner. Carbon dioxide (Matheson) and 93.6% oxygen-18 enriched C¹⁸O₂ (Miles Laboratories) were used directly. Argon mixtures Ar/CO₂=200/1 and Ar/HCl=200/1 and 100/1 were used in these experiments; each mixture was condensed at 2 mmol/h on a CsI window at 12 K for periods of 20–30 h. FTIR spectra were recorded before, once or twice during, and after sample preparation.

RESULTS

Four experiments were done with the natural isotopic carbon dioxide-hydrogen chloride system. The FTIR spectrum for a sample containing CO₂ and HCl is shown in Fig. 1; the HCl monomer $R(0)$ absorption⁵ at 2888.0 cm⁻¹ was completely absorbing and a strong product band labeled ν_3 at 2853.5 cm⁻¹ with a pronounced shoulder at 2851.7 cm⁻¹ was also completely absorbing; HCl dimer⁶ was observed at 2817.8 cm⁻¹. The strong CO₂ fundamentals at 2344 and 663 cm⁻¹ were sufficiently broad to obscure any slightly shifted product absorptions; however, the naturally occurring ¹³CO₂ doublet at 2279.5, 2273.9 cm⁻¹ exhibited a product band shoulder at 2281.5 cm⁻¹ (A =absorbance units \approx 0.12). The Fermi-resonance doublet region revealed new weak product bands identified with arrows at 1383.2 (A =0.012) and 1278.4 cm⁻¹ (A =0.007) in Fig. 2(d); this spectral region is also contrasted in Fig. 2 for HCl and C¹⁸O₂ blank experiments. A comparable amount

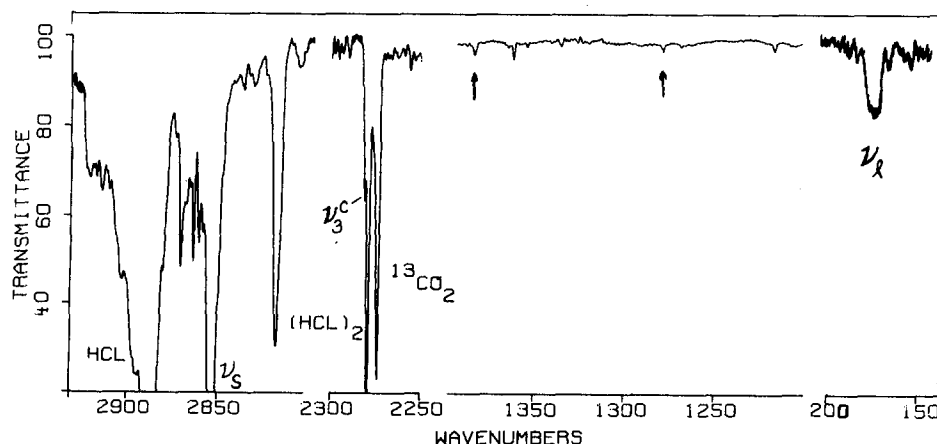


FIG. 1. Infrared spectra of samples prepared by condensing 59 mmol of Ar/CO₂=200/1 and 51 mmol of Ar/HCl=100/1 mixtures for 20 h at 12 K. The ¹³CO₂ indicated is present in natural abundance.

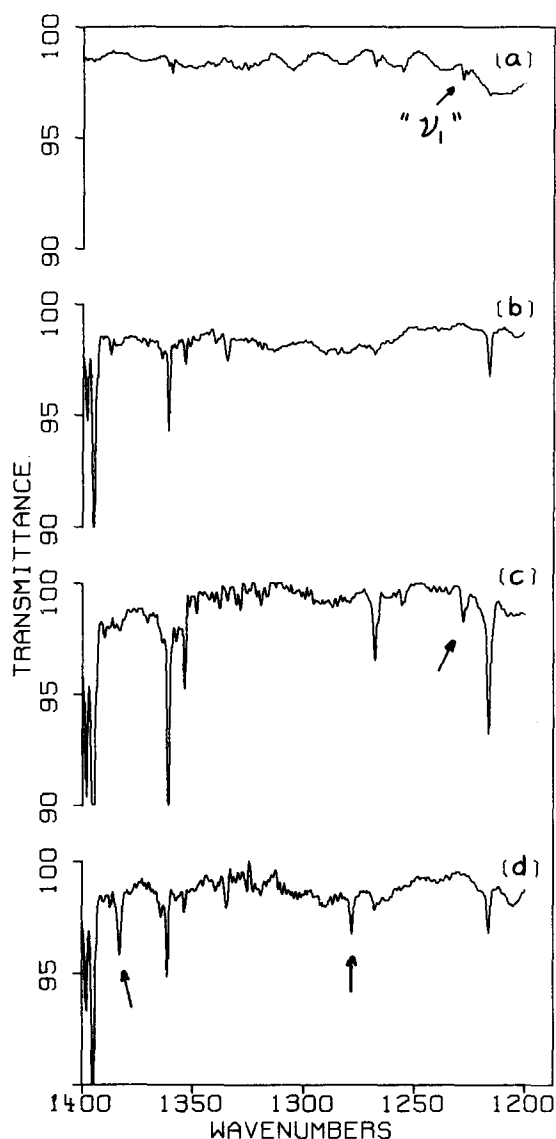


FIG. 2. Infrared spectra in the CO_2 Fermi-doublet region for HCl and CO_2 samples deposited at 12 K: (a) 37 mmol of $\text{Ar}/\text{C}^{18}\text{O}_2=200/1$, (b) 85 mmol of $\text{Ar}/\text{HCl}=200/1$, (c) 59 mmol of $\text{Ar}/\text{C}^{18}\text{O}_2=200/1$ condensed with 48 mmol of $\text{Ar}/\text{HCl}=100/1$, and (d) 59 mmol of $\text{Ar}/\text{CO}_2=200/1$ condensed with 51 mmol of $\text{Ar}/\text{HCl}=100/1$.

of the same Ar/HCl sample was condensed over the next day with a similar amount of argon as a sample blank; the completely absorbing $R(0)$ HCl band at 2888.0 cm^{-1} was accompanied by the weaker $P(1)$ line at 2553.4 cm^{-1} , without a pronounced shoulder, and the $(\text{HCl})_2$ band⁶ was observed at 2817.8 cm^{-1} ; the Fermi-doublet region contained weak bands at 1395 , 1361 , 1335 , 1267 , and 1216 cm^{-1} from trace impurities in the HCl sample and/or vacuum manifold without any detectable adsorption at 1383 and 1278 cm^{-1} , as shown in Fig. 2(b).

A similar experiment was performed with a C^{18}O_2 sample; the strong 2853.3 cm^{-1} band was observed unchanged within experimental error, a product shoulder was observed at 2245.3 cm^{-1} on the side of the $^{13}\text{C}^{18}\text{O}_2$ doublet (ν_3) at 2243.3 , 2237.8 cm^{-1} . The Fermi-doublet region exhibited a very weak product band at 1227.8 cm^{-1}

($A=0.006$), which is denoted with an arrow in Fig. 2(c); no signal was found above the noise level in the 1330 cm^{-1} region. An identical $\text{Ar}/\text{C}^{18}\text{O}_2$ sample was deposited without hydrogen chloride, and the spectrum revealed a very weak band at 1228.4 cm^{-1} ($A=0.002$) labeled " ν_1 " in Fig. 2(a), in addition to the infrared active precursor absorptions.

Another sample was prepared with CO_2 and HCl for far-infrared examination; the spectrum revealed a single band at 173 cm^{-1} ($A=0.07$, $\text{FWHM}=10\text{ cm}^{-1}$), which is shown in Fig. 1.

Two experiments were done with enriched DCl samples and CO_2 . The strong HCl absorption and reaction product were observed at 2888.0 and 2553.4 cm^{-1} as before; the strong $R(0)$ DCl absorption was observed at 2089.3 cm^{-1} and the weaker $P(1)$ line appeared at 2069.7 cm^{-1} , and a new product absorption was observed at 2065.4 cm^{-1} ($A=0.22$). The product shoulder was again observed at 2281.5 cm^{-1} ($A=0.11$), and the weak bands in the Fermi-doublet region were also observed at 1383.1 and 1278.4 cm^{-1} ($A=0.009$ and 0.004 , respectively). The far-infrared spectrum of a similar sample contained weak water lines; however, weak product absorptions were observed at 173 and 134 cm^{-1} .

The previous CO_2 and HF, DF experiments³ were re-examined in the Fermi-doublet region, which is illustrated in Fig. 3. Trace (a) shows the spectrum of 32 mmol of deposited $\text{Ar}/\text{CO}_2=300/1$ sample containing very weak, sharp bands at 1383.7 ($A=0.0028$) and 1279.5 cm^{-1} ($A=0.0017$), which are labeled " ν_1 " and " $2\nu_2$ "; for comparison the sharp 2279.5 cm^{-1} $^{13}\text{CO}_2$ band was observed with $A=0.57$. Trace (b) illustrates the spectrum of 28 mmol of an Ar/HF , $\text{DF}=300/1$ sample, which shows trace impurity bands from fluorine in this reagent sample including sharp CF_4 bands at 1274.0 cm^{-1} and OCF_2 at 1237.6 and 1232.3 cm^{-1} . Trace (c) gives the spectrum of a sample prepared from codeposited $\text{Ar}/\text{CO}_2=300/1$ and Ar/HF , $\text{DF}=300/1$ samples containing a new product band at 1383.0 cm^{-1} ($A=0.036$) and new absorption at 1275 cm^{-1} on the side of the sharp CF_4 band, which can be identified by close comparison of expanded scale spectra. The product absorptions are noted with arrows in the figure. This experiment exhibited ν_3 of $^{13}\text{CO}_2$ -HF at 2289.2 cm^{-1} ($A=0.070$). Trace (d) illustrates the spectrum of the sample prepared from $\text{Ar}/\text{C}^{18}\text{O}_2=\text{Ar}/\text{HF}$, $\text{DF}=300/1$ mixtures, and arrows note new product bands at 1333.9 ($A=0.011$) and 1228.3 cm^{-1} ($A=0.019$). Another CO_2 and HF experiment yielded 656.0 ($A\sim 0.4$), 1383.0 ($A=0.015$), 2289.2 ($A=0.032$), and 3870.9 cm^{-1} ($A=0.45$) product bands on sample condensation at 12 K. On sample warming 12–22 K, the 3871 cm^{-1} band increased 20%, weak new bands appeared at 3664 and 3851 cm^{-1} , the 1383 cm^{-1} band doubled, and a shoulder at 1275 cm^{-1} increased on the side of the sharp 1274 cm^{-1} CF_4 band. On sample warming 12–35–12 K, the 2289 and 3871 cm^{-1} bands were halved, a sharp new doublet appeared at 3842.6 , 3840.2 cm^{-1} , the 1383.0 band doubled (to $A=0.05$) and shifted to 1383.5 cm^{-1} , the 1275 cm^{-1} shoulder increased (to $A=0.02$), and strong HF aggregate bands

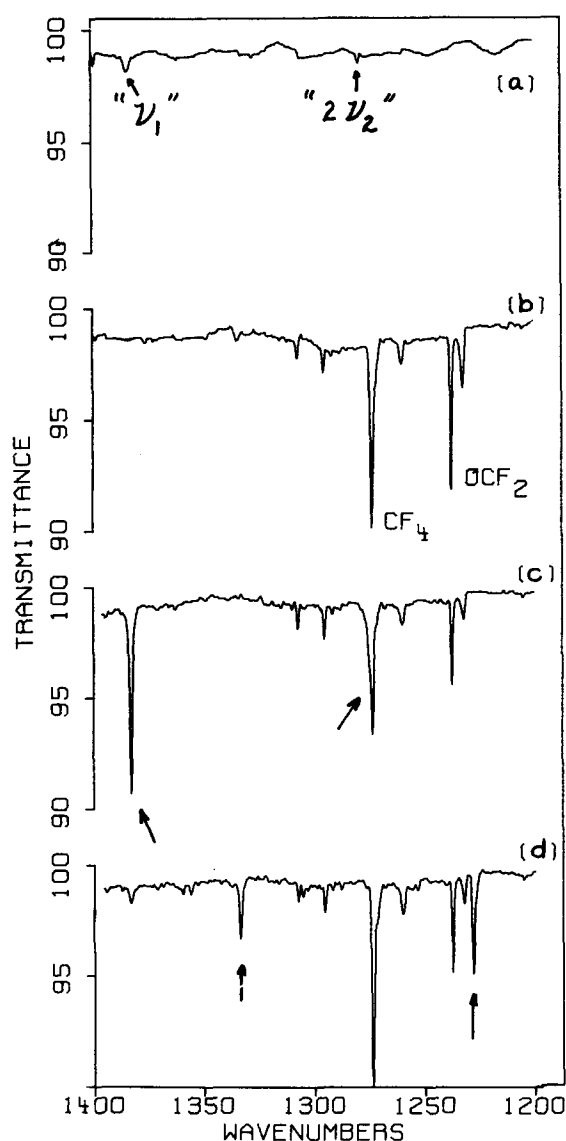


FIG. 3. Infrared spectra in the CO₂ Fermi-doublet region for HF, DF, and CO₂ samples deposited at 12 K: (a) 32 mmol of Ar/CO₂=300/1, (b) 27 mmol of Ar/HF, DF=300/1, (c) 40 mmol each of Ar/CO₂=Ar/HF, DF=300/1 samples, (d) 38 mmol each of Ar/C¹⁸O₂=Ar/HF, DF=300/1 samples.

appeared in the 3440–3410 cm⁻¹ and 3250–3190 cm⁻¹ regions.

DISCUSSION

The new product bands in CO₂ and HCl cocondensation experiments will be considered for assignment to the CO₂-HCl complex. The strongest product band at 2853.5 cm⁻¹ coincides with the *P*(1) line of HCl in solid argon⁵; however, the observed 2853.5 cm⁻¹ band has a pronounced 2851.7 cm⁻¹ shoulder and is substantially stronger than the *P*(1) line of HCl in the HCl blank experiment and in HCl experiments with CO added as a reagent.⁷ Accordingly, the sharp 2853.5 cm⁻¹ band is assigned to the H-Cl stretching fundamental ν_s in the CO₂-HCl complex. This assignment is in agreement with that of Barnes *et al.* who also observed side bands at 2836 and 2806 cm⁻¹ for CO₂-(HCl)_x species.⁸ The

latter side bands were absent in the present experiments because of faster sample condensation (less diffusion and reaction) at the lower 12 K condensation temperature. In the DCl experiments, strong 2065.4 cm⁻¹ product absorption does not coincide with the *P*(1) line of DCl in solid argon⁹ at 2069.7 cm⁻¹, which provides an unambiguous DCl counterpart for the 2853.5 cm⁻¹ product band. The HCl/DCl=2853.5/2065.4=1.382 ratio is in excellent agreement with the HCl/DCl *Q*-branch matrix ratio 2865.7/2076.0=1.380 and the *R*(0)-branch matrix ratio 2888.0/2089.3=1.382.

The 173 cm⁻¹ product band is substantially lower than the 313 cm⁻¹ ν_1 mode for the CO₂-HF complex and just below the 199 cm⁻¹ value predicted for the ν_1 mode of CO₂-HCl from the ν_1 modes of a group of hydrogen-bonded complexes listed in Table I. The weak band at 134 cm⁻¹ is probably the DCl counterpart; the observed HCl/DCl=1.291 ratio is reasonable for this motion. Observation of a single relatively sharp band for the degenerate librational mode indicates that the CO₂-HCl complex is linear, in accord with gas phase studies² and similar observations of the CO₂-HF complex in the gas phase¹ and in solid argon.³

The 2281.5 cm⁻¹ shoulder on the antisymmetric C-O stretching mode ν_3 of ¹³CO₂ at 2279.5 cm⁻¹ is assigned to this mode ν_3^s for the CO₂-HCl complex; this represents a smaller displacement $\Delta\nu_3$ for CO₂-HCl than the 10 cm⁻¹ $\Delta\nu_3$ value for the CO₂-HF complex. The ν_2^s mode was unobserved leading to the conclusion that it was not shifted outside of the ν_2 bandwidth. The weak 1383.2 and 1278.4 cm⁻¹ bands are assigned to the CO₂ submolecule Fermi-doublet modes ν_1^f and $2\nu_2^f$ in the CO₂-HCl complex made very weakly dipole allowed in the asymmetric electric environment induced by the HCl ligand. The weak bands in this region from the HCl sample arise from trace impurities at least two orders of magnitude less abundant than the HCl reagent, which makes it highly unlikely that these trace impurities contribute to the product spectrum. The present matrix observations compare favorably with the 1388.3 and 1285.5 cm⁻¹ Fermi-doublet positions in the gas phase.¹⁰ The following observations from Figs. 2 and 3 and Table II, which compare Fermi doublets for CO₂, C¹⁸O₂, and their HF and HCl complexes, confirm this assignment:

TABLE I. Comparison of H-X stretching (ν_s) and H-X librational (ν_l) modes in a group of hydrogen-bonded complexes in solid argon at 12 K.

Base	HF		HCl		Reference
	ν_s	ν_l	ν_s	ν_l	
CO ₂	3871	313	2853	173	3, this work
CO	3789	389	2815	247	7, 7
C ₂ H ₂	3745	426, 382	2764	...	a, a
HCN	3626	586	2703	375	b, b
H ₂ O	3554	721, 614	2664	...	c, 7

^aL. Andrews, G. L. Johnson, and B. J. Kelsall, *J. Phys. Chem.* **86**, 3374 (1982).

^bG. L. Johnson and L. Andrews (to be published).

^cG. L. Johnson and L. Andrews (to be published).

TABLE II. Vibrational observations in the Fermi-doublet region for several CO₂ species.

CO ₂ gas	CO ₂ in solid argon	CO ₂ -HCl complex	CO ₂ -HF complex	C ¹⁸ O ₂ gas ^b	C ¹⁸ O ₂ in solid argon	C ¹⁸ O ₂ -HCl complex	C ¹⁸ O ₂ -HF complex	ident.
1388.3	1383.7	1383.2	1383.0	1229.9	1228.4	1228.0	1228.2	ν_1
1336.9	1331.6	1330.8	1329.2	1288.5	1281.0	average
[1334.6]	[1326]	[1324] ^c	[1312]	[1314]	[1306]	[1304] ^c	[1292]	[2 \times ν_2]
1285.5	1279.5	1278	1275.4	1347.1	d	d	1333.9	2 ν_2

^aReference 10.^bReference 12.^cEstimated values.^dToo weak to observe.

(1) The CO₂ blank experiment [Fig. 2(a)] shows the weak Fermi doublet at 1383.7 and 1279.5 cm⁻¹ made very weakly infrared allowed by asymmetric matrix environment in some trapping sites. This infrared observation of the Fermi doublet of CO₂ in solid argon is in excellent agreement with the Raman Fermi doublet of CO₂ at 1382.0 and 1277.9 cm⁻¹ in solid krypton.¹¹ Based on the ¹³CO₂ ν_3 band at 2279.5 cm⁻¹ in natural abundance, the relative infrared intensity ν_3/ν_1 for CO₂ in solid argon is 20 000/1. Approximately half of the 1383.2 and 1278.4 cm⁻¹ band absorbance in the CO₂ and HCl experiments can be attributed to induced activity in the CO₂-HCl complex and the other half to unreacted CO₂ in the matrix.

(2) The HF/DF experiments with CO₂ produced ten-fold more intensity in the Fermi doublet for the CO₂-HF complex [Fig. 3(c)], although the 1275 cm⁻¹ band was partially obscured by CF₄ impurity which was absent in the HCl experiments.

(3) The HF/DF reaction with C¹⁸O₂ produced an appropriately shifted Fermi doublet at 1228.2 and 1333.9 cm⁻¹; which is in excellent agreement with gas-phase Raman 1229.9 and 1347.1 cm⁻¹ observations.¹² The lower yield HCl experiment gave the stronger component at 1228.0 cm⁻¹. The ν_1 component of the Fermi doublet exhibits a substantially greater O-18 shift than the 2 ν_2 component and the more intense ν_1 component falls lower with C¹⁸O₂, whereas the ν_1 component was higher with C¹⁸O₂.

(4) The data in Table II show that the ν_1 component is less affected by the matrix environment and the acid ligand complex environment than the 2 ν_2 component. In the CO₂-HF complex, ν_2^c shifts 7 cm⁻¹ below ν_2 whereas ν_1^c is within 1 cm⁻¹ of ν_1 .

The relative intensities of the ν_1^c and ν_2^c modes for the complex are of interest for comparison to the induced moments for the gas phase complexes. In the CO₂-HF complex, the ν_1^c mode is 50% as intense as the ν_2^c mode of the naturally occurring ¹³CO₂-HF complex, which gives an approximate ν_3/ν_1 infrared intensity ratio of 200/1; this represents a 100-fold increase in the ν_1 infrared intensity in CO₂-HF as compared to CO₂ in solid argon. Similarly, in the CO₂-HCl complex, the ν_1^c mode is approximately 5% as intense as the C-13 ν_2^c mode, and the ν_3/ν_1 intensity ratio is approximately 2000/1, which is a ten-fold increase in the ν_1 infrared intensity for the complex.

Three other matrix observations suggest that the CO₂-HCl complex is considerably weaker than the CO₂-HF complex. First, the $\Delta\nu_3^c$ value for the latter is 10 cm⁻¹ and the former is only 2 cm⁻¹; the HF ligand perturbs the ν_3 mode of CO₂ considerably more than the HCl ligand. Second, the 173 cm⁻¹ ν_1 mode is below the 199 cm⁻¹ value predicted from simple ratios with the other linear complexes in Table I; this indicates a larger librational amplitude for the CO₂-HCl complex than might be expected from the other related complexes. Third, the $\Delta\nu_3$ value for the HF complexes is 83 cm⁻¹, whereas for the HCl complex, $\Delta\nu_3$ is 13 cm⁻¹ based on Q-branch HF and HCl values.⁵ These values may be compared to $\Delta\nu_3$ values of 165 and 51 cm⁻¹ for the OC-HF and OC-HCl complexes, respectively.⁷ The ν_3 displacement for the CO₂-HCl complex is less than expected, based on the CO complexes, which is characteristic of the much weaker hydrogen bond in the CO₂-HCl complex.

Finally, some comment on the reactions that occur during matrix formation and sample warming operations is in order. The CO₂-HF and CO₂-HCl complexes are formed by diffusion and association of the reagents during sample condensation. In the HF experiments, sample warming to 20 and 22 K allows limited diffusion and further reaction of HF molecules. The growth of (HF)_n and CO₂-HF absorptions attests this point. New absorptions at 3851 and 3664 cm⁻¹ are probably due to OCO-H-F-H-F higher complex species; this latter complex should exhibit essentially the same ν_1^c mode as CO₂-HF since the latter is practically unchanged from ν_1 of CO₂ explaining additional growth of the 1383 cm⁻¹ band. A subsequent thermal cycle to 35 K markedly increased HF aggregate absorptions, decreased the ν_3 and ν_3^c modes of the simple CO₂-HF complex, increased the 1383 cm⁻¹ band, and produced a sharp new 3842.6, 3840.2 cm⁻¹ doublet. This latter band and part of the absorption at 1383 cm⁻¹ are attributed to CO₂-(HF)_n complex species.

CONCLUSIONS

The CO₂-HCl hydrogen bonded complex was formed on co-condensation of the reagents with excess argon at 12 K. Small displacements in the ν_3 and ν_3^c fundamentals and the low ν_1 mode indicate a weakly bound complex. The CO₂ Fermi doublet was very weak in the infrared spectrum of the complex. The stronger CO₂-HF complex yielded a more intense infrared Fermi doublet,

which was appropriately shifted in the C¹⁸O₂-HF complex. The relative infrared intensity ν_3/ν_1 for CO₂ in solid argon is 20 000/1 and the ratio is 200/1 for the CO₂-HF complex, showing that the HF ligand induces finite electrical asymmetry in the CO₂ submolecule.

ACKNOWLEDGMENTS

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