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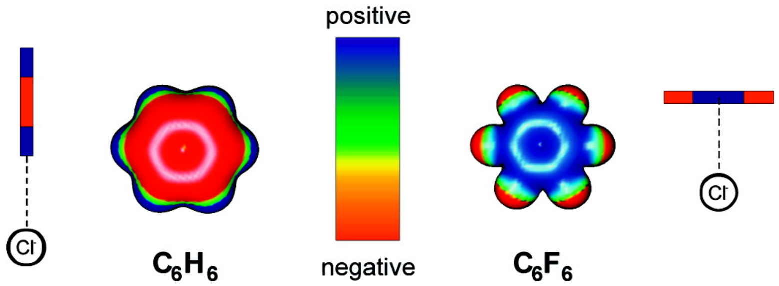
J. Am. Chem. Soc., **2007**, 129 (43), 13022-13026• DOI: 10.1021/ja073028k • Publication Date (Web): 05 October 2007



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Aromatic Molecules in Anion Recognition: Electrostatics versus H-Bonding

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Abstract: Mass-selected complexes $A^-\cdot C_6F_nH_{6-n}$ (A = Cl, I, SF_6; $n = 0-5$) were studied by infrared photodissociation spectroscopy and computational chemistry methods to investigate the interaction of negative ions and aromatic molecules, in which the charge distribution can be tuned by fluorination. Surprisingly, we find that, despite positive partial charges on the carbon atoms at high levels of fluorination, all anions under study prefer hydrogen bonding to the remaining H atoms in the ligand rather than binding to the positively charged ring. Moreover, bifurcated hydrogen bonds to two neighboring CH groups are energetically favored over linear hydrogen bonds to a single CH group.

Introduction

Aromatic molecules are an important class of chemical systems, and their interaction with charge is very important in a wide variety of chemical contexts, ranging from molecular recognition[1−6] to astrochemistry[7,8] and supramolecular chemistry (see, e.g., refs 9 and 10). Consequently, the interaction of charge with aromatic systems has received increasing attention over the past few years. Although cation−π complexes have been the main focus of most studies (see, e.g., refs 1, 2, and 11−22), an increasing amount of work, both theoretical[23−28] and experimental,[6,29−33] has recently been devoted to the investigation of anion interactions with aromatic molecules.

In clusters of anions with molecules containing H atoms, the most important contribution to the interaction potentials usually comes from ionic hydrogen bonds (H bonds). Ionic H bonds are not only based on electrostatic interactions but also involve electron transfer into the σ orbitals connecting the proton in the donating group to the rest of the molecule. Low-lying proton-transfer channels can serve to energetically favor H-bonded structures over alternative configurations that rely solely on electrostatic interactions.

Substitution makes benzene derivatives chemically very versatile. Fluorine is one of the most important substituents, and fluorine-containing organic compounds are of prime importance for pharmaceutical molecules and crop protection products, whose properties can be subtly tuned by fluorination.[34]

Every chemistry undergraduate student learns that substitution affects the charge distribution in an aromatic system, depending on the nature and the number of substituents. In the case of fluorination, the electron withdrawing nature of the F substit-

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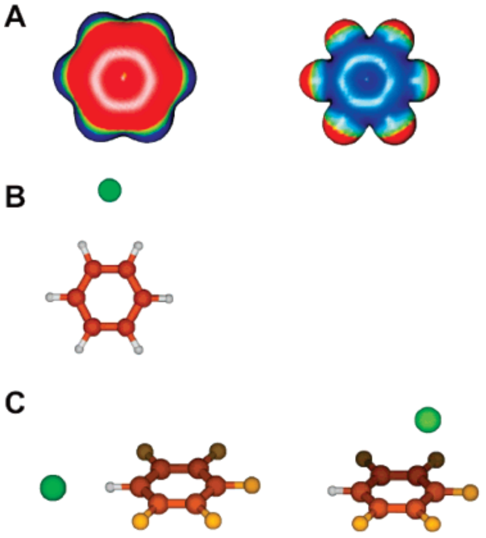

Figure 1. (A) Illustration of the electrostatic potential around C_6H_6 (left) and C_6F_6 (right), respectively (calculated with Gaussian03W, HF/3-21G* level[49]). The color coding from blue to red represents positive to negative electrostatic potentials. (B) Calculated structure for $Cl^-\cdot C_6H_6$ (B3-LYP/TZVP). (C) Calculated structures for $Cl^-\cdot C_6F_5H$ via H bonding (left) and ring bonding (right).

uents makes the electrostatic potential around the carbon ring more positive as electron density is moved to the F atoms in the periphery. This has been addressed, e.g., in a recent theoretical work by Quinonero et al.[35] and can be seen most clearly in the changes of the electrostatic potential close to the ring, which changes from negative in benzene to positive in perfluorobenzene (see Figure 1A). As the charge distribution changes with the number and positions of the F atoms, one would expect to see a change in the preferred binding site for an ion.

Bieske and co-workers[32,33] established in pioneering infrared (IR) experiments on halide-benzene complexes that the structures of these complexes are characterized by bifurcated H bonds between the anion and two neighboring CH groups (see Figure 1B). In line with the expectations described above, complexes of an anion with hexafluorobenzene have been calculated to have structures in which the anion binds to one of the carbon atoms in the ring.[35,36] In light of the different binding motifs for these two limiting cases, it is not at all clear how systems at intermediate levels of fluorination will behave. Specifically, we ask (i) how many fluorine atoms it takes to change the binding motif and (ii) how the distribution of fluorine atoms around the ring (i.e., the isomer) influences the bonding.

Combined studies employing IR spectroscopy and electronic structure calculations have been very successful for the detailed structural investigation of ion−molecule complexes and clusters (see, e.g., refs 37−48). However, experimental data on anionic clusters involving aromatic molecules is still rather rare. In the present paper, we use Ar predissociation spectroscopy to investigate the structures of $A^-\cdot C_6F_nH_{6-n}$ (A = Cl, I, SF_6; $n = 0-5$) complexes as a function of the number and positions of F atoms around the ring as well as the properties of the anion. This is the first gas-phase investigation of the structural properties of anion interactions with electron-deficient arenes.

Methods

Experiment. In the present study, we use a setup described previously.[50] In brief, Ar-solvated complexes of fluorinated benzenes with chloride anions, $Cl^-\cdot C_6F_nH_{6-n}\cdot Ar_m$ ($n = 0-5$, $m = 1-3$), are generated in a pulsed supersonic entrainment source, where $CHCl_3$ and the aromatic molecule under study were entrained into an expansion of neat Ar.[51] For the two other ions used in this study, CH_3I and SF_6 were entrained as precursors for I^- and SF_6^-, respectively. The presence of argon in the clusters ensures that the cluster ions are in or close to their equilibrium geometry. The ions are mass selected by time-of-flight mass spectrometry and then interact with the IR output of a nanosecond-pulsed optical parametric converter pumped by a Nd:YAG laser. After absorption of an IR photon resonant with a vibrational transition in the cluster, a transient, vibrationally excited cluster is formed, which subsequently decays through vibrational predissociation:

$$A^-\cdot C_6F_nH_{6-n}\cdot Ar_m + \hbar\omega \rightarrow A^-\cdot C_6F_nH_{6-n} + m\mathrm{Ar} \qquad (1)$$

(A = Cl, I, or SF_6). The formation of bare ion−molecule complexes is monitored to obtain the IR spectrum of the complexes under study, and fragment ion signals are corrected for fluctuations in the IR pulse energy. For all complexes except A = I^- and SF_6^-, we used $m = 1$. For I^- and SF_6^- complexes, we used the spectra with the best signal-to-noise ratio. We note that the dependence of the IR spectra on the number of Ar atoms is typically very weak.[52,53] Similarly, different Ar isomers usually only lead to a slight broadening of the observed bands but not to multiple clearly resolved sharp bands.

Calculations. We used density functional theory[54] (B3-LYP[55,56] method) and *ab initio* calculations at the RI-MP2[57,58] level (second-order Møller−Plesset perturbation theory applying the resolution-of-identity approximation for the evaluation of two-electron integrals) as implemented in the Turbomole suite of programs[59] to characterize structural motifs in the complexes under study. TZVP[60] basis sets were used for all atoms. Vibrational spectra (harmonic approximation) were

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also calculated on the DFT level. The harmonic frequencies from our DFT calculations have been scaled by 0.960 to account for anharmonicities.

Results and Discussion

General Remarks. On the basis of the calculated electrostatic potentials around C_6H_6 and C_6F_6, one expects that an anion will interact with benzene via H bonds to the periphery of the molecule, whereas the interaction of an anion with perfluorobenzene will involve the ring.

The IR chromophores in the present experiment are the CH stretching vibrational modes of the respective fluorinated benzene, and the binding motif is encoded in the band positions of the IR spectrum. If Cl^- binds to the ring, we expect no red-shifts for the CH stretching modes in the fluorinated benzene. The opposite is true for H bonding of Cl^- to CH groups, because ionic H bonds result in red-shifts of the CH stretching bands. We can therefore use the IR spectra of $Cl^-\cdot C_6F_nH_{6-n}$ ($n = 0-5$) to assign binding motifs to these complexes at all levels of fluorination and with all possible isomers.

Before discussing the individual spectra, we note that the spectrum of free benzene (D_{6h} symmetry) shows a characteristic “triad” of absorption bands in the CH stretching region around 3040 cm^{-1} to 3100 cm^{-1}, even though only the $\nu_{20}(e_{1u})$ mode (Wilson numbering) is infrared active. The observed series of bands (which is really a tetrad[61]) is due to Fermi resonances of the infrared active ν_{20} mode with the near-degenerate zero-order states $[\nu_1 + \nu_6 + \nu_{19}]$, $[\nu_8 + \nu_{19}]$, and $[\nu_3 + \nu_6 + \nu_{15}]$. In general, the most intense features in the IR spectrum of a H-bonded complex usually stem from ionic H bonds, in the present case between CH groups of the benzene molecule and the anion. As illustrated above for the case of free benzene, other modes close in energy may borrow intensity from the intense features through Fermi resonances. Although this can greatly complicate the observed spectra, especially through mixing of the intense CH bands with overtones and combination bands of CC/CF stretching modes, the centroid frequencies of the spectra will encode the structural properties of the complexes as detailed above.

The Roles of Fluorination Level and Isomers. Figure 2 shows the IR spectra of $Cl^-\cdot C_6F_nH_{6-n}\cdot Ar$ for all isomers at all fluorination levels. Two distinct spectral motifs can be observed: (i) a high-energy motif, which is characterized by a set of absorption bands with centroids near 3000 cm^{-1}, and (ii) a low-energy motif with absorption bands clustered around 2600 cm^{-1} (on average). The spectrum for $n = 0$ has a centroid at ~3030 cm^{-1} and is consistent with the structural assignment of a bifurcated H-bonding motif previously reported by Bieske and co-workers.[32,33] The CH stretching modes in this motif are only weakly shifted from those in bare benzene (on average ~25 cm^{-1}).

The observed motifs for the complexes under study do not only depend on the level of fluorination but also on the distribution of F atoms in the molecule. In fact, only 4 of the 12 complexes studied here exhibit the low-energy motif. These 4 molecules are 1,3,5-trifluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4,5-tetra-fluorobenzene, and pentafluorobenzene. The deciding factor is that they only have isolated CH groups. All other molecules investigated here have two neighboring CH groups, so they offer the bifurcated bonding site that is the preferred binding motif in $Cl^-\cdot C_6H_6$.

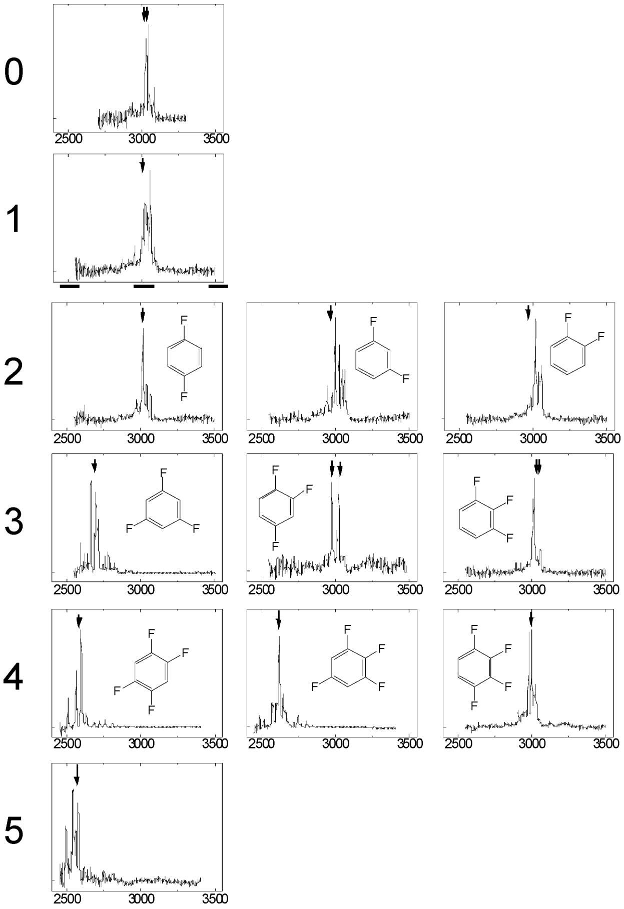

Figure 2. Ar predissociation spectra for all isomers at all fluorination levels of $Cl^-\cdot C_6F_nH_{6-n}\cdot Ar$ complexes. The horizontal axis represents the photon energy in cm^{-1}, and the vertical axis the photofragment yield in arbitrary units. The numbers on the left indicate the fluorination level, whereas structures give the isomer of the fluorobenzene moiety. The arrows indicate the calculated scaled harmonic frequencies of the most intense CH stretching bands.

Consistent with our DFT calculations (see Tables S1−S12 in the Supporting Information), we attribute the higher-energy absorptions to complexes with bifurcated bonding, whereas the lower-energy absorptions are due to complexes involving a linear bonding motif, where a H bond is formed with one CH group. This implies that Cl^- prefers bifurcated bonding to two neighboring CH groups over linear bonding. 1,2,4-Trifluorobenzene constitutes a very interesting case in this context, as it contains both possible binding sites. As expected from our above assignment, only the high-energy IR signature appears in the spectrum. Our DFT calculations place the linear structure in this complex ~160 meV (15.5 kJ/mol) above the bifurcated motif.

Vibrational Structure and Bonding Motif for $Cl^-\cdot C_6F_5H$. The pentafluorobenzene complex can serve as a case study to discuss some of the interesting features of the complexes investigated in this work, especially those with the linear binding motif. Figure 3 shows a direct comparison of the IR spectra for $n = 0$ ($Cl^-\cdot C_6H_6$) and $n = 5$ ($Cl^-\cdot C_6F_5H$). The IR signatures for $n = 5$ are centered at ~2540 cm^{-1}, far to the red of the typical CH stretching region. This indicates a H-bonded structure, because no vibrational bands were found near 3103

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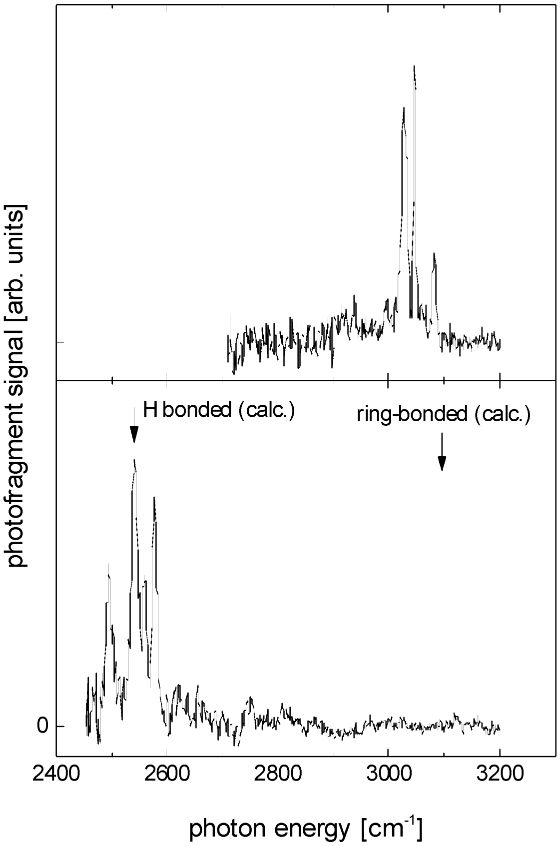

Figure 3. Ar predissociation spectra for $Cl^-{\cdot}C_6H_6{\cdot}Ar$ (top) and $Cl^-{\cdot}C_6F_5H{\cdot}Ar$ (bottom). Arrows indicate the calculated positions (scaled harmonic frequencies) of H-bonded and ring-bonded isomers for $n = 5$.

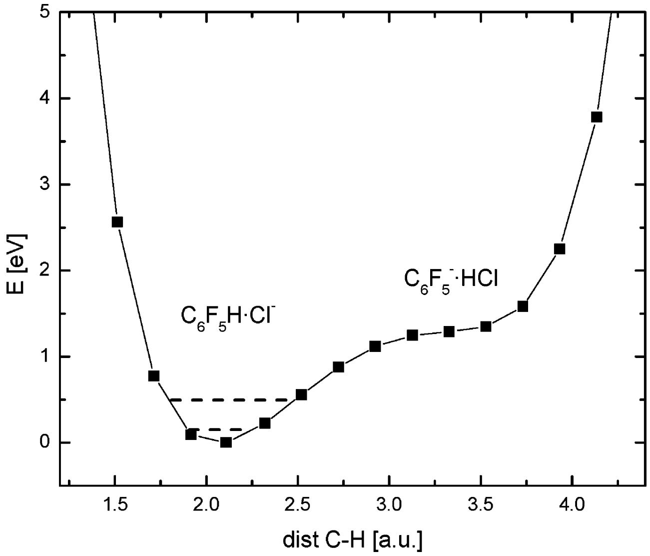

Figure 4. Calculated potential-energy surface along the CH stretching coordinate in $[C_6F_5{\cdots}H{\cdots}Cl]^-$ (MP2/TZVP). The squares are single-point energies at various C−H distances, with fixed C−Cl distance, whereas the rest of the coordinates were relaxed but constrained to C_{2v} symmetry.

cm^{-1} (the CH stretching band of free C_6F_5H[62]), where the spectroscopic signature of a ring-bonded structure is expected (scaled harmonic calculation: 3095 cm^{-1}). Our DFT calculations predict the red-shifted CH stretching vibration corresponding to a linear H bond between the Cl^- ion and the last remaining CH group in the molecule to be at 2548 cm^{-1}, in good agreement with the centroid of the spectrum.

At first glance, one would only expect one band to exist in the spectrum of $Cl^-{\cdot}C_6F_5H$, because only one CH oscillator is present in C_6F_5H. However, just as in the case of free benzene, Fermi interactions with various overtones and/or combination bands lead to the observation of additional bands which "borrow" oscillator strength from the CH stretching fundamental of the H-bonded CH oscillator. Clearly, these Fermi interactions are not the same that give rise to the "triad" in free benzene, because the mode structure is very different. We do not assign the individual bands based on our calculations, because a reliable assignment should involve anharmonic calculations, which are beyond our capabilities. However, we can identify several modes based on CC stretching and CF stretching motions that are likely candidates for causing the observed bands through combination bands and overtones (see Table S12 in the Supporting Information).

Obviously, the Cl^- ion forms an H bond even for $Cl^-C_6F_5H$ (see Figure 1C) and will only bind to the ring at complete fluorination. The ring-bonded motif is a local minimum-energy structure for $n = 5$, ~300 meV (29 kJ/mol) above the H-bonded structure (see Figure 1C). More precisely, local minima are calculated to exist above every carbon atom except that belonging to the CH group, with the minimum above the carbon para to the CH group being lowest in energy, followed by the meta and ortho positions, and the calculated energies all fall within 10 meV (1 kJ/mol). The observation of H bonds even in anion complexes with highly electron-deficient aromatics is consistent with *ab initio* and crystal structure data by Berryman et al.[6] on various other electron-deficient aromatic systems. However, Berryman et al. did not study aromatics with just one remaining CH group.

In anion−water interactions, the energy position of the OH infrared absorption bands decreases with increasing proton affinity of the anion.[63,64] Similarly, one expects that the IR absorption bands in an ionic H bond will decrease in frequency with increasing acidity of a proton in complexes involving the same anion. Consequently, one could argue that low CH stretching frequencies suggest H bonds involving a rather acidic proton.

We performed MP2 calculations to characterize the CH stretching potential-energy surface for the proton in $Cl^-{\cdot}C_6F_5H$. We find a low-lying proton-transfer channel, ~1.5 eV above the $C_6F_5H{\cdots}Cl^-$ ground state, where the resulting $C_6F_5^-{\cdots}HCl$ state shows as a shelf in the potential-energy surface (see Figure 4).

As the lower-energy absorption bands only occur for molecules that force the Cl^- ion to bind to isolated CH groups, one could argue that the proton in a CH group that is surrounded by two CF groups is more acidic than a proton belonging to one of two neighboring CH groups. However, thermochemistry data[65] reveal that the acidity of fluorobenzenes always increases with increasing fluorination level, with one of the biggest changes occurring from $n = 0$ to $n = 1$. As the complexes with

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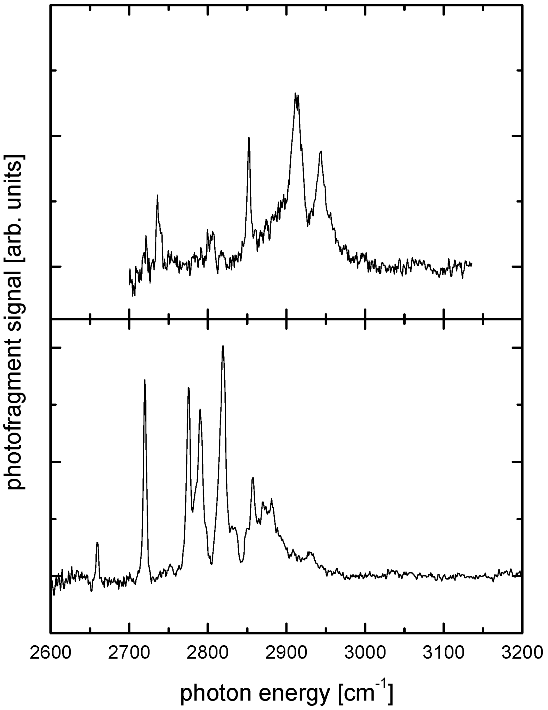

Figure 5. IR argon predissociation spectra of $X^{-}\cdot C_6F_5H\cdot Ar_3$ with X = SF_6 (top) and I (bottom).

bifurcated bonding show only a weak dependence of the CH stretching frequencies on the fluorination level, we suggest that the bifurcated bonding motif effectively shuts down the proton-transfer channel. This can be qualitatively understood through the fact that the proton-withdrawing power of the ion acts weakly on two protons rather than strongly on one. In the linear bonding motif, however, the increasing acidity is clearly observed, as the much stronger dependence of the CH stretching position on the number of F atoms shows (see Figure S1 in the Supporting Information).

Effects of Anion Size. In light of the surprising observation that Cl^- binds to the last remaining CH group in pentafluorobenzene, despite the presence of a competing positive electrostatic potential above the carbon ring, one may ask if this will be true for all anions. In this context, Pearson's hard and soft acid and base (HSAB) principle[66] implies that a softer base might be a better binding partner for the positive charge in the ring (constituting a soft acid). To test this idea, we performed IR spectroscopy on $I^{-}\cdot C_6F_5H$ and $SF_6^{-}\cdot C_6F_5H$. Iodide is usually classified as a soft base, and SF_6^- should be even softer, given its relatively large size and its highly symmetric charge distribution. Figure 5 shows the IR spectra of these complexes. Surprisingly, there is still no evidence of a ring-bound complex. The centroid frequency increases with the increasing ion radius from Cl^- (2546 cm^{-1}) to I^- (2818 cm^{-1}) to SF_6^- (2912 cm^{-1}), but the complexes are still H bonded.

Summary

Full fluorination of benzene is needed to force anions to bind to the aromatic ring. At all lower levels of fluorination, anion-fluorobenzene complexes are bound via ionic H bonds. Although the size of the anion does play a role for the distortion of the H-bonded CH groups, the binding motif remains H bonded rather than ring bonded. Our detailed investigation involving Cl^- complexes shows that bifurcated H bonds with two neighboring CH groups are preferred over bonding with a single CH group.

Acknowledgment. We gratefully acknowledge support from Grant NSF PHY0551010 and from the Donors of the Petroleum Research Fund of the American Chemical Society. We are grateful for helpful discussion with Professor G. Barney Ellison and Professor John F. Stanton.

Supporting Information Available: Figure showing centroid frequencies as a function of fluorination level; tables with all structures and calculated (unscaled) harmonic frequencies for the lowest-energy structures of all Cl^- complexes under study; complete ref 49. This material is available free of charge via the Internet at http://pubs.acs.org.

JA073028K

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