

Infrared Spectrum of the Benzene-Hydrogen Fluoride Complex in Solid Argon

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The infrared spectrum of the C_6H_6 -HF complex, formed by codeposition of Ar/benzene and Ar/hydrogen fluoride samples at 12 K, exhibits strong ν_s (H-F stretching) and ν_l (H-F librational) fundamentals at 3795 and 253 cm^{-1} and eight out-of-plane wagging fundamental and combination bands for the benzene submolecule in the complex. The positions of the ν_s and ν_l modes indicate a weaker complex than C_2H_4 -HF, and the observation of one degenerate ν_l mode with a $\nu_l(HF)/\nu_l(DF) = 1.390$ ratio that is characteristic of a harmonic vibration supports a C_{6v} equilibrium structure for the C_6H_6 complex, in accordance with microwave studies.

Introduction

Benzene is one of the most important and interesting molecules in organic chemistry. Reactions of benzene often involve attack of the π -electron system by an electrophilic reagent. There has been considerable interest in donor-acceptor complexes involving benzene since the early work of Mulliken.¹ In particular infrared spectra and structural studies of benzene-halogen molecule complexes have been interpreted to indicate both symmetric and asymmetric structures.²⁻⁹ Complexes involving the simple π bonds of ethylene and acetylene with HF were first characterized by matrix infrared studies, which proposed t-shaped structures¹⁰⁻¹² that were confirmed by later microwave spectra of these complexes produced in a nozzle beam.^{13,14} The infrared spectra exhibited blue shifts for base submolecule hydrogen deformation modes, removal of degeneracy for the $\nu_4 + \nu_5$ combination band of the acetylene submolecule, and two HF librational modes for vibration parallel and perpendicular to the π bond of the donor submolecules.¹⁰⁻¹²

The C_6H_6 -HF complex has recently been observed by the molecular beam electric resonance technique, which determined a symmetrical average structure, but large-amplitude motions in this complex made it difficult to determine an equilibrium structure.¹⁵ Theoretical considerations involving the HOMO-(benzene- e_{1g})-LUMO(HF- σ^*) interaction suggest an asymmetrical structure, and CNDO calculations propose HF interaction with one C-C bond,^{16,17} however, the electrostatic potential of benzene predicts a symmetrical structure for the complex. The infrared spectrum of C_6H_6 -HF in solid argon, to be described in this paper, reveals a degenerate HF librational mode and blue-shifted hydrogen deformation fundamental and combination modes for the benzene submolecule in the complex, which are consistent with the symmetrical equilibrium structure for the complex.

Experimental Section

The experimental methods for FTIR matrix studies of HF

TABLE I: Absorptions Due to Fundamental and Combination Bands of Benzene in Solid Argon

absorptions, cm^{-1}	assignments ^a
606	ν_{18}
676	ν_4
847	ν_{11}
967	ν_{19}
993	ν_7
1010	ν_6
1041	ν_{14}
1149	ν_{10}
1180	ν_{17}
1246	$\nu_{11} + \nu_{20}$
1390	$\nu_7 + \nu_{20}$
1483	ν_{13}
1521	$\nu_4 + \nu_{11}$
1620	$\nu_6 + \nu_{18}$
1670	$\nu_8 + \nu_{19}$
1759	$\nu_{10} + \nu_{18}$
1812	$\nu_{11} + \nu_{19}$
1956	$\nu_7 + \nu_{19}$
2600	$\nu_6 + \nu_{16}$
2618	$\nu_2 + \nu_{18} + \nu_6$
2827	$\nu_3 + \nu_{13}$
2890	$\nu_9 + \nu_{16}$
2910	$\nu_2 + \nu_{18} + \nu_9$
3047	ν_{12}
3079	$\nu_{13} + \nu_2 + \nu_{18}$
3100	$\nu_{13} + \nu_{16}$

^aReferences 6 and 20 and Shimanouchi, T. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* 1967, No. 6.

complexes have been described in earlier papers.^{12,18} Benzene (Aldrich, Gold Label) or C_6D_6 (Merck Isotopes) was diluted with argon (Ar/Bz = 200/1 to 800/1) and codeposited with HF (Matheson or $H_2 + F_2$ reaction) (Ar/HF = 100/1 to 600/1) or DF (reaction of D_2 and F_2) on a CsI window at 10-12 K at rates of 2-8 mmol/h each for 16 and 4 h, respectively. FTIR spectra were recorded on a Nicolet 7199 from 4000 to 400 cm^{-1} and from 425 to 125 cm^{-1} ; then samples were annealed at 22-24 K for 10 min and more spectra were recorded.

Results

Infrared spectra of benzene and benzene-HF cocondensation products in solid argon will be described.

Benzene. Since benzene is an important molecule with high symmetry, the infrared absorptions which can be assigned to benzene in solid argon are listed in Table I; some of these bands are shown in Figure 1a and identified with the label B. These bands show 0-4- cm^{-1} shifts from the gas-phase values,⁶ such as a 3- cm^{-1} blue shift for the strong $\nu_4(a_{1g})$ out-of-plane hydrogen deformation mode, a 1- cm^{-1} blue shift for the formally forbidden

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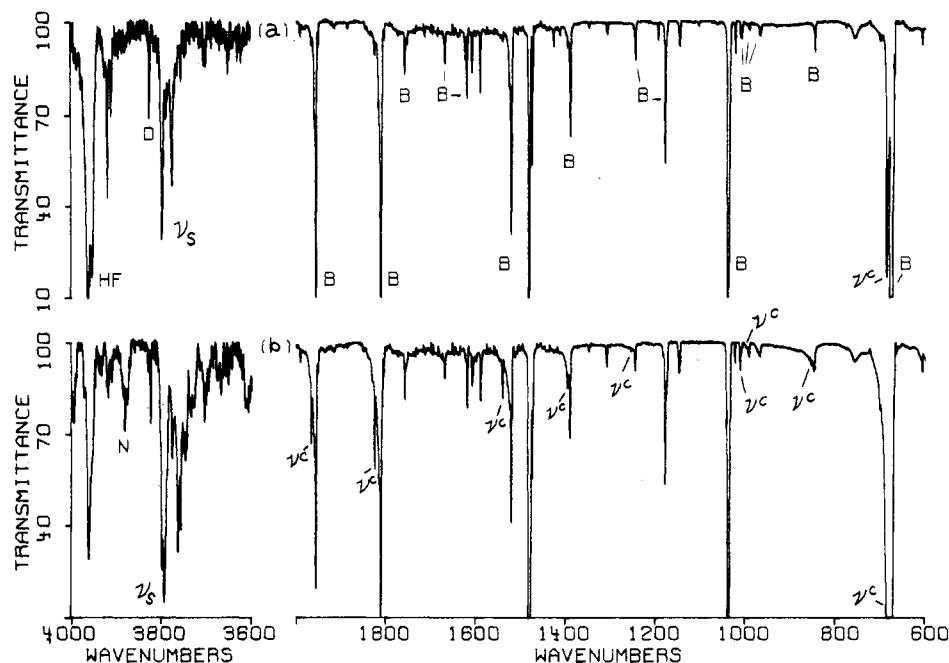


Figure 1. Infrared spectra of benzene and hydrogen fluoride. (a) Ar/Bz = 300/1 and Ar/HF = 200/1 samples codeposited at 10 K and (b) after annealing at 22 K for 10 min and recooling to 10 K.

TABLE II: Absorptions in C₆H₆ Cocondensation Experiments with Argon Diluted HF and DF

reagents	C ₆ H ₆ -HF	assignments	shifts
3919	3798	ν_s (HF)	-121
	3777	site	
1956	1968	$(\nu_7 + \nu_{19})^c$	12
1812	1826	$(\nu_{11} + \nu_{19})^c$	14
1521	1541	$(\nu_4 + \nu_{11})^c$	20
1390	1397	$(\nu_7 + \nu_{20})^c$	7
1246	1256	$(\nu_{11} + \nu_{20})^c$	10
1010	1012	ν_6	2
993	999	ν_7^c	6
847	856	ν_{11}^c	9
676	687	ν_4^c	11
	470	$(2\nu_1(\text{HF}))$	
	253	$\nu_1(\text{HF})$	
	247	site	
2877	2793	$\nu_s(\text{DF})$	-84
	2775	site	
	182	$\nu_1(\text{DF})$	
	177	site	

weak $\nu_{11}(e_{1g})$ out-of-plane hydrogen deformation mode, and up to 4-cm⁻¹ shifts for the combination bands. The benzene absorptions generally show smaller gas-to-matrix shifts in solid argon than reported for solid nitrogen.⁶

Benzene + HF. Eight codeposition experiments were done with reagents at different dilutions in argon, and three of these will be described here. Infrared spectra from the most productive experiment using Ar/Bz = 300/1 and Ar/HF = 200/1 samples are shown in Figure 1a after codeposition at 10 K and in Figure 1b after annealing to 22 K. In addition to HF monomer and dimer (labeled D) absorptions,¹⁹ strong sharp new product absorptions were observed at 3798 and 3777 cm⁻¹ (labeled ν_s) and 687 cm⁻¹ (ν_4^c); weaker satellites (labeled ν^c) were observed above the strongest four combination bands of benzene, and weak bands were observed at 1012 cm⁻¹ (ν_6^c) and 856 cm⁻¹ (ν_{11}^c). Annealing the sample to 22 K for 10 min reduced HF and benzene bands, increased the higher ν_s band markedly (7-fold) at the expense of the lower band, and shifted the major absorption to 3795 cm⁻¹. In addition, annealing produced strong new bands at 3764 and 3758 cm⁻¹ and weaker new bands at 3614 and 697 cm⁻¹, increased the ν^c absorptions 7-fold, and produced weak new ν^c absorptions

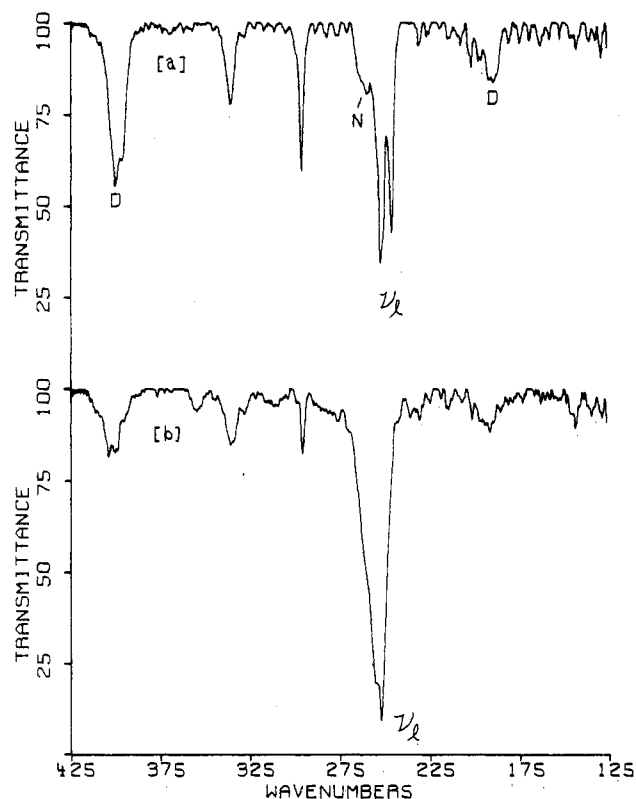


Figure 2. Far-infrared spectra of benzene and hydrogen fluoride. (a) Ar/Bz = 200/1 and Ar/HF = 100/1 sample codeposited at 10 K and (b) after annealing at 24 K for 10 min and recooling to 10 K.

at 999 and 1256 cm⁻¹ and a new band at 470 cm⁻¹ (not shown). The cocondensation product bands are listed in Table II.

A similar experiment was performed with Ar/Bz = 300/1 and Ar/HF = 600/1 samples; the new product bands given in Table II were reduced 5-fold from the Figure 1a spectrum (the three weakest bands at 856, 999, and 1256 cm⁻¹ were not detected). Sample annealing decreased HF, increased the new product bands 2-fold in concert, and produced weak new bands at 3764 and 3758 cm⁻¹. The experiment with Ar/Bz = 800/1 and Ar/HF = 400/1 samples gave initial product bands reduced 4-fold from Figure 1a, but sample annealing decreased HF and increased the Table

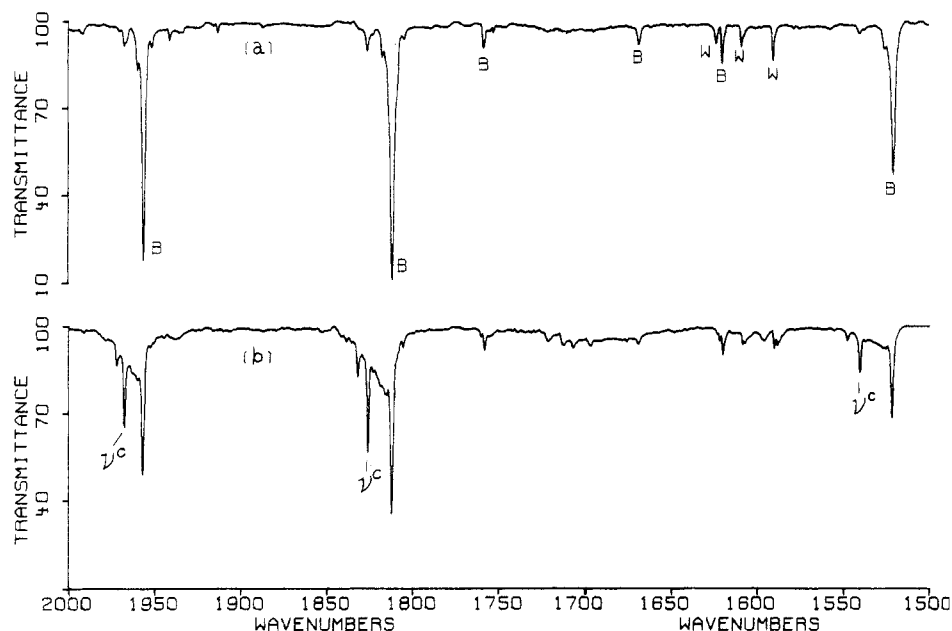


Figure 3. Infrared spectra in the 1500–2000-cm⁻¹ region for benzene and deuterium fluoride (90% DF). (a) Ar/Bz = 300/1 and Ar/DF = 150/1 samples codeposited at 10 K and (b) after annealing at 21 K for 10 min and recooling to 10 K.

II product bands 3-fold in concert.

The far-infrared region was also examined in three experiments, and spectra are shown in Figure 2a after codeposition at 10 K and in Figure 2b after annealing to 24 K. The initial spectrum shows (HF)₂ bands at 400 and 191 cm⁻¹ (labeled D) and N₂-HF at 262 cm⁻¹ (labeled N)¹⁹ and new product bands at 336, 296, 253, and 247 cm⁻¹. Sample annealing decreased (HF)₂ and the 336-, 296-, and 247-cm⁻¹ bands, increased the N band shoulder, and markedly increased the 253-cm⁻¹ band (labeled ν₁).

Benzene + DF. Two experiments were done with Ar/Bz = 300/1 samples and Ar/DF = 300/1 (60% DF) and Ar/DF = 150/1 (90% DF). Both experiments gave the 3798- and 3777-cm⁻¹ ν_s bands observed with HF and new DF counterparts at 2793 and 2775 cm⁻¹, and all of the other products bands given in Table II were observed without evidence of displacement due to DF. Sample annealing caused substantial increases in the product bands, shifted the strong ν_s bands to 3795 and 2788 cm⁻¹, and produced new bands at 2763 and 2662 cm⁻¹ in the DF stretching region and at 3755 cm⁻¹ in the HF stretching region. In the more concentrated DF experiments, annealing markedly increased the sharp ν^c bands at the expense of DF and benzene and produced a set of higher frequency satellite bands at 1972, 1832, 1548, 859, and 697 cm⁻¹ above the product bands in the initial sample. The sharp ν^c bands are illustrated in Figure 3 for the 1500–2000-cm⁻¹ region before and after sample annealing.

Five samples were prepared for far-infrared examination, and the spectra revealed (DF)₃ at 347 cm⁻¹, (DF)₂ at 300 and 162 cm⁻¹, N₂-DF at 212 cm⁻¹, and new product bands at 251, 217, 182, and 177 cm⁻¹. Sample annealing in all experiments increased (DF)₃ and N₂-DF bands, decreased (DF)₂ bands and the new products at 251, 217, and 177 cm⁻¹, and markedly increased the 182-cm⁻¹ absorption.

Benzene-d₆ + HF and DF. Two cocondensation experiments were done with benzene-d₆, and the product absorptions are given in Table III. Note small (1 cm⁻¹) red shifts in the ν_s(HF) and ν_s(DF) fundamentals. In the far-infrared experiment, the 336-cm⁻¹ band was shifted to 334 cm⁻¹ and the 296-, 253-, and 247-cm⁻¹ bands were not shifted.

Discussion

The products of the benzene-HF cocondensation reaction will be identified, and the structure of the major product will be considered.

Identification. The product bands given in Table II were not observed in separate HF or benzene samples; these absorptions change in concert on annealing and with different sample con-

TABLE III: Absorptions in C₆D₆ Cocondensation Experiments with Argon Diluted HF and DF

reagents	C ₆ D ₆ -HF	assignments	shifts
3919	3797	ν _s (HF)	-122
	3775	site	
1618	1626	(ν ₇ + ν ₁₉) ^c	8
1452	1463	(ν ₁₁ + ν ₁₉) ^c	11
1159	1174	(ν ₄ + ν ₁₁) ^c	15
497	506	ν ₄ ^c	9
2877	2792	ν _s (DF)	-85
	2774	site	
	253	ν ₁ (HF)	
	247	site	

centrations, and hence they are due to a new (Bz)_x(HF)_y complex species. The Table II bands were observed in the initial sample deposit, and the stronger ones persisted in dilute samples, which is reasonable for the 1:1 complex (*x* = *y* = 1). Annealing to allow diffusion and further association of HF and benzene increased these bands and produce a new set with an H-F stretching fundamental at 3764 cm⁻¹, further displaced from the induced HF Q branch value of 3919 cm⁻¹ in solid argon,¹⁹ and out-of-plane wagging combination bands with larger blue shifts above the isolated benzene values (Figure 3). These new bands evidence a stronger interaction between benzene and HF, and they are accordingly assigned to the 1:2 complex (*x* = 1, *y* = 2), Bz-H₂F-H₂F, where the Bz-H₂ interaction is stronger than in the 1:1 complex owing to the fluoride ion affinity of the H₂F submolecule. The observation of a second set of ν^c absorptions to higher energy than the first set (Figure 3) for the slightly stronger 1:2 complex reinforces assignment of the first (Table II) set to the 1:1 complex. The 253- and 247-cm⁻¹ bands track with the Table II Bz-HF bands on sample warming while the weaker 336- and 296-cm⁻¹ product bands exhibit different behavior and are thus due to a different complex which cannot be identified here. It should be noted that the HF/DF ratios of the latter bands (1.36, 1.34) are lower than the HF/DF ratio for the former bands (1.39).

Assignments. The strong sharp initial product bands at 3798 and 3777 cm⁻¹ and the 3795-cm⁻¹ band that replaces them on sample annealing exhibit HF/DF ratios of 1.361 ± 0.001, which is appropriate for the ν_s(H-F) stretching fundamental in a hydrogen-bonded complex. These values may be compared with the ν_s fundamentals of the C₂H₂-HF and C₂H₄-HF π complexes at 3746 and 3730 cm⁻¹, respectively.^{11,12} The latter complexes are more strongly bound than Bz-HF as indicated by shorter

base-F bond lengths¹³⁻¹⁵ and larger displacements of the ν_s modes from the HF value in solid argon.

The strong sharp 253- and 247-cm⁻¹ bands, the former of which grows markedly on sample annealing while the latter is destroyed, are assigned to the ν_1 (HF) librational modes of the 1:1 complex in two different matrix sites; the 253- and 3798-cm⁻¹ (or 3795 cm⁻¹) bands are due to the more stable matrix site, while the 247- and 3777-cm⁻¹ bands are due to a less stable matrix site. The 253-cm⁻¹ librational mode is also in accord with a weaker Bz--HF complex as compared to the C₂H₂-HF and C₂H₄-HF complexes, which exhibit higher ν_1 modes in the 382-426-cm⁻¹ range.^{11,12} The 470-cm⁻¹ band is tentatively assigned to the overtone $2\nu_1$ of the 253-cm⁻¹ fundamental. The ν_1 (HF)/ ν_1 (DF) = 253/182 = 1.390 ratio is higher than the isotopic ratios for ν_1 modes of other π complexes, (C₂H₄-HF, 1.314 and 1.338);¹² this shows that the ν_1 mode in the Bz--HF complex is an essentially harmonic vibrational motion of the acid hydrogen.

The bands denoted ν^c in the tables and figures track with the ν_s and ν_1 bands on sample annealing and are associated with fundamental or combination bands of the benzene submolecule involving hydrogen out-of-plane wagging motions with the single exception of ν_6^c which is due to a ring deformation mode.²⁰ No satellite product absorptions were observed for in-plane hydrogen bending or C-C stretching modes. The blue shifts in the complex fundamental bands, as compared to isolated benzene in solid argon, predict the shift observed for one combination band and enable 5-6-cm⁻¹ and 1-cm⁻¹ shifts, respectively, to be determined for the unobserved ν_{19}^c and ν_{20}^c complex fundamentals. The ν^c complex bands are sharp (fwhm = 2 cm⁻¹); in fact the ν_i^c bands are slightly sharper than their ν_i benzene counterparts, and there is no evidence for splitting of these bands due to lowering of symmetry for the complex.

The largest blue shift for a fundamental, 11 cm⁻¹, was observed for ν_4^c , which involves out-of-plane hydrogen bending and is the strongest infrared-active fundamental. This displacement is due, in large part, to electrostatic repulsion between the acid hydrogen and the benzenic hydrogens. The 11-cm⁻¹ blue shifts for ν_4^c of Bz--HF compares to 26 cm⁻¹ found for the out-of-plane mode of C₂H₄-HF in solid argon¹² and in the gas phase.²¹

Structure of the Complex. The relative positions of the ν_s and ν_1 infrared bands¹⁰⁻¹² and microwave measurements¹³⁻¹⁵ establish that the Bz--HF complex is more weakly bound than the C₂H₂-HF and C₂H₄-HF complexes. All of the evidence demonstrates that the latter are π complexes with the HF ligand directly over the π bond. The microwave study of Bz--HF, however, shows that the average structure is C_{6v} with fluorine on the sixfold axis, which could arise for a C_{6v} equilibrium structure or for an equilibrium structure with the fluorine close to the C₆ axis and the acid hydrogen in effect rotating around the aromatic ring.

The matrix infrared spectrum of the Bz--HF complex provides complementary structural information. First, perturbation of out-of-plane and not in-plane benzenic hydrogen fundamentals confirms the out-of-plane ligand position. Second, if the acid hydrogen remained between two adjacent carbon atoms longer than an out-of-plane wagging vibrational period the degeneracy of the combination bands would be split, and no evidence for such a splitting was observed (Figure 3). Third, the observation of a single ν_1 librational mode for the major site, in contrast to two

distinct ν_1 modes at 424 and 396 cm⁻¹ for C₂H₄-HF,¹² argues for a degenerate motion, which is consistent with the C_{6v} equilibrium geometry. Again, if the acid hydrogen spent more time between two adjacent carbons atoms than a ν_1 (HF) librational period, the degeneracy in ν_1 would be split (as observed for C₂H₄-HF), and no such splitting was observed here. Fourth, the relatively low 253-cm⁻¹ position for the ν_1 mode is indicative of a broad potential function and a large-amplitude pendulum-like vibration for HF in the Bz--HF complex with the C_{6v} equilibrium structure. This is in accord with the large size of the benzene submolecule base in contrast to the collinear complexes OCO--HF and OC--HF which have smaller bases and slightly higher ν_1 modes at 313 and 389 cm⁻¹, respectively, in solid argon.^{18,22} Fifth, the ν_1 (HF)/ ν_1 (DF) = 253/182 = 1.390 ratio describes the dynamics of the low-frequency hydrogen motion as an almost harmonic vibration, which provides further support for the C_{6v} equilibrium structure and casts doubt on a structure with the acid hydrogen constrained to rotate around the ring. Finally, it is hoped that the present ν_1 observation might stimulate potential surface calculations aimed at characterizing this low-frequency vibrational motion of the acid hydrogen in the Bz--HF complex.

Comparison with Halogen Complexes. Infrared spectra and structural studies of benzene-halogen complexes have been interpreted in terms of both symmetric and asymmetric structures.³⁻⁹ There are two notable differences with the Bz--HF complex. First, the out-of-plane wagging modes of the benzene submolecule in the complex are displaced less (for Bz--Cl₂, $\Delta\nu_4 = 9$ cm⁻¹, $\Delta(\nu_4 + \nu_{11}) = 11$ cm⁻¹, and $\Delta(\nu_7 + \nu_{19}) = 7$ cm⁻¹)⁶ for the halogen complex, suggesting a weaker interaction. Second, intensity enhancement has been observed for the ring-breathing mode $\nu_2(a_{1g})$ in the Bz--Br₂ and Bz--I₂ complexes with little shift in the band position,³⁻⁷ but ν_2^c was not detected for the Bz--HF complex. This points to a fundamental difference in the nature of the interaction between benzene and halogen on one hand and benzene and hydrogen fluoride on the other hand, and when the benzene-halogen charge-transfer complex structure is conclusively determined it may also differ from the Bz--HF complex. Ferguson and Matsen showed that enhancement of infrared intensities is inherent in charge-transfer theory and suggested that caution must be exercised in determining complex structure from "activated" infrared bands.²³

Conclusions

The simultaneous codeposition of Ar/C₆H₆ and Ar/HF samples at 12 K leads to the formation of the benzene-hydrogen fluoride complex. The infrared spectrum exhibits strong ν_s and ν_1 acid submolecule fundamentals at 3795 and 253 cm⁻¹ and eight out-of-plane wagging fundamental and combination base submolecule bands blue-shifted from benzene absorptions in solid argon. The positions of both acid submolecule modes indicate a more weakly bound, less rigid Bz--HF complex than found for C₂H₄-HF, in agreement with microwave studies. The observation of one degenerate ν_1 mode for the Bz--HF, in contrast to two different ν_1 modes for C₂H₄-HF, and a ν_1 (HF)/ ν_1 (DF) = 1.390 ratio that characterizes an almost harmonic vibrational motion provide evidence for a C_{6v} equilibrium structure for the Bz--HF complex.

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Registry No. C₆H₆, 71-43-2; HF, 7664-39-3; Ar, 7440-37-1.

(20) Normal vibrations as defined in: Herzberg, G. L. "Infrared and Raman Spectra"; van Nostrand: Princeton, NJ, 1945; p 118.

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