dichloromethane by spectrophotometric methods. The addition of a TPP solution to a dilute solution of TCNE leads to the formation of an intense absorption maximum at 470 nm which may take several minutes to reach its maximum value. (The initial rate is approximately first order in TPP and erratic with respect to TCNE.) The intensity then diminishes slowly and other maxima slowly appear. A peak is also formed at 420 nm when lower concentrations of both reagents are used; this peak is also favored when TCNE is used which has not been freshly resublimed. This species is identified as TCNE$^-$ following the arguments of Isaacs.[11] The succession of spectral changes is similar to that observed for TCNE and aromatic amines by Rappoport,[12] who suggested initial complex formation followed by rearrangement. In our case, however, the slow rate of formation suggests that the product is not formed by a direct donor–acceptor interaction. The suggestion that the species absorbing at 420 nm must be a precursor to the species at 470 nm was disproved by study of the succession of spectral changes. Tri-*m*-tolylphosphine and tri-*p*-tolylphosphine displayed the same solution behavior as triphenylphosphine. Tri-*o*-tolylphosphine failed to react, suggesting steric inhibition from the ortho methyl group.

Experimental Section

The adduct may be prepared by adding 1 ml of a saturated solution of TCNE in benzene to 50 ml of a rather concentrated solution of TPP in diethyl ether. The addition is carried out very slowly from a small syringe while stirring vigorously. A dark red solid forms within a few minutes. It is quite soluble in organic solvents, including dichloromethane and acetone. The method of adding TCNE is quite critical. If the preparation is done with solid TCNE present or by the rapid addition of TCNE solution, the product shows an additional pair of absorption maxima at 395 and 417 nm. These correspond to the maxima reported at 399 and 418 nm for the pentacyanopropenide ion.[13]

Tetracyanoethylene and phosphines were obtained from Eastman. Cyclopropyltriphenylphosphonium bromide was obtained from Aldrich Chemical Co. Purification of reagents and exclusion of the atmosphere appeared to be unimportant in preparation of the solid adduct. In solution studies TCNE was always freshly resublimed under vacuum and triphenylphosphine was recrystallized from ethanol. The solvent was freshly distilled under nitrogen. Solutions were used fresh, kept in stoppered vessels, and transferred *via* syringe, and contact with the atmosphere was minimized at all times. A few experiments done under a nitrogen blanket gave results that were unchanged.

Infrared spectra were obtained from KBr pellets and mineral oil mulls on a Beckman IR-20 spectrophotometer. Visible–uv spectra were obtained on Beckman DK-2 and Cary 14 instruments.

Anal. Calcd for $(TCNE\cdot TPP)_2$: C, 73.8; H, 3.8; N, 14.4; P, 7.9. Found: C, 73.47; H, 3.95; N, 14.18; P, 7.74.

Molecular weight was determined by Galbraith Laboratories by vapor pressure osmometry in $CHCl_3$.

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A Spectroscopic Study of IF_7 and IF_6^+ in Anhydrous Hydrogen Fluoride

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The vibrational spectra of IF_7 were first examined by Lord, *et al.*,[1] but it was later shown that their samples contained IOF_5 impurity.[2] More recently Claassen, *et al.*, have carried out a detailed examination of the gas-phase vibrational spectra.[3] As the Raman spectrum of IF_5 showed considerable frequency shifts and intensity changes on going from the gas to liquid phase,[4] it was felt worth reinvestigating the liquid-phase spectra of IF_7 to compare with the gas-phase observations.

Adducts of IF_7 with fluoride acceptors were first prepared by Seel and Detmer, who proposed an ionic structure $IF_6{}^+MF_6{}^-$.[5] Christe and Sawodny confirmed the ionic nature of $IF_6{}^+AsF_6{}^-$ by vibrational spectroscopy and showed that the cation has octahedral symmetry.[6] Their assignments were recently supported by polarization measurements on the Raman spectrum of $IF_6{}^+AsF_6{}^-$ in anhydrous hydrogen fluoride.[7] A Mössbauer study of $^{129}IF_6{}^+AsF_6{}^-$ has also confirmed the octahedral symmetry of the cation.[8] No quadrupole coupling was observed in the Mössbauer spectrum at 90°K.

Two broad-line nmr studies of solid $IF_6{}^+AsF_6{}^-$ have also been reported. The ^{19}F, ^{75}As, and ^{127}I resonances have all been observed at room temperature.[9] The ^{19}F spectrum at a 4-kG field strength features two broad overlapping peaks. A more detailed study at frequencies up to 94.1 MHz showed resolved peaks for F in $AsF_6{}^-$ and F in $IF_6{}^+$.[10]

In this paper we present the results of a Raman study of IF_7, as a liquid and dissolved in HF, and the ^{19}F nmr spectrum of $IF_6{}^+$ in HF. The Raman spectrum of $IF_6{}^+AsF_6{}^-$ in HF has already been reported,[7] so no further work was carried out on it. The nmr of IF_7 in HF was not investigated because of the extreme broadness of the IF_7 resonance (>5000 Hz).[11]

Experimental Procedures

The IF_7 was prepared as described previously.[3] Infrared spectra showed only traces of HF present with no other impurities. Arsenic pentafluoride (Ozark-Mahoning) was used without further purification. All manipulations were carried out in an all-Monel vacuum line seasoned with chlorine trifluoride except for handling of hydrogen fluoride which was transferred in a Kel-F line. Hydrogen fluoride was purified as previously described.[12]

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Raman spectra on liquid IF_7 and on hydrogen fluoride solutions were obtained by methods described earlier.[13] Fluorine-19 nmr spectra were obtained on a Varian HA-100 spectrometer operating at 94.1 MHz. Nmr samples were made up in $^3/_{16}$-in. o.d. Kel-F tubes which were subsequently sealed under vacuum.

Results and Discussion

The Raman spectrum of liquid IF_7 very closely resembles that reported for the gas (Table I). Shifts in peak positions on going to the liquid state are not significant, in no case exceeding 5 cm^{-1}. This is in marked contrast to comparisons of spectra of the vapor and liquid phases of IF_5 where peak shifts of up to 25 cm^{-1} were reported, in addition to changes in the relative intensities of the peaks.[4] Some intensity changes in the IF_7 spectrum on going to the liquid state are also observed.

TABLE I
RAMAN SPECTRUM OF IF_7

Gas[a]	Pure liquid[b]	Satd soln in HF	Assignment
310 (8)	314 (3)	311 (2.5)	ν_{10}
352 (8)	352 (2.5)	351 (2)	ν_9
510 (17)	508 (7.5)	508 (6.5)	ν_8
(598)[c] (1)	601 (0.6)	599 (0.8)	$2\nu_{10}$
635 P (100)	630 P (100)	632 P (100)	ν_2
676 P (23)	672 P (14)	675 P (14.5)	ν_1

[a] From ref 3. [b] Relative peak heights in brackets. [c] Observed very weakly but not assigned. P = polarized.

A very weak peak was shown in the gas-phase spectrum at 598 cm^{-1} but it was not assigned or commented on further.[3] We found it only as a very weak shoulder on ν_2. However, ν_2 was very much reduced in the "polarized" spectra (polarization factor ≤ 0.09) while the shoulder remained virtually unchanged in intensity, appearing as a resolved peak at 601 cm^{-1} (Figure 1). The relative intensity quoted in Table I was obtained by comparison to ν_8 in the polarized spectrum and then converted to the common base of $\nu_2 = 100$ in the normal spectrum. The 601-cm^{-1} peak is assigned to $2\nu_{10}$ which is allowed in the Raman spectrum and may have only a weakly polarized component. However, an overtone or a combination of the inactive fundamental ν_{11} (e_2'') cannot be ruled out.

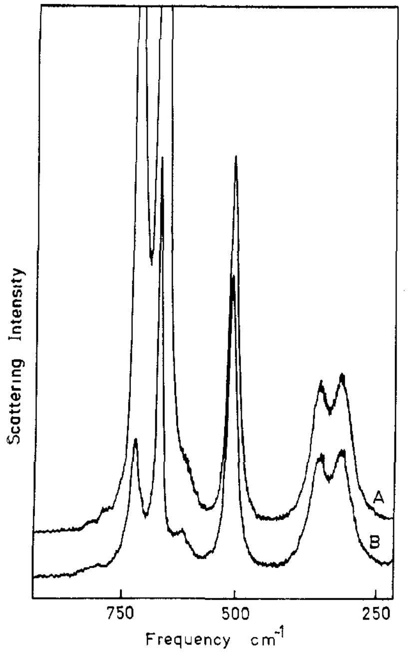

Figure 1.—Raman spectra of liquid iodine heptafluoride (slit widths 6 cm^{-1}). Incident light polarized (A) perpendicular and (B) parallel to the plane containing the slit and laser beam.

No previous studies of the IF_7–HF system have been reported. On preparation of a solution of IF_7 in HF it was found that they were not completely miscible, two liquid phases being formed. This is in sharp contrast to other halogen fluorides. Investigations of ClF_3,[14] BrF_3,[15] BrF_5,[16] and IF_5[17] have shown them to be completely miscible with HF in all proportions. The two-layer sample contained 11.3 mol % IF_7. Thus, the concentration of IF_7 in HF was unknown but less than 6.4 *m*.

The Raman spectrum of IF_7 in the upper HF-rich phase is virtually identical with that of pure IF_7 liquid (Table I). There are no frequency shifts and the relative peak intensities are the same as those found for the pure liquid.

The peak we ascribe to $2\nu_{10}$ was also clearly visible, though harder to see as the entire spectrum was less intense because of the dilution effect.

The ^{19}F nmr spectrum of $IF_6^+AsF_6^-$ was investigated in HF solution containing added AsF_5 to acidify the solution. In this way broadening of the IF_6^+ peaks caused by chemical exchange of fluorine in IF_6^+ and in the solvent by reaction 1 or 2 was suppressed, ensuring that the IF_6^+ signal would be visible without the cooling normally required to slow chemical exchange.[18] $IF_6^+AsF_6^-$ is not very soluble in HF and a

$$IF_6^+ + HF_2^- \rightleftharpoons IF_7 + HF \qquad (1)$$

$$IF_6^+ + 2HF \rightleftharpoons IF_7 + H_2F^+ \qquad (2)$$

solution which had been expected to have a concentration of 0.5 *m* contained a considerable amount of undissolved solid. However, on addition of a threefold excess of AsF_5, all the adduct dissolved.

In addition to the HF solvent line, only nmr signals attributed to IF_6^+ were observed. The nonobservance of AsF_6^- signals in anhydrous HF solutions has been reported before[18] and is explained by a rapid exchange with the solvent *via* AsF_5.

$$AsF_5 + 2HF \rightleftharpoons AsF_6^- + H_2F^+ \qquad (3)$$

The IF_6^+ peak is a sextet whose components are approximately equal in height (Figure 2). The center of the multiplet has a chemical shift of −70.5 ppm from $CFCl_3$. This can be compared to the shift of −171 ± 3 ppm for the parent IF_7.[19] The change in chemical shift of +100 ppm between the parent molecule and the fluoro cation is in the same direction but is considerably larger than the shifts reported between

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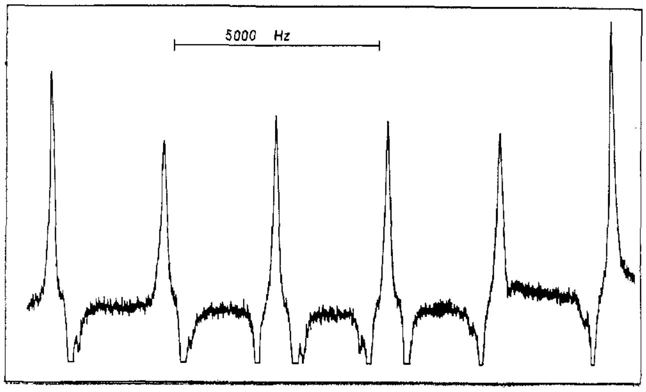

Figure 2.—The ^{19}F nmr spectrum of IF_6^+. Inverted peaks are 2500-Hz modulation side bands from base-line stabilization circuitry.

the parent fluoride and the cations SF_3^+,[18] SOF_3^+,[20] and SeF_3^+.[21] However, it is comparable to the recently observed positive shifts occurring on formation of the halogen fluoro cations ClF_2^+ and BrF_2^+.[22] The IF_6^+ peak position found in the broad-line study of IF_6^+-AsF_6^- solid was −126 ± 16 ppm from CF_3CO_2H (−46 ± 16 ppm from $CFCl_3$), in reasonable agreement with our value.[10]

The signal is split into a sextet by coupling of the six equivalent fluorines to ^{127}I (spin $^5/_2$, 100% abundance). The value of the coupling constant (J_{I-F}) is 2730 ± 15 Hz. This is the first instance of the direct measurement of an iodine–fluorine coupling constant. Only for IF_7 itself has the ^{127}I–F coupling constant been reported, obtained by computer fitting of the spectrum which is partially collapsed by quadrupole relaxation.[11] It was calculated to be 2100 Hz with an error of less than 10%, significantly lower than the coupling constant determined here. It is interesting to note that comparison of the cation SeF_3^+ with other neutral Se(IV) fluorides similarly shows a large increase in the ^{77}Se–^{19}F coupling constant.[21]

It can be seen that although the peaks of the sextet have equal intensities, their widths and thus heights are not all the same (Figure 2). The two outside peaks are sharpest, followed by the two center peaks, with the second and fifth signals being the broadest. The "sharp" outside peaks are in fact fairly broad, having a width at half-height of 1.1 × 10^2 Hz, and the broadest peaks have a width of 1.7 × 10^2 Hz. Broadening of the peaks occurs because of quadrupole relaxation of the iodine. Multiplet line contours for the resonance of equivalent nuclei coupled to a high-spin nucleus undergoing quadrupole relaxation have been calculated by Suzuki and Kubo as a function of the parameter α.[23] For a nucleus of spin $^5/_2$

$$\alpha = \frac{125}{3}\,\frac{1}{T_1}\,\frac{1}{2\pi J}$$

where T_1 is the relaxation time of the quadrupole nucleus and J is the coupling constant to the nuclei being observed. The spectrum we obtain is best described by that calculated for α = 250.[23] Cooling the sample from 34 to 0° causes the IF_6^+ peaks to broaden somewhat further, as expected for coupling to a nucleus undergoing quadrupole relaxation. In contrast, were the broadening of the room-temperature peaks caused by a chemical-exchange process, cooling the sample would slow the exchange and cause the peaks to narrow.

Quadrupole relaxation of a high-spin nucleus occurs if there is an electric field gradient at the nucleus. For an ion of O_h symmetry, such as IF_6^+, the electric field gradient at the iodine will be zero and quadrupole broadening would not be expected to occur. In fact, the broadening is quite large, and a well-resolved spectrum is seen only because of the large value of the ^{127}I–^{19}F coupling constant. Similar results have been previously reported for highly symmetric species. The ^{17}O nmr spectrum of MnO_4^- shows considerable broadening and the six components caused by coupling of ^{17}O to ^{55}Mn (I = $^5/_2$) form one peak envelope with six maxima.[24] Although quadrupole relaxation of ^{17}O itself contributes to the broadening, it was not possible to describe the band shape solely in terms of this effect. A significant broadening caused by quadrupole relaxation of ^{55}Mn also had to be taken into account to fit the observed spectrum. Quadrupole relaxation of the central nucleus has been explained by deformation of the ion, producing an electric field gradient at the nucleus. This can be due to collisions with other molecules in solution, which cause momentary distortions of symmetry.[24,25]

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The Reaction of Hydridopentacyanocobaltate(III) with Ferricyanide

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While the hydridopentacyanocobaltate(III) ion, $Co(CN)_5H^{3-}$, has been found to exhibit pronounced reactivity toward substrates such as free radicals[1] and conjugated olefins[2] to which it can transfer a hydrogen atom, it appears to be intrinsically rather unreactive toward simple "electron transfer" type oxidants such as ferricyanide. Reactions of the latter type are, however, frequently promoted by OH^- and occur readily at sufficiently high pH. Under these conditions $Co(CN)_5H^{3-}$ was found to react with $Fe(CN)_6^{3-}$ in aqueous solution in accord with the stoichiometry

$$Co(CN)_5H^{3-} + 2Fe(CN)_6^{3-} + OH^- \longrightarrow [(NC)_5FeCNCo(CN)_5]^{6-} + Fe(CN)_6^{4-} + H_2O \quad (1)$$

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