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The Reaction of HF with Polyacetylene

by

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Chemistry

THE REACTION OF HF WITH POLYACETYLENE

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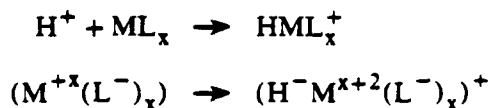
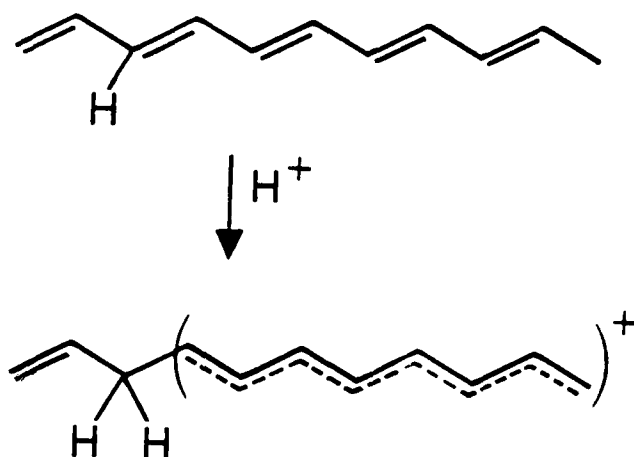
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ABSTRACT: Anhydrous HF reacts with polyacetylene to produce a material with metallic conductivity. Infrared spectra of lightly doped samples show bands characteristic for a delocalized positive charge along the polymer chain. Upon heavier doping, conductivities of $1-10 (\Omega\text{-cm})^{-1}$ are measured. Addition of ammonia produces an ammonium ion on the chain, and destroys the conductivity of the material. A discussion of the doping mechanism and related reactions is given.

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Two general mechanisms have been reported to occur upon reaction of various dopants with polyacetylene.¹ In a formal oxidation, electrons are removed from the polyacetylene by an oxidizing agent ($I_2 \rightarrow I_3^-$,² $3AsF_5 \rightarrow 2AsF_6^- + AsF_3$,³ etc.). Much experimental work supports this formal oxidation mechanism. The second mechanism has been called "proton acid doping." In this mechanism, a proton attaches to a carbon atom, forming a covalent C-H bond using 2 electrons from the double bond (or valence band). The polyacetylene is oxidized, although the electrons never leave the polymer. This proton oxidation



is formally analogous to the oxidative addition of hydrogen to transition metal complexes, where the metal is oxidized.

H_2SO_4 and $HClO_4$ are claimed to be effective proton dopants¹ in generating metallic levels of conductivity, while HBr and HCl are ineffective. Japanese workers⁴ have made semiconducting solar cells from methanol- HCl solutions recently, but their conductivities were less than 10^{-3} (S-cm). Yet these examples of "proton doping" are ambiguous, since the acid anhydrides SO_3^5 and Cl_2O_7 would formally oxidize $(CH)_x$, while no anhydride exists

for HCl or HBr. Thus, the reported "proton oxidation" may actually be proceeding through a formal oxidation by the anhydride. In this work, the reaction of HF with polyacetylene to make a highly conducting polymer is reported. This result clearly supports the model of proton doping, and also clarifies several other reported reactions where HF is probably the active species.

EXPERIMENTAL

$(\text{CH})_x$ and $(\text{CD})_x$ were made by published methods,⁶ and were mixtures of cis and trans materials. HF (Matheson) was made anhydrous by adding to excess K_2NiF_6 (Alfa Ventron) in a Teflon FEP tube attached via Swagelock connectors to a stainless steel vacuum line. The solution was pumped at -96°C to remove residual SiF_4 . Gas phase infrared spectra showed no impurities. The FEP is somewhat permeable, so the solution was frozen at -196°C and pumped on to remove any air or oxygen evolved within the container before each reaction. NH_3 (anhydrous, Matheson) was condensed at -196°C and evacuated. The ammonia was warmed to -78°C and the polyacetylene was exposed to the vapors (~ 46 torr) for about one hour. ND_3 was prepared from D_2O (Aldrich, 99.8% Gold Label) vapors passed onto Li_3N (Alfa Ventron, 94%), distilled, and kept at -78°C during exposure to the polyacetylene. Samples were handled in a Vacuum Atmospheres Drilab with argon. One to ten milligrams of polyacetylene were weighed in the Drilab on a Perkin Elmer AD2-Z electrobalance to an accuracy of less than $\pm 1 \mu\text{g}$. ESR data was collected on a Varian E-3 spectrometer.

Transmission IR of lightly doped samples of $(\text{CH})(\text{HF})_{0.0163}$ and $(\text{CD})(\text{HF})_{0.0115}$ are shown in Fig. 1, and summarized in Table 1. It is apparent that both samples share common features. A broad absorption occurs above 2000 cm^{-1} , which obscures the C-H stretches,

but not the C-D stretch near 2200 cm^{-1} . A second broad absorption (about 1420 cm^{-1}) is centered just above the cis C-H bend (1335 cm^{-1}). A similar band is observed about 1200 cm^{-1} just above the corresponding 1050 cm^{-1} peak of $(\text{CD})_x$. A sharp peak at 1295 cm^{-1} is apparent in the $(\text{CH})(\text{HF})_{0.0163}$ sample, and has been observed in several other doped $(\text{CH})_x$ samples. While it is tempting to ascribe this peak to a C-F stretch, this peak is not seen in the $(\text{CD})(\text{HF})_{0.0115}$ sample, and does occur in $(\text{CH})(\text{I}_3^-)_x$ samples^{5,7} where it cannot be assigned to C-F bonds. The third broad absorption is seen enveloping the cis and trans C-H bending modes, and the equivalent region of the $(\text{CD})(\text{HF})_{0.0115}$ sample. The remaining features are from the original material.

The similarity of these three bands, with those which appear upon formal oxidation of the polyacetylene by AsF_5 , is striking.⁸ Yet in this case, HF has no formal oxidizing ability, and can only protonate the polymer. This protonation can localize the electrons of the π bond in a new C-H bond. The protonated carbon is changed from sp^2 to sp^3 hybridization, and the positive charge is delocalized along the polymer chain. The polymer region containing this positive charge would be identical to the region after undergoing a formal oxidation, except for the shorter chain length due to the protonated ends. It is not surprising that the strong absorptions that arise from vibrations within these delocalized electron regions would appear identical to the formally oxidized polymers.

Further reaction of these samples with HF lead to conducting polymers (Table 2). These materials are opaque in the infrared. On two samples, sufficient current was passed to completely polarize any free acid, but no change in the conductivity was noted. These two experimental facts are consistent with a metallic, and not ionic, conductivity. In air, the conductivity slowly dropped over 24 hours to form an insulator.

The composition versus conductivity curves are noteworthy. Others have reported the insulator-metal transition with 0.1-1.0% doping.¹ Yet, these $(\text{CH})(\text{HF})_x$ samples at 1% doping still do not show metallic conductivity. Most likely, not every molecule of HF protonates the polyacetylene. The free fluoride coordinates other HF molecules. The largest known hydrogen-fluoride anion is the tetrahedral H_4F_5^- ,⁹ so a composition $(\text{CH})(\text{HF})_{5x}$ could be $(\text{CH})(\text{H}^+)_x(\text{H}_4\text{F}_5^-)_x$. One notes that if H_4F_5^- is the counter ion, then the compositions, as a function of degree of protonation, bracket the previously established insulator-metal transition compositions deduced from formal oxidation studies.

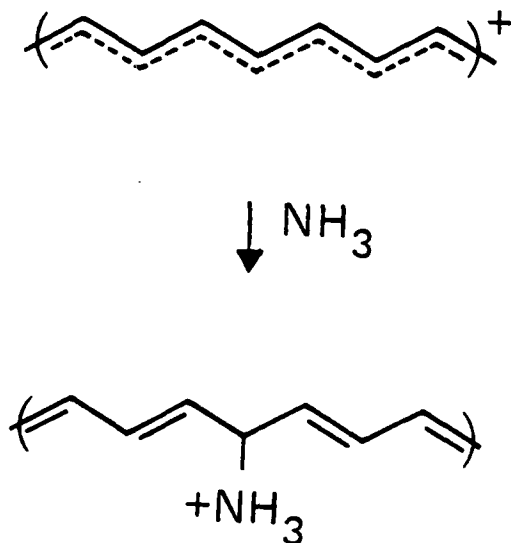
ESR data from these samples were collected. The peak-to-peak width was 1.0G in the protonated $(\text{CH})_x$, and 1.2G in the deuterated material. The g values were unchanged from the original polymer g value (2.003 ± 0.002) of a trans $(\text{CD})_x$ reference. The resonance line appeared to be symmetric, and not Dysonian.

Figure 2 shows the IR spectra of $(\text{CH})(\text{HF})_x$ and $(\text{CD})(\text{HF})_x$ samples after addition of NH_3 or ND_3 vapors at -78°C . All four samples lost their metallic conductivity. Remnants of the three broad bands remain, but many functional moieties are also apparent. Table 3 summarizes the data and the assignments.

The most obvious feature in all four spectra is the loss of any peaks associated with cis-polyacetylene, while prominent peaks occur at 1000 cm^{-1} (trans $(\text{CH})_x$) and 740 cm^{-1} (trans $(\text{CD})_x$). This observation is consistent with past reports that cis is converted to trans upon doping.¹⁰ Protonation of the cis material can lead to a sp^3 carbon intermediate which can revert to the more stable trans material. However, as is shown below, there is no

evidence that rapid H-D exchange occurs. Thus the cis-trans isomerization is performed over the delocalized positive charge region, rather than at the protonation site.

The second significant feature is the strong 2000 cm^{-1} absorption in both $(\text{CH})(\text{HF})_{0.0459}(\text{NH}_3)_{0.0147}$ and $(\text{CD})(\text{HF})_{0.0758}(\text{NH}_3)_{0.0189}$. Nakanishi¹¹ has shown that primary aliphatic amine hydrochlorides have a band at $2100\text{-}1900\text{ cm}^{-1}$, which is not present in the free amine. The bands near 1600 and 1500 cm^{-1} are also characteristic of primary ammonium salts. This is spectroscopic evidence that a reductive addition of ammonia to the oxidized polyacetylene occurs and localizes the conducting hole on the ammonium group.



Nakanishi also points out that for these primary amine hydrochlorides, the N-H absorption is broad and centered near 3000 cm^{-1} , as opposed to 3300 cm^{-1} in NH_3 and 3150 cm^{-1} in NH_4^+ . Therefore, the N-H absorptions overlap the C-H stretches of sp^3 carbons ($2950\text{-}2850\text{ cm}^{-1}$) and may contribute to the broad baseline absorptions in this region. The absence of the 2000 cm^{-1} peak in the ND_3 cases further supports the assignment that the 2000 cm^{-1} band is characteristic of N-H stretches of a R-NH_3^+ .

In both, $(\text{CD})(\text{HF})_{0.0596}(\text{ND}_3)_{0.0333}$ and $(\text{CH})(\text{HF})_{0.0639}(\text{ND}_3)_{0.0255}$, a peak near 2900 is also seen which supports a C-H stretch from protonation. The signal is stronger in the latter compound, since protonation of the $(\text{CH})_x$ chain creates two sp^3 C-H stretches, as opposed to one in the $(\text{CD})_x$ material. No sp^2 C-H stretches are seen in the $(\text{CD})_x$ sample above 3000 cm^{-1} which shows that H-D exchange does not occur.

It is curious, that the weight uptake of ammonia did not equal the amount of HF determined by weight uptake. One might have expected one mole of ammonia for each mole of HF to make the ammoniated material. If hydrogen fluoride anions are present, one might expect some ammonium fluoride or ammonium hydrogen fluorides to be found. However, our experiments did not support this expectation. X-ray diffraction of the $(\text{CH})(\text{HF})_{0.0459}(\text{NH}_3)_{0.0147}$ sample showed no lines of NH_4F , nor any other ammonium salt. The IR does not conclusively rule out the presence of ammonium fluoride, but only a very small peak occurs at 3100-3200 where ν_3 of NH_4^+ occurs. These two facts imply that, if NH_4F is also present, it is at most in tiny particles or in small amounts in the film. It may also be that some HF was lost from the sample upon addition of NH_3 , so that the amount of NH_3 added is greater than the weight uptake. After addition of ammonia (but not before), a fine ring of white powder remains where the polymer touched the glass. Lastly, washing of the polymer with water did not reduce the N%. In the $(\text{CH})(\text{HF})_{0.0483}$ sample, no amount of nitrogen was detected by elemental analysis. Some nitrogen (1-2%) was detected after NH_3 was added to the sample, and remained after washing the sample with water and air drying. This washing should have removed any NH_4F in the polymer. The experimental evidence supports the contention that the bulk of the nitrogen is bound to the polymer, and is not observed as ammonium fluoride. The stoichiometry remains unsettled, although it is

noteworthy that MacDiarmid also observed less than a 1:1 ratio of $N(Et)_3:I$ in polyacetylene.¹

These samples treated with ammonia were stored in sealed containers, under argon, in the Drilab for two weeks. After that time, their infrared properties had changed dramatically. These changes further aided the assignment of the bands (Fig. 3). The most prominent change was the loss of the band at 2000 cm^{-1} in the NH_3 samples. The related band at 1490 had also disappeared. A band at 1650 cm^{-1} has appeared which can be assigned an $R-NH_2$ bend. Therefore, it appears that the $R-NH_3^+$ has transformed to RNH_2 , with loss of HF.

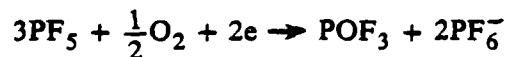
The second feature is most prominent in the ammoniated $(CD)(HF)_x$ samples, where a very strong sp^3 C-H stretch has grown in at 2900 cm^{-1} and 2850 cm^{-1} . In the $(CH)(HF)_x(NH_3)_y$ samples, these two peaks are also prominent along with the sp^2 C-H at 3010 cm^{-1} . In the poly(acetylene- d_2) doped samples, only the sp^3 C-H stretches are apparent. Exchange of the sp^2 carbons, D for H, apparently does not occur.

A similar experiment was made to look for H-D exchange in the protonated material. To a sample of $(CD)(HF)_{0.149}$ which had been left in the Drilab for three weeks and was still quite conducting, NH_3 was added. The resulting spectra showed a large growth of sp^3 C-H peak relative to the sp^2 C-D peak. However, no exchange of sp^3 C-H to sp^2 C-H is observed. Rapid exchange of H for D does not occur in either the initially protonated material or the ammoniated polymer.

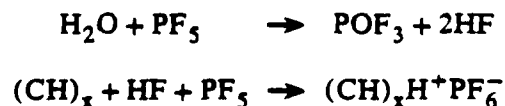
To the $(\text{CD})(\text{HF})_{0.0758}(\text{NH}_3)_{0.0189}$ sample, further HF vapors were added for about one hour. The sample was about 40-fold less conducting than the original $(\text{CD})(\text{HF})_{0.0758}$. When a small current was passed for 24 hours, the conductivity dropped about 1000-fold further, and within a week was insulating. In this compound, the second addition of HF apparently created some ionic conductivity within the polymer.

DISCUSSION

These reactions of HF also explain several other reactions of fluorides with $(\text{CH})_x$. MacDiarmid et al. have shown that PF_5 reacts very slowly, if at all, with $(\text{CH})_x$. However, the addition of "lab air" along with PF_5 caused an immediate reaction.¹ We have duplicated his results, and seen POF_3 in the gas phase products by infrared. An alternative possible formal oxidation reaction is



However, the addition of pure O_2 and PF_5 resulted in a negligibly slow reaction. Even though this reaction is a strong oxidation, there must be a kinetic barrier of breaking the O-O bond. When one exposes $(\text{CH})_x$ to PF_5 , and then admit some water vapors, the infrared immediately shows the presence of POF_3 and the $(\text{CH})_x$ material becomes metallic. In the absence of $(\text{CH})_x$, PF_5 plus water also results in POF_3 (Figure 4). This latter experiment shows that a supply of electrons (from polyacetylene) is not required for this production of POF_3 . These spectra suggest that the following reactions occur:



This final product, rather than PF_5OH^- , is the more chemically plausible chemical final material. Since gas phase IR of an HF and PF_5 mixture shows only the presence of these two gases, and no HPF_6 , HF is the active reagent in this reaction. The fluoride ion affinity of PF_5 would increase the acidity of HF to aid its protonation.

The protonation of $(\text{CH})_x$ must be governed by the acidity of the acid. The acidity trend in aqueous solution



or in the gas phase reaction¹², $\text{HX}_{(g)} \rightarrow \text{H}_{(g)}^+ + \text{X}_{(g)}^-$, appears to contradict this assertion, since HBr and HCl do not increase the conductivity to metallic levels. However, these measures of acidity reflect the H-X bond strength, and ignore the ability of HF to form polyanions. The stability of bifluoride and larger polyanions causes the acidity of HF to increase dramatically as the concentration approaches 100% HF.¹³ The other hydrogen halides have little drive to form such polyanions, so their acidity does not increase as dramatically. The acidity of pure HF becomes much greater than those of the other pure hydrogen halides, and thus, it is capable of protonating polyacetylene to metallic levels.

CONCLUSIONS

Anhydrous HF protonates polyacetylene and raises its conductivity to metallic levels. HF is the first reported nonoxidizing acid to clearly demonstrate the protonation mechanism. The addition of ammonia to the protonated material produces the primary ammonium ion, which reduces the polymer by localizing the hole on the ion. H-D exchange does not occur, so the cis-trans isomerization does not occur at the protonation site, but rather along the metallic chain.

ACKNOWLEDGMENT

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Table 1

	<u>(CH)(HF)_{0.0459}</u> <u>(NH₃)_{0.0147}</u>	<u>(CH)(HF)_{0.0639}</u> <u>(ND₃)_{0.0255}</u>	<u>(CD)(HF)_{0.0758}</u> <u>(NH₃)_{0.0189}</u>	<u>(CD)(HF)_{0.0596}</u> <u>(ND₃)_{0.0333}</u>	
	3210m		3100w		
trans = C = H stretch - C - H asym ⊕ sym; -N-H ₃	3010s 2900sh 2850 ± 60vs	3000m 2900vs 2850sh	2900sh 2850 ± 50s	2900m 2850sh	
	2260	2320	2260sh 2220s	2320s	asym = C-N-D = C-D sym = C-N-D
		2150s		2210vs 2150vs	
-C-N-H ₃ [⊕] 	2000s		2000s		
	1890s 1720m	1890s 1720m		1900m.b	
-C-N _{sciss} -H ₂ ; C-N-H ₃ [⊕] deformation	1600sh	1600sh		1620m	
-C-N-H ₃ [⊕] 	1495vs	1480m	1490s	1490vw	
⊕NH ₃ C-H; C-N 	1400vs	1400vs			
	1295s	1295s			
	1250				
			1225m	1225m	C-N-D ₃ bend (ν ₂ ND ₄ ⁺)
(C-H) ⁺	1180	1175			
C-C{			1150 ± 50	1150 ± 50	NH ₃ C-D
	1120 ± 20	1115		1120 - 1100	C-N-D bend (~ν ₄ ND ₄ ⁺)

Table 1 (Continued)

	$\frac{(\text{CH})(\text{HF})_{0.0459}}{(\text{NH}_3)_{0.0147}}$	$\frac{(\text{CH})(\text{HF})_{0.0639}}{(\text{ND}_3)_{0.0255}}$	$\frac{(\text{CD})(\text{HF})_{0.0758}}{(\text{NH}_3)_{0.0189}}$	$\frac{(\text{CD})(\text{HF})_{0.0596}}{(\text{ND}_3)_{0.0333}}$	
trans = $\overset{\text{I}}{\text{C}}-\text{H}$	1000	1000			
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \\ \text{R} \\ \text{H} \end{array}$	890w	885w	910vw	910vw	
			850sh 800s	850sh 800s	$\begin{array}{c} \\ -\text{C}-\text{D} \\ \\ \text{rock/in plane bend} \end{array}$
	740w		740vs	745vs	trans = $\overset{\text{I}}{\text{C}}-\text{D}$ rock
	475		470		
		450		455	
		400m		400m	
	290	285	~300	~300	
		265	~265	~270	

Table 2

Summary of Polyacetylene-HF Data

x of (CH)(HF) _x Based on Gravimetry	σ (S-cm) ⁻¹	Other Experiments
0.0115*	3×10^{-5}	Lightly doped for IR.
0.0154	8.7×10^{-4}	
0.0163	10^{-4}	Lightly doped for IR.
0.0227	conducts	
0.0459	0.30	(CH)(HF) _{0.0459} (NH ₃) _{0.0147} , both samples for IR.
0.0483**	0.21	Sample showed no N% in elemental analysis. After NH ₃ was added, (CH)(HF) _{0.0483} (NH ₃) _{0.0188} showed N% in sample and sample washed in water.
0.0596*	4.1	(CD)(HF) _{0.0596} (ND ₃) _{0.0333} , both samples for IR.
0.0639	—	(CH)(HF) _{0.0639} (ND ₃) _{0.0255} , both samples for IR.
0.0673	conducts	ESR 1.25G 1/2 width.
0.0737	1.1	
0.0758*	1.42	(CD)(HF) _{0.0758} (NH ₃) _{0.0189} , both samples for IR.
0.0839	2.74	Current passed to exceed the amount of acid-still metallic. ESR 1.1G 1/2 width, g=2.003.
0.0855	10	

Table 2 (Continued)

x of (CH)(HF) _x Based on Gravimetry	σ (S-cm) ⁻¹	Other Experiments
0.115	5.5	Current passed to exceed the amount of acid-still metallic.
0.0149	30	ESR 1.0G 1/2 width, g=2.003. Sample had NH ₃ added to it 3 weeks later, and no H-D exchange was seen.
0.183*	1.2	ESR 1.25G 1/2 width, g=2.003.

* (CD)_x** Rohm and Haas (CH)_x

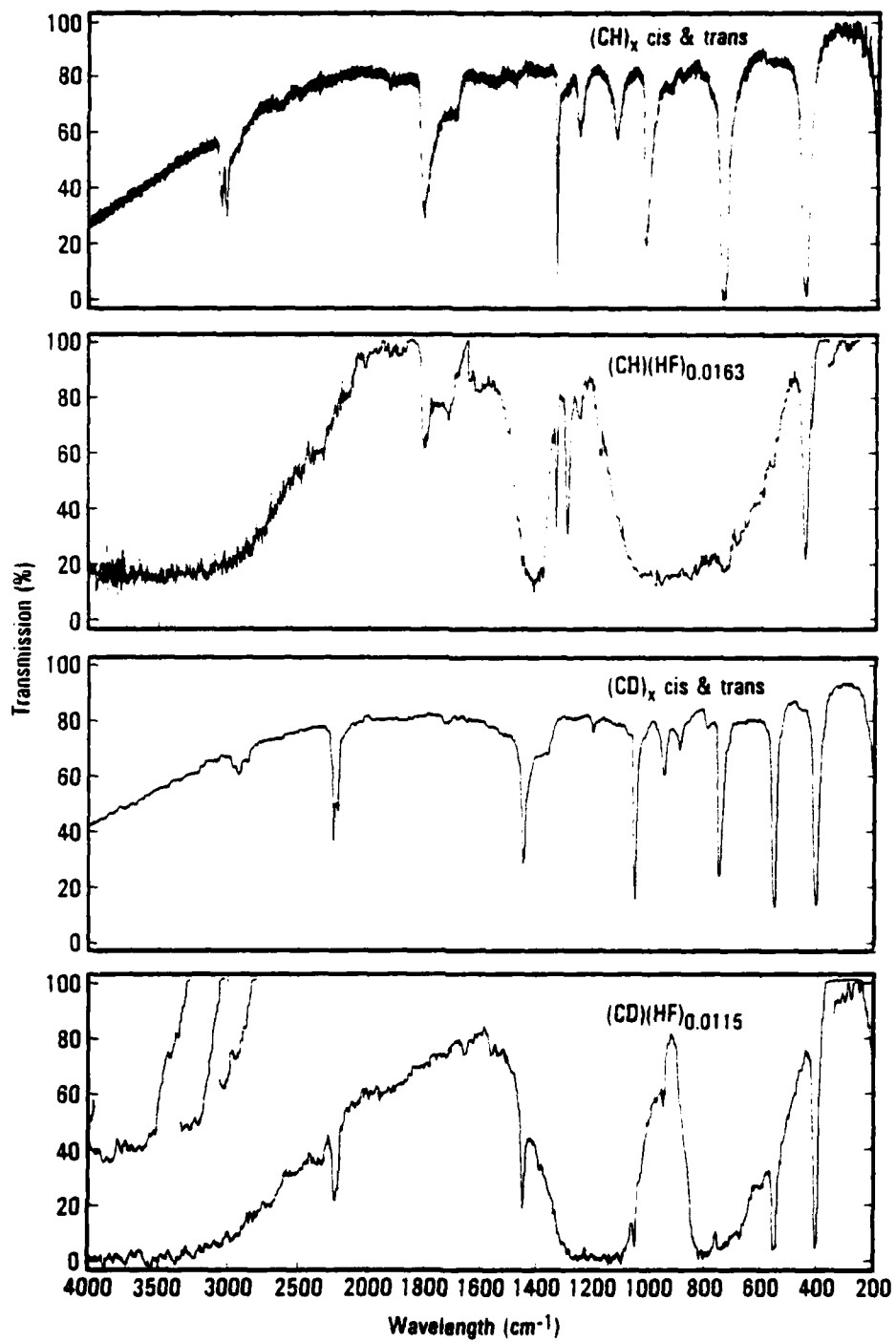


Figure 1. Transmission IR of polyacetylene and lightly doped samples.

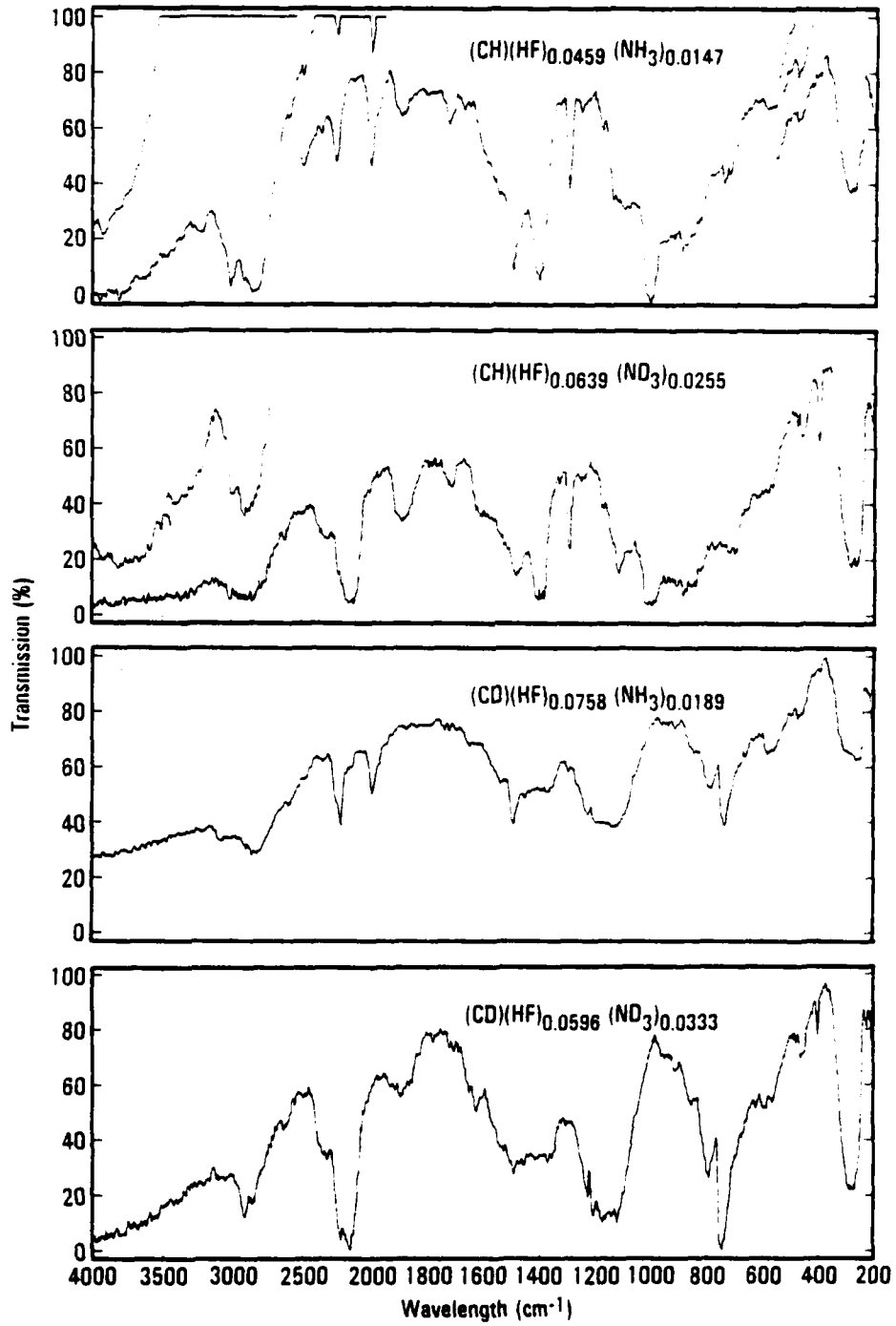


Figure 2. Transmission IR of heavily doped samples after addition of ammonia.

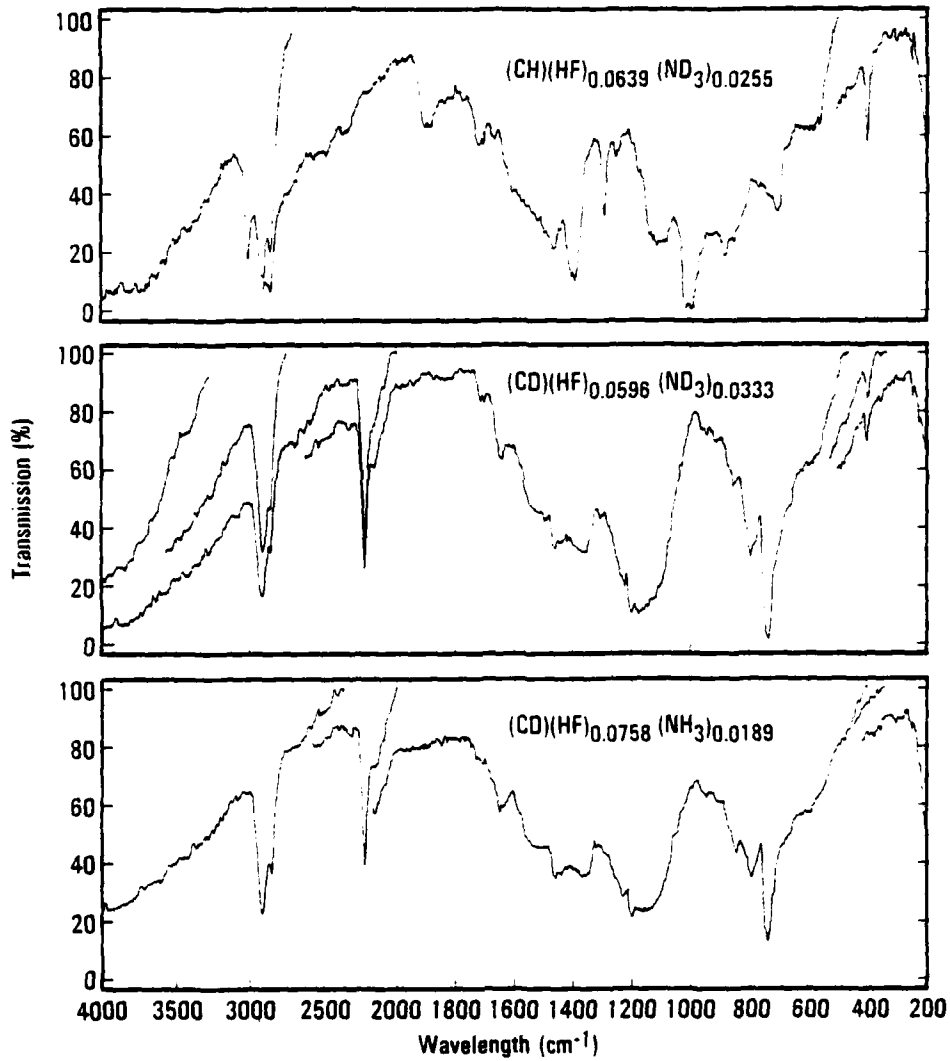


Figure 3. Transmission IR of ammoniated samples after two weeks.

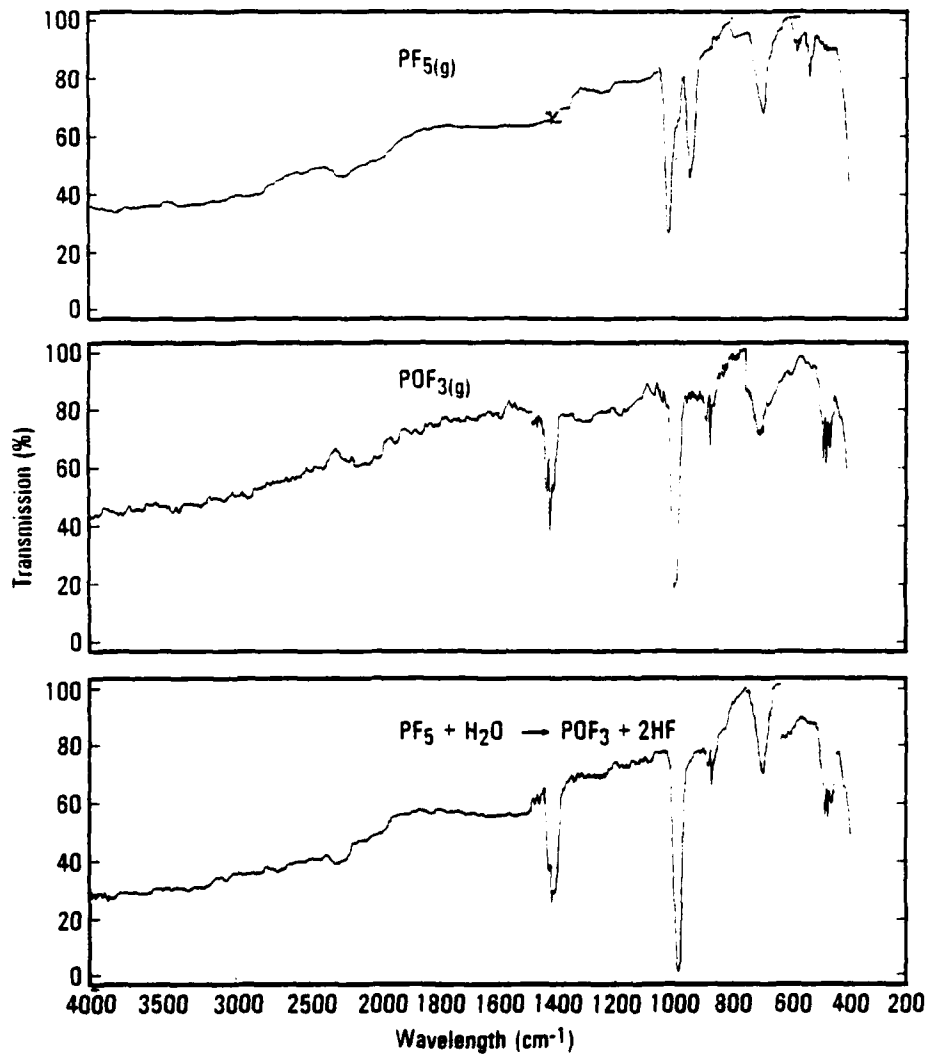


Figure 4. Gas phase IR of reaction products. (The broad peak near 700 cm⁻¹ is AsF₆⁻ on the AgCl passivated windows.)

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