states are present between the porphyrin S_1 and S_2 states and below the S_1 state, while OEPErOH emits only S_1 fluorescence. Quenching of S_2 emission in OEPErOH, like other diamagnetic metal OEP complexes,[2] is attributed to a fast relaxation to the S_1 state. Since the S_1 and S_2 excited states are a 50:50 admixture of two common $^1(\pi,\pi^*)$ excited configurations in accidental degeneracy, the energy surfaces of the lowest excited singlets are almost parallel. These parallel surfaces, however, are displaced from the ground-state surface. In fact, the Franck–Condon overlap is so small that only a weak $Q_{0,0}$ band is observed in the TPP complexes. In the OEP complexes, on the other hand, the peripheral substituents partially lift the accidental degeneracy and thus yield some difference in shift between the S_1 and S_2 surfaces. This makes an increase in the Franck–Condon overlap, which intensifies the $Q_{0,0}$ band of OEP complexes, and also allows the fast $S_2 \rightsquigarrow S_1$ relaxation.

TPPEr(dpm) exists in two conformations in methanol/ethanol glassy medium at 77 K. Conformer I, with the central metal ion in the porphyrin plane, emits S_2 fluorescence, while conformer II, with the central metal ion displaced out of the porphyrin plane, emits no S_2 fluorescence. The quenching of S_2 emission in conformer II is attributable to an increase in the interaction of S_1 and S_2 states but not to an enhancement of spin–orbit coupling in the central metal ion.

Upon irradiation in an absorption band of coordinated dpm around 300 nm, we observe not only phorphyrin S_2 emission but also coordinated β-diketone T_1 emission. This implies that the rate of interligand energy transfer from the β-diketone S_1 state to the porphyrin S_2 state is not as fast as intersystem crossing within the β-diketone. Also energy transfer between the β-diketone T_1 and porphyrin S_2 states, even if in an accidental degeneracy, is rather inhibited.

Acknowledgment. The authors are grateful to Professor I. Tanaka for his continuous interest and encouragement.

Registry No. TPPErOH, 102941-86-6; TPPEr(dpm), 102941-87-7; OEPErOH, 60452-84-8; TPPGdOH, 102941-88-8; OEPGdOH, 60452-83-7.

Infrared Spectra of Diacetylene–Hydrogen Fluoride Complexes in Solid Argon

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(Received: September 6, 1985; In Final Form: February 10, 1986)

Diacetylene–hydrogen fluoride complexes and their deuterated counterparts have been characterized in solid argon at 10 K by infrared spectroscopy. The observation of two new sets of H–F stretching, C–H stretching, and C–H bending absorptions indicates that two primary product 1:1 complexes were trapped in the matrix. These absorption bands characterize a C_4H_2--HF π complex and a C_4H_2--FH σ complex whose relative yields exhibit a deuterium substitution dependence consistent with a preference for deuterium in the bonding position. The relative values of the ν_s (H–F stretching) and ν_l (H–F librational) modes for the diacetylene--HF and acetylene--HF π complexes reveal weaker hydrogen bonding in the diacetylene--HF complex. Annealing produced comparable increased yields of both 1:1 complexes, suggesting comparable stabilities, and a marked increase in a C_4H_2--$(HF)_2$ complex.

Introduction

A variety of techniques have recently been applied to understanding the hydrogen-bonding interaction with π-bonded systems. Infrared spectroscopy was first used to observe alkene–HI complexes in matrix isolation;[1-3] results of later studies on ethylene–HF and acetylene–HF in solid argon indicated T-shaped complexes, with the hydrogen halide attached to the π bond.[4-6] Microwave spectra of ethylene–HF and acetylene–HF confirmed the T-shaped structures deduced from the matrix spectra.[7,8] Analogous complexes between HF and methyl-substituted ethylenes[9] and acetylenes[10] have been studied in matrix isolation, and rotational spectra of propyne–HF suggested that the geometry is slightly distorted by the methyl group.[11]

Interest in conjugated π systems as bases followed from experimentation with localized π bonds. Molecular beam electric resonance spectra of benzene–HF indicated that the average structure placed HF on the C_6 axis perpendicular to the benzene ring,[12] and matrix infrared spectra supported this structure.[13] The weak hydrogen bonding in the complex and the breadth of the potential for the proton apparently favor a complex where HF oscillates markedly from this average position. Infrared spectra of conjugated diene–HF complexes in solid argon suggested a similar oscillation of HF from an average position above the central C–C bond.[14] Conjugation of the two π systems also exists in diacetylene, so that a similar oscillating structure might be expected; however, due to the geometry of this molecule, the distance separating the two π bonds is greater than for conjugated dienes and a greater barrier may exist between the potential minima.

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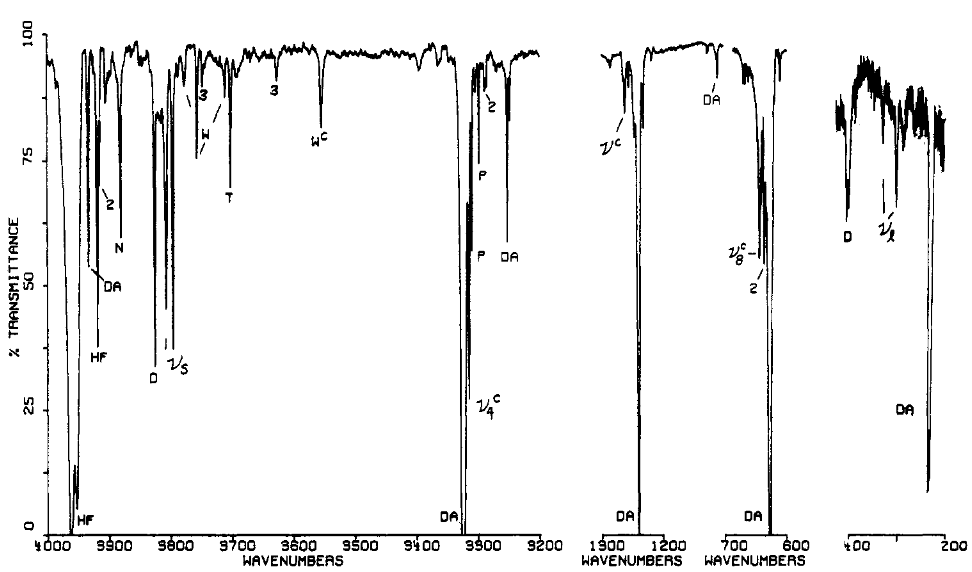

Figure 1. Infrared spectrum of the 600–4000-cm^{-1} region prepared by codepositing 13 mmol of Ar/C_4H_2 = 200/1 and 19 mmol of Ar/HF = 150/1 samples for 4.5 h at 10 K. Infrared spectrum of the 200–400-cm^{-1} region recorded for 50% more sample codeposited in 7 h. DA denotes diacetylene bands.

Here follows a detailed matrix isolation study of the diacetylene–hydrogen fluoride system.

Experimental Section

The Nicolet 7199A Fourier-transform infrared spectrophotometer, cryogenic apparatus, and vacuum and gas mixture delivery systems employed in the mid-infrared experiments have been discussed previously;[5,15] 1.0-cm^{-1} resolution was employed and band measurement accuracy is ±0.3 cm^{-1}. Far-infrared data were obtained with a Perkin-Elmer 983 dispersive infrared spectrophotometer operated from 4000 to 180 cm^{-1} in order to obtain correspondence between far-IR and mid-IR absorptions of the complex; frequency accuracy is ±0.5 cm^{-1}. Spectra were recorded after sample codeposition at 10–12 K and then after annealing first to 17–19 K and second to 22–24 K to allow diffusion of trapped reagents. Diacetylene was prepared by double elimination from 1,4-dichloro-2-butyne (Aldrich Chemical Co.) in heated aqueous KOH with 10% dioxane and collected in a trap cooled by a CCl_4 slush bath.[16] Diacetylene-d_2 was prepared in a similar manner with the following changes: (a) the elimination was performed in D_2O with dissolved KOH, (b) a gas washing bottle containing D_2O with dissolved sodium metal was included before the condensing trap to complete deuteration, and (c) N_2 carrier gas was used.[17] The diacetylene-d_2 sample contained less than 10% diacetylene-*d* based on relative band intensities. Diacetylene samples were stored in Pyrex vessels with Teflon stopcocks maintained at 200 K; before use, the samples were degassed at 77 K. Hydrogen fluoride (Matheson) was condensed and evacuated, and deuterium fluoride was prepared by reacting equal amounts of deuterium and fluorine in a 3-L stainless steel can; the sample was degassed at 77 K before dilution with argon. Sample concentrations for argon/diacetylene and argon/hydrogen fluoride ranged from 100/1 to 1200/1 in an extensive series of matrix experiments.

Results

Argon–diacetylene mixtures were deposited alone and then annealed to identify bands arising from uncomplexed base and its polymers, and these absorptions are listed in Table I. Assignments of complex bands are based upon their displacement from bands of the uncomplexed base as well as their increase in intensity upon annealing and location with respect to previously observed alkyne–HF complex absorptions.[6,10] The diagnostic modes sought for the product complexes are ν_s, the hydrogen-fluorine stretch, ν_l, the two librations of HF constrained by the hydrogen bond, and the base submolecule C–H stretching and bending modes, $\nu_4{}^c$ and $\nu_8{}^c$, respectively.[18,19]

TABLE I: Absorptions (cm^{-1}) of Diacetylene and Diacetylene-d_2 in Solid Argon

C_4H_2 matrix	C_4H_2 gas	C_4D_2 matrix[a]	assignt[b]
3934.4	3948	3079.3, 3054.4	$\nu_1 + \nu_8$ or $\nu_4 + \nu_6$
3326.7	3329	2593.4	$\nu_4(\sigma_u{}^+)$
3316.6		2590.8	p
3304.2		2577.0	p
3285.9		2554.7	p
3252.1	3247		$\nu_5 + 2\nu_8$
2186[c]	2184	2067[d]	$\nu_2(\sigma_g{}^+)$ p
2020.9	2020	1891.0	$\nu_5(\sigma_u{}^+)$
1298.5		1034.2	p
1280.2		1023.1	p
1283.7		1018.8	p
1256.6		1004	p
1247.3		998	p
1240.6	1241	993.2	$\nu_6 + \nu_8$
1114.7	1113	955.0	$\nu_7 + \nu_8$
848.8	846	703.4	$\nu_6 + \nu_9$
709.7	701	675.5	$\nu_7 + \nu_9$
707.8		673.1	
661.3			p
656.7			p
653.7		515.0	p
647.6		511.5	p
639.3		502.0	p
633.6		499.4	p
627.8	628	495.6	$\nu_8(\pi_u)$
619.8	627		$\nu_6(\pi_g)$ p
227.8	220	209.6	$\nu_9(\pi_u)$
224.9		206.5	

[a] Additional sharp, weaker bands were observed at 3325.2, 2563.0, 1239.6, 846.1, 703.4, 627.0, and 222 cm^{-1} for the mixed isotope C_4HD. [b] Assignments are based on the gas-phase spectra of ref 18 and 19. Bands assigned to dimer and polymer, denoted p, increased markedly on sample warming. [c] In addition to the 2186-cm^{-1} absorption, which is probably due to dimer, bands at 2183 and 2180 cm^{-1} are probably due to higher aggregates. [d] Sipos and Phibbs (Sipos, P. A.; Phibbs, M. K. *Can. J. Spectrosc.* **1974**, *19*, 159) deduce a gas-phase Raman value of 2067 cm^{-1}. Sample warming increased this band and absorption at 2062 and 2057 cm^{-1} probably due to higher polymers.

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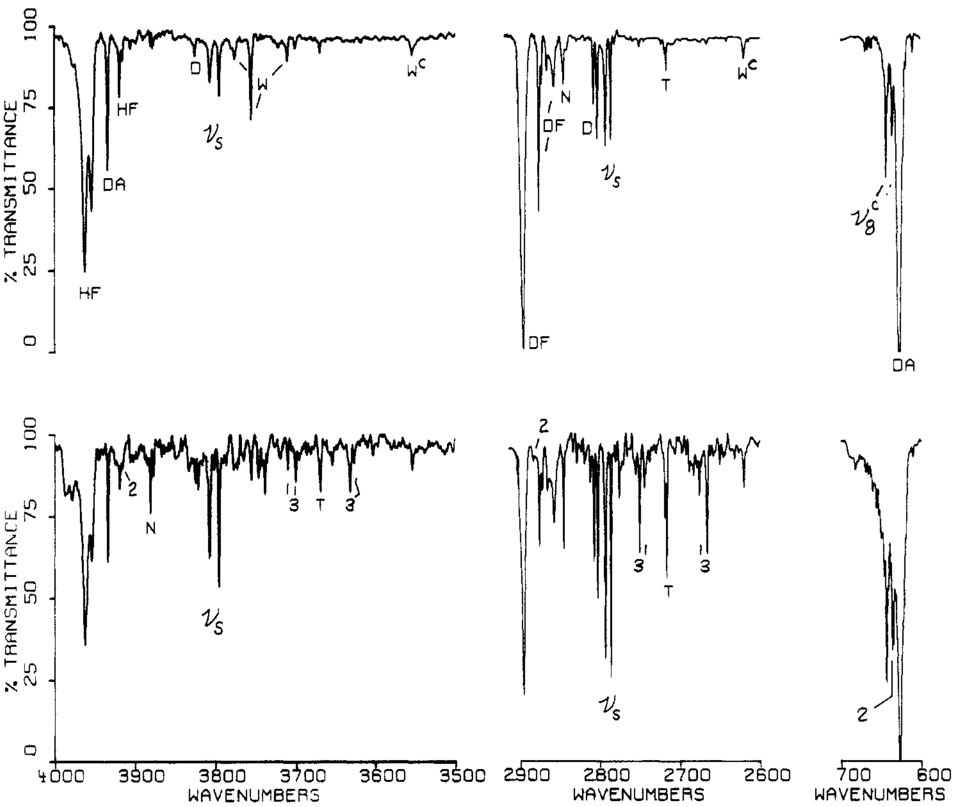

Figure 2. (top) Infrared spectrum of matrix prepared by codepositing 15 mmol of Ar/C_4H_2 = 200/1 and 22 mmol of Ar/(HF + DF) = 150/1 (80% DF enrichment) at 10 K. (bottom) Infrared spectrum recorded after warming to 24 K for 10 min and then recooling to 10 K. DA denotes diacetylene bands.

Diacetylene and HF give rise to two ν_s bands at 3808.2 and 3796.6 cm^{-1}; the 3796-cm^{-1} band is stronger, as shown in Figure 1, and it increased 10% more than the 3808.2-cm^{-1} band during annealing at 17 and 24 K. Warming the matrix to 17 K for 10 min caused each band intensity to increase by 30–40%, and after 24 K diffusion for 10 min, the bands are 2.3 and 2.5 times as intense as in the original deposited sample; a weak new band at 3914 cm^{-1} (labeled 2) grew similarly on sample warming. (In two other experiments a marked decrease in the 3919-cm^{-1} HF band on annealing clearly revealed the new 3914-cm^{-1} band.) The spectrum also shows HF monomer and aggregates (marked D and T),[20] water (W), and water complex (W^c).[21] Weaker bands at 3747.7 and 3627.4 cm^{-1} (marked 3) increased markedly (10-fold) on diffusion. A similar pair of ν_s bands appeared for diacetylene–DF at 2794.0 and 2787.0 cm^{-1} with a weak new 2884-cm^{-1} band (marked 2), which follow approximately the same growth pattern upon diffusion as their HF counterparts as illustrated in Figure 2. Sample warming markedly increased (12-fold) weak bands at 2751.1 and 2667.5 cm^{-1} and revealed satellite features at 2745.2, 2677.0, 3740.0, and 3632.2 cm^{-1}, in addition to weak 3747.7- and 3627.4-cm^{-1} bands, marked 3, in Figure 2. Increasing the DF enrichment favored the 2751.1-, 2667.5-cm^{-1} pair relative to the satellites and the 3747.7-, 3627.4-cm^{-1} pair. Thus, the data have revealed two different sets of product bands that increased 2-fold on annealing and one set that increased 10-fold on annealing. This and the following evidence support the identification of two 1:1 complexes (ν_s and 2) and one 1:2 complex (3) in these samples.

The infrared-active C–H bend ν_8 gave rise to two new product absorptions above the free diacetylene value[18,19] of 627.8 cm^{-1}: sharp bands at 644.1 cm^{-1} (marked ν_8^c) and 636.4 cm^{-1} (marked 2). These two bands were of comparable intensity in HF experiments, and they increased parallel to the ν_s doublet and 3914-cm^{-1} bands and to each other, on sample annealing. Since neither perturbed ν_8 band is completely resolved from the intense precursor band and weaker polymer bands, only qualitative comparisons of relative intensity changes are possible. Under higher resolution, the 636.4-cm^{-1} band shows evidence of splitting at 635.4 cm^{-1}. It is noteworthy that with DF the 644.1-cm^{-1} band is about 50% stronger than the 636.4-cm^{-1} band as can be seen by comparing Figures 1 and 2; the absolute 636.4-cm^{-1} band yield is approximately constant after deposition and annealing to the same temperature in these experiments. The combination of ν_8 with the Raman-active C–H bend, ν_6, gave a product at 1262.9 cm^{-1} (marked ν^c) above the base mode at 1240.6 cm^{-1}. A strong sharp new band at 3314.9 cm^{-1} (marked ν_4^c) and a weak new band at 3291 cm^{-1} (marked 2) appeared below ν_4 of C_4H_2 at 3326.7 cm^{-1} and above the polymer at 3285.9 cm^{-1}. In three separate far-infrared experiments, the HF librational modes ν_l(HF) appeared at 326.6 and 297.4 cm^{-1}, which are also illustrated in Figure 1. The DF counterpart of the 326.6-cm^{-1} band was found at 261.7 cm^{-1}, but the other libration was obscured by the doubly degenerate skeletal bend ν_9, a doublet at 227.8, 224.9 cm^{-1}; the lack of N_2 impurity in these experiments was verified by the lack of N_2--DF absorption at 214 cm^{-1}.[22] A possible ν_2^c band at 2186.7 cm^{-1}, while coincident with a diacetylene polymer band, shows markedly greater growth upon diffusion than do other diacetylene polymer bands, but a contribution from the diacetylene polymer is suspected.

Codeposition of diacetylene-d_2 with HF again produced the strong ν_s bands at 3807.9 and 3796.3 cm^{-1}, in agreement with C_4H_2 values within measurement error, which are shown in Figure 3. DF counterparts for these bands at 2794.0 and 2786.8 cm^{-1} increased 5-fold on sample warming, as illustrated in Figure 4. The HF librational modes were observed at 326.6 and 297.4 cm^{-1} in separate far-infrared experiments. The DF counterparts were observed at 259.3 and 228.8 cm^{-1}, which are shown in Figure 5; again, the lack of nitrogen impurity is demonstrated by the absence of absorption at 214 cm^{-1}.[22]

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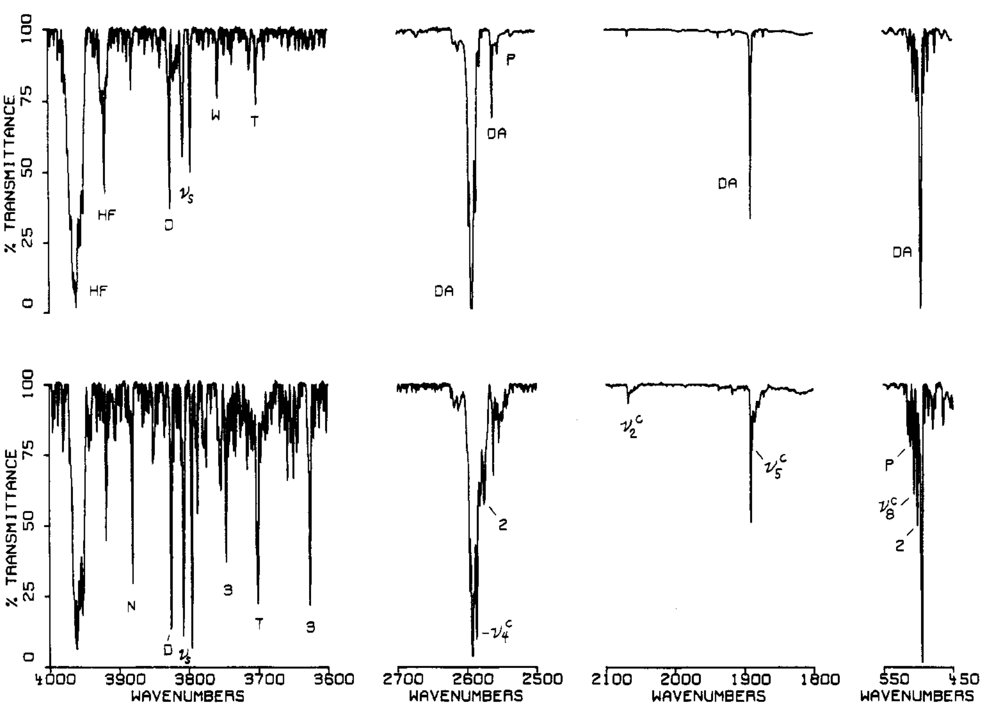

Figure 3. (top) Infrared spectrum of sample formed by condensing 23 mmol of Ar/C_4D_2 = 400/1 and 28 mmol of Ar/HF = 200/1 at 10 K. (bottom) Infrared spectrum recorded after warming to 24 K for 10 min and then recooling to 10 K.

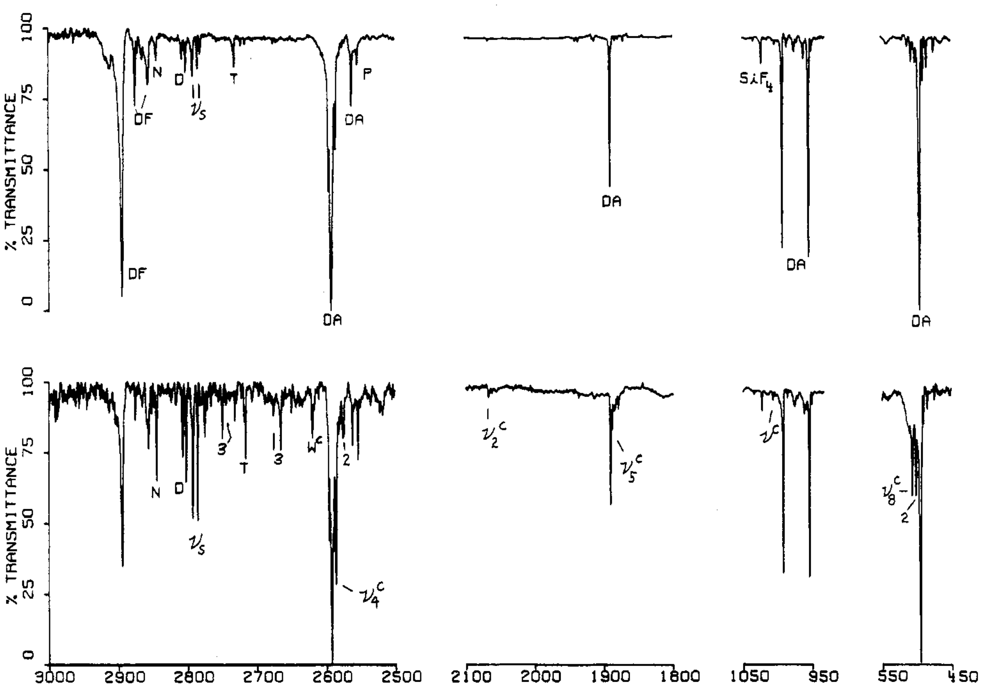

Figure 4. (top) Infrared spectrum of matrix prepared by codepositing 22 mmol of Ar/C_4D_2 = 600/1 and 26 mmol of Ar/(HF + DF) = 200/1 (80% DF enrichment) for 5 h at 10 K. (bottom) Infrared spectrum recorded after warming to 24 K for 10 min and then recooling to 10 K.

Deuteration of the diacetylene skeleton permits greater resolution of many of the complex bands and also produces a considerable intensity increase in ν_5, the infrared-active triple-bond stretch due to coupling with ν_4. The strong antisymmetric C–D stretch (ν_4^c) at 2587.4 cm^{-1} and a new weak 2575-cm^{-1} band (marked 2) were observed below the 2593.4-cm^{-1} value for the base. The ν_5 mode was reduced from 1891.0 cm^{-1} for the base to 1889.0 cm^{-1} for the complex. Also, growth upon diffusion of a weak band at 2067.4 cm^{-1}, appropriate for the complex-activated ν_2^c mode, is found to be inconsistent with the growth of diacetylene-d_2 polymer bands observed in the ν_2 and ν_8 regions; the 2067.4-cm^{-1} band is believed to be due primarily to the HF complex. Perturbed counterparts of ν_8 were observed strongly at 507.2 and 501.9 cm^{-1} above diacetylene-d_2 at 495.6 cm^{-1} (Figures 3 and 4). HF favored (by 3 to 2) the lower of these two bands relative to DF, and accordingly, Figure 3 shows an increased yield of the bands marked 2 relative to Figure 4. A single new combination $\nu_6 + \nu_8$ appeared at 1007.2 cm^{-1}. These bands and their DF complex counterparts are listed in Table II. Diacetylene-d_2 precursor bands are also given in Table I.

Discussion

As necessary background work for the study of diacetylene complexes, the C_4H_2 and C_4D_2 precursors were examined in solid argon. Infrared absorptions for C_4H_2 and C_4D_2 are compared in Table I since there is no C_4D_2 spectrum in the literature. Interesting differences for C_4D_2 are the greater intensity for ν_5 (antisymmetric C≡C stretch) due to mixing with ν_4 (antisymmetric C–D stretch) and the observation of Fermi resonance for ($\nu_6 + \nu_8$) and ($\nu_7 + \nu_8$), which enhances the latter band intensity.

TABLE II: Absorptions (cm^{-1}) for the Vibrations of Diacetylene and Diacetylene-d_2 1:1 Complexes with HF and DF

C_4H_2–HF	C_4H_2- -DF	C_4H_2	C_4D_2- -HF	C_4D_2- -DF	C_4D_2	assignt
3914	2884					$\nu_s(2)$
3808.2	2794.0		3796.3	2786.8		$\nu_s(1)$
3796.6	2787.0		3796.3	2786.8		$\nu_s(1)$
3314.9	3314.9	3326.7	2587.4	2586.7	2593.4	$\nu_4(1)$
3291	3291	3326.7	2575	2575	2593.4	$\nu_4(2)$
2186.7	2186.7	*a*	2067.4	2067.4	*a*	$\nu_2(1)$
		2021	1888.8	1888.8	1891.0	$\nu_5(1)$
1262.9	1263.4	1240.6	1007.2	1007.3	993.2	$\nu_6 + \nu_8(1)$
644.1	644.2	627.8	507.2	507.7	495.6	$\nu_8(1)$
636.6	636.8	627.8	501.9	501.9	495.6	$\nu_8(2)$
326.6	261.7		327.6	259.6		$\nu_1(xz)(1)^b$
297.4			298.1	228.8		$\nu_1(yz)(1)^b$

[a] Infrared inactive in free diacetylene. [b] Axes defined: *x* axis through base, *z* axis through HF.

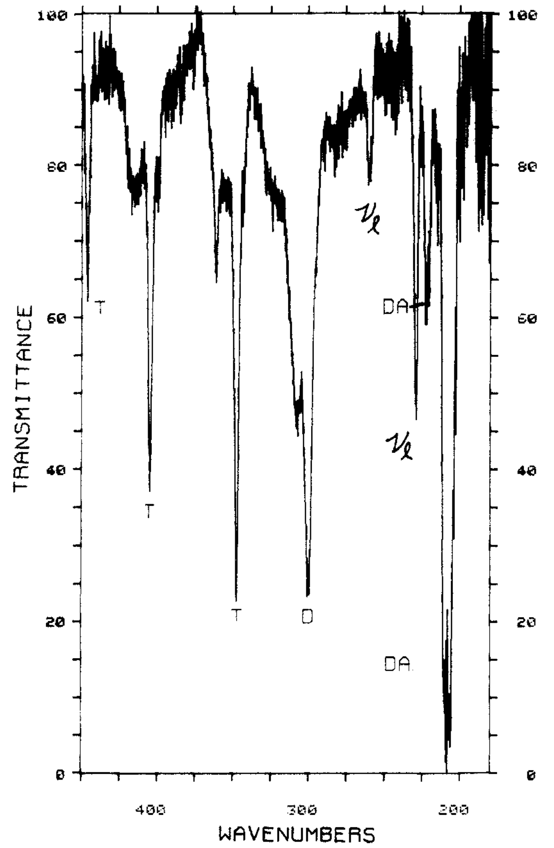

Figure 5. Far-infrared spectrum of matrix prepared by codepositing 45 mmol of Ar/C_4D_2 = 200/1 and 36 mmol of Ar/(HF + DF) = 100/1 (90% DF enrichment) for 7 h at 10 K.

Hydrogen bonding in dimer and higher polymers also leads to new bands in the ν_4, ν_5, ν_8, and ($\nu_6 + \nu_8$) regions, and these bands are also listed in Table I.

C_4H_2- -HF Complexes. Diacetylene, like 1,3-butadiene, possesses two sites of equal basicity in conjugation. As a result, some electron density at each basic site is withdrawn into the region of the single bond, as MO calculations demonstrate by obtaining a longer C≡C bond length than that of acetylene[23] and a shorter C—C bond length than the experimental value for propyne.[24] The hydrogen bond of diacetylene–HF is expected to be weaker than that of 1,3-butadiene–HF, in analogy to acetylene–HF vs. ethylene–HF, implying that a greater freedom of HF motion will be allowed in this complex. Infrared data provide evidence for the trapping of two different 1:1 complexes in the argon matrix. The observation of two different structures for a 1:1 complex in solid argon is not without precedent; both HCN- -HF and HF- -HCN were observed in matrix codeposition experiments.[25]

The ν_8 (C–H bending) region of diacetylene clearly revealed two different product complex absorptions, a sharp band at 644.1 cm^{-1} and a doublet at 636.4, 635.4 cm^{-1} above diacetylene at 627.8 cm^{-1}. These two bands maintained the same relative intensities upon deposition throughout seven experiments where the argon/diacetylene ratio was varied from 200/1 to 1200/1 and where Ar/HF was independently varied over the 150/1 to 1200/1 range. However, considerably different relative intensity behavior for these two ν_8 complex bands with the DF acid indicates that they do not arise from the same 1:1 complex. Diacetylene-d_2–HF gives two distinct counterparts at 507.2 and 501.9 cm^{-1}, and the 501.9-cm^{-1} band is favored by 3 to 2 relative to diacetylene-h_2–HF counterparts. The ratios of frequencies $\nu(C_4H_2\text{–}HF)/\nu(C_4D_2\text{–}HF)$ are only slightly different: 644.1/507.2 = 1.270 and 636.4/501.9 = 1.268. Replacement of HF with DF, on the other hand, *decreased the intensity of the lower component relative to the higher component* for both diacetylene–DF and diacetylene-d_2–DF. This behavior shows that the two bands arise from two distinct complexes and that the complex corresponding to the upper ν_8 component is relatively more favorable with DF.

The two strong ν_s absorptions of nearly equal intensity separated by 11 cm^{-1} behave appropriately for matrix site splittings of the same complex, and the HF/DF ratios (1.363 and 1.362) characterize an H–F stretching fundamental. Although we cannot be absolutely certain that each one does not belong to a slightly different complex structure, the data do not provide sufficient detail to support such a hypothesis. On the other hand, the weaker 3914-cm^{-1} band is clearly due to a different complex and its HF/DF ratio (1.357) also characterizes an HF motion.

The ν_4 (antisymmetric C–H and C–D stretching) regions each reveal two product bands: strong 3315-cm^{-1} and weak 3291-cm^{-1} bands *below* C_4H_2 at 3327 cm^{-1} and strong 2587-cm^{-1} and weak 2575-cm^{-1} bands *below* C_4D_2 at 2593 cm^{-1}. The strong 3315-cm^{-1} band is red-shifted 12 cm^{-1}, slightly more than the 8-cm^{-1} red shift for this mode in the C_2H_2- -HF π complex; however, the weaker 3291-cm^{-1} band is red-shifted a much greater 36 cm^{-1}, which indicates hydrogen bonding of the alkyne C–H itself. In the reverse HF- -HCN complex in solid argon,[25] the C–H stretching mode was red-shifted 33 cm^{-1}. Similar observations came from C_4D_2 experiments: the strong band was red-shifted only 6 cm^{-1} whereas the weaker band appeared 17 cm^{-1} below C_4D_2 itself. These C–H (D) stretching data also characterize two different primary complexes. The product absorptions discussed so far are sufficient to characterize two 1:1 product complexes: **1**, a weak π complex, and **2**, a weak reverse σ complex. The vibrational data do not allow discrimination between the oscillating model **1′**, for the π complex, where HF oscillates between the potential minima, and the localized model **1**, where HF is hydrogen bonded to one of the triple bonds in the diacetylene base. These two models represent two different wave functions on the same potential surface, where **1** is a consequence of a high barrier to exchange of the H–F submolecule between the two triple bonds and **1′** would arise for a relatively low barrier.

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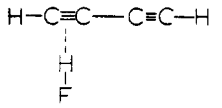

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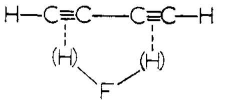
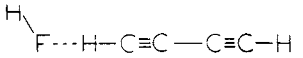


1′



2

For complexes with less symmetry than a 3-fold rotational axis, the difference between the two nondegenerate HF librations ν_l reflects the anisotropy of the potential encountered by the HF proton; for all HF complexes, the librational frequencies relate generally to the strength of the hydrogen bond. Two ν_l modes were observed for the diacetylene–HF π complex at 326.6 and 297.4 cm^{-1}, considerably lower than the acetylene–HF modes at 426.2 and 382.0 cm^{-1}, but due to interference from the strong ν_9 C_4H_2 band, only the upper counterpart was observed at 261.7 cm^{-1} in DF experiments. Based on the lack of N_2–DF complex at 214 cm^{-1}, any N_2–HF absorption at 262 cm^{-1} can be ruled out.[22] The available isotopic substitution ratio $\nu_l(C_4H_2\text{–}HF)/\nu_l(C_4H_2\text{–}DF)$ is 326.6/261.7 = 1.248, indicating greater anharmonicity than is the case for either of the acetylene–HF ν_l modes.[6] The anisotropy of the ν_l(HF) modes is less than is the case for acetylene–HF, which is consistent with the π complex. No evidence was found for HF librational modes for the reverse complex, which are expected below 200 cm^{-1} by using the "free" HF submolecule[26] in $(HF)_2$ as a model.

Deuteration of the diacetylene skeleton, while having little effect on ν_s, caused small shifts in the ν_l frequencies. The upper ν_l of diacetylene-d_2–HF appeared at 327.6 cm^{-1}, a 1.0-cm^{-1} increase from diacetylene–HF, but its DF counterpart appeared at 259.6 cm^{-1}, a 2.1-cm^{-1} decrease from diacetylene–DF. The lower ν_l was observed at 298.1 cm^{-1}, 0.7 cm^{-1} above that for diacetylene, and the DF counterpart was observed at 228.8 cm^{-1}, free of interference from the diacetylene-d_2 ν_9 mode at 209.6 and 206.5 cm^{-1}. Isotopic substitution ratios indicate a greater anharmonicity for the upper ν_l: 327.6/259.6 = 1.262 and 298.1/228.3 = 1.303. The difference in anharmonicities for the two motions can be caused by the difference between proton motion in the complex plane or perpendicular to the complex plane. Greater anharmonicity would be expected in the motion which is interfered with by repulsions from base submolecule hydrogens, as has been the case for both alkenes and alkynes,[5,6] so that the motion with the lower isotopic substitution ratio, the ν_l of higher frequency, is assigned as the libration in the complex plane (xz) and the ν_l of lower frequency is assigned as that perpendicular to the complex plane (yz).

No evidence was found for splitting or doubling of the ν_l modes for the π complex. The $\nu_l(xz)$ mode is expected to be most sensitive to the effect of a double-minimum potential required by **1′** if the barrier height is comparable to the ν_l level, and the absence of splitting can be taken as evidence against this oscillating model.

The remaining weak perturbed base submolecule modes observed here and listed in Table II are probably due to the π complex **1**, although these modes are not particularly sensitive to structure and contributions from **2** cannot be ruled out. The ν_4^c shift in diacetylene-d_2 is only −6 cm^{-1} because of greater coupling between ν_4^c and the antisymmetric C≡C stretch ν_5^c. This latter mode itself shows a perturbation of −2 cm^{-1} for diacetylene-d_2–HF, but ν_5^c of diacetylene–HF is not observed due to the markedly lower intensity of ν_5, which is itself attributed to a lack of coupling with the C–H stretch. Of the possible IR-active perturbed components of the combination ($\nu_6 + \nu_8$), only one was observed: a band shifted 22 cm^{-1} above the diacetylene absorption at 1241 cm^{-1}.

The ν_s modes assigned here to the C_4H_2- -HF π complex **1** (3808 and 3796 cm^{-1}) exhibit less displacement from the isolated HF fundamental[15] at 3919 cm^{-1} than does the C_2H_2- -HF π complex with ν_s = 3745 cm^{-1}. Likewise, the ν_l modes for the diacetylene complex (326 and 297 cm^{-1}) are substantially lower than those for the acetylene complex (426 and 382 cm^{-1}). The ν_4^c and ν_8^c modes assigned to **1** also exhibit less displacement from C_4H_2 than counterparts in C_2H_2 + HF experiments.[6] These observations clearly indicate a longer and weaker hydrogen bond in the diacetylene complex.

On the other hand, the 3914-cm^{-1} H–F stretching value for the reverse complex shows little perturbation and a weak interaction for the reverse complex **2**. This contrasts the stronger reverse complex HF- -HCN, where the H–F fundamental was observed at 3892 cm^{-1}. Unfortunately, without the intensity enhancement due to hydrogen bonding, the 3914-cm^{-1} H–F stretching mode in the reverse complex was substantially weaker than found for the π complex, which made its observation more difficult. The C_4H_2 submolecule modes marked 2 are assigned to the reverse complex **2**; the 636.4-, 635.4-cm^{-1} doublet for the perturbed doubly degenerate bending mode exhibits much less displacement than did the bending mode for HCN in the reverse complex, but the C–H stretching modes involved in hydrogen bonding show comparable displacements.[25]

It is interesting to note that the reverse complex was not observed for C_2H_2 and HF,[6] and calculations show that HF- -HC≡CH is less stable by about 0.5 kcal/mol than the observed π complex.[27] However, diacetylene is a stronger acid than acetylene, owing to the σ-withdrawing effect of the acetylide group, and a weaker π donor than acetylene due to delocalization. These two factors work together to enhance the stability of **2** relative to **1** for diacetylene as compared to acetylene. The matrix experiments show that **2** is closer in stability to **1** than for the corresponding acetylene species, but the present work cannot determine which is more stable, **1** or **2**.

In contrast with acetylene, fluoroacetylene, like diacetylene, exhibited both σ and π complexes with HF,[10] and the inductive effect of fluorine rationalizes the increased acidity of the hydrogen and reduced basicity of the π bond in fluoroacetylene that is responsible for the stabilization of both structures for fluoroacetylene–HF. Diacetylene can be viewed in like fashion with one HC_2– group affecting the other like F– in fluoroacetylene. However, methylacetylene, like acetylene, exhibited only a π complex, and this complex was stabilized by the electron-donating effect of the methyl substituent, which resulted in a larger displacement for ν_s and higher ν_l modes.[10]

Finally, the relative yields of **1** and **2** with deuteration of both acid and diacetylene submolecules merit comment. It is well-known in hydrogen-bonded systems that, other things being equal, D in the bonded position is more stable than H. This is best illustrated with (HF)(DF), which is more stable than (DF)(HF).[27] In the case of C_4H_2 with HF and DF, deuterium prefers the bonding role, as in the π acid complex, which gives more of **1** relative to **2** with DF as compared to HF; hence, the **2** bands are stronger in HF experiments than in DF studies (compare Figures 1 and 2 or Figures 3 and 4). In the case of C_4H_2 and C_4D_2 with each acid in turn, more of **2** is expected relative to **1** with C–D in the bonding role, and indeed, the **2** bands are stronger in C_4D_2 studies than in C_4H_2 experiments (compare Figures 1 and 3 or Figures 2 and 4).

An estimate of the relative stabilities of C_4H_2- -DF and DF- -H_2C_4 can be made assuming the change in relative intensities of the two displaced ν_8 bands in Figure 2, as normalized in Figure 1 with HF, can be ascribed to different populations owing to the enhanced stability of deuterium in the bonding role. Since the annealing process gives the best defined temperature, the 3/2

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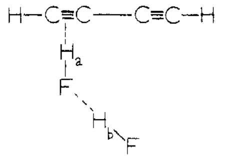
population produced on annealing at 24 K yields an estimated relative energy difference of 70 cm^{-1} from a simple Boltzmann calculation; this value is on the order of the relative energy between the (HF)(DF) and (DF)(HF) dimers.[28] Finally, we suspect that the relative yield of **1** and **2** in these experiments is more under kinetic than thermodynamic control since the relative intensities of the two perturbed ν_8 bands are the same for production during condensation of gases at 10 K or annealing the solid to 24 K. The matrix cage is expected to inhibit the rotation of HF around the end of diacetylene to interconvert **1** and **2**.

C_4H_2- -$(HF)_2$ Complexes. Annealing enhances a 1:2 complex present as a minor product in the initial sample deposit (bands marked 3 in figures); this complex, diacetylene-$(HF)_2$, is comparable to N_2- -$(HF)_2$ where N_2 has been replaced with the slightly stronger base diacetylene.[29] The addition of H_b–F to structure **1** to give structure **3** increases the hydrogen-bond strength and shifts the H_a–F mode to 3627.4 cm^{-1}, and the H_b–F mode appears at 3747.7 cm^{-1}, below the $(HF)_2$ value[20] of 3825.5 cm^{-1}. Other vibrations for complex **3** were not observed owing to growth of diacetylene polymer in these spectral regions. Formation of this 1:2 complex took place much more readily than did that of 1,3-butadiene–$(HF)_2$ under similar conditions,[14] and $\nu_s(H_a–F)$ is a sharp, single peak compared with the numerous splittings observed for the $\nu_s(H_a–F)$ mode for 1,3-butadiene–$(HF)_2$.



3

The observation of mixed HF–DF absorptions for the 1:2 complex verifies the stoichiometry and provides a basis for comparison with the 1:2 complexes in the N_2 and H_2O systems.[21,22,29] First, the mixed isotopic bands are assigned as follows:

C_4H_2- -H_a–F- -D_b–F		C_4H_2- -D_a–F- -H_b–F	
3632.2	2745.2	2677.0	3740.0

Comparison of the H_a–F and H_b–F modes in the mixed dimers, where practicaly no interaction occurs, with C_4H_2- -H_a–F- -H_b–F modes at 3747.7 and 3627.4 cm^{-1} and a like comparison of mixed dimer D–F modes with C_4H_2- -D_a–F- -D_b–F modes at 2667.5 and 2751.1 cm^{-1}, shows that some interaction does occur between the acid submolecule stretching modes for **3**. This interaction is less than in the N_2- -$(HF)_2$ and OC- -$(HF)_2$ complexes with weak bases, where extensive interaction occurs and the mixed isotopic modes fall midway between H_a–F and H_b–F values,[29] but the present interaction is more than that found in the H_2O- -$(HF)_2$ complex with the stronger base where insufficient interaction occurs between the acid submolecule stretching modes at 3690 and 3272 cm^{-1} to even resolve mixed isotopic splittings on the latter bands.[21]

Conclusions

The diacetylene–HF and diacetylene–$(HF)_2$ complexes, along with their deuterated analogues, have been prepared by codeposition of argon gas solutions of diacetylene and hydrogen fluoride at 10 K and studied with infrared spectroscopy. The observation of two sets of H–F stretching, C–H stretching, and C–H bending absorptions shows that two different 1:1 complexes are trapped in the matrix. The data demonstrate that one of these is a π complex, by comparison with the C_2H_2- -HF species, and that the other is a reverse σ complex, HF- -H_2C_4, by comparison with HF- -HCN. The relative positions of the ν_s(H–F stretch), ν(C–H stretch), ν(C–H bend), and ν_l(H–F libration) modes for the C_4H_2- -HF and C_2H_2- -HF π complexes reveal a weaker hydrogen bond in the diacetylene π complex. The two H–F stretching modes for the diacetylene–$(HF)_2$ complex show stronger hydrogen bonding than in the 1:1 complex, which is typical of 1:2 complexes. Further study of the 1:1 diacetylene–HF complex, particularly rotational spectra, will be necessary to determine the more stable complex geometry in the gas phase.

Acknowledgment. We acknowledge financial support from National Science Foundation Grant CHE82-17749 for this research and helpful discussions with F. A. Carey and C. E. Dykstra.

Registry No. HF, 7664-39-3; D_2, 7782-39-0; diacetylene, 460-12-8.

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Excited States and Transients Formed in Laser Flash Photolysis of Ir(III) Complexes of 2,2′-Bipyridine

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Transients generated in pulsed laser excitation of both fully N-bonded and mixed N-bonded, C-bonded isomers of *tris*-(2,2′-bipyridine) complexes of Ir(III) have been characterized by differential absorption techniques over the range 350–450 nm. Three transients with lifetimes ranging from 10 μs to 0.1 s have been observed for each of the isomers. The short-lived transients are excited states whose electron distributions are related to the positions of their differential absorption features. Longer-lived transients are associated with species arising from cleavage of Ir–N bonds following excited-state formation. A discussion of the potential use of differential absorption spectra in establishing excited-state electron distributions is presented.

Introduction

The low-lying excited states of metal complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) have been subjected to a multitude of spectroscopic, photophysical, and photochemical studies utilizing a wide variety of experimental techniques. Particular emphasis has been placed on tris complexes of d^6 transition-metal ions, exemplified by the prototype $Ru(bpy)_3^{2+}$.[1-8] In general, tris-bpy and -phen complexes are found to have photoproperties that indicate the existence of several closely spaced low-lying excited states of different orbital parentage whose energetics can be altered by substituents at remote sites of the bpy

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