Dreiding models of the cycloheptene can access twist angles for the sp² carbons of the triplet in excess of 90°. The models thus confirm that the hindrance to twisting is minimal.

For 1-anisylcyclohexene (68 ns) and 1-phenylcyclohexene (56 ns) the somewhat longer lifetime suggests a moderate hindrance to twisting, confirmed by the observation of a maximum twist angle of 50–55° for the Dreiding model.

The much longer lifetimes for the arylcyclopentenes are similarly consistent qualitatively with the nearly negligible capacity to twist, as expected a priori. Dreiding models suggest a maximum twist of 10–15°.

We conclude that the effect of ring size is easily understood on the basis of constraint to twisting. In view of the general similarity for the seven-membered ring compound to the acyclic triplet lifetime model, we suggest that its lifetime is determined purely by intersystem crossing at the twisted geometry as for the acyclics. For the six- and five-membered ring compounds, the longer lifetimes may result from an energy barrier to reaching a more fully twisted geometry,[33] from a decrease in spin–orbit coupling at the relaxed geometry of the triplet, or a combination of the two.

Our value for phenylcyclohexene triplet lifetime is in perfect consonance with the value reported by Bonneau,[9] but the previous study[33] of phenylcycloalkene triplet lifetimes afforded much longer values than those we report. Since that work involved steady-state studies with unavoidable assumptions, and since the two independent flash kinetic studies agree for phenylcyclohexene, we believe that the flash kinetic lifetimes are the correct ones. Phenylcyclopentene is a possible exception since we cannot rule out the possibility of impurity control in our case.

Summary

We have determined the lifetimes of a series of arylalkene and aryycycloalkene triplets and have discussed possible origins for the effects of degree of substitution, deuterium substitution, and ring size on those lifetimes. To us, the most interesting extrapolation of the present results is the possible role of nuclear motions in govening intersystem crossing rates in triplet biradicaloid species. Further work is planned to examine this hypothesis, since its correctness would have rather general implications for triplet-state photochemistry.

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Fourier Transform Infrared Matrix Spectra of Substituted Alkene–Hydrogen Fluoride Complexes

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Abstract: FT IR matrix spectroscopy has been used to characterize hydrogen-bonded complexes prepared by condensing argon-diluted samples of substituted alkenes and hydrogen fluoride. The ν_s and ν_l modes for methyl-substituted alkenes indicate stronger hydrogen bonding than with ethylene, and the observation of only perturbed out-of-plane C–H₂ modes shows that H–F is perpendicular to the molecular plane in these π complexes. The vinyl fluoride (VF) complex exhibits a weaker hydrogen bond, perturbed in-plane and out-of-plane bending modes, and a displaced C–F stretching mode, which suggest a σ complex with H–F attached to fluorine at an acute angle with the molecular plane.

Introduction

There has been a considerable amount of recent research activity on hydrogen-bonded π complexes of ethylenes or acetylene and hydrogen halides.[1–5] Infrared matrix-isolation[1,2] and microwave[5] spectra have been interpreted to indicate an out-of-plane alkene π complex (Chart I) with the acid perpendicular to the plane of the alkene. Earlier workers reported complexes of HI and substituted alkenes in matrix-isolation experiments.[6–8] The out-

Chart I
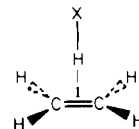
of-plane CH₂ wagging modes of the alkene were particularly sensitive to perturbation by the HX ligand, which provided evidence for an out-of-plane π complex.[1,2,7] A complex involving three molecules of HCl and one propylene (PR) molecule has been

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Substituted Alkene–Hydrogen Fluoride Complexes

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proposed as an intermediate in the addition of HCl to propylene from kinetic data.[9]

Recent matrix-isolation studies of the C_2H_2--HF and C_2H_4--HF complexes[1-3] revealed strong ν_s(H–F) modes at 3745.5 and 3730.7 cm^{-1}, respectively; the red shift from the 3953.8-cm^{-1} isolated HF value is a measure of the hydrogen-bond strength. In addition, the librational mode ν_l of HF in the complex is split, indicating anisotropy in the hydrogen-bonding potential, and ν_l is also characteristic of the hydrogen-bond strength.[2,3] Accordingly, complexes of HF and methyl-substituted ethylenes have been prepared to examine FT IR spectra and to correlate hydrogen-bonding strength in the series. Several HF–fluoroethylene complexes will also be reported for comparison.

Experimental Section

The cryogenic and vacuum apparatus, experimental technique, and FT IR system have been described in earlier papers.[2,3,10] Alkene–hydrogen fluoride complexes were prepared by codepositing Ar/reagent = 300/1 and Ar/HF = 300/1 samples from separate manifolds at about 2 mM/h onto a 12 K CsI plate for 1–20 h. Similar samples of each reagent were condensed without hydrogen fluoride to measure reagent and impurity absorptions in the sample in both the near- and far-IR regions; hydrogen fluoride samples were also condensed without reagent to measure all hydrogen fluoride monomer and dimer absorptions and impurities unique to the fluoride system. Close comparison of high-quality FT IR matrix spectra with accurately reproducible absorbance and frequency measurements allows absorptions due to the acid–base cocondensation reaction to be identified with confidence. Ethylene, propylene, *trans*-2-butene, isobutylene, and vinyl chloride (VC) (Matheson) and fluoroethylene and 3,3,3-trifluoropropene gases (Peninsular Chemresearch) were condensed at 77 K and vacuum distilled from glass beads to remove any volatile impurities. Liquid samples of 2-methyl-2-butene, 2,3-dimethyl-2-butene (DMB), vinyl bromide (VB), and dichloroethanes (Aldrich) were also condensed at 77 K and evacuated. Hydrogen fluoride was prepared with minimum water contamination by reacting equimolar quantities of the elements at low pressure (~2 torr) in a well-passivated stainless-steel vacuum system. Enriched deuterium fluoride was prepared from D_2 and F_2 gases; after the system was exchanged with fresh DF samples for several days, the DF enrichment was approximately 75%.

Infrared spectra were recorded on a Nicolet 7199A FT IR using 1.0-cm^{-1} resolution in the 4000–400-cm^{-1} region (KBr beam splitter) and 2.0-cm^{-1} resolution in the 425–125 cm^{-1} region (6.25-μm Mylar beam splitter): frequency accuracy is ±0.3 and ±0.5 cm^{-1}, respectively, in these two regions.

Results

Experiments codepositing substituted alkenes with hydrogen fluoride at high dilution in argon will be described in turn.

Alkenes. The ethylene–hydrogen fluoride cocondensation reaction has been investigated in detail previously;[2] very intense, sharp product absorptions were observed at 3730.7, 973.0, 423.6, and 396.1 cm^{-1}; the 4000–3500- and 600–400-cm^{-1} regions in the spectrum are compared in Figure 1a with spectra for methyl-substituted ethylene reaction products with hydrogen fluoride. The strong HF absorptions near 3960 cm^{-1} sharp bands at 3920, 3881, 3826, 3702, 561, and 446 cm^{-1} (labeled D), due to hydrogen fluoride monomers and dimers, are common to all of the spectra.[11] The weak water absorption (labeled W) at 3756 cm^{-1} and the H_2O--HF complex at 3554 cm^{-1} (labeled W^c), which has been prepared in greater yield in H_2O and HF cocondensation experiments in this laboratory, are also common absorptions.

Three experiments were done with propylene (PR) and hydrogen fluoride. A very strong, sharp 3690.3- and 3678.3-cm^{-1} (A = 1.0) doublet (labeled ν_s) and a strong, sharp 453.2- and 439.6-cm^{-1} (A = 0.25) doublet (labeled ν_l) are illustrated in Figure 1b; additional sharp product bands were observed at 1640.0 cm^{-1} (A = 0.05) below PR at 1650.5 cm^{-1} at 1009.6 cm^{-1} (A = 0.02) above PR at 997.8 cm^{-1}, at 929.6 cm^{-1} (A = 0.4) above PR at 909.9 cm^{-1}, at 600.8 cm^{-1} (A = 0.03) above PR at 578.6 cm^{-1}, and at 793.6 cm^{-1} (A = 0.05). Sample warming to 22 K over

(9) Haugh, M. J.; Dalton, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 5674.

(10) Andrews, L.; Johnson, G. L. *J. Chem. Phys.* **1982**, *76*, 2875.

(11) Argon-matrix HF and DF spectra and assignments are discussed in: Mason, M. G.; VonHolle, W. G.; Robinson, D. W. *J. Chem. Phys.* **1971**, *54*, 3491; when not completely absorbing, HF appears as a sharp doublet at 3962.4 and 3953.8 cm^{-1} and DF as a single sharp 2895.8-cm^{-1} band.
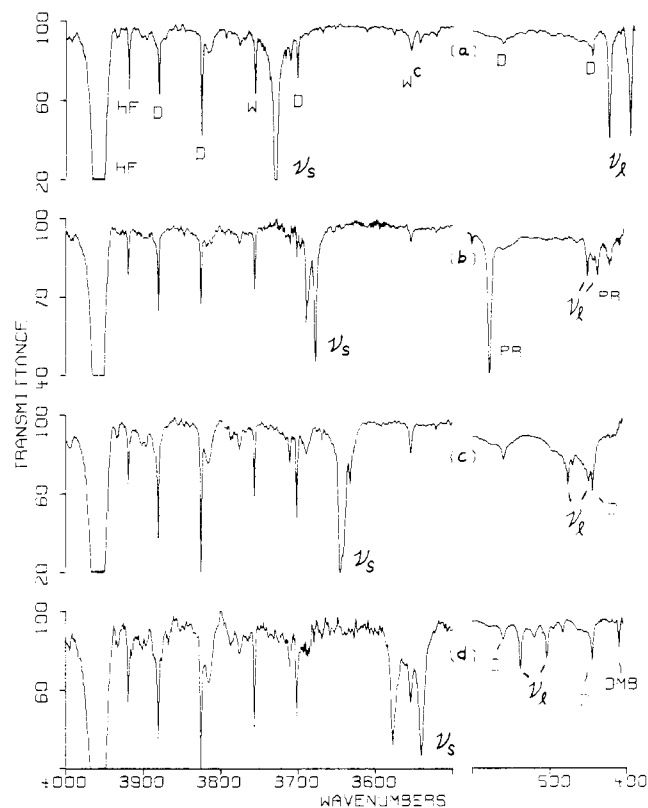

Figure 1. FT IR spectra for complexes prepared by codepositing Ar/alkene = 300/1 and Ar/HF = 300/1 samples at 12 K for 16–20 h: (a) ethylene, (b) propylene, (c) *trans*-2-butene, (d) 2,3-dimethyl-2-butene. The bands labeled D are due to HF dimers or aggregates, W denotes H_2O, and W^c indicates H_2O--HF complex. PR and DMB indicate reagent absorptions.
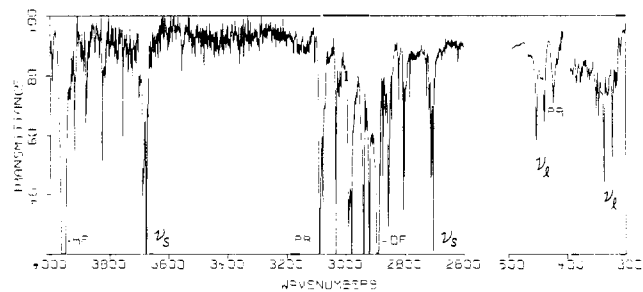

Figure 2. Infrared spectra of matrix prepared by codepositing Ar/propylene = 300/1 and Ar/(HF + DF) = 300/1 samples at 12 K for 20–22 h. PR denotes propylene absorptions. The far-IR experiment used a more completely enriched DF sample.

a 10-min period increased the above product absorptions by 60%. The spectrum from an experiment using an HF and DF mixture is illustrated in Figure 2. The very strong product bands were observed at 3677.8 cm^{-1} (3690.1-cm^{-1} splitting) and 2705.8 cm^{-1} (2713.8-cm^{-1} splitting) (labeled ν_s in the figure), the weaker 1640.0-, 1009.6-, 793.4-, 600.8-, and 595.8-cm^{-1} bands and a sharp 929.6-cm^{-1} absorption are not shown, and strong product bands were observed at 453.1 and 439.9 cm^{-1} (ν_l). The far-IR spectrum of a similar sample gave sharp, strong product bands at 338.5 and 324.3 cm^{-1} (labeled ν_l in the figure).

Experiments were performed with two dimethylethylene isomers. The first with *trans*-2-butene gave a very strong, sharp 3646.1-cm^{-1} band (A = 0.8) (ν_s) and sharp 481.1- and 451.0-cm^{-1} bands (A = 0.1) (ν_l), which are shown in Figure 1c; in addition a weak 996-cm^{-1} band was observed above the 977-cm^{-1} precursor absorption. The second with 2-methylpropene produced a very strong, sharp 3633.3-cm^{-1} band (A = 101), a 1646-cm^{-1} shoulder below the 1657-cm^{-1} precursor band, a sharp 904.7-cm^{-1} band (A = 0.22) above the 890.0-cm^{-1} precursor absorption, and a sharp 475.5-, 472.2-cm^{-1} doublet (A = 0.20, 0.25).
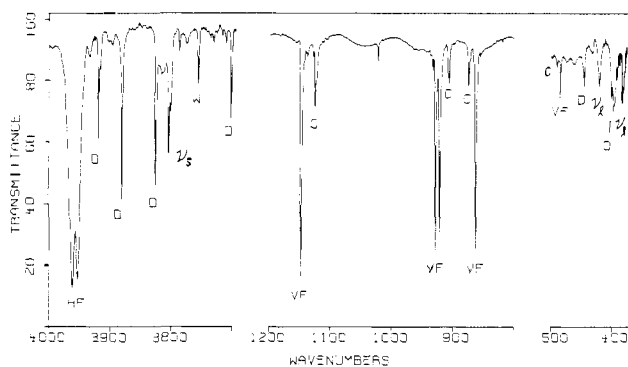
Figure 3. Infrared spectra of complex formed by cocondensing Ar/ C_2H_3F = 400/1 and Ar/HF = 200/1 samples at 12 K. The labels ν_s, ν_l, and C denote product complex bands, and VF indicates vinyl fluoride.

Two experiments were done with 2-methyl-2-butene and hydrogen fluoride; a very strong, sharp absorption was observed at 3593.7-cm^{-1} (A = 0.5) with weaker splittings at 3600.7 and 3584.4 cm^{-1} and a sharp doublet was observed at 507.9 and 491.8 cm^{-1} (A = 0.06).

Several studies were carried out with 2,3-dimethyl-2-butene (DMB). The first experiment gave a strong, split product band at 3577.8, 3555.0, and 3540.8 cm^{-1} (A = 0.52) (ν_s) and a doublet at 538.8 cm^{-1} (A = 0.11) and 504.0 cm^{-1} (A = 0.08) (ν_l) with weaker satellites at 520.7 cm^{-1} (A = 0.03) and 484.0 cm^{-1} (A = 0.025), which are illustrated in Figure 1d. This experiment was repeated with Ar/HF = 600/1 hydrogen fluoride concentration, and the relative intensities of the 3577.8- and 3540.8-cm^{-1} bands were not changed, but the 3555.0-cm^{-1} band increased relative to the 3540.8-cm^{-1} band (A = 0.30), and, in the lower-frequency region, the absorbance ratios of the 538.8-, 520.7-, 504.0-, and 484.0-cm^{-1} bands were unchanged. Temperature cycling this sample to 22 K markedly increased the components of the strong triplet near 3540 cm^{-1} and the doublet at 538.8 and 504.0 cm^{-1} giving a final spectrum similar to that shown in Figure 1d. This reagent was condensed with a DF/HF $\approx$ 2/1 sample, and the intense triplet near 3540 cm^{-1} was reduced in absorbance, a strong new triplet appeared at 2637.1, 2621.2, and 2611.2 cm^{-1}, with the same relative intensities as the 3540-cm^{-1} triplet and the triplet in Figure 1d, and the 538.8- and 504.0-cm^{-1} doublet was reduced in absorbance. A similar far-IR experiment gave new product bands at 398.7 and 378.6 cm^{-1} with weaker satellites at 384 and 363 cm^{-1}.

Haloalkenes. Similar cocondensation experiments were conducted with hydrogen fluoride and a series of halogen-substituted ethylenes. Two experiments were done with vinyl fluoride (VF), and Figure 3 illustrates part of the FT IR spectrum, which contained a sharp 3804.6-cm^{-1} band (A = 0.22) with a 3801.4-cm^{-1} splitting, new bands at 1656, 1125, 907, and 875 cm^{-1} near completely absorbing vinyl fluoride bands at 1650, 1149, 923, and 863 cm^{-1}, a new band at 706 cm^{-1} below VF at 712 cm^{-1}, a new band at 491 cm^{-1} above VF at 485 cm^{-1}, and new bands at 421 and 384 cm^{-1} with shoulders at 431 and 391 cm^{-1}. The product bands are collected in Table II. A similar experiment with vinyl chloride gave a sharp 3773.8-cm^{-1} (A = 0.10) product band, a sharp 905-cm^{-1} band above vinyl chloride at 894 cm^{-1}, a weak 703–698-cm^{-1} doublet below the 713–708-cm^{-1} precursor doublet, and a weak 425-cm^{-1} band. A like study with vinyl bromide produced a sharp 3758.7-cm^{-1} band (A = 0.10) with a 3753.5-cm^{-1} splitting, a sharp 907-cm^{-1} band above vinyl bromide at 898 cm^{-1}, and a weak 601-cm^{-1} band below the precursor at 607 cm^{-1}.

An analogous series of experiments was done with the difluoroethylene (DFE) isomers and hydrogen fluoride. The *cis*-DFE precursor gave a sharp 3865-cm^{-1} band (A = 0.15), a sharp 1710-cm^{-1} band below the intense 1716-cm^{-1} precursor band, a strong new 1112-cm^{-1} band near the precursor multiplet at 1127–1118 cm^{-1}, and new product bands at 398 and 338 cm^{-1}. The 1,1-DFE precursor gave a sharp 3876-cm^{-1} band, a sharp 1731-cm^{-1} shoulder on the 1734-cm^{-1} precursor band, a sharp 1276-cm^{-1} band below the 1290-cm^{-1} precursor band, and a sharp
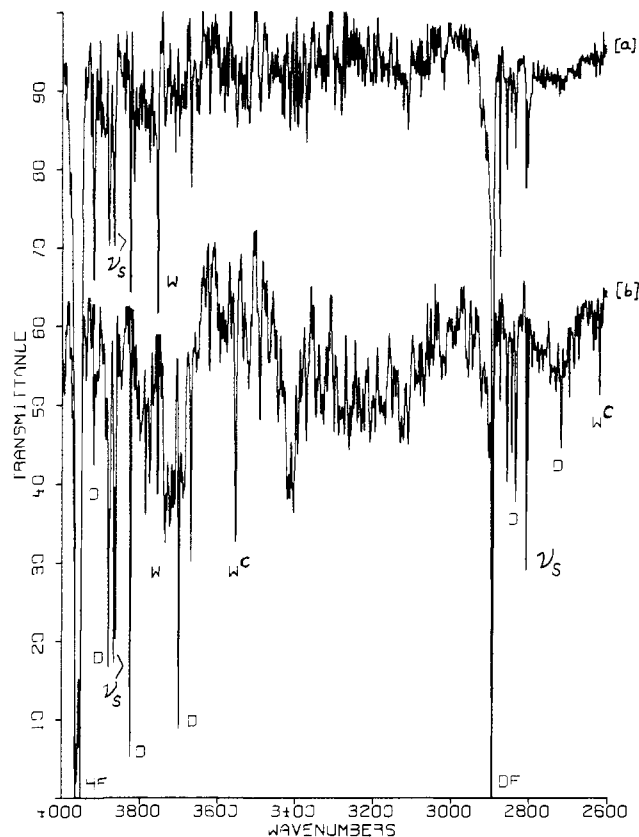

Figure 4. FT IR spectra of matrix prepared by condensing Ar/$C_2H_3CF_3$ = 300/1 and Ar/(HF + DF) = 300/1 samples. The bands labeled D are due to HF and DF aggregates, W denotes H_2O, and W^c indicates H_2O--HF and H_2O--DF complexes; (a) initial samples condensed at 12 K, (b) sample warmed to 24 K for 10 min then recooled to 12 K (transmittance scale displaced).

817-cm^{-1} absorption above the 803-cm^{-1} precursor band. A similar experiment with a *trans*-DFE sample containing *cis*-DFE impurity gave a sharp, strong product band at 3833 cm^{-1} and a weaker product band at 3865 cm^{-1}. An argon resonance photolysis experiment, which gave HF photoelimination in previous studies,[1,3] was performed with 1,1,2-trifluoroethane; three new product bands were observed at 3876, 3865, and 3833 cm^{-1} with comparable absorbances (A = 0.02). One experiment was done with trifluoroethylene and hydrogen fluoride; a weak new product doublet was observed at 3878 and 3868 cm^{-1}.

An experiment was done with 3,3,3-trifluoropropene and an HF/DF mixture. The spectrum, illustrated in Figure 4a, shows the strong HF doublet at 3962.4 and 3953.8 cm^{-1} and weaker HF band at 3920 cm^{-1}, and bands at 3881, 3826, and 3702 cm^{-1} due to HF dimers (labeled D), a new product absorption at 3867.2 cm^{-1} (A = 0.15) with a 3863.1-cm^{-1} shoulder (A = 0.06) (labeled ν_s), water at 3756.4 cm^{-1} (labeled W), and the H_2O--HF complex at 3554.6 cm^{-1} (labeled W^c). In the DF region, the strong DF absorption was observed at 2895.8 cm^{-1}, DF dimer and aggregate bands were observed at 2877, 2858, 2846, 2808, and 2804 cm^{-1} (labeled D), and a sharp new product doublet was observed at 2835.9 and 2833.1 cm^{-1} (A = 0.11 and 0.06) (labeled ν_s). No new product absorptions were observed near very strong precursor absorptions based upon comparison with a sample deposited without hydrogen fluoride. This sample was warmed to 24 K for 10 min to allow diffusion and reaction of trapped HF and DF and then recooled to 12 K, and the recorded spectrum is contrasted in Figure 4b. A number of changes were observed: HF and DF monomer, including bands at 3919 and 2876 cm^{-1}, and water absorption decreased. The D bands increased, the new product doublets increased, 3867.2 and 3863.1 cm^{-1} to A = 0.36 and 0.30 and 2835.9 and 2833.1 cm^{-1} to A = 0.25 and 0.12, and the water-complex bands at 3554.6 and 2721.3 cm^{-1} (labeled W^c) increased.

Ethylene and fluorine samples (200/1) were codeposited at 18 K for 23 h; the initial spectrum revealed a number of product bands including strong new absorptions at 3805.0 (A = 0.8) 1656, 1125, 907, 875, 706, 491, 421, and 384 cm^{-1} and vinyl fluoride bands at 1650, 1139 (site), 923, and 863 cm^{-1}. Photolysis by a water-filtered high-pressure mercury arc for 30 min markedly increased the 3805-, 1656-, 1125-, 907-, 875-, 706-, and 491-cm^{-1} bands and 431- and 391-cm^{-1} bands with little effect on the vinyl fluoride absorptions. Several additional product bands will be considered in a separate report.

Vinyl chloride was codeposited with hydrogen chloride in the manner described previously for ethylene;[1] a new product absorption was observed at 2786 cm^{-1} (A = 0.05), a weak 901-cm^{-1} band was observed above the 894-cm^{-1} precursor absorption, and a weak 699-cm^{-1} band with a 694-cm^{-1} shoulder was observed below the 713–708-cm^{-1} precursor doublet. Argon resonance photolysis experiments with 1,1- and 1,2-dichloroethane samples, Ar/R = 400/1, which gave HCl photoelimination in previous studies,[1,3] produced strong 2786-cm^{-1} (A = 0.6) and 2712-cm^{-1} (A = 0.3) absorptions and sharp 901- and 699-cm^{-1} absorptions that were not present in the reagent samples. A similar experiment with 1,2-dichloroethane-d_4 produced strong 2018- and 1965-cm^{-1} absorptions, which were not present in the precursor sample.

Discussion

The new product absorptions observed in cocondensation reactions of hydrogen fluoride with substituted alkenes will be assigned to hydrogen-bonded complexes, and structural and bonding implications and substituent effects will be considered.

Assignments. The infrared spectrum of a hydrogen-bonded complex can be assigned by comparison with the isolated acid and base molecule spectra. As has been discussed previously,[2,3] the strongest acid submolecule modes are ν_s, the H–F stretching fundamental, and ν_l, the H–F librational fundamental, where the latter may be split depending on the anisotropy of the hydrogen-bonding potential. Owing to the relatively weak hydrogen-bonding interaction, the base submolecule modes are perturbed slightly by the HF ligand and the base molecule serves as a model for the base submolecule in the complex.

The strong, sharp 3677.8-cm^{-1} absorption in propylene experiments is assigned to ν_s for the C_2H_3M–HF π complex (M = methyl) based on the position below ν_s for the C_2H_4–HF complex[2] (3730.7 cm^{-1}) and the HF/DF ratio 3677.8/2705.8 = 1.3592, which is in close agreement with the ratio for the C_2H_4–HF complex (3730.7/2742.0 = 1.3606) and for isolated hydrogen fluoride 3953.8/2895.8 = 1.3654. In like fashion the 453.1-, 439.1-cm^{-1} doublet is assigned to the two nondegenerate ν_l modes owing to the position above the ν_l modes for the C_2H_4–HF complex and the HF/DF ratios 453.1/338.5 = 1.3386 and 439.9/324.3 = 1.3565, which are in agreement with the 423.6/322.5 = 1.3138 and 396.1/296.1 = 1.3381 ratios for C_2H_4–HF. The 793.6-cm^{-1} band could be the overtone of one of the ν_l modes in the C_2H_3-H–HF complex. Although the HF/DF ratio 793.6/595.8 = 1.331 and the overtone/fundamental ratios are reasonable, this possible assignment must be considered tentative. The ν_s and ν_l values for the ethylene and propylene complexes are compared in Table I.

The base molecule fundamentals most likely affected by the HF ligand are the C=C stretching mode and out-of-plane hydrogen motions. Four product bands in the PR experiments correlate with strong PR absorptions corresponding to these vibrations.[12] The 1640.0-cm^{-1} band below the 1650.5-cm^{-1} C=C stretching mode of PR is assigned to this mode for the complex; the 1009.6-cm^{-1} band above the 997.8-cm^{-1} C—H wagging mode of PR, the 929.6-cm^{-1} band above the 909.9-cm^{-1} C—H$_2$ wagging mode of PR, and the 600.8-cm^{-1} band above the 578.6-cm^{-1} C—H$_2$ twisting mode of PR are assigned to these modes for the C_2H_3M–HF complex. Note that the C=C stretching fundamental is *decreased* 10 cm^{-1} in the complex and the out-of-plane hydrogen motions are *increased* 12, 20, and 22 cm^{-1}, respectively, as given in Table I.

(12) Johnson, G. L.; Andrews, L. *J. Am. Chem. Soc.* **1982**, *104*, 3043.

Table I. Acid and Base Molecule and Submolecule Modes (cm^{-1}) for HF and DF π Complexes (C) with Alkenes

$C_2H_3CF_3$	C	Δ^a	assign
	3867.2	−86.6	ν_s (HF)
	2835.9		ν_s (DF)
C_2H_4	**C**	**Δ**	**assign**
	3730.7	−223.1	ν_s (HF)
	2742.0		ν_s (DF)
947.4	973.0		$\nu_7{}^c$
	423.6		ν_l (HF)
	396.1		ν_l (HF)
$C_2H_3CH_3$	**C**	**Δ**	**assign**
	3677.8	−276.0	ν_s (HF)
	2705.8		ν_s (DF)
1650.5	1640.0	−10.5	$\nu_{C=C}$
997.8	1009.6	11.8	$\nu_{C—H}$ rock
909.9	929.6	19.7	ν_{CH_2} rock
578.6	600.8	22.2	ν twist
	453.1		ν_l (HF)
	439.9		ν_l (HF)
	338.5		ν_l (DF)
	324.3		ν_l (DF)
MC_2H_2M	**C**	**Δ**	**assign**
	3646.1	−307.7	ν_s (HF)
977	996	19	$\nu_{C—H}$ rock
	481.1		ν_l (HF)
	451.1		ν_l (HF)
$C_2H_2M_2$	**C**	**Δ**	**assign**
	3633.3	−320.5	ν_s (HF)
1657	1646	−11	$\nu_{C=C}$
890.0	904.7	14.7	$\nu_{C—H_2}$ rock
	475.5		ν_l (HF)
	472.2		ν_l (HF)
C_2HM_3	**C**	**Δ**	**assign**
	3593.7	−360.1	ν_s (HF)
	507.9		ν_l (HF)
	491.8		ν_l (HF)
C_2M_4	**C**	**Δ**	**assign**
	3540.8	−413.0	ν_s (HF)
	2611.2		ν_s (DF)
	538.8		ν_l (HF)
	504.0		ν_l (HF)
	398.7		ν_l (DF)
	378.6		ν_l (DF)

^{a} Δ is complex-molecule difference. The HF fundamental is 3954 cm^{-1} in solid argon.

Following the trends established above, the strong, sharp absorptions and the sharp doublets summarized in Table I are assigned to the ν_s and ν_l modes of the given alkene–HF complexes. The HF/DF ratios for the C_2M_4–HF complex 3540.8/2611.2 = 1.3560, 538.8/398.7 = 1.3514, and 504.0/378.6 = 1.3312 are in close agreement with HF/DF ratios for the C_2H_3M–HF complex reported above. Notice that ν_s decreases while ν_l increases with increasing methyl substitution. In the *trans*-2-butene experiment, the 996-cm^{-1} product band above the 977-cm^{-1} C–H wagging mode of the base is assigned to this mode for the complex. The 2-methylpropene reaction gave a 1646-cm^{-1} shoulder below the 1657-cm^{-1} precursor C=C stretching mode[7] and a sharp 904.7-cm^{-1} band above the 890.0-cm^{-1} precursor C—H$_2$ wagging mode, which are assigned to these modes for the complex.

Two of the alkene–hydrogen fluoride complexes studied here, PR and DMB (Figure 1, b and d), exhibited a substantial splitting in the ν_s mode at higher frequency (smaller $|\Delta\nu_s|$). In the PR case the band at 3690.1 cm^{-1} is 12.3 cm^{-1} above the stronger band. The new band at 3577.8 cm^{-1} is 37.0 cm^{-1} *above* the stronger absorption for the DMB complex, and another pair of librational modes was observed 20 ± 1 cm^{-1} *below* the stronger ν_l bands. The above data indicate a subtle difference in the complexes giving

rise to the two sets of absorptions; possibilities include two HF molecules bonded to the same alkene and a slightly different alkene–HF orientation caused by the matrix atom packing arrangment around the guest complex. If a second HF hydrogen bonded to the first HF in the alkene complex, a substantially different ν_s would be expected, as found for the 1/1 and 1/2 ammonia–hydrogen fluoride complexes.[13] It is also expected that the polarizability of the π system and its resulting proton affinity would be reduced enough by the first hydrogen-bonded HF to reduce the bond strength of a second HF to the same alkene π system more than the observed energy splitting. Furthermore, HF concentration changes and sample warming to allow diffusion and further reaction of trapping HF demonstrate that the strongest two ν_s bands behave similarly, which shows that both species contain the same number of acid ligands. The more likely possibility is a slightly different orientation of the HF ligand in the two DMB species presumably caused by the matrix cage, one giving rise to a weaker hydrogen bond ($\nu_s = 3577.8$ cm^{-1}; $\nu_l = 520.7, 484.0$ cm^{-1}) and the other giving rise to a slightly stronger hydrogen bond ($\nu_s = 3540.8$ cm^{-1}, $\nu_l = 538.8, 504.0$ cm^{-1}).

The product absorptions in vinyl halide reactions with hydrogen fluoride also follow a trend. The 3805-, 1656-, 907-, 875-, 706-, 491-, (431-, 421-, (391-) and 384-cm^{-1} bands were observed upon codeposition of C_2H_3F and HF and upon cocondensation of C_2H_4 and F_2; these bands increased slightly on sample warming in the former experiment and markedly on photolysis in the latter experiment, which verifies their assignment to a C_2H_3F--HF complex.[1] Similar bands observed in nitrogen matrix samples of C_2H_4 and F_2 exposed to glowbar radiation were identified as C_2H_3F--HF following a four-center-reaction.[14] The sharp 3804.6-cm^{-1} band is assigned to the ν_s mode, and the 421-, 384-cm^{-1} absorptions with 431-, 391-cm^{-1}, splittings are assigned to the ν_l modes. The sharp 1656-cm^{-1} band above the 1650-cm^{-1} C=C stretching mode of VF is assigned to this mode of the complex. The sharp 875-cm^{-1} band above the 863-[-1] C–H$_2$ wagging and the weak 706-cm^{-1} below the 712-cm^{-1} torsion of VF[15] are assigned to these out-of-plane modes for the complex. The product bands at 1125 and 907 cm^{-1} below the C–F stretching and C–H$_2$ rocking modes of VF at 1149 and 923 cm^{-1}, and the 491-cm^{-1} band above the 485-cm^{-1} C–C–F bending mode of VF[15] are probably due to these modes for the complex, although perturbed in-plane modes have not been observed for any of the other complexes reported here.

The sharp band at 3773.8 cm^{-1} in vinyl chloride (VC) experiments is assigned to ν_s in the C_2H_3Cl--HF complex. The 905-cm^{-1} band above the 894-cm^{-1} C–H$_2$ wagging mode of VC[16] and the 703–698-cm^{-1} product doublet below the 713–708-cm^{-1} C–Cl mode of VC are assigned to these modes for the complex. The sharp 3758.7-cm^{-1} band in vinyl bromide (VB) studies is assigned to ν_s in the C_2H_2Br--HF complex. The 905-cm^{-1} absorption above the 898-cm^{-1} C–H$_2$ wagging mode of VB and the 601-cm^{-1} band below the 607-cm^{-1} C–Br mode of VB are assigned to these modes in the complex.

The vinyl chloride-hydrogen chloride complex was prepared by codeposition of the reagents and vacuum-ultraviolet photolysis of 1,2-dichloroethane. A new product band at 2786 cm^{-1} in these experiments is assigned to ν_s of the C_2H_3Cl--HCl complex. The weak 901-cm^{-1} band above the 894-cm^{-1} C–H$_2$ wagging mode and the 699-cm^{-1} band below the C–Cl mode of VC are attributed to these modes for the complex. The strong 2786-cm^{-1} band shifted to 2018 cm^{-1} in a similar 1,2-dichloroethane-d_4 experiment; the HCl/DCl ratio (1.381) is near that for the diatomic molecule $(2888/2089 = 1.382)$. The strong band at 2711 cm^{-1} in 1,2-dichloroethane photolysis experiments shifted to 1965 cm^{-1} with deuteration. These bands are tentatively assigned to the complex C_2H_2--HCl--HCl. The HCl/DCl ratio (1.380) is appropriate for a ν_s mode; the displacement to lower wavenumber is attributed to the stronger hydrogen bond formed by the "inside" HCl owing

to the chloride ion affinity of the "outside" HCl in the complex.

The hydrogen fluoride experiments with difluoroethylenes gave product bands which are probably due to complexes. The *cis*-DFE precursor gave a sharp 3865-cm^{-1} band, which is assigned to ν_s, a sharp 1710-cm^{-1} product below the C=C stretching mode[17] of the precursor at 1716 cm^{-1}, and a new 1112-cm^{-1} band below the C—F stretching mode of the precursor at 1127 cm^{-1}, which are attributed to these modes for the complex. The 1,1-DFE reagent gave a sharp 3876-cm^{-1} band, which is assigned to ν_s, and a 1731-cm^{-1} shoulder below the 1734-cm^{-1} C=C stretching mode of the precursor, which is assigned to this mode for the $C_2H_2F_2$--HF complex. In addition, a sharp 1276-cm^{-1} absorption below the C–F$_2$ stretching mode of the precursor[18] at 1290 cm^{-1} and a sharp 817-cm^{-1} absorption above the precursor C–H$_2$ wagging mode at 803 cm^{-1} are attributed to these modes for the complex. A *trans*-DFE sample gave a sharp band at 3833 cm^{-1}, which is assigned to ν_s for the complex. The observation of ν_s bands for the three isomeric $C_2H_2F_2$--HF complexes from vacuum-UV photolysis of 1,1,2-trifluoroethane, which can reasonably be expected to photodissociate to $C_2H_2F_2$ and HF, provides support for the identification of the difluoroethylene–hydrogen fluoride complexes.

The sharp new doublets in the $C_2H_3CF_3$ experiment with HF and DF at 3867.2, 3863.1 cm^{-1} and 2835.9, 2833.1 cm^{-1} exhibit an HF/DF ratio of 1.3637 ± 0.0001, which substantiates their assignment to ν_s of the $C_2H_3CF_3$--HF complex. These bands increased dramatically upon sample warming (Figure 4b) with relatively more increase in the upper components. The two bands in each ν_s doublet are attributed to slightly different orientations of the acid ligand in the complex. The relatively larger increase in the absorbance for the HF species is not without precedent in HF/DF cocondensation experiments. No other absorptions were observed for the complex.

Structure and Bonding. The base submolecule modes in the $C_2H_xM_{4-x}$--HF complexes ($x = 0, 1, 2, 3, 4$) provide information on the structure of the complexes. The observation of a strong C–H$_2$ out-of-plane wagging mode for the C_2H_4--HF complex 25.6 cm^{-1} above this mode for C_2H_4 without an in-plane C–H$_2$ rocking mode removed from the C_2H_4 value indicated an out-of-plane position for the HF ligand in the complex (Scheme I).[1,2] The propylene (PR) complex C_2H_3M--HF exhibited C—H and C—H$_2$ out-of-plane wagging and C—H$_2$ twisting modes above the molecule values and a C=C stretching fundamental 10.5 cm^{-1} below the PR value without any in-plane C—H$_2$ or C—H modes removed from the PR values. These data, summarized in Table I, indicate an out-of-plane π complex analogous to Scheme I. The *trans*-2-butene and 2-methylpropene complexes exhibited out-of-plane C—H and C—H$_2$ wagging modes, respectively, above precursor values and the latter gave a C=C stretching mode 11 cm^{-1} below the base molecule value. These observations are again consistent with an out-of-plane structure for these π complexes; the reduction in the C=C strecthing mode in the complexes implies that the HF ligand withdraws a small amount of π electron density.

The splitting in the ν_l modes for the alkene–hydrogen fluoride complexes demonstrates anisotropy in the hydrogen-bonding potential, which is expected for a π complex. It is interesting to note that the separation between ν_l modes varies between a minimum of 3.3 cm^{-1} for the CH_2CM_2--HF complex and 34.8 cm^{-1} for the C_2M_4--HF complex; this reflects a change in anisotropy in the π system as a function of position and number of conjugating methyl substituents.

The vinyl fluoride–hydrogen fluoride complex, however, exhibits major differences from the propylene complex. The ν_s and ν_l modes indicate a weaker hydrogen bond than in the ethylene complex, whereas the propylene complex forms a stronger hydrogen bond. The out-of-plane C—H$_2$ wagging mode behaves the same as in the propylene complex; however, as the comparison

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Table II. Acid and Base Molecule and Submolecule Modes (cm^{-1}) for HF Complexes with Haloethylenes

C$_2$H$_3$F	C	Δ^a
	3805	−149
1650	1656	+6
1149	1125	−24
923	907	−16
863	875	+12
712	706	−6
485	491	+6
	421	
	384	
C$_2$H$_3$Cl	**C**	**Δ**
	3774	−180
894	905	+11
713	703	−10
	425	
C$_2$H$_3$Br	**C**	**Δ**
	3759	−195
899	907	+8
607	601	−6
1,1-C$_2$H$_2$F$_2$	**C**	**Δ**
	3876	−78
1738	1731	−3
1290	1276	−14
803	817	+14
cis-C$_2$H$_2$F$_2$	**C**	**Δ**
	3865	−89
1716	1710	−6
1127	1112	−15
	400	
	338	
trans-C$_2$H$_2$F$_2$	**C**	**Δ**
	3833	−121

^{a} Δ is complex–molecule difference. The HF fundamental is 3954 cm^{-1} in solid argon.

in Table II shows, the in-plane C—H$_2$ rocking and C—F stretching modes exhibit counterparts below the precursor, the C=C stretching and C—C—F bending modes for the complex are above VF, and the torsion mode is below VF values. The HF complexes with VC and VB and the HCl complex with VC show similar behavior; the C–H$_2$ wag and C–X stretch in the complexes, respectively, appear above and below the precursor values. The substantial reduction in the C–X stretching fundamental in the C$_2$H$_3$X--HX complexes provides strong evidence for a σ complex where the HX ligand is attached to the electron-rich halogen atom rather than the π system. Similar behavior has been found for the CH$_3$F--HF complex, which exhibits a 3774-cm^{-1} ν_s mode and a 35-cm^{-1} decrease in the C–F mode for the complex as compared to the precursor.[19] The trend of slightly decreasing ν_s (increasing $|\Delta\nu_s|$) for the C$_2$H$_3$X--HF complexes (X = F, Cl, Br) indicates a stronger hydrogen bond of HF to the larger more polarizable halogen substituent, which parallels an increase in proton affinity as shown by the CH$_3$X series.[20] The decreasing effect on the C–X stretching mode with the stronger hydrogen bond to HF is due to the increase in carbon motion vibrating against the heavier X atom where the HF ligand has little effect. The increasing displacement in the C–Cl stretching mode for VC with HCl (Δ = −14) compared to the stronger bonding ligand HF (Δ = −10) may be explained as a greater damping due to the heavier, although weaker hydrogen-bonding, HCl ligand. The decreasing effect on the C–H$_2$ wagging mode with increased hydrogen-bond strength is opposite the effect for C$_2$H$_4$ π complexes,[2] but the trend is consistent with the σ complex proposed above since the HF
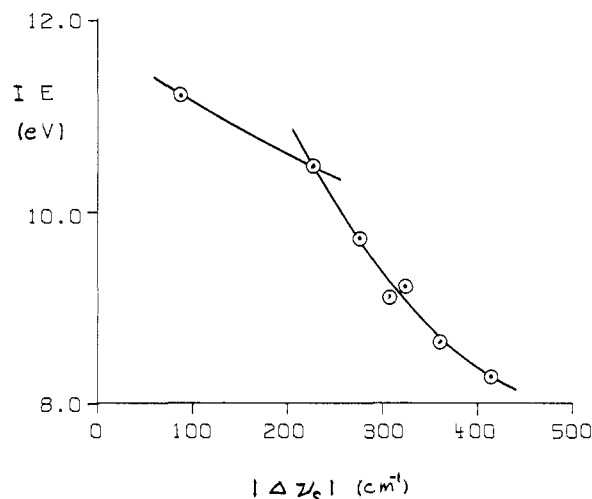

Figure 5. Wavenumber shifts ($\Delta\nu_s$) for the H–F fundamental in alkene–HF π complexes plotted against the first ionization energy of the alkene.

ligand becomes progressively further removed from the C–H$_2$ group with the heavier vinyl halide.

The strong perturbation of four in-plane and two out-of-plane VF submolecule modes in the C$_2$H$_3$F--HF complex suggests that the HF ligand is oriented at some acute angle to the molecular plane. The splitting in ν_l modes indicates substantial anisotropy in the hydrogen-bonding potential implying a nonlinear C–F--H–F unit, and the appearance of an additional matrix site splitting for each ν_l band suggests that two orientations of the HF ligand may be stabilized by the matrix.

Similar behavior was found for two difluoroethylene complexes. In the *cis*-DFE case, the C=C and C—F stretching modes were reduced in the complex, and in the 1,1-DFE case, in-plane C=C and C—F$_2$ stretching modes were reduced and the out-of-plane C—H$_2$ wagging mode was increased by the perturbation. It is suggested that the HF ligand is bonded to fluorine and that its axis deviates from perpendicular to the base molecule plane in the C$_2$H$_2$F$_2$--HF complexes.

Although it is not possible to characterize the structure of the C$_2$H$_3$CF$_3$--HF complex from base submolecule modes, a hydrogen-bonding interaction involving the π bond is suggested. The small displacement in ν_s resulting from a weaker hydrogen bond is explained by the very strong inductive effect of the CF$_3$ group,[21] which results in a decrease in basicity of the π system.

Substituent Effects. The strength of HF hydrogen-bonded π complexes with alkenes varies markedly with methyl substitution as measured by $\Delta\nu_s$, the difference between the ν_s mode for the complex and the isolated HF fundamental (3954 cm^{-1}). This trend is also followed by increasing ν_l values with increasing hydrogen-bond strength.

The increasing $\Delta\nu_s$ in hydrogen iodide complexes with substituted alkenes has been correlated with ionization energy (IE) of the alkene where an increasing $\Delta\nu_s$ follows a decrease in IE.[7] A plot of $\Delta\nu_s$ for the hydrogen fluoride–methyl-substituted alkene π complexes vs. IE of the alkene[22] is illustrated in Figure 5. The strength of the hydrogen bond correlated with ease of electron removal owing to the transfer of electron density from the π system of the alkene to the σ^* orbital of HF. The complex C$_2$H$_3$CF$_3$--HF was prepared as a test case since this olefin has a higher IE (11.24 ± 0.04 eV)[23] owing to the very strong inductive effect of the CF$_3$ group.[20] The C$_2$H$_3$CF$_3$--HF complex exhibited a substantially smaller $\Delta\nu_s$, consistent with the correlation, although the curve through the CH$_3$–ethylene data has a greater slope than the curve fit to the CF$_3$–ethylene observations. In the former case, the CH$_3$ substituents donate a small amount of electron density[21,24] whereas,

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in the latter, the CF_3 group withdraws electron density.[21]

A similar relationship is found between hydrogen-bond strength and proton affinity[20] of the base molecule. Both ionization energy and proton affinity reflect the stability of the product ion in its lowest-energy configuration. The alkene–hydrogen fluoride complex is a model species for the intermediate proton addition complex, similar to that formed by proton attachment *before* rearrangement, as has been the subject of theoretical calculations on the ethyl ion with open and bridged configurations.[25]

Conclusions

Cocondensation of substituted alkenes and hydrogen fluoride at high dilution in argon on a 12 K substrate has produced hydrogen-bonded complexes for characterization by FT IR matrix spectroscopy. In the case of methyl-substituted alkenes, the ν_s (H–F stretch) and ν_l (H–F libration) modes show that stronger hydrogen bonds are formed than with ethylene, and the observation of only perturbed out-of-plane $C–H_2$ base submolecule modes shows that H–F is perpendicular to the alkene plane in these π complexes. The split ν_l modes provide a measure of the anisotropy of the hydrogen-bonding interaction, which shows a dependence on the position and number of methyl substituents. In the case of vinyl fluoride, the ν_s and ν_l modes show that a weaker hydrogen bond is formed compared to ethylene, the observation of a substantially red-shifted C–F stretching mode indicates that H–F attaches to the electron-rich fluorine rather than the π bond, and the observation of four perturbed in-plane modes, two perturbed out-of-plane modes, and two separate ν_l modes for the complex suggests that H–F forms an acute angle with the molecular plane. The observation of acid and base submolecule vibrations in matrix FT IR studies of hydrogen-bonded complexes provides a characterization of the hydrogen-bond strength and the geometry of the complex.

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Structure of Perfluoromethanimine by Microwave, Infrared, and Raman Spectroscopy, Electron Diffraction, and ab Initio Methods

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Abstract: A normal coordinate analysis for CF_2=NF based on infrared, Raman, and microwave data has been performed. The geometric structure was determined experimentally by a joint analysis of electron diffraction and microwave data. The structures of CH_2=NH and CF_2=NF were optimized by ab initio calculations using 4-21G basis sets. For CF_2=NF very short C–F bonds (1.300 (3) Å) and a very long N–F bond (1.389 (2) Å) are determined. These results are in agreement with the corresponding force constants. The N=C bond lengths in CH_2=NH and CF_2=NF are equal within error limits. The bonding properties of CF_2=NF are discussed on the basis of the ab initio calculations.

Introduction

Methanimine, CH_2=NH, is the simplest imine and it has been the subject of considerable chemical and theoretical interest.[1] However, the compound is exceedingly unstable and the gas-phase pyrolysis of amines is the only method for its synthesis. Perfluoromethanimine, CF_2=NF, on the other hand, is a stable compound, much more amenable to experimental study. The latter was first obtained in 1952,[2] but difficult methods of synthesis have limited its structural characterization to ^{19}F NMR and a survey infrared spectrum.[3]

Recently, new preparative methods were found for CF_2=NF,[4] and these allow a detailed investigation of the chemical properties[5] and structure. Here we report the structure of CF_2=NF as determined by infrared, Raman, and microwave spectroscopy, by gas electron diffraction, and by ab initio methods. The results are compared with CH_2=NH and related isoelectronic species O=CF_2, CF_2=NCl, CF_2=CHF, and also CH_2=CF_2.

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Experimental Section

Sample. Perfluoromethanimine was prepared from ClCN according to the literature method.[4] The sample for IR and Raman were purified by GLC on a 20 ft × ¹/₄ in. column packed with 40% perfluorotributylamine on Chromosorb P. The sample for electron diffraction and microwave spectroscoy was purified by distillation and the purity was checked by IR spectra.

Vibrational Spectra. The IR spectra were recorded at ambient temperature in the gas phase (10-cm cell with CsI windows and ca. 10 torr pressure) with a Perkin-Elmer Model 180 spectrophotometer (resolution of 0.8 cm⁻¹). The Raman spectra were taken with a Spex 14018 double monochromator with photon-counting detection. Excitation was via the 514.5-nm line of an Ar⁺ ion laser using 150–350 mW of power. Depolarization ratios were determined by method IV as described by Claassen et al.[6] A low-temperature glass cell similar to that described by Brown

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