ORIENTATIONS AND ORDERING OF CH_4, CFH_3, CHF_3, AND CF_4 MOLECULES ON A GRAPHITE SUBSTRATE

By

William Ross Hammond

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ABSTRACT

ORIENTATIONS AND ORDERING OF CH_4, CFH_3, CHF_3, AND CF_4 MOLECULES ON A GRAPHITE SUBSTRATE

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We study the energetics of single CH_4, CFH_3, CHF_3, and CF_4 molecules physisorbed on a graphite substrate, and of molecular pairs in free space. The model used in our calculations is based on the Lennard-Jones 12-6 and Coulomb pair potentials. The ground state of single molecule systems is determined, and some conjectures, although no conclusive determination, are made as to the ground state structure of monolayer systems. We also discuss orientational ordering, commensurate *vs* incommensurate structures, substrate mediated effects, and the range at which the interactions (Coulomb and Lennard-Jones) are significant.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SECTION I

INTRODUCTION

The study of interactions on surfaces has opened up experimental and greatly broadened theoretical exploration of several areas of physics including the phenomena of molecular physisorption(1) and phase transitions in two dimensional molecular overlayers.(2) Specific phenomena of interest include orientational order–disorder transitions,(2,3) commensurate–incommensurate phase transitions,(2,4) substrate mediated orientational ordering,(5) and two dimensional melting.(6) There have been a large number of recent studies, both experimental and theoretical, on physisorption and ordering of rare gas atoms and simple multiatom systems such as nitrogen, oxygen, methane and CF_4 on a graphite substrate. However, to date we know of only a few experimental(7) and no theoretical studies of relatively more complicated systems such as CHF_3 or CFH_3. These asymmetric molecules posses larger multipole moments as compared to their symmetric counterparts CH_4 and CF_4; thus one may see dominance of the electrostatic contributions in both the molecule-substrate and intermolecular interactions. One therefore expects the orientations of a single molecule on a graphite substrate and the orientational structures of molecular overlayers of CHF_3 and CFH_3 to be completely different from CH_4 and CF_4.

In this thesis we make a careful investigation of the equilibrium position and orientation of a single physisorbed molecule of CH_nF_{4-n} (where n=0,1,3,4) on a graphite substrate to find out how these change with n. In addition we explore the orientation and position of a pair of interacting molecules in order to get some insight into the orientational and center of mass structure of monolayer or submonolayer systems. We use data from models of the intermolecular interaction of CH_nF_{4-n}(8,9,10) and attempt to determine from the characteristics of these molecules precisely how they will position and orient on a graphite substrate in the ground state and possibly other low lying locally stable excited configurations. To do this we calculate the interaction energy between a molecule and the substrate, and between a pair of molecules using the Lennard-Jones 12-6 and the Coulomb pair potential. In the single molecule case the total energy of an adsorbed molecule is obtained by summing over all the contributions to the interaction between each atom of the molecule and the carbon atoms of the graphite lattice. The interaction between molecular pairs was obtained by summing over all contributions to the interaction between each atom of one molecule and each atom of the other molecule.

In the second and third sections of this thesis we review of what is known experimentally and theoretically about the systems under investigation. Section IV details the determination of the parameters appearing in the intermolecular interactions. In section V we describe the methods used for calculating equilibrium position, orientation, ground state energy, and translational energy barriers for a single molecule. In addition we discuss the method used to obtain the intermolecular interaction energy for a pair of molecules for a large portion of the available phase space. Sections VI gives the results of our study and then discusses and summarizes them.

SECTION II

REVIEW OF EXPERIMENTAL DATA

The four molecules that we have chosen are structurally very similar.[11] The C-F bonds are about 30% longer than the C-H bonds, and the angles between bonds of the asymmetric molecules (CHF_3 and CFH_3) differ from the symmetric bond angle of 109.47° by less than one degree as shown in Figure 1. The electrical characters of the asymmetric molecules, however, are very different from that of the symmetric molecules in that CHF_3 and CFH_3 have large dipole moments, while the octapole moment is the first non-zero moment for CH_4 and CF_4.

The most well studied of these four systems (molecules adsorbed on graphite) is methane.(2,8) This is also the simplest system since the ground state of sub-monolayer to monolayer methane (shown in Figure 2) is commensurate with the graphite substrate, and the only other solid phase of methane,* which is stable at a higher temperature, is isotropically expanded by approximately 1%.(3) Both CF_4 and CHF_3 (to the best of our knowledge there is no data on CFH_3) form incommensurate ground states,(7,13) and have other stable high temperature solid phases that are not as simply related to the ground state as methane's high temperature phase is related to its ground state.

The ground state of methane on graphite is a triangular $\sqrt{3} \times \sqrt{3}$ R30° commensurate lattice with nearest neighbor distance 4.263Å. Here we use the standard

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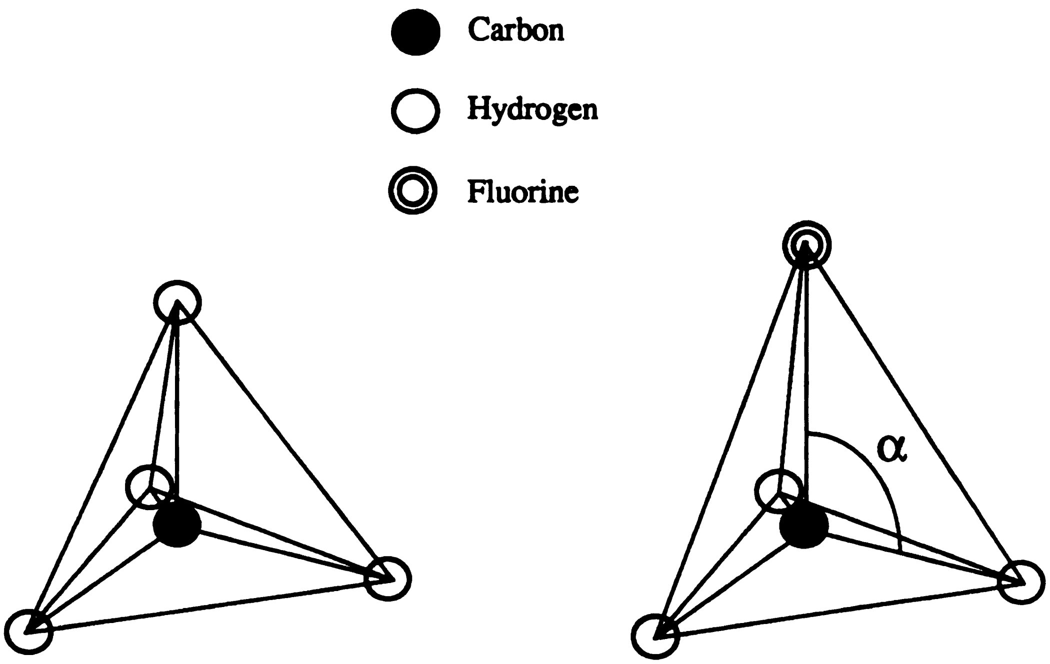
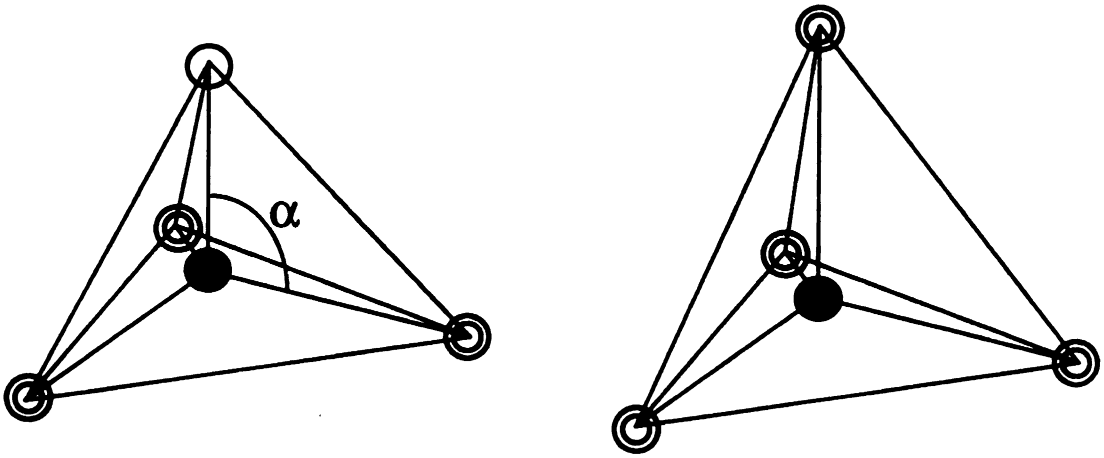
* Although we have not noted it elsewhere, Smalley *et al.*[12] have mentioned a compressed phase of methane at coverages above 0.9 monolayer.



Methane all bond angles 109.47°, all bond lengths 1.091 Å

CFH$_3$ $\alpha = 108.5^{\circ}$
C-F bond length is 1.382 Å
C-H bond length is 1.095 Å



CHF$_3$ $\alpha = 110.1^{\circ}$
C-F bond length is 1.098 Å
C-H bond length is 1.332 Å

CF$_4$ all bond angles 109.47°, all bond lengths 1.32 Å

Figure 1. Scale drawing of adsorbate molecules.

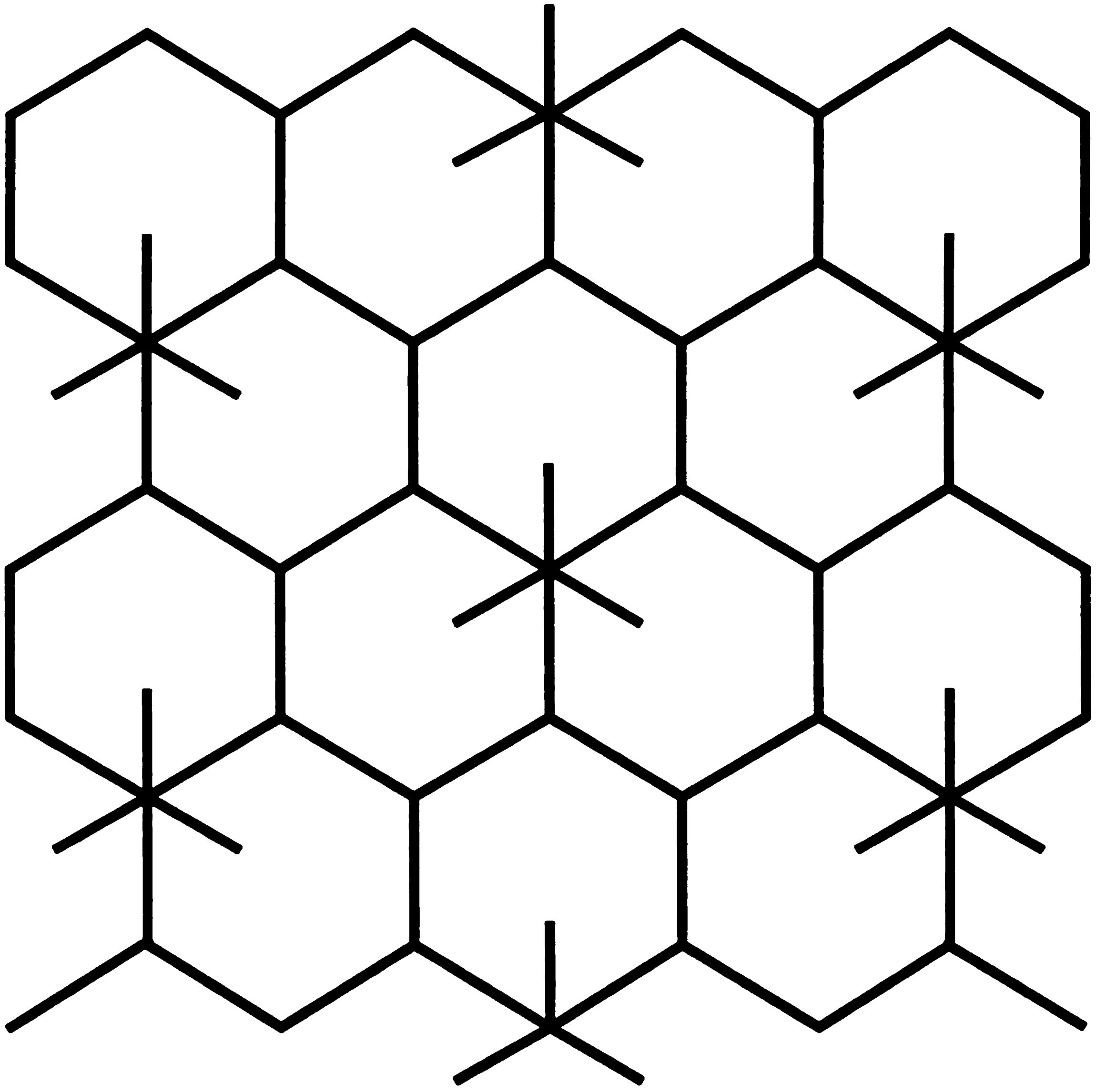


Figure 2. Methane on graphite ground state commensurate structure.

nomenclature(14) where the base unit cell is the unit cell of graphite shown in Figure 3a, and the R30° implies that the methane lattice is rotated by 30° with respect to the graphite lattice. This unit cell describes only one layer of the graphite; natural graphite has an A-B-A scheme with the A and B layers related to each other as shown in Figure 3b. It has been suggested that in the minimum energy configuration, shown in Figure 4, the center of a methane molecule sits 3.3Å above the graphite plane with one C-H bond pointing straight up normal to the graphite plane, and the other three C-H bonds pointing out and slightly down into the substrate.(15) The incommensurate phase of methane on graphite mentioned above has only been noted in the last ten years(16) due to the very small (1%) increase in nearest neighbor separations. This phase is orientationally disordered and slightly expanded as compared to the commensurate phase. Melting to the two dimensional liquid phase occurs from this incommensurate phase which is stable between 50K and 70K.

In contrast to CH_4, the CF_4 on graphite system shows a large variety of structures.(13) There are five "two-dimensional" solid phases of CF_4 only one of which is commensurate. The commensurate phase which is stable at higher temperatures is shown in Figure 5. (The preferred orientation of a single molecule on the substrate has three fluorines pointing down into the centers of the surrounding graphite hexagons, however, our calculations show that the intermolecular interactions will rotate the preferred orientations of the molecules to those shown in the figure.) The intermolecular separation is 4.923Å, and the phase shown has a 2×2 triangular structure unlike the $\sqrt{3} \times \sqrt{3}$ R30° triangular structure of methane. In Figures 2 and 5 we have placed the CH_4 and CF_4 molecules at the atop sites.

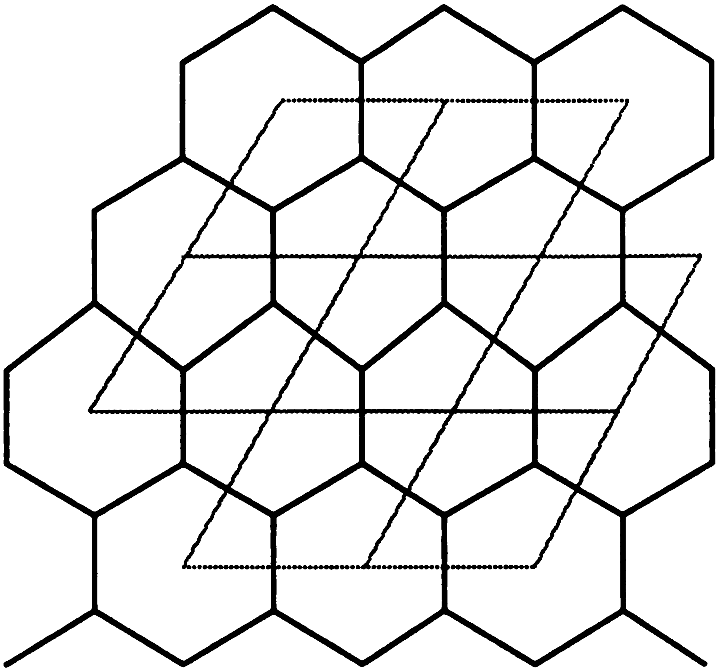


Figure 3a. The unit cell of graphite. Seven cells are drawn (dashed rhombuses) superimposed on the familiar graphite hexagons.

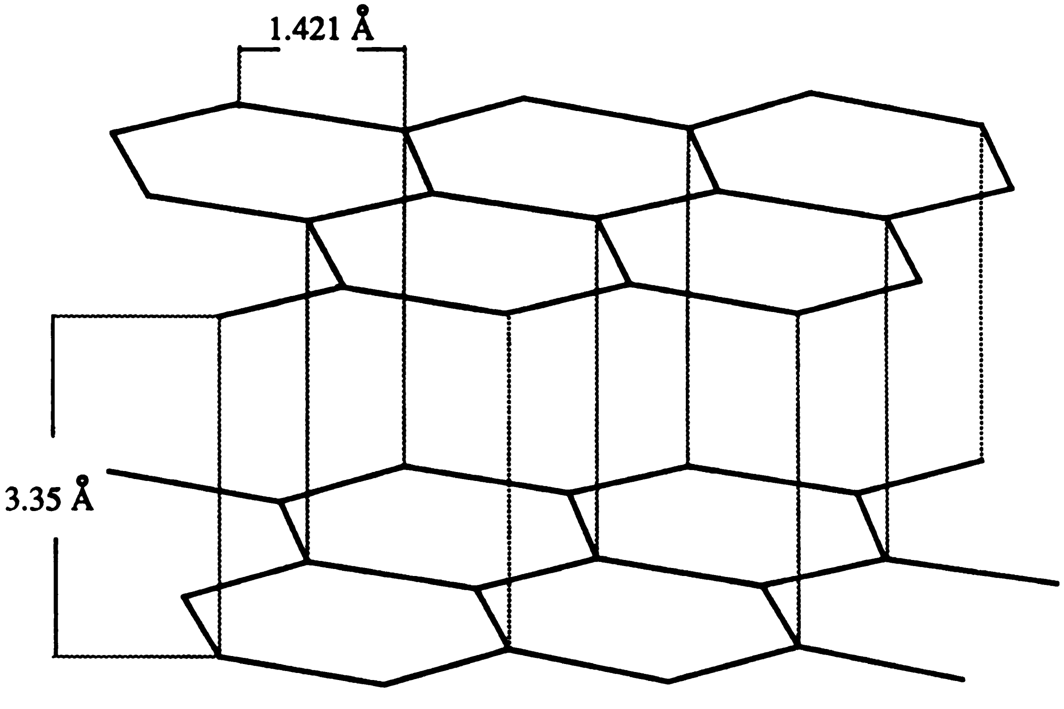


Figure 3b. Two layers of graphite.

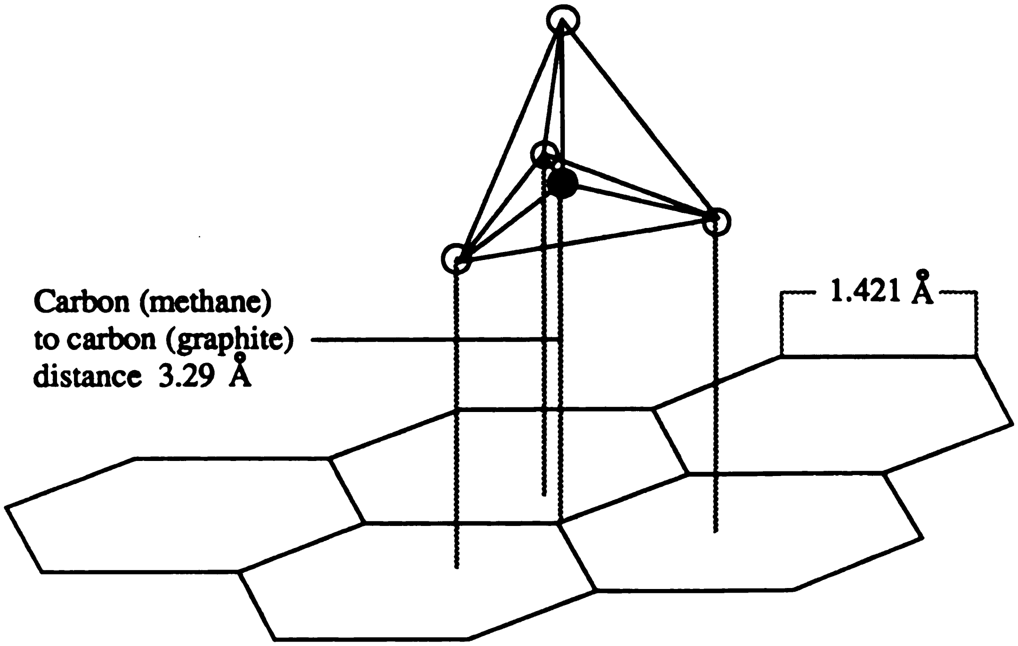


Figure 4. Methane in the atop site on graphite.

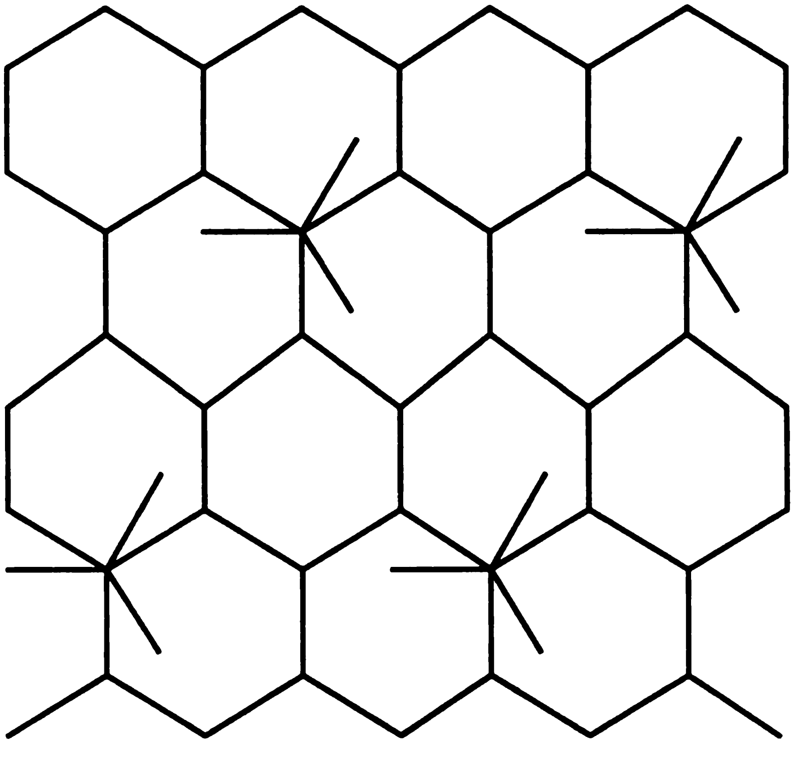


Figure 5. CF_4 on graphite commensurate high temperature solid phase.

Although there is no direct experimental evidence of this positioning there are some symmetry based theoretical arguments,(17) and our own calculations strongly support this placement.

The exact structure of the ground state of CF_4 has not been identified, and is referred to in the literature as a three peaked phase;(2,13) the three peaks refer to peaks seen in X-ray diffraction experiments. There have also been several LEED(18) and neutron scattering(19) experiments on CF_4, however the experimental resolution of the data has been too poor to make any further conclusions on the precise structures, in particular on the orientations of the molecules in the different phases. One of our aims is to use theoretical calculations to find our about the molecular orientation of CF_4 on the substrate.

As far as we know there is only one experimental study of CHF_3 on graphite, done by Knorr and Wieckert.(7) For coverages less than or equal to 0.92 (in units of one molecule per 3 graphite hexagons *i.e.* the commensurate structure of methane discussed earlier) and temperatures less than 85K, their results indicate a triangular orientationally disordered lattice incommensurate with the substrate, and with slightly smaller intermolecular distances (CHF_3 has an area per molecule of 16.5Å^2 in the ground state) than the CF_4 on graphite system (CF_4 has an area per molecule of 21Å^2 in the 2 × 2 phase). Below approximately 45K the molecules become orientationally ordered and the unit cell is uniaxially compressed; the single Bragg peak also splits into two peaks, indicating that one molecule in the triangular lattice moves closer to one of the other two molecules and farther from the other. This is similar to the ground state structure of O_2 on graphite for coverages of approximately 0.9 monolayer.(20)

Figure 6a shows the triangular orientationally disordered phase of CHF_3 along with the rectangular unit cell containing two molecules proposed by Knorr *et al.*$^{(7)}$ The rectangular unit cell is preferred by Knorr *et al.* in describing the distorted triangular lattices of Figures 6b and 6c. The molecules in Figures 6 are represented by circles approximately outlining the area beyond which there is no significant probability of finding electrons from that molecule. Figures 6b and 6c show the two orientationally ordered and uniaxially compressed structures proposed as possible configurations of the ground state. The arrows indicate the direction of the dipole moment which is parallel to the C–H bond and conjectured to be on the average approximately parallel to the graphite plane. These two structures were found by simply drawing molecules on a surface and minimizing the overlap while maintaining their calculated area per molecule of 16.5Å^2 (the area of three graphite hexagons is 15.7Å^2). This method of proposing structures is not meant to provide a conclusive determination of the structure of the ground state, but to give an initial guess that can be checked by further experiment or theoretical calculations.

Both the structures given in Figures 6b and 6c have an in plane (parallel to the substrate) antiferroelectric moment, however, the herringbone structure (Figure 6b) is antiferroquadrupolar while the structure of Figure 6c is ferroquadrupolar. The long–range antiferroelectric order appears below 45K. In a Cartesian coordinate system with origin at the lower left (as drawn) vertex of the unit cell, the coordinates of the molecule in the center of the cell are (0.75a, 0.5b) for the herringbone structure and (0.3a, 0.5b) for the ferroquadrupolar structure. The electric dipole moments of the molecules in the ferroquadrupolar structure are, as shown, either all parallel or all antiparallel to the short axis of the unit cell, while the dipole moments in the

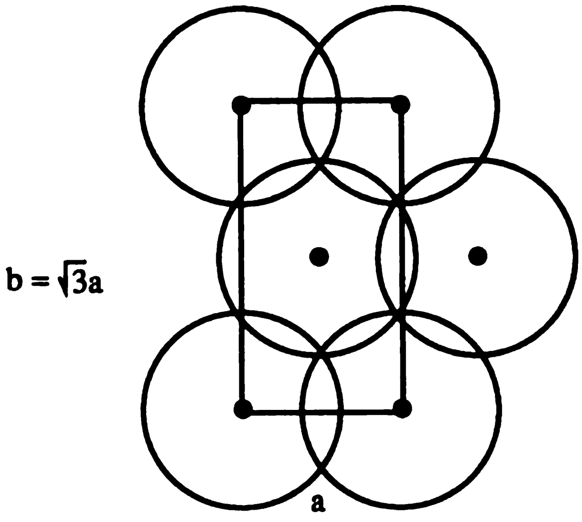


Figure 6a. Orientationally disordered structure.

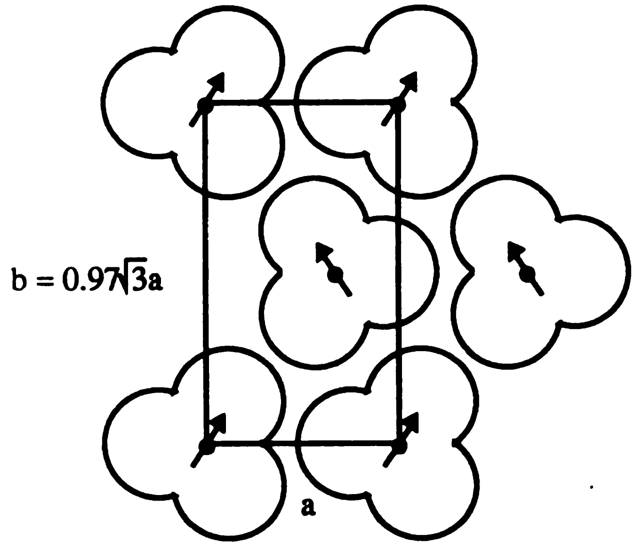


Figure 6b. Uniaxially compressed herringbone structure.

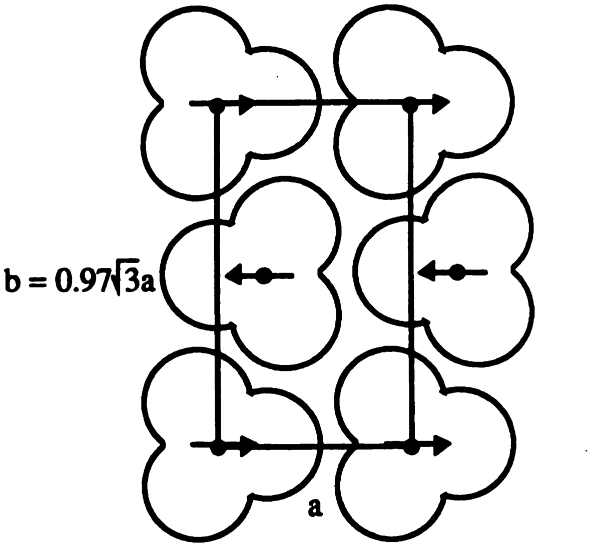


Figure 6c. Uniaxially compressed ferroquadrupolar structure.

Figure 6. CHF$_3$ monolayer lattice proposed structures.

herringbone structure are, either all at 60° or all at 120° to the short axis of the unit cell. Both structures are consistent with the splitting of their diffraction peak and appear equally probable as candidates for the ground state of CHF_3 on graphite.

Knorr and Wieckert$^{(7)}$ have claimed that there are some physical similarities between their CHF_3 on graphite system and a molecular dynamics study of diatomic oxygen on graphite by S. Tang, S.D. Mahanti, and R. Kalia$^{(20)}$ showing the energies of a ferroquadrupolar structure and a herringbone structure to be quite close, and that a high density of defects such as vortex-antivortex pairs may change the ground state locally from the ferroquadrupolar to the herringbone structure. Knorr *et al.* note, however that the experimental structure factor of CHF_3 on graphite system is very consistently 2 ± 0.4, whereas the calculated structure factor for the ferroquadrupolar structure (Figure 6c) is 4.0 and for herringbone structure is 0.5. However, the precise value of the structure factor is very sensitive to the exact position of the molecules in the lattice, so it is possible for either configuration to shift slightly and have a structure factor of approximately 2.0.

The three physisorbed systems we have discussed in this section are all very different despite the internal structural similarity of the adsorbed molecules. Only methane on graphite has had its ground state structure precisely identified, and one of the few experimentally known facts about the ground state of the other two systems is that they are, unlike methane, incommensurate with the substrate. Even the ground state of methane on graphite has not been completely identified since we do not know for certain what the preferred adsorption site is. Despite careful experiments on these systems only conjectures about the ground state structure and orientations of CF_4 and CHF_3 on graphite exist, and to the best of our knowledge there is no experimental basis to conjecture about the ground state orientation or structure of the CFH_3 on graphite system. In this thesis we investigate the energetics of these four physisorbed systems to understand what the precise ground state structure of a single physisorbed molecule is, why the ground state structures are different for different molecules, what interactions drive the different structures, and attempt to gain some insight into the ground state structures in the submonolayer to monolayer region for each of the four systems.

SECTION III

REVIEW OF THEORETICAL MODELS

A. Methane on graphite

Methane is the most studied system that we have considered in this thesis. It is also the only system among CH_nF_{4-n} (where n=0,1,3,4) where the characteristics of the ground state have been carefully investigated.(8,14) In these studies the ground state of methane on graphite was investigated using an atom-atom Lennard-Jones potential

$$V = \sum_{i,j} 4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^{6}], \tag{1}$$

where the i's are atoms in an adsorbed methane molecule, and the j's are the atoms in the graphite substrate.

This potential was used to obtain both adsorbate-substrate and adsorbate-adsorbate interaction energies. Phillips *et al.*(8) also investigated the energetics with an exponential-sixth potential, where the repulsive part of the Lennard-Jones potential is replaced by an exponential function. The exponential-sixth model, however, did not give results which agreed with experiment in general.(8) In particular the preferred adsorption site for methane using the exponential-sixth potential was found to be the bridge site instead of the atop site found by the Lennard-Jones 12–6 potential, the latter being consistent with the prediction using symmetry arguments for CF_4.(20) The parameters for the Lennard-Jones potential used by Phillips *et al.* were taken from several experimental intermolecular studies and are discussed further in section IV.

The results of Phillips and Hammerbacher agree well with experiment(15) in finding the equilibrium height of a methane molecule at 3.28Å above the graphite plane measured from carbon to carbon. They also calculate the minimum energy of a single molecule due to the substrate as -1663 K/molecule. This agrees reasonably well with the isosteric heat reported by Thomy and Duval(21) which is given as 3.3Kcal/mole, *i.e.* 1660 ± 25K at coverage 0.1 in units of one molecule per three graphite hexagons. The above agreement gives us some confidence in both the potential model and the parameters which we used in our own calculations, as will be discussed further in sections IV (Determination of Parameters) and V (Methods of Numerical Calculations).

B. Intermolecular Potentials for CH_4, CFH_3, CHF_3, CF_4

In considering the intermolecular interactions of CH_nF_{4-n} we have chosen to use an atom-atom potential as the best method of describing the potential interactions since other simple methods do not adequately explain some experimental results.(8) Unlike the case for a molecule adsorbed on graphite, there is substantial amount of information available on intermolecular interactions using atom-atom potentials.(8,9,23) In our calculations we use data from intermolecular studies of CH_nF_{4-n} to determine some of the parameters (the ϵ's and σ's of equation 1, and q the partial charge on an atom in a molecule), and we also compare the results of our intermolecular pair calculations with results from the literature.

The self consistent field (SCF) model has been used recently to study CH_nF_{4-n} intermolecular systems.(9,23) The intermolecular interaction is expressed as a pairwise sum of interatomic potentials between atoms of different molecules. The interaction energy between two atoms i and j is given by:

$$\Delta V_{ij} = exp(\frac{-(R_{ij} - s_i - s_j)}{p_i + p_j}) + \frac{q_i q_j}{r_{ij}} - F_{ij}\frac{C_{ij}}{r_{ij}^6}, \tag{2}$$

where r_{ij} is the distance between the interacting atoms, q_i and q_j are the partial charges on each atom, and the other constants in the equation are parameters obtained from *ab initio* methods.(22) One problem, however, with the parameter F_{ij} in the above equation is that it is defined differently in different papers. F_{ij} is a damping function which is defined as:

$$F_{ij} = exp(-(\frac{1.28R_{vdw}}{r_{ij}} - 1)^2), \quad r_{ij} < 1.28R_{vdw} \tag{3a}$$

in one paper,(9) and in another(23) as:

$$F_{ij} = exp(-(\frac{1.28R_{vdw}}{r_{ij}} - 1)^2), \quad r_{ij} \leq R_{vdw} \tag{3b}$$

In both definitions F is defined as 1 outside of the appropriate above noted ranges, and R_{vdw} is related to the Van der Waals radius that will be discussed in section IV. Further discussion of equation 2 will also be presented in section IV. It should be noted that the above equation describes the physical interaction between an atom of one molecule and another atom of a different molecule; and it does not describe any changes that might occur in the two molecules as they are brought near to each other. In the above version of the equation all parameters are in atomic units, *i.e.* 1a.u. of length =0.53Å, 1a.u. of charge =1e, and 1a.u. of energy =13.6eV. The parameters from several molecules and the energy at the Van der Waals minimum *i.e.* $r_{ij} = R_{vdw}2^{1/6}$ are given in Table 1.

Table 1. SCF data

Atom	q	R_0	ρ_i	σ_i	C_{ii}	from	V_{SCF} (K)
C	-0.2469	7.2118	0.18078	1.42232	27.09	CFH_3	29.6
C	+0.7649	7.2118	0.32383	0.60460	26.98	CHF_3	15.4
C	-0.3374	7.2118	0.20794	1.50191	30.69	$\underline{C}H_3CN$	43.8
C	+0.488	7.2118	0.28362	1.08998	47.36	$CH_3\underline{C}N$	31.1
H	+0.1473	5.090	0.27846	0.15619	3.352	CFH_3	0.75
H	+0.0214	5.090	0.24426	0.18180	3.338	CHF_3	20.4
H	+0.1564	5.090	0.27093	0.26402	4.644	CH_3Cl	7.4
H	+0.201	5.090	0.26653	0.14604	5.858	CH_3CN	33.8
F	-0.1950	6.2362	0.22596	1.03083	11.30	CFH_3	15.2
F	-0.2621	6.2362	0.22242	1.05472	11.26	CHF_3	15.7

The V_{SCF} of Table 1 shows the energy (in K) of a pair of atoms (what kind of atoms is specified by the first column of the table) at a separation of R_0. (All entries in Table 1 except V_{SCF} are in the atomic units defined earlier.) R_0 is defined as $R_0 = R_{vdw}2^{1/6}$, thus V_{SCF} should equal $-\epsilon$ (the ϵ of equation 1) as will be discussed in the next section. Note that we obtain the tabulated energy only when both atoms are taken from the indicated molecule. Also the q's, the partial charge on the atoms, were ignored in the calculation of V_{SCF}, which is given by equation 2, since in the next section we wish to compare the energy of the non-Coulomb part of the SCF interaction to the energy of the Lennard-Jones interaction.

SECTION IV

DETERMINATION OF PARAMETERS

Several experimental studies have been done on methane to determine the Lennard-Jones parameters, ϵ and σ, (see equation 1) of the constituent carbon and hydrogen. The results of these studies are summarized by Severin and Tildesley(14) who studied the ground state properties of a 400Å^2 monolayer of methane on graphite with periodic boundary conditions. Based on their calculations Severin and Tildesley adjusted the parameters (ϵ and σ) to those noted in Table 2. Although the intention of this thesis is not to further refine the values of these parameters, we found it useful to run some tests with various values of ϵ and σ taken from the literature. The values of the various ϵ's and σ's we chose to test are also given in Table 2. All possible combinations of these parameters were tested by assigning them to a methane molecule and determining the potential energy in the preferred orientation of the molecule–substrate interaction 3.3Å above the atop and center sites of the graphite substrate. The results of this investigation are given in Table 2, and based on a comparison of these results with the isosteric heat of Thomy and Duval(21) (-1663K) we adjusted our choice of parameters used in this (methane-graphite) interaction to those (parameters *i.e.* A, C, G, and M) noted in the table.

The parameters we use (ϵ's and σ's) are all parameters for an atom-atom potential, thus when we choose a value for a parameter (*e.g.* $\epsilon_{C-graphite}$) we use that value of that parameter in all of our systems (*i.e.* for all n in CH_nF_{4-n}, where

Table 2. Parameters tested

Parameters used	Combination tested	Energy at atop site*	Energy at center site*
A ϵ_{C-g}=47.68^{a,f}	A,C,F,I	1533K	1540K
B ϵ_{C-g}=51.198^{b}	A,C,F,J	1571K	1572K
	A,C,F,K	1592K	1588K
C σ_{C-g}= 3.30^{a,f}	A,C,F,L	1598K	1593K
D σ_{C-g}= 3.35^{b}	A,C,F,M	1605K	1598K
E σ_{C-g}= 3.40^{c}	A,C,F,N	1649K	1620K
	A,C,G,I	1587K	1592K
F ϵ_{H-g}=15.79^{d}	A,C,G,J	1628K	1627K
G ϵ_{H-g}=17.00^{a,f}	A,C,G,K	1651K	1644K
H ϵ_{H-g}=23.798^{b}	A,C,G,L	1658K	1650K
	A,C,G,M	1665K	1654K
I σ_{H-g}= 2.90^{c}	A,C,G,N	1712K	1678K
J σ_{H-g}= 2.95	A,C,H,I	1890K	1896K
K σ_{H-g}= 2.98^{a}	A,C,H,J	1948K	1934K
L σ_{H-g}= 2.99^{b}	A,C,H,K	1980K	1958K
M σ_{H-g}= 3.00^{f}	A,C,H,L	1990K	1966K
N σ_{H-g}= 3.10^{c}	A,C,H,M	1999K	1972K
	A,C,H,N	2065K	2006K
	A,D,F,I	1558K	1572K
	A,D,F,J	1596K	1604K
	A,D,F,K	1617K	1621K
	A,D,F,L	1623K	1625K
	A,D,F M	1630K	1630K
	A,D,F,N	1674K	1652K
	A,D G,I	1612K	1624K
	A,D,G,J	1653K	1659K
	A,D,G,K	1676K	1676K
	A,D,G,L	1682K	1682K
	A,D,G,M	1689K	1686K
	A,D,G,N	1737K	1711K
	A,D,H,I	1915K	1918K
	A,D,H,J	1973K	1966K
	A,D,H,K	2005K	1990K
	A,D,H,L	2015K	1998K
	A,D,H,M	2024K	2004K
	A,D,H,N	2090K	2038K
	A,E,F,I	1574K	1596K
	A,E,F,J	1613K	1630K
	A,E,F,K	1634K	1646K
	A,E,F,L	1640K	1651K

Table 2 (cont'd.).

Parameters used	Combination tested	Energy at atop site*	Energy at center site*
A $\epsilon_{C-g}=47.68^{a,f}$	A,E,F,M	1646K	1655K
B $\epsilon_{C-g}=51.198^{b}$	A,E,F,N	1690K	1677K
	A,E,G,I	1628K	1650K
C $\sigma_{C-g}=3.30^{a,f}$	A,E,G,J	1670K	1684K
D $\sigma_{C-g}=3.35^{b}$	A,E,G,K	1692K	1702K
E $\sigma_{C-g}=3.40^{c}$	A,E,G,L	1699K	1707K
	A,E,G,M	1706K	1712K
F $\epsilon_{H-g}=15.79^{d}$	A,E,G,N	1753K	1736K
G $\epsilon_{H-g}=17.00^{a,f}$	A,E,H,I	1932K	1943K
H $\epsilon_{H-g}=23.798^{b}$	A,E,H,J	1990K	1991K
	A,E,H,K	2021K	2016K
I $\sigma_{H-g}=2.90^{c}$	A,E,H,L	2031K	2023K
J $\sigma_{H-g}=2.95$	A,E,H,M	2041K	2030K
K $\sigma_{H-g}=2.98^{a}$	A,E,H,N	2107K	2063K
L $\sigma_{H-g}=2.99^{b}$	B,C,F,I	1593K	1603K
M $\sigma_{H-g}=3.00^{f}$	B,C,F,J	1632K	1635K
N $\sigma_{H-g}=3.10^{e}$	B,C,F,K	1653K	1652K
	B,C,F,L	1659K	1656K
	B,C,F,M	1665K	1661K
	B,C,F,N	1710K	1683K
	B,C,G,I	1647K	1656K
	B,C,G,J	1689K	1690K
	B,C,G,K	1711K	1707K
	B,C,G,L	1718K	1713K
	B,C,G,M	1725K	1718K
	B,C,G,N	1772K	1742K
	B,C,H,I	1941K	1949K
	B,C,H,J	2009K	1997K
	B,C,H,K	2040K	2022K
	B,C,H,L	2050K	2029K
	B,C,H,M	2060K	2036K
	B,C,H,N	2126K	2069K
	B,D,F,I	1620K	1638K
	B,D,F,J	1659K	1670K
	B,D,F,K	1680K	1686K
	B,D,F,L	1686K	1691K
	B,D,F,M	1692K	1695K
	B,D,F,N	1736K	1718K
	B,D,G,I	1674K	1690K
	B,D,G,J	1716K	1724K

Table 2 (cont'd.).

Parameters used	Combination tested	Energy at atop site*	Energy at center site*
A ϵ_{C-g}=47.68[a,f]	B,D,G,K	1738K	1732K
B ϵ_{C-g}=51.198[b]	B,D,G,L	1745K	1747K
	B,D,G,M	1752K	1752K
C σ_{C-g}= 3.30[a,f]	B,D,G,N	1799K	1776K
D σ_{C-g}= 3.35[b]	B,D,H,I	1978K	1983K
E σ_{C-g}= 3.40[c]	B,D,H,J	2036K	2031K
	B,D,H,K	2067K	2056K
F ϵ_{H-g}=15.79[d]	B,D,H,L	2077K	2063K
G ϵ_{H-g}=17.00[a,f]	B,D,H,M	2087K	2070K
H ϵ_{H-g}=23.798[b]	B,D,H,N	2153K	2104K
	B,E,F,I	1638K	1665K
I σ_{H-g}= 2.90[c]	B,E,F,J	1676K	1697K
J σ_{H-g}= 2.95	B,E,F,K	1697K	1713K
K σ_{H-g}= 2.98[a]	B,E,F,L	1704K	1718K
L σ_{H-g}= 2.99[b]	B,E,F,M	1710K	1722K
M σ_{H-g}= 3.00[f]	B,E,F,N	1754K	1745K
N σ_{H-g}= 3.10[e]	B,E,G,I	1692K	1717K
	B,E,G,J	1734K	1752K
	B,E,G,K	1756K	1759K
	B,E,G,L	1763K	1774K
	B,E,G,M	1770K	1779K
	B,E,G,N	1817K	1803K
	B,E,H,I	1996K	2010K
	B,E,H,J	2054K	2058K
	B,E,H,K	2085K	2083K
	B,E,H,L	2095K	2090K
	B,E,H,M	2104K	2097K
	B,E,H,N	2171K	2131K

[*] All energies are negative.

[a] From Severin and Tildesley(14) for molecule-substrate interaction.

[b] From Severin and Tildesley for intermolecular interaction.

[c] From Bondi.(10)

[d] From mixing rules.(1)

[e] From Severin and Tildesley (quoted but not used in their work).

[f] Value used in our calculations.

$n = 0, 1, 2, 3, 4$). This assumes that the character of each atom in CH_nF_{4-n} does not change significantly with n. This assumption need not be true, as can be inferred from Table 1, and following the example of others in the literature$^{(8,14)}$ we did not assume that interactions with a carbon atom from the substrate were described by the same parameters as similar interactions with a carbon atom from a CH_nF_{4-n} molecule. However, our assumption provided at least an initial estimate of several needed parameters. We have not yet specified the values of the parameters for the fluorine-graphite and intermolecular interactions. The values of the ϵ's for the (intermolecular) carbon-carbon and hydrogen-hydrogen interactions were taken from the work of Severin and Tildesley. However, the values of the σ's for the (intermolecular) carbon-carbon and hydrogen-hydrogen as well as the fluorine-fluorine interactions were taken from the work of Bondi$^{(10)}$ (who tabulated values of various σ's using experimental data), to which the SCF calculations are fit. Test runs on a pair of methane molecules at a separation of 4.26Å (the intermolecular distance of methane in the commensurate structure on graphite) showed that the σ's of Bondi and the σ's of Severin and Tildesley gave the same energies to within 5K per molecule (10K per pair of molecules).

A calculation of the value of ϵ for the fluorine-fluorine interaction was made by equating the F-F potential energy well depth of the Lennard-Jones potential to the F-F potential energy well depth of the SCF model. By differentiating equation 1 and setting dV/dr=0 it is immediately obvious that the Lennard-Jones potential minimum occurs at $r = R_0 = \sigma \times 2^{1/6}$. Substituting this value for r back into equation 1 shows that the potential well depth is just equal to ϵ. Therefore $\epsilon = -V_{vdw}(r = R_0) = -V_{SCF}(r = R_0)$. In calculating the SCF energy (V_{SCF}) we chose to use equation 3b for the definition of F_{ij} of equation 2 since the paper containing this particular definition of F_{ij} gave a more complete table of parameters. Definition 3a would make $F_{ij} = 0.98$, and thus would not make much of a difference. Note that R_{vdw}, the Van der Waals radius of equations 3, is exactly the same as σ of equation 1.(10,23)

As can be seen from Table 1 the SCF energy of the carbon-carbon and hydrogen-hydrogen interactions vary across a very large range, while that of the fluorine-fluorine interaction is very consistent (ϵ =15.2K and 15.7K for CFH_3 and CHF_3 respectively). Despite the apparent consistency of the potential well for fluorine, the large variations in V(SCF) for carbon and hydrogen indicate that the potential well for the fluorine-fluorine interaction may not be very accurate, or may not be unique depending on the system under consideration. We have used an *ad hoc*, but simple method of obtaining another estimate of the value of ϵ for the fluorine-fluorine interaction from a knowledge of the ϵ's for carbon and hydrogen, and from the C_{SCF}'s, the constant in the attractive part of the SCF potential given in Table 1. The method involved multiplying the value of $C_{(SCF\ for\ F)}$ by the average ratios of $\epsilon_{carbon}/C_{(SCF\ for\ carbon)}$ and $\epsilon_H/C_{(SCF\ for\ H)}$, *i.e.*

$$\epsilon_F = C_{(SCF\ for\ F)}\frac{1}{2}\left[\frac{\epsilon_{carbon}}{C_{(SCF\ for\ carbon)}} + \frac{\epsilon_H}{C_{(SCF\ for\ H)}}\right], \qquad (4)$$

where the ϵ's are the ϵ's of equation 1 and the C's are obtained from the SCF data in Table 1. The resulting value of ϵ for fluorine is 18.0K.

Test runs with ϵ_F =15.5K and ϵ_F =18.0K showed that the two different parameters gave the same minimum energy value and minimum energy configuration for a single molecule (of any kind, *i.e.* for any n =0,1,3,4 in CH_nF_{4-n}) on the substrate to within 0.1K and 0.01Å. Test runs of molecular pairs showed that the total energy of a pair of molecules increased by less than 9K for CF_4, less than 5K for CHF_3, and less than 2K for CFH_3. There was no significant change in the minimum energy configuration of any molecular pairs with the change in ϵ_F. Based on a comparison of our potential well depth for CHF_3 pairs (-911K) with the average of results from the literature$^{(9)}$ (-1155K and -760K are quoted for an average of approximately -955K) we chose to use the value of 18.0K for ϵ_F for further calculations.

The mixing rules for calculating the σ's and ϵ's between different kinds of atoms (*e.g.* fluorine and hydrogen) are quite well known,$^{(1)}$ and have consistently given results that agree well with experiment. The mixing rules are:

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2, \tag{5a}$$

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}. \tag{5b}$$

The values obtained from these mixing rules are noted in Table 2. The atoms in the molecules were also considered to have a partial charge since the electron affinities of carbon, hydrogen, and fluorine are very different. The partial charges on the atoms were taken from the intermolecular SCF models$^{(9,23)}$ mentioned earlier except for the case of CF_4 which was not considered in the referenced works. However, based on the assumption that the difference in the partial charge on a hydrogen atom between CFH_3 and CH_4 molecules (which is close to 0 as can be seen in Table 1) is nearly equal to the difference in the partial charge on a fluorine atom in CHF_3 and CF_4, the partial charge on an F in CF_4 was extrapolated to -0.262e.

The only parameters needed in the model that have not yet been mentioned are the bond lengths and angles which were obtained from references 8, 11, and 24, and the polarizability of graphite. The atomic polarizability of carbon which we used in our calculations is given by E.M. Purcell in his undergraduate text Electricity and Magnetism as 1.5×10^{-24} cm^3.

SECTION V

METHODS OF NUMERICAL CALCULATIONS

A. Set-up of model

In this section we detail the precise physical setup of the model we used in our calculations, and explain exactly what we calculated and how we calculated it. For the physical setup of our model we first generated a 30 × 30 × 3 graphite substrate which should be large enough to contribute all the significant energy of an infinite lattice (this is discussed and tested later). The graphite lattice was formed by first stepping down the Y-axis in units of one bondlength, assigning one carbon atom to the first two of every three steps. With the Y-axis defined this way the X coordinates of an atom must be:

$$X(n,m) = n \times \mathit{bondlength} \times \frac{(3)^{1/2}}{2}, \tag{6}$$

where n is the number of atoms out from the Y-axis the atom in question is, and m is the number of atoms out from the X-axis. The Y coordinates are then staggered. If an atom is an even number of atoms out from the Y-axis then its Y coordinate is the same as the Y coordinate of the atom on the Y-axis, Y(0). If an atom is an odd number of atoms out from the Y-axis in the X direction, then:

$$Y(n,m) = Y(0,m) \qquad \mathit{for\ n\ even} \tag{7a}$$

$$Y(n,m) = Y(0,m) - \mathit{bondlength}/2 \qquad \mathit{for\ n\ and\ m\ odd} \tag{7b}$$

$$Y(n,m) = Y(0,m) + \mathit{bondlength}/2 \qquad \mathit{for\ n\ odd\ and\ m\ even} \tag{7c}$$

The Z coordinate of the atoms in the top graphite plane are 0, for the second plane Z is -3.35Å, and for the third plane Z is -6.7Å. The *bondlength* in the above equations is 1.421Å. In natural graphite the planes are shifted in relation to each other in an A-B-A scheme. To simulate this in the model the X coordinate of every atom in the second plane is increased by *bondlength* × $\frac{(3)^{1/2}}{2}$ and the Y coordinate is increased by one half *bondlength*; the resultant lattice is shown in Figure 3. Once the lattice has been set up, the adsorbate can be added to the system. The adsorbed molecule has six degrees of freedom, three translational and three rotational. The three rotational coordinates used are the Euler angles(25) θ, ϕ, and ω, where θ is a rotation about the molecules Z-axis, ϕ is a rotation about the Y′-axis, and ω is a rotation about the Z″-axis as defined in Figure 7. If the four atoms about the carbon are labeled form one to four, then for $(\theta, \phi, \omega) = (0, 0, 0)$ the positions of atoms 1, 2, 3 and 4 are defined in figure 8.

B. Description of the molecule-substrate interaction

Once the position of the molecule is known in phase space (*i.e.*, X, Y, Z, θ, ϕ and ω are all known, where the X, Y and Z always refer to the coordinates of the carbon atom) the X, Y, and Z coordinates of all the constituent atoms can be found using the Euler transformation matrix which is given in Figure 9. The Lennard-Jones interaction is then summed pairwise between each atom of the adsorbed molecule and the substrate.

The Coulomb contribution to the potential energy for ion-atom pairs is well known,(1) and is given by:

$$V_C = -\frac{1}{2}\alpha\frac{q^2}{r^4}, \tag{8}$$

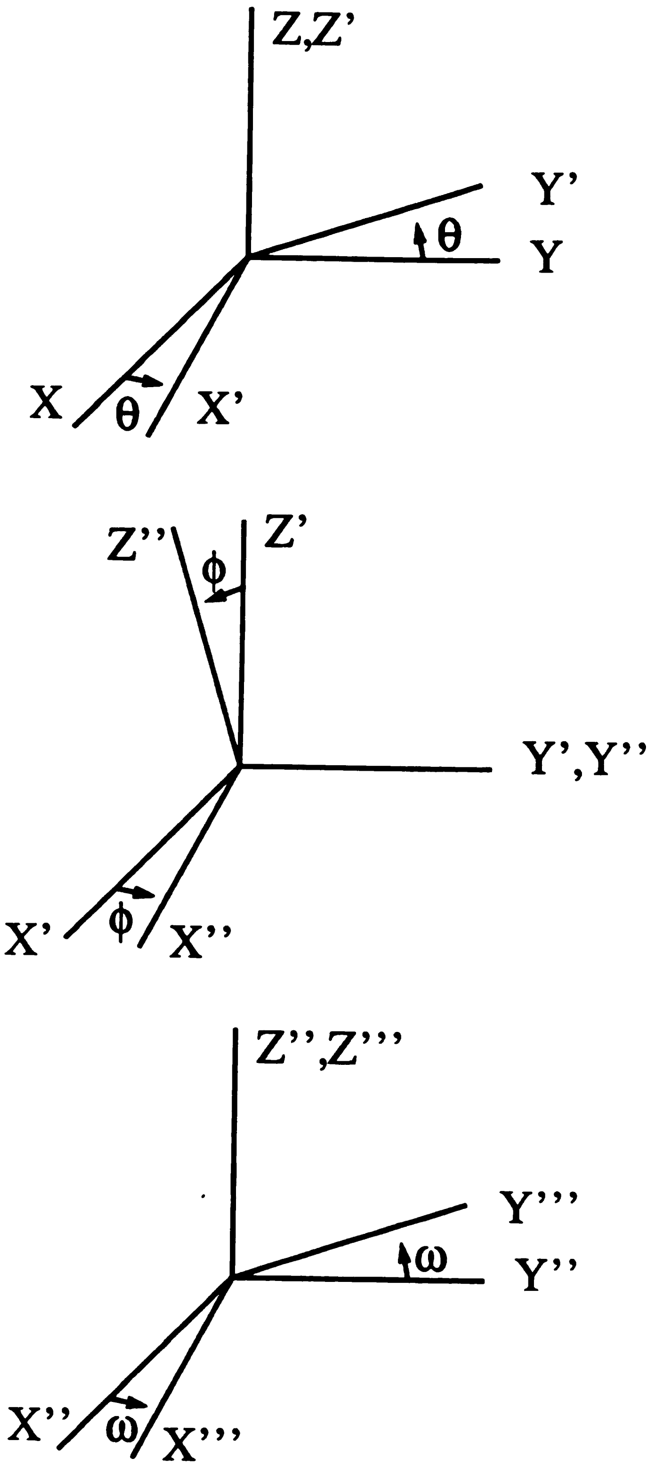


Figure 7. Euler angles

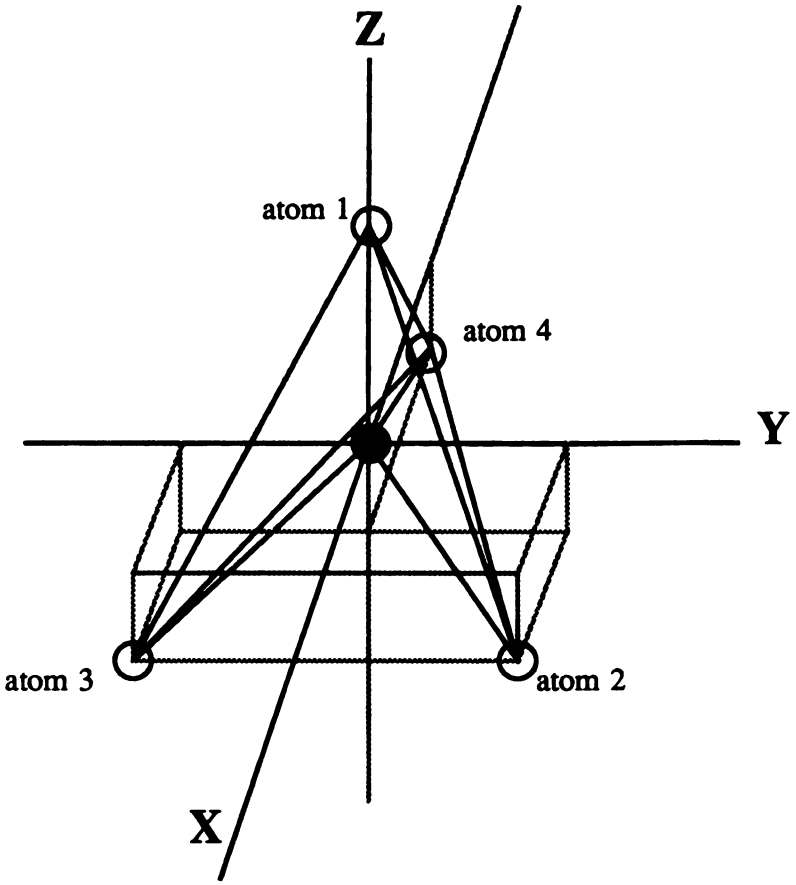


Figure 8. Methane showing positions of atoms 1, 2, 3 and 4 with Euler angles (0,0,0).

$$\begin{bmatrix} \cos\theta \cos\phi \cos\omega - \sin\theta \sin\omega & -\cos\theta \cos\phi \sin\omega - \sin\theta \cos\omega & \cos\theta \sin\phi \\ \sin\theta \cos\phi \cos\omega + \cos\theta \sin\omega & \cos\theta \cos\omega - \sin\theta \cos\phi \sin\omega & \sin\theta \sin\phi \\ -\sin\theta \cos\omega & \sin\theta \sin\omega & \cos\phi \end{bmatrix}$$

Figure 9. The Euler transformation matrix.

where α is the polarizability of the atom, q is the charge on the ion, and r is the distance between the ion and the atom. In order to calculate the net interaction between the different ions of an adsorbed molecule and an atom in the substrate it is necessary to first calculate the net polarization of the atom due to the molecule. To accomplish this, equation 8 is separated into cartesian coordinates (X, Y, Z) and the cartesian components of the electric field at the atom, the E_X's, E_Y's, and E_Z's, are summed separately. Equation 8 now becomes:

$$V_C = -\frac{1}{2}\alpha[(\Sigma_i E_{X_i})^2 + (\Sigma_i E_{Y_i})^2 + (\Sigma_i E_{Z_i})^2]^{1/2} \times |\Sigma_i \frac{q_i}{r_i^2}\hat{r}_i|, \tag{9}$$

where the sum is over the ions in the molecule. The first factor ($\frac{1}{2}\alpha$ times the sum) in equation 9 is the response (polarization) of the atom, and the second factor is the magnitude of the net field at the atom due to the ions of the molecule (which is parallel to the polarization of the atom). Since the two sums are exactly equal to each other, equation 9 reduces directly to:

$$V_C = -\frac{1}{2}\alpha[(\Sigma_i E_{X_i})^2 + (\Sigma_i E_{Y_i})^2 + (\Sigma_i E_{Z_i})^2]. \tag{10}$$

Thus it is only necessary to calculate the cartesian component of the electric field at each atom due to every ion and sum up the energies (multiplied by $\frac{1}{2}\alpha$ and a conversion factor since we want to use Kelvin units to compare with the energies due to the Lennard-Jones interaction).

At any distance more than a few angstroms from a given molecule in the X or Y directions, interactions between a second adsorbed molecule and the substrate will probably interfere with the X and Y components of the polarization of the graphite due to the first molecule. In order to get some idea of possible effects of this interference effect the model has two cutoff distances for the coulomb potential, one cutoff distance in any direction, and the other cutoff depending only on the sum of the squares of the X and Y components of the distance. The effects of these various cutoffs are discussed further in the next section.

C. Description of the intermolecular interaction

For speed of calculation of the intermolecular interaction the Cartesian coordinates of the individual ions of the adsorbate calculated for the adsorbate-substrate interaction are stored and sent to the subroutine calculating the intermolecular potential. Once these parameters are determined the sums are done in the same way as for the graphite lattice. The only difference is that every atom has its own partial charge, and thus the Coulomb interaction is described by an ion-ion potential:

$$V_C = \Sigma_{i,j} \frac{q_i q_j}{r_{ij}}, \tag{11}$$

where the i's and j's are ions of different molecules.

SECTION VI

RESULTS

A. Single molecule

In this section we give the results of our energy calculations for a single molecule on a substrate and the conclusions based on these results. As will be discussed throughout this section our results agree quite well with all available theoretical and experimental data including adsorption site, adsorption potential, and most favored orientation. We should also note that the energy values we quote are generally given to 1K, which may be up to four digits of accuracy. As the results given in Table 2 show, we can expect our results to be accurate to no more than two or three digits. However, some of the energy differences we wish to quote here require greater accuracy, and we therefore quote the additional digits in our results. We note that the energy differences, except for the depth of the corrugation of the substrate potential (see Table 2), are accurate to the quoted number of digits for reasonable choices of Lennard-Jones and Coulomb parameters.

In order to test whether or not our physical set up (*i.e.* the computer model of the graphite lattice described in section V) was adequate to describe the system, we ran several tests on an expanded lattice of dimensions (90 atoms, 90 atoms, 9 layers) or approximately (108Å, 187Å, 30Å). (As a comparison our (30 atoms, 30 atoms, 3 layers) lattice measures approximately (34Å, 60Å, 10Å) with a surface area a little over 2000Å^2.) To the extent of this expanded lattice we found only the Coulomb interaction from CH_4 and CF_4 to go to zero with six digits of accuracy.

However, even though the interaction energies did not go to zero within our tested accuracies, the interaction of a molecule with the smaller lattice provided 99% of the molecule-substrate interaction energy of the larger lattice for all four molecules. Furthermore all of the energy differences (such as between different sites, or for different orientations) were the same to within four digits of accuracy for test runs on both lattices. Since calculations with both lattices produced the same minimum energy configurations for all molecules and the same minimum energies to within approximately 1%, and because of the great computational time saved, we chose to use the smaller lattice for our investigations. Thus the energy values of adsorbed molecules (not the values of the energy differences) we quote throughout this section may be one or two percent low, however, all physical conclusions based on these values should be valid.

We found that if the interactions were cutoff outside of a distance of approximately 12Å the results of our calculations were quite consistent with the results calculated using very large cutoffs on the enlarged lattice. At a cutoff distance of 14Å (15Å for CF_4), which implies interacting with only about 500 graphite atoms, all four single molecule systems have 98% of the total energy calculated for the enlarged lattice (where we used a cutoff of 54Å). The physical characteristic most sensitive to short distance cutoffs is the vertical height of a molecule above the graphite plane. At a cutoff of approximately 10Å (with approximately 94% to 95% of the energy at large cutoff) the calculated preferred height of a molecule begins to increase, but the preferred (minimum energy) orientations remain the same for both the symmetric and asymmetric molecules.

We found the minimum energy configuration of a single methane molecule on graphite to be 3.29Å above an atop site with the three tripod legs pointing towards the centers of the surrounding graphite hexagons (see Figure 4). In this configuration the potential energy, *i.e.* the isosteric heat, is -1665K. This value agrees very well with the value of -1663K obtained by Phillips and Hammerbacher.(8) The small difference is due to a combination of the inclusion of a larger volume of the graphite substrate by Phillips *et al.* in their calculation of the Lennard-Jones energy, and our own inclusion of the Coulomb interaction. The potential energies for methane on a bridge site (which we found to be the least favored adsorption site) and on a center site (which we found to be a saddle point) are -1654K and -1642K respectively. Thus the corrugation potential in which a methane sits is not very deep. Therefore it seems that there should be little favoring of a commensurate structure over an incommensurate structure. However, a final analysis of the relative stabilities of a commensurate and incommensurate structure will depend on the pair energies and the pair potential minimum. These will be discussed later.

The rotational barrier for methane is 53K if the height above an atop site is fixed at 3.29Å, and 47K if it is allowed to relax up to Z=3.33Å. The barriers to rotation are found to be larger than the barriers to translation, which seems to argue that descriptions of methane as a spherical molecule in the orientationally disordered solid phase are not sufficient to describe the system.

CF_4 is somewhat more interesting than methane on graphite since CF_4 has such a large number of solid phases, and because the ground state structure has not been precisely identified. There are, however, a large number of similarities to methane. We find that the preferred position of CF_4 is also an atop site 3.47Å above the graphite plane, and in this configuration a molecule will have a potential energy of -2448K. Unlike CH_4, however, the center site is the least preferred adsorption site for CF_4 and has a potential energy of -2350K when Z=3.53Å. Over a bridge site the potential energy is -2380K if Z is allowed to relax to 3.51Å above the graphite plane. The corrugation of the potential is approximately 100K, which suggests that there is little favoring of a commensurate phase over an incommensurate phase. The barrier to rotation about the Z-axis is 142K if held, and 117K if the molecule is allowed to relax in the Z direction to 3.54Å. Despite a considerable amount of work on the CF_4 on graphite system in the literature,(2,13) we have found no data to compare to our calculations of the adsorption potential (isosteric heat) or corrugation of the potential.

We find CHF_3 to be the most interesting in the CH_nF_{4-n} on graphite system, because of the existence of two very different locally stable configurations which are close in energy. The actual ground state has the CHF_3 in the atop site with the Euler angles (see Figures 7 and 8) $\theta = 30°$, $\phi = 123°$, $\omega = 0°$, and has Z=3.33Å. This orientation has one F pointing up, the H and two F's approximately parallel to the graphite plane and pointing at the centers of the surrounding graphite hexagons and a potential energy of -2482K. (This configuration is similar to that found in experiment.(7)) The local minimum has Euler angles (0,0,90), *i.e.* the H pointing up and the three F's pointing at the centers of the three surrounding graphite hexagons. The energy of this configuration is -2434K at Z=3.49Å above the graphite plane. The rigid and relaxed rotational barriers are respectively 126K and 104K for the global, and 39K and 6K for the local minimum. The preferred orientation at the bridge site is $\theta = 30°$, $\phi = 124°$, $\omega = 0°$ with Z=3.36Å and an energy of -2436K.

In the center site CHF_3's preferred orientation is $\theta = 0°$, $\phi = 124°$, $\omega = 0°$ with Z=3.37Å and an energy of -2414K. The corrugation of the potential is thus intermediate to the corrugation potentials of CH_4 and CF_4.

In CFH_3 there is a global and local minimum energy similar to that for CHF_3, and similarly, the "tipped" phase of CFH_3 has a lower energy than does the orientation with the single F pointing straight up. When the F points up there is a local minimum with the three tripod legs in the usual position, a Z of 3.25Å and an energy of -1911.5K/molecule. In the "tipped" orientation CFH_3 has angles $\theta = 30°$, $\phi = 103°$, $\omega = 0°$, with Z=3.31Å and an energy of -2117K. The rigid and relaxed barriers are respectively 60K and 52K for the local minimum, and 100K and 73K for the global minimum. The orientation of the minimum energy configuration at the bridge site is $\theta = 0°$, $\phi = 105°$, $\omega = 0°$, with Z=3.34Å and an energy of -2085K. For the center site the angles are $\theta = 0°$, $\phi = 101°$, $\omega = 0°$, with Z=3.33Å and an energy of -2072K.

For all adsorbates we found the Lennard-Jones interaction to dominate over the Coulomb. This was most pronounced for the symmetric molecules (which have a net octapole moment) where the Coulomb interaction died off completely (within an accuracy of five digits) inside of 14Å and provided only about -3K to the total energy of methane and about -20K for CF_4. CHF_3 was able to get approximately -100K from the Coulomb interaction when $\phi = 0°$, and -420K when $\phi = 180°$. (The minimum energy orientation for only the Coulomb interaction of CHF_3 and CFH_3, which both have net dipole moments, is with $\phi = 180°$.) These calculations were done with the carbon atom of the molecule held fixed at Z=3.3Å for CFH_3 and

Z=3.32Å for CHF_3. In both these molecules the carbon atom is close to, but not at, the center of charge.

The Coulomb interaction for CFH_3 provided approximately twice the total energy as it did for CHF_3. At $\phi = 0°$ the Coulomb contribution to the total energy was approximately -160K. Unlike the case for CHF_3, the Coulomb interaction for CFH_3 has a shallow local maximum near, but not at, $\phi = 0°$. The minimum energy of the Coulomb interaction for CFH_3 is approximately -820K at $\phi = 180°$.

The dominating force of the single molecule-substrate interaction for the symmetric molecules is the Lennard-Jones interaction with almost no contribution from the Coulomb interactions. However, for the asymmetric molecules the ground state structure is determined by the competition between the Coulomb interaction which wants to have as large a ϕ as possible, and the steric repulsion between the substrate and atom "one" (see Figure 8, atom one is the H in CHF_3 and the F in CFH_3), thus the repulsion tries to push atom one of the molecule up, *i.e.* towards smaller ϕ's.

B. Pair of molecules

In the previous section we investigated the energetics of a single molecule adsorbed on a graphite substrate. We now investigate the energetics of a pair of interacting molecules in free space to gain some insight as to how monolayer or submonolayer systems of CH_nF_{4-n} will act on a graphite substrate. We calculate the most favored orientation and separation of a pair of molecules, and consider, but do not explicitly calculate the substrate mediated interactions.

We have used the molecule-substrate cutoff's discussed earlier to attempt to get some idea of the possible substrate mediated interactions. For CF_4, CHF_3, and CFH_3 the Coulomb interactions with the substrate (which cause the substrate mediated effects) act significantly over a range far larger than the intermolecular nearest neighbor distances (which will be discussed later). However, the Coulomb interaction for CH_4 is quite small and dies off very rapidly. The Coulomb interaction energy for methane goes to zero in approximately 10Å, and when at the atop site, approximately three quarters of the Coulomb energy, or 2.9K, (methane generally gains between 3K and 4K from the Coulomb interaction) comes from the interaction with the carbon atom above which the molecule sits 3.29Å away (in the minimum energy configuration). The extremely short range of this significant part of the Coulomb interaction (the carbon atom beneath one methane molecule should be beyond the range where a second methane molecule can significantly influence it) implies that there should be little or no substrate mediated interference effects. Having not made an explicit calculation of the substrate mediated effects, however, we can not conclusively state that they are insignificant.

For methane the minimum energy occurs at a separation of 4.00Å with one H from each molecule pointing straight up and a tripod leg from one of the two molecules pointing into the V of the other molecule. The interaction energy is -167K. To see how the minimum energy separation corresponds to various commensurate lattice separations on a graphite lattice (see Figure 10, where we place a molecule at site 0 and another at site n where n=1,2,3,... and all lattice points equidistant from site 0 are given the same n), Table 3 shows the pair energy at most favored orientation at the sites shown in Figure 10. At site four with a separation of 3.76Å

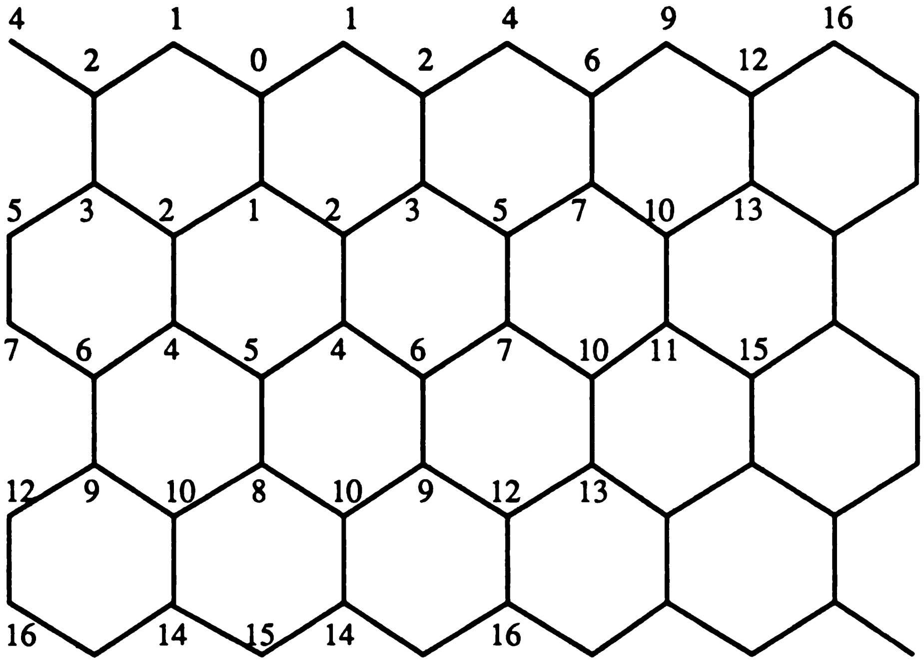


Figure 10. Definition of sites used in Table 3. Sites equidistant from site 0 are assigned the same site number.

Table 3. Minimum intermolecular energy for pairs of CH_4 and CF_4

Site number	Separation from site 0 in Å	Energy in K	
		for CH_4	for CF_4
1	1.421	>0	>0
2	2.461	>0	>0
3	2.842	>0	>0
4	3.760	-165	>0
5	4.263	-142	-127
6	4.923	-68	-198
7	5.124	-55	-167
8	5.684	-29	-93
9	6.194	-18	-52
10	6.512	-12	-38
11	7.105	-7	-22
12	7.384	-6	-17
13	7.519	-5	-15
14	7.912	-4	-11
15	8.526	-2	-7
16	8.644		-6

two molecules would have an interaction energy of -165K. There is no way, however, to form a cluster (let alone a monolayer) with three or more nearest neighbors all having this separation (3.76Å) without losing the commensuration energy. The first site at which it is energetically reasonable for methane to form a commensurate lattice is site five, which corresponds to the triangular $\sqrt{3} \times \sqrt{3}$ R30° lattice shown in Figure 2. Site five has an interaction energy of -142K which is approximately 30K above the minimum of the pair potential. Since this is larger than the corrugation of the molecule-substrate potential the incommensurate phase appears to be the ground state of methane on graphite. This does not agree with experiment, however, some calculations by Phillips *et al.*(5) indicate that a combination of the substrate mediated interaction and the zero point oscillations of methane (which we did not calculate) will shift the equilibrium energy and position so that the commensurate phase is the ground state.

We have also considered the orientational order-disorder transition of methane on graphite. One odd thing about the system is that for CH_4 at a separation of 4.00Å the barrier against rotation due to an adjacent molecule is 23K. The barrier against rotation at 4.263Å is 29K. This occurs because the Lennard-Jones interaction and the Coulomb interaction are opposing each other. When one interaction is at a maximum, the other is at a minimum. The net effect is that the variations in the potential tend to cancel each other out except that the Coulomb interaction always varies more with orientation than does the Lennard-Jones potential. At a separation of 4.263Å the Lennard-Jones potential is much flatter than at 4.00Å, and thus the variation in the Coulomb potential is more evident.

Table 3, mentioned earlier in this section, gives some data on the pair interaction of both methane and CF_4. For CF_4 the minimum of the pair potential is -224K, and the pair potential at site six is -198K. Since the difference (26K) is less than the difference between the atop site and other sites it looks like the ground state of CF_4 should be the commensurate phase. However, in the 2 × 2 structure the CF_4's are forced to orient themselves away from the minimum energy configuration of the substrate-CF_4 interaction. This reduces the commensuration energy to below 26 K/molecule, and thus it is probable that the ground state of CF_4 on graphite is incommensurate. We note here that the zero point oscillations which apparently affect the minimum energy configuration of methane should not have as large an effect on the minimum energy configurations of CF_4 since a fluorine atom has almost twenty times the mass of a hydrogen atom and the C–F bond lengths are about 30% longer than the C–H bond lengths. Thus the moment of inertia of CF_4 is over 100 times larger than the moment of inertia of CH_4.

The CFH_3 and CHF_3 systems on graphite are quite complex and a complete analysis of these systems is very difficult. The tables in appendix A show the energy of a pair of interacting molecules throughout a large portion of the available phase space. We have isolated at least a local minimum for the intermolecular pair potential at (carbon to carbon) separations of 4.0Å for CFH_3 and 4.5Å for CHF_3. These minima were found by rotating both molecules through all Euler angles at initial separations of 4.4Å for CFH_3 and 4.5Å for CHF_3, and then varying the separation until a minimum was found. This minimum energy separation agrees well with the experimental results of Knorr and Weickert(7) for the separation of molecules of CHF_3 on a graphite. The potential well depths mentioned earlier were found by simply calculating the pair energy at the minimum energy pair configurations (*i.e.* $\phi_1 = 16°$, $\phi_2 = 196°$, $X_1 = 0$, $X_2 = 3.33Å$ for CFH_3 and $\phi_1 = 2°$, $\phi_2 = 208°$, $\omega_2 = 60°$, $X_1 = 0$, $X_2 = 3.76Å$ for CHF_3 with all coordinates not mentioned equal to zero) of an SCF calculation.$^{(5)}$ The tables in appendix A do not show any configuration that can completely dominate the structure of a molecular monolayer for either CFH_3 or CHF_3.

Since it is possible that the orientations of molecules in clusters or monolayers of CFH_3 and CHF_3 on graphite may be determined by the molecule-substrate interaction we have further investigated the intermolecular interaction of pairs of molecules in the orientations preferred by the molecule-substrate interaction. Both systems have two molecular orientations preferred by the graphite-adsorbate interactions, namely having all ϕ's equal to 0°, and having $\phi = 103°$ or $\phi = 123°$ for CFH_3 and CHF_3 respectively. The configuration with all ϕ's equal to 0° is highly unfavorable, the intermolecular interactions being repulsive for both CHF_3 and CFH_3. The "tipped" configurations (where $\phi = 123K$ for CHF_3 and $\phi = 103K$ for CFH_3), however, have some orientations that are very favorable (have very low energy), as well as some orientations that are very unfavorable (have extremely high interaction energy). The figures in appendix B show the interaction energies of various orientations (θ's) with the ϕ's held to 125° or 100° for CHF_3 and CFH_3 respectively which are close to the "tipped" configurations' values. Maxima and minima as well as points of zero energy are shown to display regions of attractive and repulsive potentials which cover nearly equal areas of the phase space. In a triangular lattice each molecule will have six nearest neighbors spaced 60° apart. Thus, even assuming that all molecules will have only one rotational degree of freedom (for instance θ with ϕ and ω set to the values preferred by the substrate interaction, as shown in appendix B) finding the exact ground state orientations is not a trivial problem, and we do not attempt to do this in this thesis.

Our present study does not represent a complete analysis of the systems we have investigated, and in view of the uncertainty in our parameters the molecule-substrate potentials are uncertain to several (we estimate 2 to 4) tens of degrees (K). However, energy differences due to changes in orientations or intermolecular configurations should be accurate to the digits we have quoted. We believe we have found several new and interesting results including the preferred orientation of CF_4 in the 2×2 commensurate phase, the preferred orientations and adsorption sites of single CFH_3 and CHF_3 molecules, and approximate values for the isosteric heats and vertical heights above the graphite plane for CF_4, CHF_3, and CFH_3. Our results agree well with available experimental data such as the vertical height of methane above the carbon plane, the preferred orientation of CH_4, the (theoretical) preferred adsorption site for CH_4 and CF_4, and the isosteric heat of physisorbed methane. Although we did not perform a complete calculation of the ground state of molecular monolayers, our calculations suggest an incommensurate phase for the ground state of CF_4 on graphite, and "tipped" phases for the ground states of CFH_3 and CHF_3. We can not predict any preferred orientational structure for the ground states of large systems of the asymmetric molecules on graphite. We can, however, conclude that there should be little favoring of an orientationally ordered phase over a disordered phase, this conclusion is supported by the low (45K) temperature at which orientational ordering of CHF_3 on graphite is observed.(7)

APPENDIX A

The tables in this appendix give the pair energy minima of the asymmetric molecules, CHF_3 and CFH_3, for various configurations of the two molecules. The configurations of the molecules are described by the Euler angles θ, ϕ, and ω defined in section V of the thesis, where $\theta_1=0$ is the direction from atom 1 to atom 2, $\theta_2=0$ points away from atom 1, and Δ is the carbon to carbon separation of the molecules. The three energies quoted in Tables 4 and 5 are the total energy, E_{min}, at the pair potential minimum, and the contributions to this energy from the Coulomb interaction, E_C, and the Lennard-Jones interaction, E_{LJ}.

Although our pair calculations were done in free space for simplicity, the main objective of this thesis is to consider systems physisorbed on graphite. Since all pair configurations with both ϕ's small are energetically unfavorable, and the molecule-substrate interaction prevents any configurations with large ϕ's, we give here those ϕ_1's with "tipped" orientations in the region where the molecule-substrate interaction is energetically favorable. For each molecule we also give one table with $\theta_1=0$ and vary ϕ_1 through 180°. In calculating the pair energies, we rotated molecule two through all possible θ and ϕ in steps of 10° or 15°. For CFH_3 we constrained $\omega_2=0$, since the pair energies are not very sensative to changes in ω and the molecule-substrate interaction for "tipped" configurations has a very strong preference for $\omega=0$. The Δ's were chosen by making pair energy tables at initial guesses of $\Delta=4.5$Å for CHF_3, and $\Delta=4.4$Å for CFH_3. The configuration corresponding to the largest (most negative) entry from each set of tables was then tested at various Δ's until minima were found at 4.5Å and 4.0Å for CHF_3 and CFH_3 respectively. We note that the experimental separation of CHF_3 on graphite$^{(7)}$ is close to our chosen Δ and the experimental separation of CH_4 is close to our chosen Δ for CFH_3.

Table 4. Pair energies for CHF_3.

Table 4a.

CHF_3 ϕ_1=50° ω_1=0° Δ=4.5Å

θ_1	θ_2	ϕ_2	ω_2	E_{min}	E_C	E_{LJ}
-15	60	150	0	-701	-598	-103
0	0	160	60	-693	-596	-97
15	300	150	0	-701	-598	-103
30	270	140	90	-714	-570	-144
45	270	140	90	-719	-580	-139
60	240	140	60	-703	-517	-186
75	240	130	60	-707	-524	-183
90	240	130	60	-675	-497	-177
105	210	140	30	-639	-440	-198
120	210	130	30	-583	-381	-202
135	210	120	60	-563	-361	-202
150	210	100	60	-578	-391	-187
165	210	100	60	-587	-414	-174
180	180	110	60	-597	-439	-158

Table 4b.

CHF_3 ϕ_1=70° ω_1=0° Δ=4.5Å

θ_1	θ_2	ϕ_2	ω_2	E_{min}	E_C	E_{LJ}
-15	30	140	90	-624	-562	-62
0	0	140	60	-614	-532	-83
15	330	140	30	-624	-562	-62
30	300	130	0	-666	-587	-80
45	270	120	90	-717	-576	-142
60	270	120	90	-701	-565	-136
75	240	130	60	-670	-479	-191
90	240	120	60	-685	-496	-189
105	210	130	60	-643	-486	-184
120	210	120	60	-613	-422	-192
135	210	110	60	-559	-361	-199
150	180	100	30	-521	-332	-189
165	180	90	60	-509	-325	-184
180	180	90	60	-505	-324	-181

Table 4c.

CHF$_3$ ϕ_1=90° ω_1=0° Δ=4.5Å

θ_1	θ_2	ϕ_2	ω_2	E_{min}	E_C	E_{LJ}
-15	30	60	60	-584	-448	-137
0	330	70	60	-560	-439	-121
15	330	60	60	-584	-447	-137
30	300	100	90	-646	-571	-75
45	270	100	90	-685	-552	-133
60	270	100	90	-718	-560	-159
75	270	90	60	-654	-461	-192
90	240	110	90	-681	-496	-185
105	240	100	60	-658	-470	-188
120	210	110	60	-643	-483	-160
135	210	100	60	-591	-405	-186
150	210	100	60	-533	-361	-172
165	180	90	60	-481	-295	-186
180	180	90	60	-456	-270	-186

Table 4d.

CHF$_3$ ϕ_1=110° ω_1=0° Δ=4.5Å

θ_1	θ_2	ϕ_2	ω_2	E_{min}	E_C	E_{LJ}
-15	30	40	60	-623	-487	-137
0	330	50	60	-607	-494	-113
15	330	40	60	-623	-487	-137
30	300	50	60	-669	-584	-85
45	300	40	60	-691	-555	-135
60	270	80	90	-712	-543	-169
75	270	60	60	-643	-446	-198
90	240	90	90	-686	-498	-188
105	240	90	60	-671	-489	-181
120	210	80	90	-657	-538	-119
135	210	90	60	-629	-479	-150
150	180	70	90	-570	-402	-168
165	180	90	60	-520	-342	-178
180	180	90	60	-489	-302	-187

Table 4e.

CHF_3 $\phi_1=130°$ $\omega_1=0°$ $\Delta=4.5Å$

θ_1	θ_2	ϕ_2	ω_2	E_{min}	E_C	E_{LJ}
-15	30	10	90	-698	-600	-99
0	0	10	0	-690	-611	-79
15	330	10	30	-699	-600	-99
30	300	20	60	-715	-584	-131
45	270	40	90	-703	-535	-168
60	270	50	90	-698	-523	-175
75	270	40	60	-628	-428	-200
90	240	70	90	-685	-495	-190
105	240	70	60	-678	-498	-180
120	210	60	90	-692	-566	-126
135	210	70	60	-662	-533	-130
150	180	60	90	-625	-469	-156
165	180	70	60	-570	-389	-181
180	180	70	60	-538	-346	-193

Table 4f.

CHF_3 $\theta_1=0°$ $\omega_1=0°$ $\Delta=4.5Å$

ϕ_1	θ_2	ϕ_2	ω_2	E_{min}	E_C	E_{LJ}
0	180	170	0	-630	-437	-193
10	210	170	30	-662	-469	-192
20	180	180	0	-691	-512	-179
30	60	170	0	-708	-543	-166
40	0	170	60	-716	-578	-139
50	0	160	60	-693	-596	-97
60	0	150	60	-652	-579	-72
70	0	140	60	-614	-532	-83
80	0	130	60	-584	-465	-119
90	330	70	60	-560	-439	-121
100	330	60	60	-577	-472	-199
110	30	50	60	-607	-495	-113
120	30	40	60	-641	-503	-138
130	0	10	0	-690	-611	-79
140	0	0	0	-725	-581	-144
150	210	10	30	-726	-556	-170
160	180	20	60	-720	-539	-181
170	180	30	60	-725	-551	-174
180	180	40	60	-725	-581	-144

Table 5. Pair energies for CFH_3.

Table 5a.

CFH_3 ϕ_1=70° ω_1 =ω_2=0° Δ=4.0Å

θ_1	θ_2	ϕ_2	E_{min}	E_C	E_{LJ}
-15	15	100	-490	-633	+143
0	0	110	-383	-681	+297
15	345	100	-490	-633	+143
30	345	130	-636	-579	-57
45	255	120	-781	-620	-161
60	255	120	-828	-613	-215
75	240	110	-809	-606	-203
90	240	110	-765	-572	-193
105	225	110	-744	-633	-111
120	225	110	-724	-565	-159
135	220	110	-700	-546	-153
150	210	120	-663	-520	-142
165	210	110	-628	-550	-79
180	160	120	-611	-528	-83

Table 5b.

CFH_3 ϕ_1=80° ω_1 =ω_2=0° Δ=4.0Å

θ_1	θ_2	ϕ_2	E_{min}	E_C	E_{LJ}
-15	15	90	-319	-684	+365
0	0	100	-108	-722	+614
15	345	90	-319	-684	+365
30	330	90	-599	-596	-3
45	255	110	-732	-615	-117
60	255	110	-827	-616	-211
75	240	110	-814	-610	-204
90	240	110	-776	-587	-189
105	225	110	-720	-652	-68
120	225	100	-716	-590	-127
135	225	100	-675	-511	-164
150	210	120	-645	-510	-135
165	210	110	-618	-531	-87
180	210	110	-597	-520	-77

Table 5c.

CFH_3 $\phi_1=90°$ $\omega_1=\omega_2=0°$ $\Delta=4.0Å$

θ_1	θ_2	ϕ_2	E_{min}	E_C	E_{LJ}
-15	15	90	-239	-704	+465
0	---	---	>0	---	---
15	345	90	-239	-704	+465
30	330	80	-591	-621	+30
45	285	80	-717	-635	-82
60	255	100	-823	-616	-207
75	240	100	-819	-614	-204
90	240	100	-787	-602	-185
105	225	80	-713	-628	-86
120	225	90	-701	-602	-99
135	225	100	-666	-517	-149
150	210	120	-626	-508	-118
165	210	110	-608	-526	-82
180	180	50	-590	-471	-119

Table 5d.

CFH_3 $\phi_1=100°$ $\omega_1=\omega_2=0°$ $\Delta=4.0Å$

θ_1	θ_2	ϕ_2	E_{min}	E_C	E_{LJ}
-15	15	80	-327	-691	+364
0	0	80	-106	-722	+616
15	345	80	-327	-691	+364
30	315	70	-627	-667	+40
45	285	70	-732	-628	-104
60	255	90	-819	-614	-204
75	240	90	-823	-616	-207
90	240	90	-793	-609	-184
105	225	70	-719	-606	-112
120	225	80	-687	-598	-90
135	225	90	-657	-528	-129
150	210	70	-623	-554	-69
165	180	50	-607	-477	-130
180	180	50	-605	-471	-134

Table 5e.

CFH_3 $\phi_1=110°$ $\omega_1=\omega_2=0°$ $\Delta=4.0Å$

θ_1	θ_2	ϕ_2	E_{min}	E_C	E_{LJ}
-15	15	70	-496	-653	+157
0	0	80	-381	-660	+280
15	345	70	-496	-653	+157
30	315	60	-692	-641	-50
45	285	60	-749	-608	-141
60	255	80	-814	-611	-204
75	240	80	-827	-616	-211
90	240	80	-797	-609	-188
105	225	70	-723	-652	-71
120	225	70	-679	-580	-99
135	225	80	-647	-527	-119
150	210	60	-631	-502	-130
165	180	50	-626	-499	-127
180	180	50	-624	-487	-136

Table 5f.

CFH_3 $\theta_1=0°$ $\omega_1=\omega_2=0°$ $\Delta=4.0Å$

ϕ_1	θ_2	ϕ_2	E_{min}	E_C	E_{LJ}
0	180	140	-801	-518	-213
10	180	150	-806	-586	-220
20	180	160	-816	-603	-213
30	180	160	-813	-630	-183
40	20	180	-763	-599	-163
50	0	160	-741	-631	-110
60	0	140	-611	-684	+74
70	0	110	-384	-681	+297
80	0	100	-108	-722	+614
90	---	---	>0	---	---
100	0	80	-106	-722	+616
110	0	80	-381	-660	+280
120	340	60	-581	-627	+46
130	60	10	-747	-628	-119
140	60	0	-807	-640	-168
150	140	20	-846	-648	-199
160	150	30	-828	-622	-206
170	200	30	-807	-638	-169
180	180	30	-771	-643	-128

APPENDIX B

The figures in this appendix show the pair energies of the asymmetric molecules, CHF_3 and CFH_3, for various θ's with the ϕ's and ω's (the θ's, ϕ's, and ω's used here are the Euler angles defined in section V of this thesis) set to the orientations noted in the captions of Figures 11 and 12. These noted orientations are close (within 2 degrees) to the minimum energy orientations of the single molecule-substrate interactions.

Each drawing in Figures 11 and 12 shows two molecules with molecule one represented by a single dark line pointing in the direction of the dipole moment of the molecule. Molecule two is represented by a circle centered on the carbon atom, and showing the approximate radius of the molecule. For each orientation (θ) of molecule one, molecule two is rotated through 360 degrees (in steps of 10°) and all local energy maxima and minima are shown by drawing a radial line in the direction of the dipole moment at the maximum or minimum and noting the total pair energy of the configuration and the angle (θ_2) at which this energy was found. We also show the approximate angles at which the pair energy is zero, and, as an aid to the eye, we have shaded the regions of positive energy (*i.e.* if the dipole moment of molecule two lies in a shaded region, as drawn, then the pair interaction energy is positive). As can be seen from the figures, regions of positive and negative energy occupy nearly equal areas of the available (as we have constrained it) phase space. The intermolecular separations, r, of the molecules represented in Figures 11 and 12 are 4.5Å and 4.0Å for CHF_3 and CFH_3 respectively; these separations were chosen to match the intermolecular separations which we have discussed in appendix A.

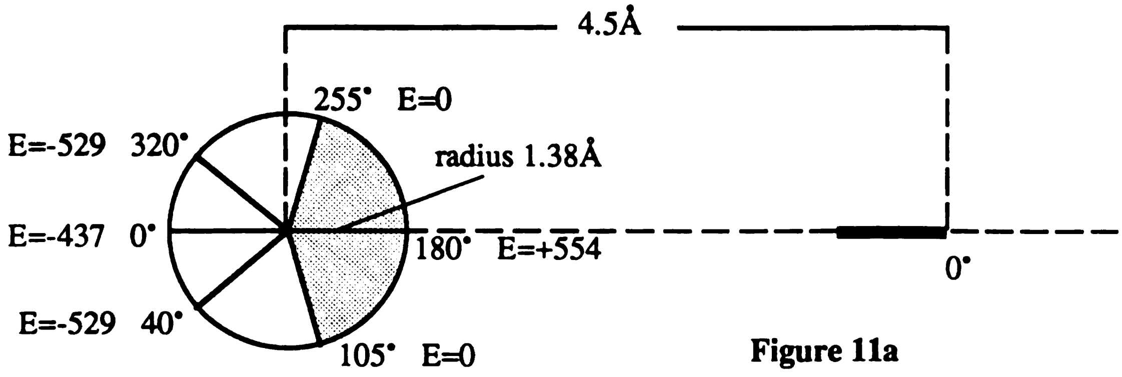


Figure 11a

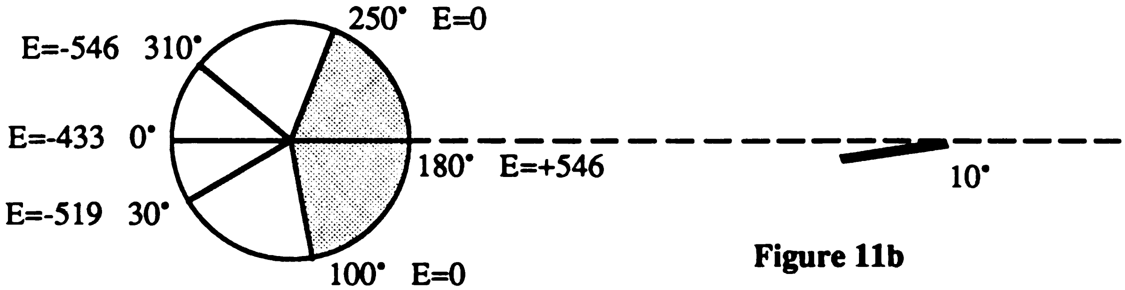


Figure 11b

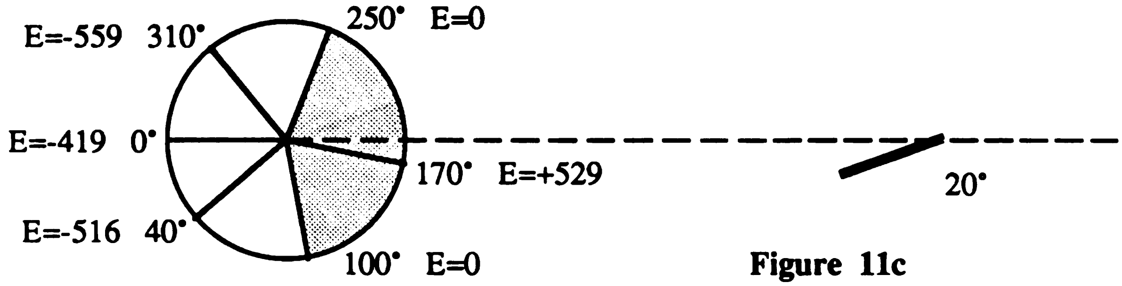


Figure 11c

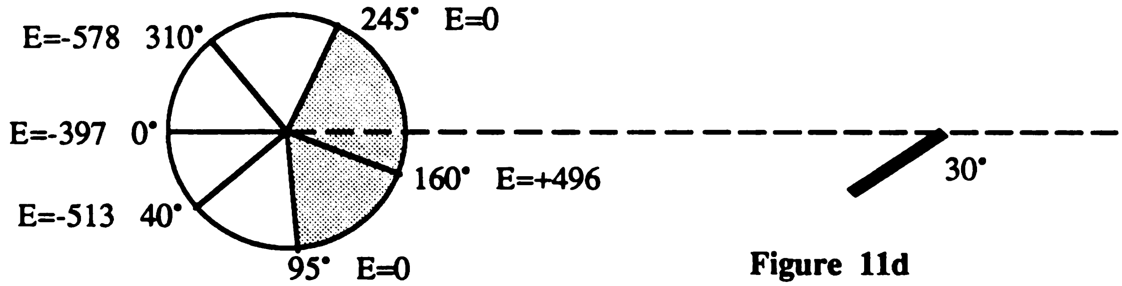


Figure 11d

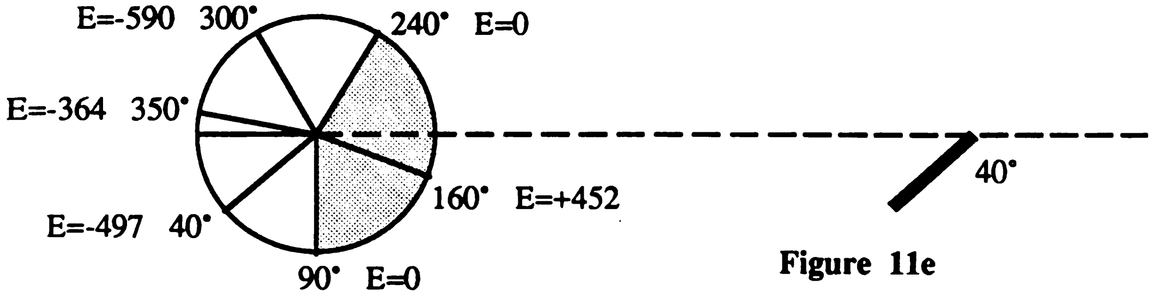


Figure 11e

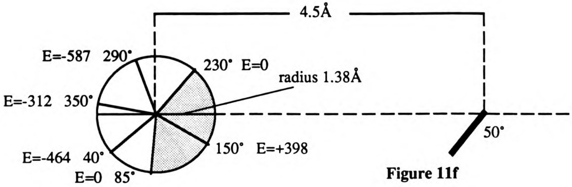


Figure 11f

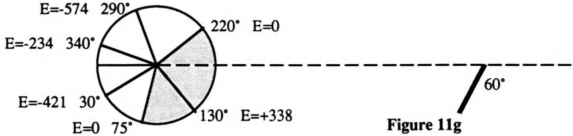


Figure 11g

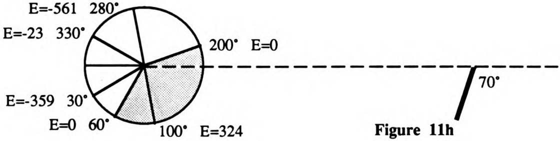


Figure 11h

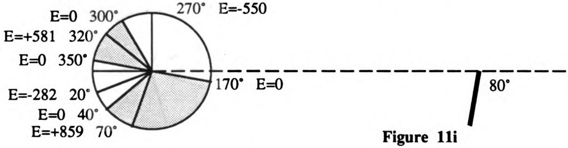


Figure 11i

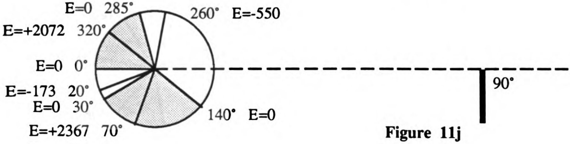


Figure 11j

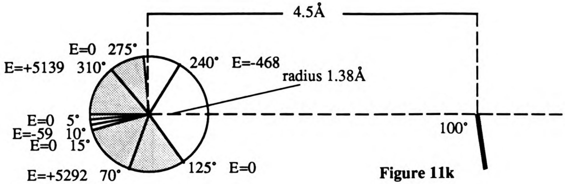


Figure 11k

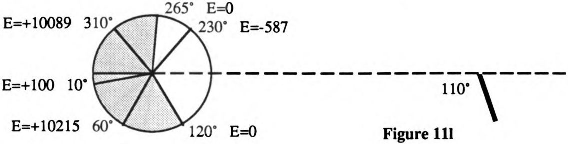


Figure 11l

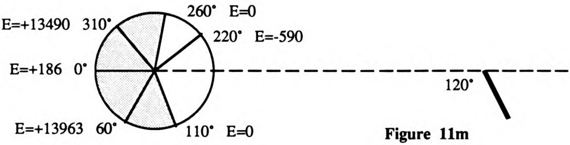


Figure 11m

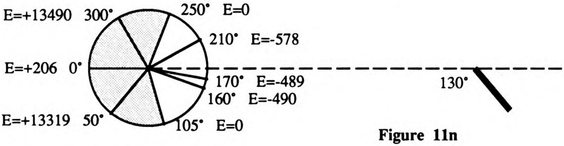


Figure 11n

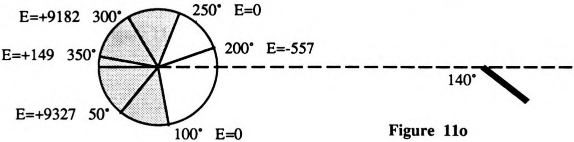


Figure 11o

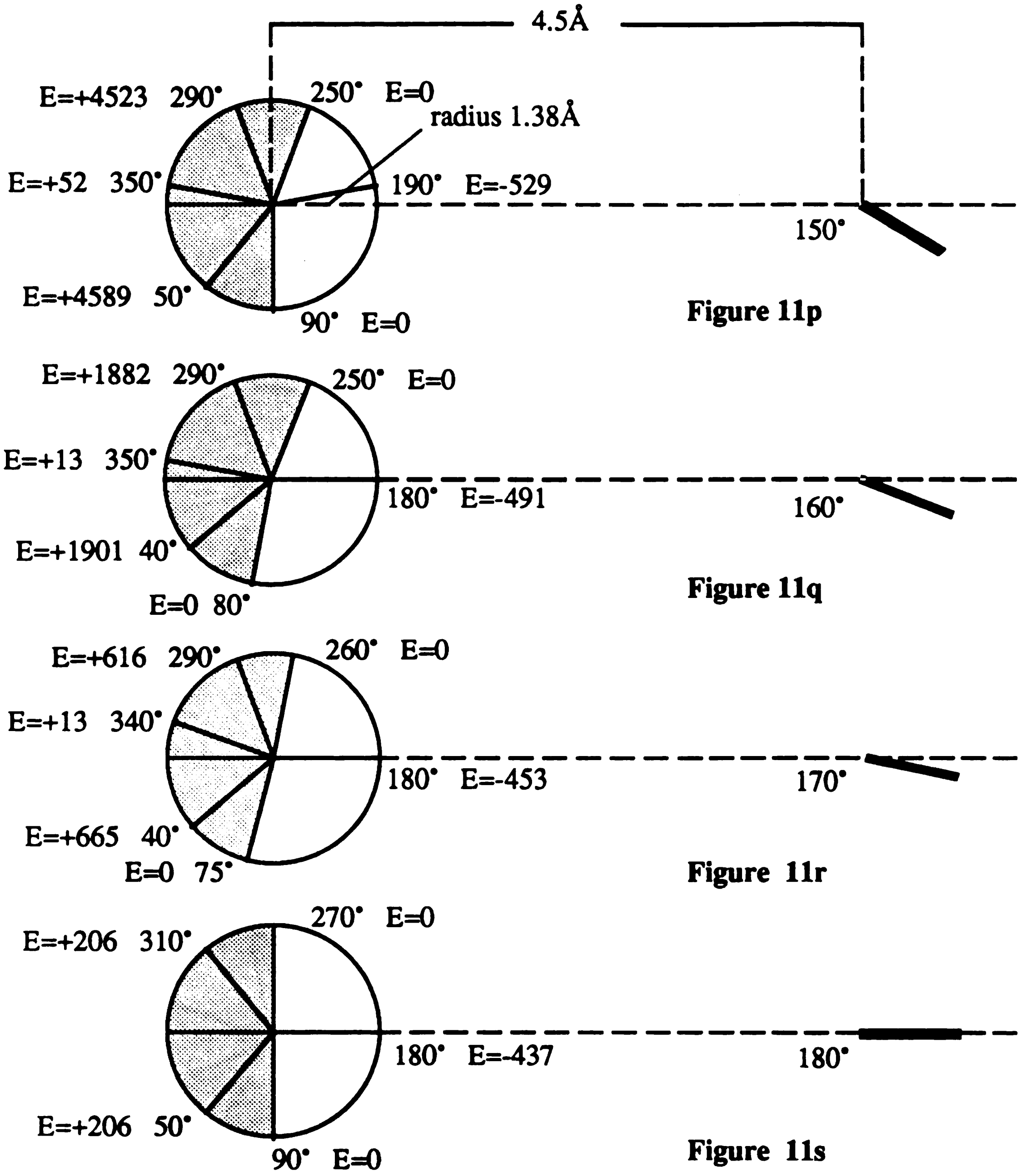


Figure 11p

Figure 11q

Figure 11r

Figure 11s

Figure 11. CHF$_3$ pair energies for $\phi_1=\phi_2=125°$, r=4.5Å

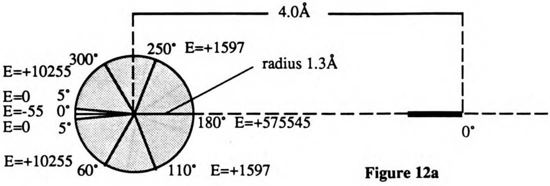


Figure 12a

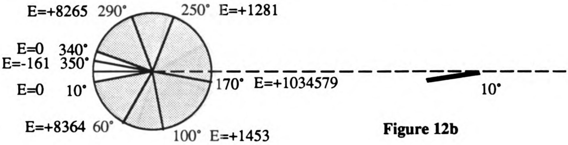


Figure 12b

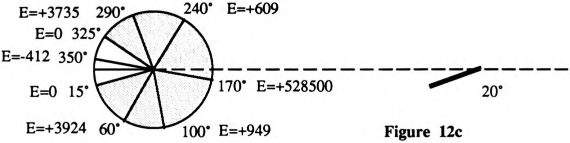


Figure 12c

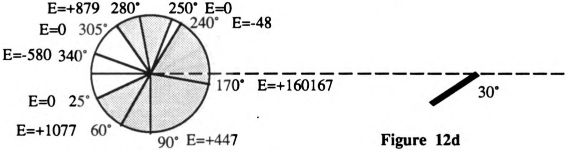


Figure 12d

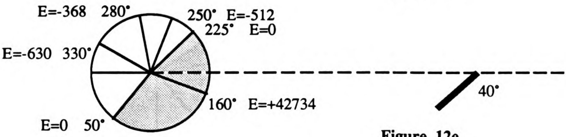


Figure 12e

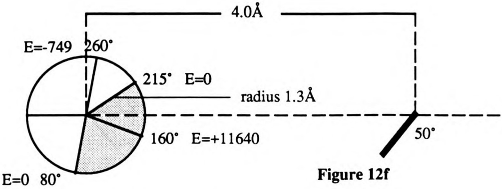


Figure 12f

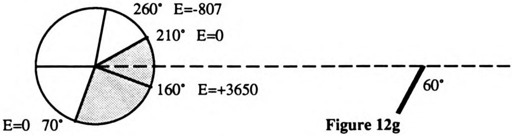


Figure 12g

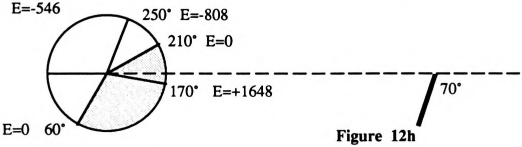


Figure 12h

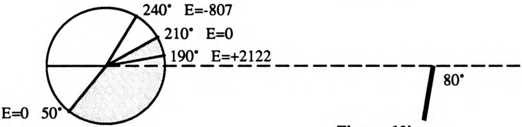


Figure 12i

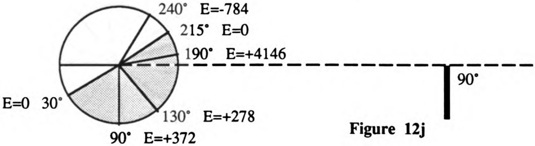
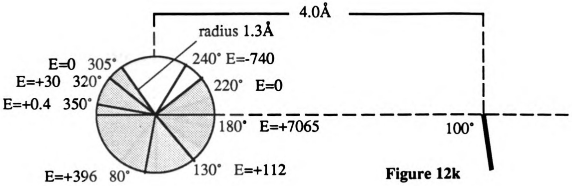


Figure 12j



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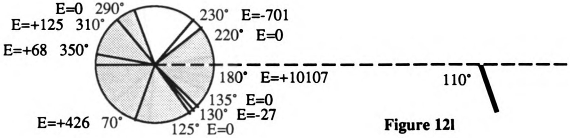

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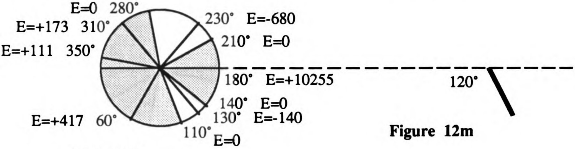

Figure 12m

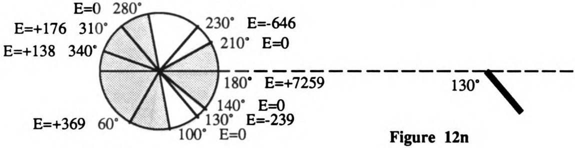

Figure 12n

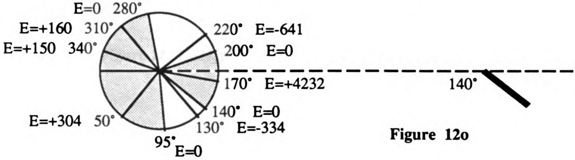

Figure 12o

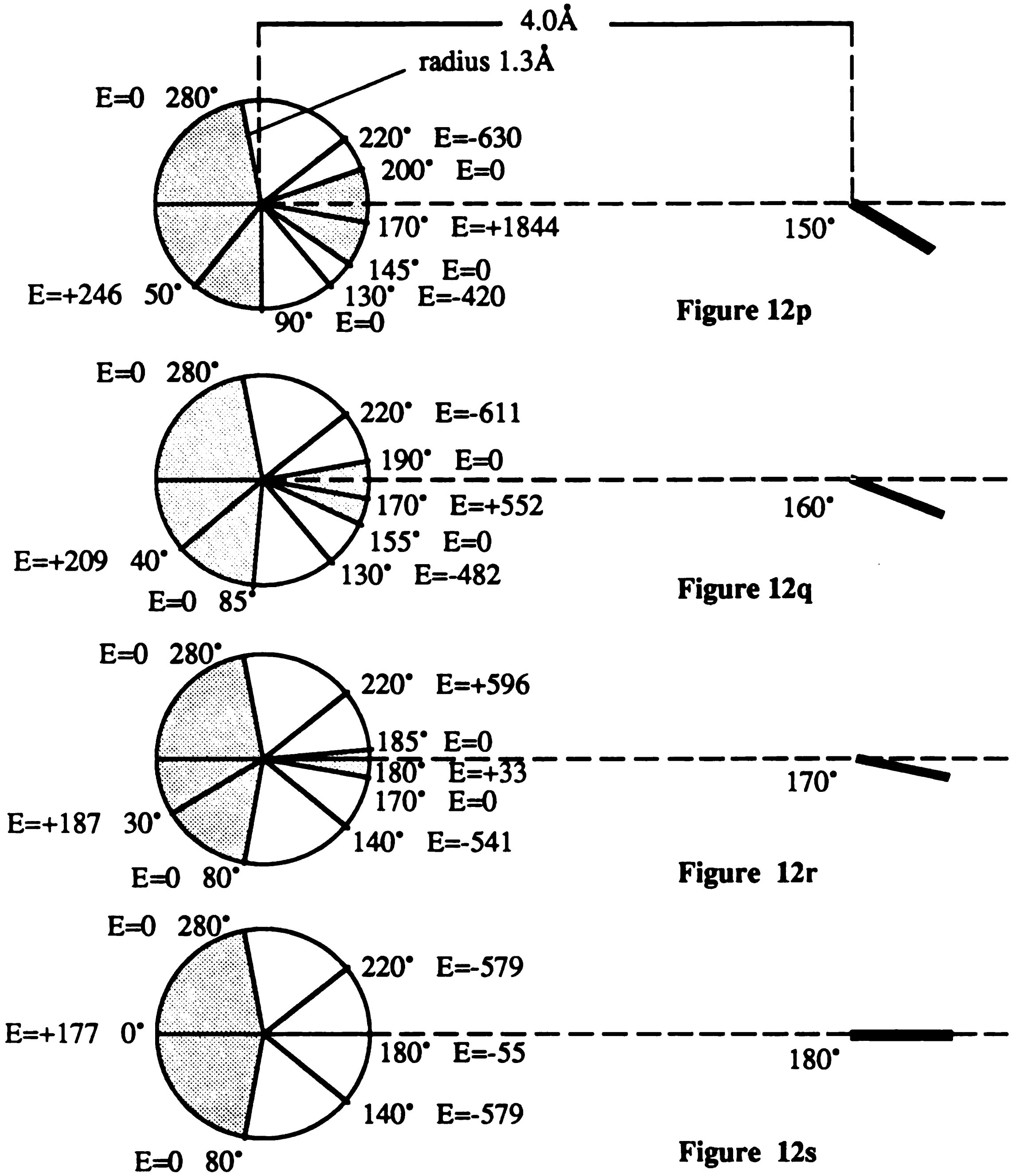

Figure 12p

Figure 12q

Figure 12r

Figure 12s

Figure 12. CFH$_3$ pair energies for $\phi_1=\phi_2=100°$, r=4.0Å

LIST OF REFERENCES

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