

**Figure 6.** Histogram of the lowest 201 vibrational modes in bovine pancreas trypsin inhibitor. Data reproduced from Gō et al.<sup>35</sup> Superimposed are normalized densities of vibrational states (eq 1) varying as  $\nu^2$  (Debye model) and  $\nu^{0.34}$  (fractal model). The latter  $\rho(\nu)$  is derived from the estimated  $d$  for BPTI, assuming the spectral exponent is equal to the fractal dimension.

for a regular three-dimensional solid,  $\rho(\nu) \propto \nu^2$ . Inspection of Figure 6 demonstrates convincingly that the fractal model provides a more accurate description of the low-frequency variation of modes. (An unweighted nonlinear least-squares analysis of the data between  $0 \leq \nu \leq \nu_{\max}$  yields a best-fit normalized  $\rho(\nu) \propto \nu^{0.24}$ .) We conclude that over this magnitude of frequencies some of the details from a complex protein dynamics calculation may be anticipated from an estimate of the fractal dimension. At frequencies above the estimated  $\nu_{\max}$ , the results of Gō et al. and of a more detailed study by Brooks and Karplus<sup>36</sup> both show that

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the distribution of modes decreases toward a nearly constant value (see Figure 6). Since vibrations at these higher frequencies correspond to more localized modes, they are outside the scope of both the fractal model and the vibrations that contribute to the Raman relaxation mechanism.

In summary, fractal models of protein structure and dynamics provide the best explanation for the diversity observed in the temperature dependence of the Raman relaxation rates in paramagnetic proteins. The fractal nature of a protein is characterized by a fractal dimension—a conformational index sensitive to secondary structures and supra-secondary domains—that defines the distribution of vibrational states associated with the collective motions of the polypeptide backbone. Future studies will concentrate on additional paramagnetic proteins, either natural or spin-labeled, that extend the experimental verifications of the proposed fractal models.

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**Registry No.** Reductase, 9037-80-3; dehydrogenase, 9035-82-9; kinase, 9031-44-1; hydrolase, 9027-41-2; cytochrome P450, 9035-51-2; cytochrome c, 9007-43-6; cytochrome c-555, 9048-77-5; trypsin inhibitor, 9035-81-8; pancreatic basic trypsin inhibitor, 9087-70-1.

**Supplementary Material Available:** Table listing protein fractal dimensions for the 70 proteins described in Figure 5 (3 pages). Ordering information is given on any current masthead page.

(37) Earlier work on *P. putida* cytochrome P450<sup>38</sup> indicated  $n$  and  $m$  are essentially independent of changes in the magnetic field position. The variation in  $n$  that was observed from measurements at three magnetic fields, which correspond to the three principal axes of the P450  $g$  tensor (2.42, 2.25, 1.92), is comparable to the precision ( $\pm 0.06$ ) of a single determination of the temperature exponent of the Raman rate. Relatively small changes in the position of the magnetic field are thus inconsistent with the large differences in  $n$  and  $m$  that are observed in the present C551 data.

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## Fourier Transform Infrared Spectra of Conjugated Diene and Cumulene Complexes with HF in Solid Argon

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**Abstract:** Codeposition of conjugated diene and substituted conjugated diene samples with HF produced new absorptions due to  $\nu_s$ (HF) stretching,  $\nu_l$ (HF) librational, and  $\nu^c$ (base) modes in the complexes. Comparison to similar alkene complexes suggests a structural model with HF on the  $C_2$  axis of butadiene and the acid hydrogen oscillating between the regions of maximum  $\pi$  electron density of both  $\pi$  bonds. On the other hand, the degeneracy in the allene  $CH_2$  wagging mode is lifted in the allene-HF complex, which provides evidence for hydrogen bonding of HF to one  $\pi$  bond in allene.

The hydrogen-bonding interaction has attracted considerable attention in recent years. Infrared studies of a wide variety of gas mixtures and matrix isolated samples have been performed.<sup>1-4</sup> Rotational spectra and structural data have been obtained by using pulsed expansion of gases from a supersonic nozzle and Fourier-transform microwave spectroscopy,<sup>5,6</sup> molecular beam electric resonance,<sup>7,8</sup> and direct observations upon gas mixtures for stronger complexes.<sup>9,10</sup> Predissociation and photodissociation spectra for

HF complexes and polymers have been obtained,<sup>11,12</sup> as has rotational fine structure for these species using infrared laser

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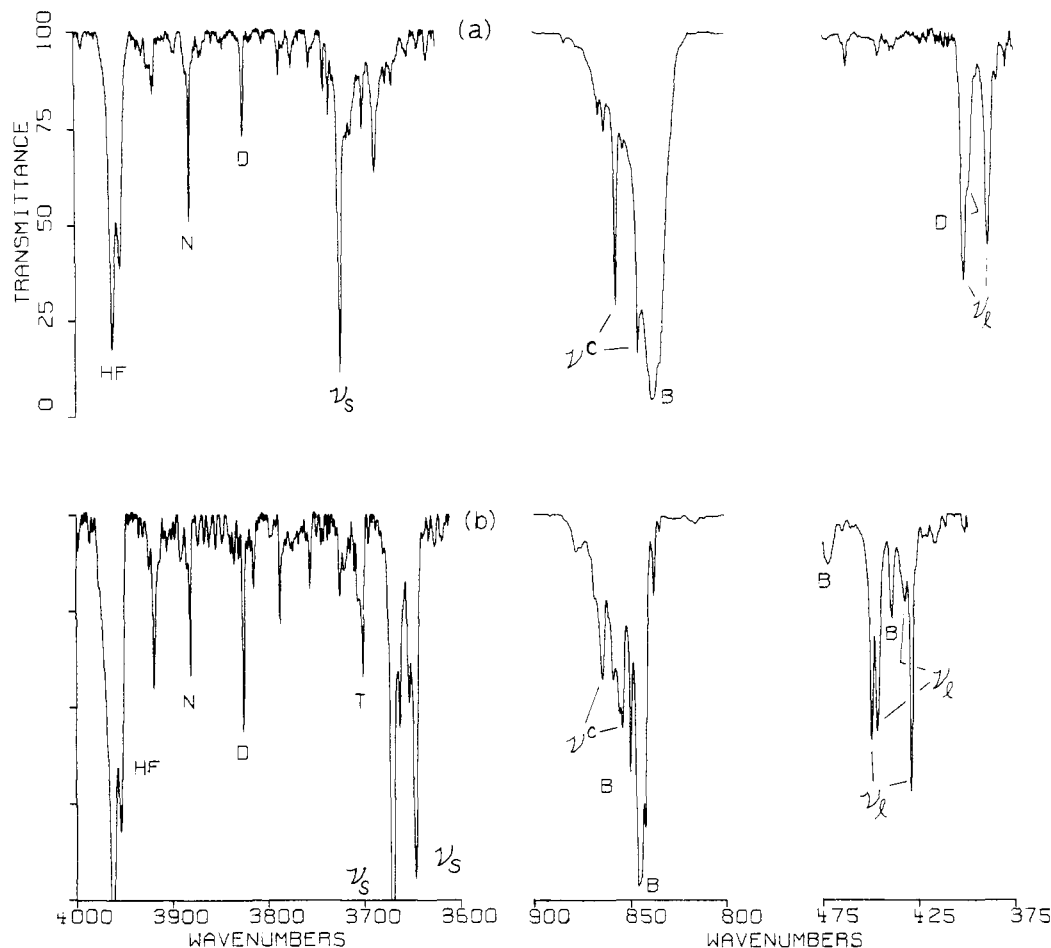
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**Figure 1.** FTIR spectra of cumulene-HF complexes produced by codepositing Ar/HF = 200/1 samples at 10 K: (a) with Ar/allene = 400/1; (b) with Ar/3-methyl-1,2-butadiene = 200/1. B designates absorptions of the cumulene base, HF designates hydrogen fluoride absorptions, N labels the  $N_2$ -HF complex, and D and T denote HF polymers.

spectroscopy.<sup>13,14</sup> Fourier-transform matrix infrared spectroscopy provides complementary information on hydrogen-bonded complexes; in addition to increased sensitivity for observation of H-F stretching modes, H-F librational modes and base submolecule vibrations can be observed for matrix-isolated complexes.

Complexes between  $\pi$  bonds and hydrogen halides were first studied by matrix isolation, where substituted alkene-HI complexes were reported.<sup>15-17</sup> Subsequent matrix infrared spectra obtained for  $C_2H_2$ -HF and  $C_2H_4$ -HF first proposed T-shaped  $\pi$  complexes,<sup>18</sup> which were supported by further studies of ethylene-HF,<sup>19</sup> acetylene-HF,<sup>20</sup> and methyl-substituted ethylenes

and acetylenes with HF.<sup>21,22</sup> Structural information from microwave spectra of ethylene-HF<sup>5</sup> and acetylene-HF<sup>23</sup> and the matrix infrared experiments indicate that HF binds perpendicular to the carbon-carbon bond.

The observation of complexes between localized  $\pi$  bonds and HF generated interest in complexes between conjugated  $\pi$  systems and HF. Both molecular beam electric resonance<sup>24</sup> and matrix infrared<sup>25</sup> spectra of benzene-HF revealed that the average structure of the complex places HF on the sixfold axis perpendicular to the benzene ring; however, the proton of HF apparently oscillates from this position due to the broad potential caused by the extent of the basic site. Complexes resulting from conjugated  $\pi$  systems combined with HF were studied in order to characterize the interaction of HF as localized to one  $\pi$  bond or as oscillating between the  $\pi$  bonds in the conjugated system.

## Experimental Section

The procedure for matrix deposition and the high-vacuum cell, refrigeration, and Nicolet 7199A Fourier-transform infrared spectrophotometer have been described in previous papers.<sup>4,26</sup> Allene and 1,3-butadiene (Matheson Gas Products) and 1,3-butadiene- $d_4$  (MSD Isotopes) were metered directly into the gas manifold and diluted with high-purity argon to the desired concentration in a 2-L stainless steel can. The other compounds (Aldrich Chemical Co.) were twice cooled to 77 K and

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**Table I.** Absorptions ( $\text{cm}^{-1}$ ) for Cumulene-Hydrogen Fluoride Complexes in Solid Argon

mode	allene			3-methyl-1,2-butadiene		
	HF complex	DF complex	uncomplexed base	HF complex	DF complex	uncomplexed base
$\nu_s^a$	3725.0	2737.5		3671.0	2701.4	
				3648.0	2684.0	
C=C=C as str	1949.6	1949.6	1955.5	1967.4	1967.4	1976.9
CH <sub>2</sub> scissors	1391.6	1391.7	1389.7	1368.8	1368.7	1366.4
CH <sub>2</sub> rock	unresolved	unresolved	996.0	1005.2	1005.3	1001.9
CH <sub>2</sub> wag	857.7	858.0	838.5	864.8	863.8	846.1
	846.0	846.3	838.5	854.8	854.9	846.1
CH <sub>2</sub> torsion				580.6	580.3	585.3
$\nu_1$	402.3	303.3		450.0	323.8	
				447.1	322.0	
$\nu_1$	389.8	295.5		429.4	302.9	
				432.5	301.9	
$\nu_s(\text{H}_a\text{-F})^b$	3512.7	2589.7		3400.5	2514.9	
$\nu_s(\text{H}_b\text{-F})^b$				3726.0	2736.6	
CH <sub>2</sub> wag <sup>b</sup>	866.7	866.7	838.5			
	864.0	862.2	838.5			

<sup>a</sup> The H-F fundamental is  $3919.5\text{ cm}^{-1}$  in solid argon; increased displacements from this value indicate increased hydrogen bond strength in the complex. <sup>b</sup> Base-(HF)<sub>2</sub> complex.

outgassed. Hydrogen fluoride (Matheson) was metered into a separate manifold and diluted after degassing at 77 and 179 K; deuterium fluoride was prepared by reacting the elements at low pressure.<sup>26</sup> The gas mixtures were codeposited upon a CsI window maintained at 10 K at average rates of 6 mM/h for each mixture; depositions, in general, required 4 h. The spectra were collected over the frequency range 4000 to  $400\text{ cm}^{-1}$  with  $1\text{ cm}^{-1}$  resolution and from 425 to  $125\text{ cm}^{-1}$  with  $2\text{ cm}^{-1}$  resolution, resulting in frequency accuracies of  $\pm 0.2$  and  $\pm 0.5\text{ cm}^{-1}$ , respectively.

## Results

Each of the compounds was studied in a mid-infrared experiment in which approximately 20 mmol of 200 parts Ar to 1 part base were codeposited with an equal amount of Ar/HF = 200/1. Spectra were recorded and samples were annealed at 22 or 24 K for 10 min to allow diffusion and further association of HF with base molecules. Similar argon-base mixtures were codeposited with Ar/DF = 150/1 with 90% DF enrichment. Assignments of HF stretching ( $\nu_s$ ) and librational ( $\nu_l$ ) modes are based upon changes in band intensity during diffusion, displacement from bands known to originate from HF aggregates<sup>27</sup> or contaminants,<sup>28</sup> and position with respect to the previously observed stretches and librations for alkene-HF complexes.<sup>18,21</sup> Assignments to base submolecule modes are made to new bands displaced from modes observed for the free base that track with  $\nu_s$  and  $\nu_l$  modes upon diffusion but do not appear in separate experiments where a given base-argon mixture was deposited alone and annealed.

Table I lists absorptions arising from the allene-HF and allene-DF complexes. The strong band shown at  $3725.0\text{ cm}^{-1}$  in Figure 1a is close to the ethylene-HF  $\nu_s(\text{HF})$  fundamental, and it may be assigned to the allene-HF  $\nu_s(\text{HF})$  mode; the much weaker  $3689\text{-cm}^{-1}$  band increased relatively more on annealing and is attributed to a different site with a stronger matrix interaction. The  $3725.0\text{-cm}^{-1}$  band is strong and sharp in the initial sample deposit, and upon diffusion at 22 K for 10 min, it more than doubled in intensity. The allene-DF  $\nu_s(\text{DF})$  mode was observed at  $2589.7\text{ cm}^{-1}$ . The bands at  $857.7$  and  $846.0\text{ cm}^{-1}$ , above the free allene absorption at  $838.5\text{ cm}^{-1}$ , are assigned as the CH<sub>2</sub> wagging motions of the allene submolecule in the allene-HF complex; these absorptions increased approximately twofold upon diffusion as well. The librational modes of HF for the allene-HF complex were observed at  $402.3$  and  $389.8\text{ cm}^{-1}$  ( $\nu_l$  in Figure 1a), just below the ethylene-HF librational modes.<sup>19</sup> It should be noted that the  $402.3\text{-cm}^{-1}$  band is close to the HF dimer librational doublet at  $401$  and  $396\text{ cm}^{-1}$ ; but, as is shown in Figure 1a, the stronger  $\nu_s$  motion for the dimer, labeled D, is relatively weak and the  $401\text{-cm}^{-1}$  absorption does appear as a shoulder on the  $402.3\text{-cm}^{-1}$  band in the far-infrared experiment done under similar conditions. New  $303.3\text{-}$  and  $295.5\text{-cm}^{-1}$  bands

are assigned to the allene-DF librational modes. The C=C antisymmetric stretch and CH<sub>2</sub> scissors bend<sup>29</sup> are also observed to be perturbed in the complex; no perturbed CH<sub>2</sub> rock, however, was observed, which may be due in part to severe band broadening upon annealing. In addition to growth in allene-HF complex bands, the allene-(HF)<sub>2</sub> complex was formed upon annealing, as observed from the appearance of  $\nu_s(\text{H}_a\text{-F})$  at  $3514.5\text{ cm}^{-1}$  and its DF counterpart at  $2589.7\text{ cm}^{-1}$ . The  $\nu_s(\text{H}_b\text{-F})$  mode was not observed and is presumed to be insufficiently intense for observation.

3-Methyl-1,2-butadiene and HF produced two  $\nu_s(\text{HF})$  modes at  $3671.1$  and  $3648.0\text{ cm}^{-1}$ , an antisymmetric C=C=C stretch at  $1967.4\text{ cm}^{-1}$  below the base value of  $1976.9\text{ cm}^{-1}$ , two CH<sub>2</sub> out-of-plane wagging modes at  $854.8$  and  $864.8\text{ cm}^{-1}$ , above the  $846.1\text{ cm}^{-1}$  base value, the C=C=C in-plane bend at  $580.6\text{ cm}^{-1}$  decreased from  $585.3\text{ cm}^{-1}$ , and two pairs of librational modes, as listed in Table I. Upon controlled diffusion, the above bands increased in intensity; in addition, strong new bands appeared at  $3726.0$  and  $3400.5\text{ cm}^{-1}$ , which are assigned, respectively, as H<sub>b</sub>-F and H<sub>a</sub>-F motions for the complex of two hydrogen fluoride molecules with one base molecule. This base and DF gave a complex which differed primarily in  $\nu_s$  and  $\nu_l$  frequencies, which are listed in Table I.

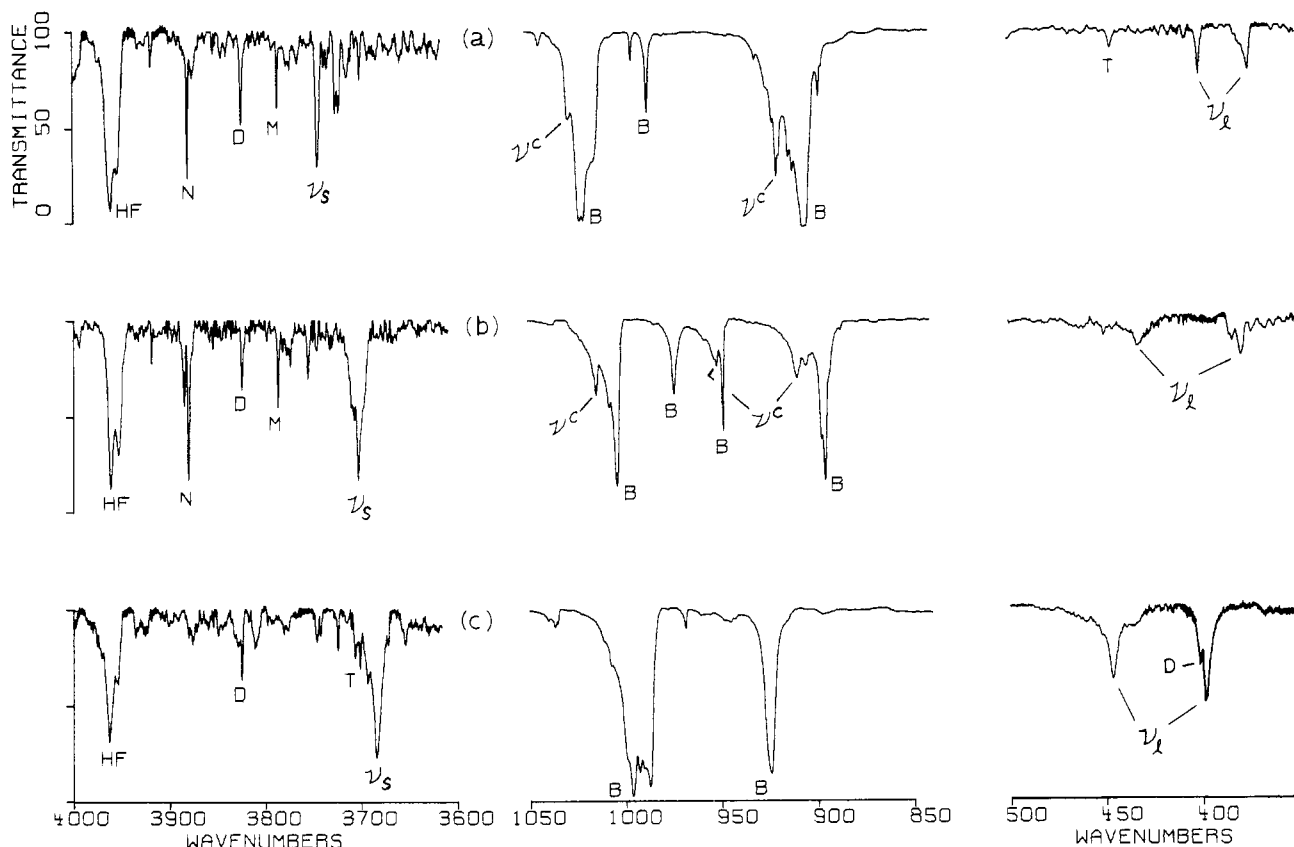
Cocondensation of 1,3-butadiene and HF in excess argon produced two  $\nu_s$  bands at  $3746.0$  and  $3726.5\text{ cm}^{-1}$ . Both of these bands grew a similar extent during annealing at 17 K; annealing at 24 K, however, reduced the intensity of the  $3726.5\text{-cm}^{-1}$  band and increased that of the  $3746.0\text{-cm}^{-1}$  band by a factor of 2; the latter spectrum is shown in Figure 2a. The experiment was repeated with more dilute 1,3-butadiene, then with more dilute HF; these experiments indicate that both  $\nu_s$  bands arise from 1/1 complexes, with the  $3726.5\text{-cm}^{-1}$  band arising from a more strongly interacting matrix acid-base configuration that is not favored on annealing. The DF counterparts at  $2752.1$  and  $2738.8\text{ cm}^{-1}$  exhibit similar behavior upon annealing. Librational modes were observed for the complex at  $400.9$  and  $375.3\text{ cm}^{-1}$  ( $\nu_l$ ) with DF counterparts at  $304.4$  and  $281.4\text{ cm}^{-1}$ , respectively. Although the  $400.9\text{-cm}^{-1}$  band is near the (HF)<sub>2</sub> librational mode,<sup>27</sup> the low dimer yield in these experiments and growth paralleling that of the  $375.3\text{-cm}^{-1}$  band after diffusion argue for minimal (HF)<sub>2</sub> absorption at  $401\text{ cm}^{-1}$ . Several 1,3-butadiene-base submolecule modes were observed and are assigned to bands as listed in Table II; the C=C antisymmetric stretch is decreased  $2\text{ cm}^{-1}$  and the hydrogen bending, rocking, and wagging motions are increased  $2\text{--}15\text{ cm}^{-1}$  from free butadiene values.<sup>30</sup> The diffusion behavior of these bands parallels that of the  $3746.0\text{-cm}^{-1}$  band rather than that of

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**Figure 2.** FTIR spectra of conjugated diene-HF complexes obtained after 24 K diffusion for 10 min of Ar/HF = 200/1 samples codeposited: (a) with Ar/1,3-butadiene = 200/1; (b) with Ar/*trans*-1,3-pentadiene = 400/1; (c) with Ar/*trans*-2,trans-4-hexatriene = 400/1. The band labeled M arises from N<sub>2</sub>-(HF)<sub>2</sub> complex; B designates bands of the conjugated diene base.

**Table II.** Absorptions (cm<sup>-1</sup>) for 1,3-Butadiene and 1,3-Butadiene-*d*<sub>4</sub>-Hydrogen Fluoride Complexes in Solid Argon

mode	1,3-butadiene-HF	1,3-butadiene-DF	1,3-butadiene
ν <sub>s</sub> (stable)	3746.0	2752.1	
ν <sub>s</sub> (unstable)	3726.5	2738.8	
ν <sub>s</sub> (H <sub>a</sub> -F) <sup>a</sup>	3515.3	2593.2	
ν <sub>11</sub> + ν <sub>15</sub>	1843.2	1843.8	1815.6
ν <sub>20</sub> (C=C)	1593.9	1593.7	1595.9
ν <sub>21</sub> (CH <sub>2</sub> bend)	1381.3 sh	1381.2	1379.5
ν <sub>10</sub> (CH wag)	1027.8	1027.9	1022.6
ν <sub>23</sub> (CH <sub>2</sub> rock)	988.4 sh	988.4	987.0
ν <sub>11</sub> (CH <sub>2</sub> wag)	919.8	920.2	905.0
ν <sub>1</sub>	400.9	304.4	
ν <sub>1</sub>	375.3	281.4	

mode	1,3-butadiene- <i>d</i> <sub>4</sub> -HF	1,3-butadiene- <i>d</i> <sub>4</sub> -DF	1,3-butadiene- <i>d</i> <sub>4</sub>
ν <sub>s</sub> (stable)	3745.2	2751.3	
ν <sub>s</sub> (unstable)	3725.9	2738.4	
ν <sub>11</sub> + ν <sub>15</sub>	1471.0	1471.0	1450.7
ν <sub>20</sub> (C=C)	1530.7	1530.7	1534.2
ν <sub>10</sub> (CH wag)	973.5	973.5	967.7
ν <sub>11</sub> (CD <sub>2</sub> wag)	736.2	736.2	726.5

<sup>a</sup> For the inside HF submolecule in butadiene-(HF)<sub>2</sub> which increased on annealing. Several site splittings of this band were observed; the frequency given is that of the most intense peak.

the 3726.5-cm<sup>-1</sup> band. Cocondensation of HF and DF with 1,3-butadiene-*d*<sub>4</sub> gave small shifts in the ν<sub>s</sub> modes and new base submolecule modes that are listed in Table II.

Similar experiments were done with *trans*-1,3-pentadiene and HF, and infrared spectra are shown in Figure 2b. The 3703.7-cm<sup>-1</sup> ν<sub>s</sub>(HF) mode of the *trans*-1,3-pentadiene-HF complex was observed to grow by a factor of 3 upon annealing at 17 K, and annealing at 24 K produced approximately 50% more intensity; the DF counterpart was observed at 2723.3 cm<sup>-1</sup>. The librations (ν<sub>1</sub>) appear at 431.8 and 378.5 cm<sup>-1</sup>, while DF librations are

**Table III.** Absorptions (cm<sup>-1</sup>) for *trans*-1,3-Pentadiene Complexes in Solid Argon

mode	1,3-pentadiene-HF	1,3-pentadiene-DF	1,3-pentadiene
ν <sub>s</sub>	3703.7	2723.2	
ν(C=C)	1602.6	1602.4	1607.2
ν <sup>c</sup> (CH wag)	1014.4	1014.5	1004.5
ν <sup>c</sup> (CH wag)	957.6	958.0	948.4
CH <sub>2</sub> wag	909.7	910.0	895.6
twist	821.5	821.6	818.0
ν <sub>1</sub>	431.8	328.4	
ν <sub>1</sub>	378.5	287.4	

observed at 328.3 and 287.4 cm<sup>-1</sup>. For the HF complex, the *trans*-CH=CH wag of higher frequency, corresponding to the methylated double bond,<sup>31</sup> was shifted to 1014.4 cm<sup>-1</sup> from 1004.5 cm<sup>-1</sup>; the other *trans*-CH=CH wag increased from 948.4 cm<sup>-1</sup> for the base molecule to 957.6 cm<sup>-1</sup> for the complex. These and several other perturbed base submolecule modes are listed in Table III.

The *trans*-2,trans-4-hexadiene-HF complex was studied and the spectrum is shown in Figure 2c; the CH wags were not resolved from the base spectrum. The ν<sub>s</sub>(HF) band, however, was observed at 3685.0 cm<sup>-1</sup> and increased by a factor of 2 after annealing at 24 K. One librational mode appears at 447 cm<sup>-1</sup>; this band, which is close to the (HF)<sub>3</sub> libration at 446 cm<sup>-1</sup>, is too intense to be due solely to the trimer, as may be observed from the smaller intensity of the trimer band at 3702.3 cm<sup>-1</sup>. In a separate far-infrared experiment, the other ν<sub>1</sub> mode was observed at 399 cm<sup>-1</sup>. Unlike other HF complexes, the *trans*-1,3,5-hexatriene-HF complex was not observed until after diffusion at 17 K; diffusion at 24 K produced ν<sub>s</sub> at 3742.6 cm<sup>-1</sup> with intensity approximately half that of the 1,3-butadiene-HF ν<sub>s</sub> motion under similar con-

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**Table IV.** Absorptions ( $\text{cm}^{-1}$ ) for 1,3,5-Hexatriene-Hydrogen Fluoride Complexes

mode	complex	base
$\nu_s$	3742.6	
$\nu(\text{C}=\text{C})$	1613.9	1623.7
$\nu_{19}(\text{CH wag})$	1018.0	1012.1
$\nu_{20}(\text{CH wag})$	990.3	986.4
$\nu_{21}(\text{CH}_2 \text{ wag})$	918.2	906.0
unassigned $A''$	829.5	818.9
$\nu_{22}$ twist	595.2	588.7

ditions. This motion, a perturbed  $\text{C}=\text{C}$  antisymmetric stretch, and several CH wags<sup>32,33</sup> are listed in Table IV.

The two nonconjugated dienes, when complexed with HF, gave spectra which were comparable with the propylene-HF complex<sup>21</sup> in regions of concern. The bands produced by 1,4-pentadiene-HF and by 1,5-hexadiene-HF after diffusion are summarized in Table V. Both dienes, however, exhibited a  $\nu_s$  intensity reversal upon annealing; upon deposition, the 1,4-pentadiene-HF  $\nu_s$  appeared at  $3700.9 \text{ cm}^{-1}$ , whereas that of 1,5-hexadiene-HF appeared at  $3685.4 \text{ cm}^{-1}$ . Annealing increased these bands, and also produced bands at  $3677.2 \text{ cm}^{-1}$  for 1,4-pentadiene-HF and at  $3669.0 \text{ cm}^{-1}$  for 1,5-hexadiene-HF in equal or greater intensity.

### Discussion

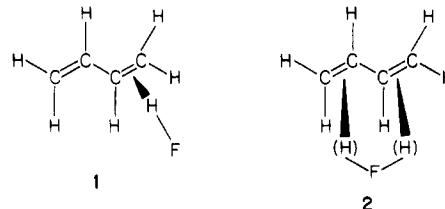
Hydrogen bonding causes variations in the vibrational fundamentals of both the base and hydrogen fluoride submolecules; in addition, the hydrogen fluoride rotations are restrained by the hydrogen bond and become the librational modes ( $\nu_l$ ). In previous studies of complexes between alkenes and HF,<sup>18,21</sup> the vibrational motions of interest were the hydrogen-fluorine stretch ( $\nu_s$ ), the carbon-carbon  $\pi$  bond stretch, and the C-H out-of-plane wagging motions ( $\nu^c$ ). The benzene-HF complex<sup>25</sup> exhibited smaller displacements in both  $\nu_s$  and the C-H out-of-plane wags from isolated molecule values than did the ethylene-HF complex,<sup>19</sup> indicating a weaker hydrogen bond, which is expected based on the lower  $\pi$  bond order for benzene as compared with ethylene. Bond length data suggest that the  $\pi$  bond order at the electron density maxima for 1,3-butadiene is slightly less than that of ethylene; also, appreciable  $\pi$  electron density is present in the single bond of 1,3-butadiene. Observations show that weaker hydrogen bonding is the case for conjugated dienes with HF than for similarly substituted alkenes and suggest that oscillation of the HF proton along the  $\pi$  system occurs in a similar fashion to that for benzene-HF. The  $\pi$  bond order for allene is comparable to that of ethylene, so that a similar hydrogen bonding interaction would be expected. The data show that the allene-HF complex is slightly stronger than ethylene-HF, but that oscillation of HF between the  $\pi$  systems is unlikely.

**Nonconjugated Diene Complexes.** The vibrations of both 1,4-pentadiene-HF and 1,5-hexadiene-HF complexes bear a striking resemblance to those of the propylene-HF complex, as demonstrated in Table V. The three complexes have similar  $\nu_s$  and  $\nu_l$  frequencies. Thus, the nonconjugated diene-HF complexes are believed to have an analogous structure to the propylene-HF complex; HF is out-of-plane and interacts directly with one  $\pi$  bond. Shifts on the CH and  $\text{CH}_2$  out-of-plane wags upon complexation are somewhat less for the nonconjugated dienes than for propylene; this can be accounted for by coupling of the motions for the uncomplexed  $\pi$  system with those of the complexed  $\pi$  system.

**Conjugated Diene Complexes.** The effects of increasing methyl substitution upon the 1,3-butadiene system are analogous to those of increasing methyl substitution upon the ethylene system: added methyl groups increase the basicity of both systems in a nonlinear fashion, as observed by the  $\nu_s$  mode of the HF complexes. However, the 1,3-butadiene system exhibits less basicity than does the ethylene system for any given extent of methyl substitution:

	$\nu_s(\text{HF})$ (R/R')	$\nu_s(\text{HF})$ (R/R')
R = H, R' = H	3730.7	3746.2
R = H, R' = $\text{CH}_3$	3677.8	3703.7
R = $\text{CH}_3$ , R' = $\text{CH}_3$	3646.1	3685.0

Hydrogen fluoride thus interacts slightly less with the conjugated diene system than with a single  $\pi$  bond. In addition, the  $\nu_l$  motions also appear at lower frequencies for conjugated dienes than for alkenes of comparable substitution. These results would be expected from the slightly lower  $\pi$  electron density at the double bonds than for ethylene, as reflected by the longer double bond ( $1.341 \text{ \AA}$  for 1,3-butadiene<sup>34</sup> as compared with  $1.337 \text{ \AA}$  for ethylene).<sup>35</sup> A significant difference is the small effect of methyl substitution upon the lower-frequency  $\nu_l$  motion for conjugated diene-HF complexes: a methyl substitution in 1,3-butadiene increases the lower-frequency  $\nu_l$  by only  $3.2 \text{ cm}^{-1}$ , whereas substitution in ethylene increases the lower-frequency  $\nu_l$  by  $43.7 \text{ cm}^{-1}$ . The small substituent effect for the  $\nu_l$  motion indicates that the region of favorable potential for the HF proton is significantly longer along a conjugated diene than along a nonconjugated  $\pi$  system. These comparisons cast doubt on a structure with HF interacting with a single  $\pi$  bond in the diene like those found for alkenes. The out-of-plane CH wagging modes for both the alkenes and the dienes are increased in frequency mostly by electrostatic repulsion between the HF proton and the hydrogens of the base submolecule. Thus, the shift is expected to be directly proportional to the number of base hydrogens participating in a given CH out-of-plane wag in a complexed  $\pi$  system. In considering the 1,3-butadiene-HF complex as per structure 1 with HF perpendicular to the molecular plane, the coupling of motions between the hydrogens about the complexed  $\pi$  bond and those about the noncomplexed  $\pi$  bond are expected to reduce the shift observed somewhat, as was the case for the CH and  $\text{CH}_2$  of 1,4-pentadiene-HF complex as compared with propylene-HF. The CH wag,  $\nu_{10}$ , is expected to undergo perturbation of somewhat less than  $1/4$  ( $25.6 \text{ cm}^{-1}$ ) =  $6.4 \text{ cm}^{-1}$ , and the observed shift is  $5.2 \text{ cm}^{-1}$ .



The  $\text{CH}_2$  wag  $\nu_{11}$  is expected to be perturbed less than  $12.8 \text{ cm}^{-1}$ ; the observed perturbation, however, is  $14.8 \text{ cm}^{-1}$ . This higher perturbation contradicts not only the  $\nu_{10}$  perturbation but also the lower  $\nu_s$  shift of the 1,3-butadiene-HF complex relative to ethylene-HF, which indicates that HF interacts less effectively with 1,3-butadiene and is, therefore, farther away from the hydrogen atoms in butadiene. This observation suggests structure 2 for the complex where HF is perpendicular to the plane of the molecule and the acid H oscillates between the  $\pi$  bonds with F on the  $C_2$  axis. It must be pointed out that, while the more prominent  $3746.0\text{-cm}^{-1}$   $\nu_s(\text{HF})$  mode is assigned here to the delocalized complex 2, the weaker  $3726.5\text{-cm}^{-1}$  band described above could be due to a localized complex like 1, which is produced in smaller yield in these experiments than 2 and is unstable upon  $24 \text{ K}$  diffusion with respect to 2.

Additional support for structure 2 is obtained from isotopic substitution of the terminal hydrogens in 1,3-butadiene. In the case of ethylene, deuteration of one carbon,  $\text{CH}_2\text{CD}_2$ , decreased  $\nu_s$  for the HF complex from  $3730.3$  to  $3728.9 \text{ cm}^{-1}$ . This apparent slight increase in hydrogen bond strength upon deuteration of the base may be attributed to less electrostatic repulsion between deuterium atoms with smaller amplitudes of motion and the HF proton than between hydrogen atoms with larger amplitudes of

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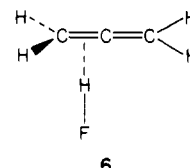
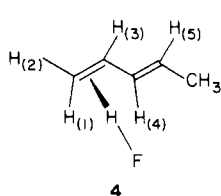
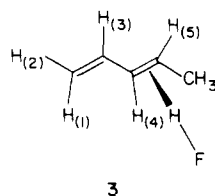
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**Table V.** Comparison of Vibrational Modes ( $\text{cm}^{-1}$ ) of Complexes with Propylene and with Nonconjugated Dienes

mode	propylene-HF		1,4-pentadiene-HF		1,5-hexadiene-HF	
	complexed	uncomplexed	complexed	uncomplexed	complexed	uncomplexed
$\nu_s$	3677.8	3919.5	3677.2	3919.5	3669.0	3919.5
$\nu_1$	453.1		453.3		458.3	
	439.9		425.4		439.4	
CH wag	1009.6	997.8	1003.4	995.6	1016.3	996.6
CH <sub>2</sub> wag	929.6	909.9	934.1	917.5	931.9	911.7

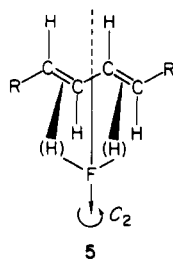
motion and the HF proton. Deuteration of the four terminal positions of 1,3-butadiene, however, leads to a smaller decrease in  $\nu_s$  (from 3746.0 to 3745.2  $\text{cm}^{-1}$ ) than found for the ethylene case described above. This indicates that the decrease in electrostatic repulsions upon deuteration of the terminal carbons of 1,3-butadiene is less than for ethylene, as would be expected for the oscillating structure **2**, but not for a localized structure, like **1**. The shift in the CH wag for the complex also increased slightly for 1,3-butadiene- $d_4$ -HF, but this is attributed mostly to reduced coupling between the CH wag and the CD<sub>2</sub> wag in the base submolecule.

The 1,3-pentadiene-HF complex was initially prepared in order to observe whether the HF attached to the substituted end of the conjugated diene  $\pi$  system, according to structure **3**, or to the opposite end, according to structure **4**, with HF perpendicular to the molecular plane. The observation of only one  $\nu_s$  band for the 1,3-pentadiene complex clearly demonstrates that both **3** and **4** were not produced. This  $\nu_s$  band is substantially different from the  $\nu_s$  observations for ethylene and propylene complexes, and it indicates a weaker hydrogen bonding interaction than found for the propylene complex; in fact, the observed  $\nu_s$  is approximately the average of ethylene and propylene complex values. This comparison points to a longer HF-ligand distance like that suggested for the oscillating model **5** where one R = H and the other R = CH<sub>3</sub>. The perturbations of CH out-of-plane motions ex-



pected for structure **3** are a large perturbation in the *trans*-CH<sub>4</sub>=CH<sub>5</sub> wag and small perturbations in both the CH<sub>2</sub> wag (H<sub>1</sub> and H<sub>2</sub>) and the *trans*-CH<sub>1</sub>=CH<sub>3</sub> wag; the opposite relationship in the perturbation would be expected for structure **4**. Data indicate a combination of the two structures. The CH<sub>2</sub> wag is perturbed by 14.1  $\text{cm}^{-1}$ , comparable to the 1,3-butadiene perturbation. The *trans*-CH<sub>1</sub>=CH<sub>3</sub> wag is increased by 9.2  $\text{cm}^{-1}$ , whereas the *trans*-CH<sub>4</sub>=CH<sub>5</sub> wag is increased by 9.9  $\text{cm}^{-1}$ . Coupling of these two vibrations is presumably significant for this molecule; nevertheless, the fact that the two shifts are nearly, but not exactly, the same suggests that *bonding of HF to one  $\pi$  bond to the exclusion of the other is unlikely*, the same conclusion reached above from the  $\nu_s$ (HF) mode dependence on methyl substitution for alkenes and conjugated dienes.

The apparent interactions of the HF with the entire  $\pi$  system of a conjugated diene suggest the oscillating HF model **5** for the conjugated diene-HF complexes. This model places the HF center of mass along the C<sub>2</sub> axis of a conjugated diene possessing C<sub>2h</sub> symmetry; hydrogen bonding interaction then occurs above and



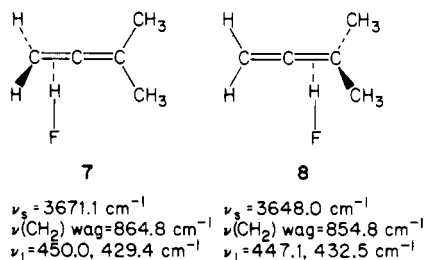
at an angle to each  $\pi$  bond, as the HF molecule oscillates or librates along the  $\pi$  system from its average position on the C<sub>2</sub> axis. The oscillation is assisted by the presence of considerable  $\pi$  electron density between the two double bonds, as indicated by the shorter C-C bond length of 1,3-butadiene, 1.463 Å,<sup>34</sup> as compared with that of propylene, 1.501 Å.<sup>36</sup> The small substituent effect upon the  $\nu_1$  motion of lower frequency is explained by assigning this libration to the motion of H along the  $\pi$  system. Both the smaller  $\nu_1$  frequencies and the smaller  $\nu_s$  shift as compared with similarly substituted alkenes indicate that the HF proton is, on average, farther away from a conjugated diene than from an alkene, which is consistent with observations for the benzene-HF complex.<sup>24,25</sup>

**Cumulene Complexes.** The allene-HF complex exhibits a similar extent of interaction between the  $\pi$  system and HF as does the ethylene-HF complex, as is deduced from the similar  $\nu_s$  frequencies and C=C antisymmetric stretch perturbation, which is slightly less than half of the shift found for propylene-HF. The important observation is that *two* perturbed CH<sub>2</sub> wags appear at 857.7 and 846.0  $\text{cm}^{-1}$  above the degenerate 838.5  $\text{cm}^{-1}$  allene value, indicating that the equivalence of the two allene CH<sub>2</sub> groups is removed in the complex. Both of the  $\nu_1$  modes are slightly lower than for the ethylene HF complex, indicating similar librational freedom and, therefore, a comparable region of favorable potential. These data are most consistent with a structure in which HF interacts with only one  $\pi$  bond, as in **6**. A structure similar to

the oscillating model for conjugated diene-HF complexes is not inconsistent with the  $\nu_s$  and  $\nu_1$  frequencies, but it is ruled out by the observation of two different CH<sub>2</sub> wagging motions, which demonstrate inequivalence in the two CH<sub>2</sub> groups in the complex.

The 3-methyl-1,2-butadiene-HF spectrum is more complicated due to the possible presence of two different complexes. Two strong  $\nu_s$  bands were observed at 3671.1  $\text{cm}^{-1}$  and at 3648.0  $\text{cm}^{-1}$ ; the former is approximately twice as intense as the latter. A single perturbed antisymmetric C=C stretch was resolved with a similar shift as for the C=C stretch for 2-methylpropene-HF. Two pairs of  $\nu_1$  motions appear; the frequencies are more appropriate for propylene-HF than for 2-methylpropene-HF. The most significant feature of the spectrum is two different perturbed CH<sub>2</sub> wags at 864.8 and 854.8  $\text{cm}^{-1}$ ; while the latter of the two is more intense, it is not completely resolved from the free base absorption. From the simultaneous presence of two different CH<sub>2</sub> wags, the formation of the two complexes **7** and **8** is suggested. A delocalized model is again difficult to rationalize based on the two different CH<sub>2</sub> wagging modes. An alternate explanation for these observations, the possibility of matrix site effects, cannot be ruled out completely, but the absence of a preference on sample annealing suggests two different structures.

Proposing two different structures for the 3-methyl-1,2-butadiene-HF complex requires that the two double bonds be similar both in basicity and in ease of approach of HF to the bond. Since the intensity of bands for structure **7** is greater than for those of structure **8**, the unsubstituted end of the molecule is apparently



more readily approached. The basicity of the substituted  $\pi$  bond, however, is somewhat greater, as indicated by the greater  $\nu_s$  displacement for structure 8; the  $\nu_s$  value for this structure, in fact, is only  $13.7 \text{ cm}^{-1}$  greater than that of 2-methylpropene-HF,<sup>21</sup> and the difference may reflect electrostatic repulsions from an allenic proton in the plane of the hydrogen bond. Unlike structure 8, no hyperconjugation with the methyl groups is available to structure 7, but this complex undergoes greater  $\nu_s$  displacement than does allene-HF. The  $\sigma$  bonds of the methyl substituents can be expected to interact with the unsubstituted  $\pi$  bond and donate some electron density to that  $\pi$  bond, especially when an electrophilic ligand such as HF binds.

## Conclusion

The HF complexes of a series of conjugated dienes, 1,3,5-hexatriene, two nonconjugated dienes, and two cumulenes have been produced in solid argon matrices. The nonconjugated dienes, 1,4-pentadiene and 1,5-hexadiene, give complexes strongly analogous to propylene-HF, and no evidence is found for complexes in which HF interacts with both  $\pi$  bonds. The conjugated dienes, on the other hand, form complexes with 1/1 stoichiometry such that HF interacts with the entire  $\pi$  system, rather than with an individual  $\pi$  bond, with the HF proton oscillating between the  $\pi$  electron density maxima. An analogous structure is expected for *trans*-1,3,5-hexatriene; however, the possibility that HF interacts with only two of the three  $\pi$  bonds cannot be excluded entirely. Allene and HF produce a complex in which the degeneracy of the  $\text{CH}_2$  groups is split, indicating a complex to one localized  $\pi$  bond with HF. While the possibility of matrix site splitting cannot be absolutely ruled out, 3-methyl-1,2-butadiene apparently produces two different complexes with HF ligation at one of the two different  $\pi$  bonds.

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## Interaction of Frontier Orbitals of Group 15 and Group 16 Methides with the Frontier Orbitals of Benzene<sup>†</sup>

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**Abstract:** Electron transmission spectroscopy has been employed to determine the energies of low-lying negative ion states of group 15 ( $M = \text{N}, \text{P}, \text{and As}$ ) and group 16 ( $M = \text{O} \text{ and S}$ ) methides,  $M(\text{CH}_3)_n$ , as well as *p*-benzenes containing the related substituents,  $M(\text{CH}_3)_{n-1}$ . Spectral peaks are observed corresponding to electron capture into benzene  $\pi^*$  orbitals perturbed by interactions with the substituents and into substituent  $\sigma^*$  orbitals. Nitrogen substituents give a substantial splitting and destabilization of the benzene LUMO ( $\pi_{4,5}^*$ ) while P and As substituents cause little splitting and a slight stabilization of this orbital. Virtual orbital eigenvalues from minimum basis set SCF-MO calculations on the monosubstituted benzenes show the same trends. Reduction in the *p* character of the substituent lone pair, reduction in the magnitude of interactions, and increased stabilization of the benzene LUMO's by mixing with the substituent  $\sigma^*$  orbitals along the  $\text{N} \rightarrow \text{As}$  series may all contribute to this trend. Similarly, O substituents give a substantial  $\pi_{4,5}^* - \pi_{5,5}^*$  splitting while S substituents give primarily an inductive stabilization of the  $\pi_{4,5}^*$  orbitals.

Main group hydrides,  $\text{MH}_n$ , and their alkyl derivatives, such as  $M(\text{CH}_3)_n$ , have an important role as ligands in coordination and organometallic chemistry. Transition-metal complexes with the group 15 and 16 hydrides and methides are especially well-known. In these complexes, the metal-ligand bond is described as resulting from the donation of a lone pair of electrons from the ligand to form a coordinate covalent bond. A problem with this description of metal-ligand bonding is the buildup of formal negative charge on the metal. However, in many cases, including those considered here, the ligand is more electronegative than the metal and can thus exercise an electron-withdrawing or inductive effect which will permit a delocalization of electron density to stabilize the system. A second means of stabilizing a metal-ligand

coordinate covalent bond involves the donation of charge density from the metal to metal-ligand orbitals of  $\pi$  symmetry arising from resonance interaction<sup>1</sup> of metal *d* orbitals and unfilled ligand orbitals of  $\pi$  symmetry with respect to the metal-ligand bond axis ( $d\pi - \pi$  back-donation).<sup>2</sup> In either case, the frontier molecular orbitals of the ligand are paramount in determining the donor-acceptor properties of the ligand.

The highest occupied molecular orbitals of nearly all the main group hydrides and their methyl derivatives have been characterized by photoelectron spectroscopy (PES). Recently, we have undertaken analogous studies of properties associated with the lowest unoccupied orbitals of these compounds using the technique of electron transmission spectroscopy (ETS).<sup>3</sup>

The extent of participation of a formally unoccupied ligand orbital in a coordinate covalent bond depends upon both energetics

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<sup>†</sup> In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The *d*-transition elements comprise groups 3 through 12, and the *p*-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)

<sup>‡</sup> University of Maryland.

<sup>§</sup> Institut für Anorganische Chemie der Universität Frankfurt.

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