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# Unpaired and $\sigma$ Bond Electrons as H, Cl, and Li Bond Acceptors: An Anomalous One-Electron Blue-Shifting Chlorine Bond

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Ab initio, DFT, and AIM theoretical studies on H-, Cl-, and Li-bonded complexes have been carried out with typical lone pair ($H_2O$), $\pi$ ($C_2H_4$) and $\sigma$ ($H_2$) bonded pairs, and unpaired ($CH_3$) electrons as acceptors and HF, ClF, and LiF as donors. Optimization and frequency calculations have been carried out at reasonably high levels (MP2, DFT(B3LYP), and QCISD) with large basis sets up to aug-cc-pVTZ. Not surprisingly, all HF complexes show red shift in stretching frequency and the shift is correlated to the binding energy. However, the FCl···$CH_3$ complex shows a large blue shift (about 200 $cm^{-1}$), which appears to be the largest blue shift predicted for any weakly bound complex yet. Analysis of the normal modes of the complex indicates that the shift is due to the mixing of modes between donor and acceptor and it is qualitatively different from the blue shifts reported thus far in hydrogen-bonded complexes. For Cl- and Li-bonded complexes, a correlation between frequency shift and binding energy is not found. However, AIM theoretical analysis shows the similarity in all these interactions. The electron density at the bond critical point shows a strong correlation with the binding energy for H-, Cl-, and Li-bonded complexes. This appears to be the first report on a one-electron chlorine bond.

## I. Introduction

Intermolecular interactions play a very important role in chemistry and biology that cannot be overemphasized.[1,2] These have been traditionally classified as hydrogen bonding and van der Waals interactions, and the term “noncovalent interactions” has been used in recent times.[3] Though van der Waals interactions and hydrogen bonding have been in the literature for about a century now, there has been a continuous debate about what these terms mean.[1−12] Initially, hydrogen bonding was identified between a H atom bonded to an electronegative element X and another electronegative element Y which has a lone pair of electrons, and it was usually represented as X−H···Y.[13] Many of the characteristic defining features of the H bonding have been shown to apply to only the strong H bonds. Notable among them are the requirement of “most electronegative elements” as donor/acceptor and a red shift of X−H bond stretching frequency.[13] It was soon realized that $\pi$ electrons could act as H bond acceptors as well, and it has been discussed in the earliest books on hydrogen bonding.[11,12] Recently, it has been pointed out that the unpaired electron[14,15] as in $CH_3$ radical and $\sigma$ electrons as in $H_2$ molecule[16,17] can also act as acceptors of “H bonds”. Today H bonds by C−H groups are well established,[6] and some of them exhibit a blue shift in C−H stretching frequency.[18,19] There have been numerous studies on the origin of blue shifting, and it appears that in most instances there is a concomitant shortening and strengthening of the C−H bonds.[18−24]

Another question that has been debated in parallel is whether hydrogen bonding is unique or not. The answer is quite subjective, and one can safely say that hydrogen bonding is as unique in intermolecular interactions as hydrogen is in the periodic table. Let us consider the following statements: (1) H is one of the 100 plus elements and (2) H is the number one element and the only one without an inner electron core. Both are not far from the truth. There have been several reports about analogous chlorine bonding[25−28] and lithium bonding[29−32] with lone pair and $\pi$ acceptors. A communication on blue-shifting Li bonds[31] and a theoretical study on blue-shifting halogen bonds[28] have appeared as well. The latter work considered $CF_3$-Cl as a Cl bond donor similar to the $CF_3H$ complexes that were found to show blue shift. The main objective of this work was to find out if Cl and Li bonding could be observed with unpaired and $\sigma$ electrons as acceptors. Ab initio and AIM theoretical methods have been used in this study to answer this question. It has led to the observation of a strongly blue-shifting one-electron Cl bond in the $H_3C$···ClF complex. AIM theoretical analysis highlights the similarity of interactions in all these complexes. The details are presented in this article. After the completion of this work, we came across a recent article on a one-electron Li bond that considered several XLi···$CH_3$ complexes, including FLi···$CH_3$.[32] The work presented here appears to be the first report on one-electron chlorine bonding.

## II. Computational Methods

Four acceptors were chosen to represent lone pair ($H_2O$), $\pi$ bonded pair ($C_2H_4$), unpaired ($CH_3$), and $\sigma$ bonded pair ($H_2$) electrons. The interaction energy for H bonds decreases in this order as well. The donors chosen were typical for these interactions: HF, LiF, and ClF. Geometries of all H/Li/Cl-bonded complexes were fully optimized at MP2/aug-cc-pVDZ, MP2/6-311++G**, MP2/aug-cc-pVTZ, B3LYP/6-311++G**, and QCISD/6-311++G** levels, using Gaussian 98[33] and/or Gaussian 03[34] quantum chemical packages. All MP2 calculations reported in this work did not use the frozen core approximation, and they may be denoted as MP2(FULL). Frequency calculations were done at all these levels (except QCISD/6-311++G**) to ensure that the complex structures were true minima and also

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**TABLE 1: Optimized X−A Bond Distances and ∠DXA Bond Angles in D−X···A Complexes (X = Cl, Li, or H)**

| | MP2(FULL)/6-311++G** | | B3LYP/6-311++G** | | QCISD/6-311++G** | | MP2(FULL)/aug-cc-pVDZ | | MP2(FULL)/aug-cc-pVTZ | |
|---|---|---|---|---|---|---|---|---|---|---|
| dimers[a] | $R_{X-A}$ | ∠DXA | $R_{X-A}$ | ∠DXA | $R_{X-A}$ | ∠DXA | $R_{X-A}$ | ∠DXA | $R_{X-A}$ | ∠DXA |
| $H_2O-ClF$<br>3.2 | 2.587 | 179.8 | 2.459 | 179.7 | 2.661 | 179.3 | 2.526 | 180.0 | 2.488 | 179.9 |
| $C_2H_4-ClF$<br>3.5 | 2.736 | 180.0 | 2.584 | 180.0 | 3.023 | 180.0 | 2.530 | 180.0 | 2.456 | 180.0 |
| $H_3C-ClF$<br>3.5 | 3.054 | 180.0 | b | b | 3.014 | 180.0 | 2.823 | 180.0 | 2.616 | 180.0 |
| $H_2-ClF$*<br>3.0 | 2.985 | 179.4 | 2.685 | 179.7 | 3.045 | 179.6 | 2.690 | 179.3 | 2.659 | 179.7 |
| $H_2O-LiF$<br>3.2 | 1.950 | 174.6 | 1.941 | 179.8 | 1.956 | 171.4 | 1.919 | 180.0 | 1.910 | 180.0 |
| $C_2H_4-LiF$*<br>3.5 | 2.361 | 179.7 | 2.393 | 179.7 | 2.375 | 179.6 | 2.350 | 179.7 | 2.336 | 179.7 |
| $H_3C-LiF$<br>3.5 | 2.406 | 180.0 | 2.416 | 180.0 | 2.412 | 180.0 | 2.361 | 180.0 | 2.373 | 180.0 |
| $H_2-LiF$*<br>3.0 | 2.122 | 177.5 | 2.103 | 180.0 | 2.122 | 177.5 | 1.962 | 177.4 | 2.055 | 177.4 |
| $H_2O-HF$<br>2.6 | 1.730 | 177.7 | 1.703 | 177.6 | 1.752 | 177.7 | 1.711 | 178.0 | 1.694 | 178.0 |
| $C_2H_4-HF$*<br>2.9 | 2.200 | 177.9 | 2.175 | 180.0 | 2.270 | 179.8 | 2.133 | 180.0 | 2.094 | 180.0 |
| $H_3C-HF$<br>2.9 | 2.251 | 180.0 | 2.101 | 180.0 | 2.280 | 180.0 | 2.183 | 180.0 | 2.118 | 180.0 |
| $H_2-HF$*<br>2.4 | 2.113 | 176.7 | 1.955 | 178.8 | 2.114 | 176.8 | 1.971 | 177.1 | 2.001 | 177.1 |

[a] Number in this column represents the sum of van der Waals radii of the two atoms X and A. A is O, C, C, and H for the $H_2O$, $C_2H_4$, $CH_3$, and $H_2$, respectively. See text for the van der Waals radii used. See also section III.4 for discussions on the use of van der Waals radii. [b] Optimization of $H_3C···ClF$ at this level was not successful and led to the reaction forming $H_3CCl$ and F.

to determine the frequency shift in X−F (X = H, Li, or Cl) stretching following the complex formation. The interaction energies were corrected for basis set superposition error (BSSE) following the Boys−Bernardi counter poise procedure.[35] Electron densities and Laplacian of the electron densities were calculated using Bader's[36] Atoms in Molecules (AIM) theory as implemented in the AIM2000[37] package. Ab initio wave functions were generated from Gaussian 03 at MP2(FULL)/aug-cc-pVTZ using the OUTPUT=WFN and "DENSITY=CURRENT" options.

## III. Results and Discussion

**III.1. Geometrical Features.** The complexes under investigation in this study may be written as D−X···A, representing the donor group D−X having the X atom H, Li, or Cl, and an acceptor atom/group A, which has a lone pair of electrons or $\pi/\sigma$ bonded pair of electrons or an unpaired electron. The most important geometrical parameters for such a complex D−X···A are the distances between D and X, $R_{DX}$, and X and A, $R_{XA}$, and the angle, ∠DXA. In the past, the presence of H bonding in D−H···A was expected to make the D−A distance smaller than the sum of van der Waals radii of D and A[13,38] However, now it is well recognized[6−12] that this criterion for H bond is too limiting and is only applicable for strong hydrogen bonds. Also, such a criterion cannot be applied for Cl/Li-bonding interactions. Interpretation of the X−A distance has been shown to be a better alternative for confirming or ruling out X bonds.[39−42] The ∠DXA angle is expected to be close to 180° in these isolated complexes.

The X−A distance and ∠DXA angles from the optimized geometries are given in Table 1. Indeed, the ∠DXA angles are very close to 180° in all complexes. A closer scrutiny reveals that, for all Cl-bonded complexes at all levels of calculations considered here, the ∠DClA values lie between 179.3° and 180.0°. The ∠DHA has the lowest value of 176.7° for the $\sigma$ H-bonded $H_2-HF$ complex at the MP2/6-311++G** level, and the ∠DLiA is lowest at 171.4° at the QCISD/6-311++G** level for $H_2O-LiF$ complex. Legon previously reported extensive experimental results that show Cl bonding to be more linear than H bonding.[26] The main reason is that the small size of H enables long-range secondary interaction between D and A. In the case of the Cl bond, the D is further away and the primary interaction constrains the ∠DClA to be 180°. Interestingly, our results show that the one-electron X-bonds in $H_3C···XF$ are more linear than the corresponding bonds in the other A···XF complexes. Table 1 compares the sum of van der Waals radii to $R_{XA}$ for all the complexes considered here. The van der Waals radii (in angstroms) for H (1.2), C (1.7), O (1.4), Cl (1.8), and Li (1.8) were taken from Pauling's book.[13] The $R_{XA}$ values were observed to be below the sum of van der Waals radii for all these complexes. Clearly, these complexes could be characterized as Cl-, Li-, and H-bonded complexes. Another approach would be to compare the nonbonded and bonded radii for these atoms and estimate the penetration of the two atoms into the other atom's electron cloud, as described by Koch and Popelier.[43] This analysis is described in section III.4 along with the results from AIM theoretical calculations.

The geometrical parameters reported here compare well with previously published work at similar levels of calculations. For $FH···CH_3$, our results are identical to those reported by Alkorta et al.[15] at MP2(Full) and DFT(B3LYP) calculations using the 6-311++G** basis set. For $H_3C···LiF$, $R_{C-Li}$ is calculated to be 2.373 Å at MP2(Full)/aug-cc-pVTZ compared to 2.457 Å reported by Li et al.[32] at the MP2/aug-cc-pVTZ level. This difference could be because Li et al. have used frozen core approximation. For $H_2···HF$, our results are in very good agreement with those of Grabowski et al.[17] at the same level of calculations. These authors have discussed the effects of basis set and level of calculations, and it is clear that the MP2(Full)/aug-cc-pVTZ level of calculations is quite reasonable for the complexes under investigation.

**TABLE 2: Shift in X−F Stretching Frequency ($\Delta\nu$)[1] and Change in X−F Distance, $\Delta R_{XF}$, for All DX···A Complexes**

| | MP2(FULL)/6-311++G** | | B3LYP/6-311++G** | | MP2(FULL)/aug-cc-pVDZ | | MP2(FULL)/aug-cc-pVTZ | |
|---|---|---|---|---|---|---|---|---|
| complex | $\Delta\nu^a$ | $\Delta R_{XF}$ | $\Delta\nu^a$ | $\Delta R_{XF}$ | $\Delta\nu^a$ | $\Delta R_{XF}$ | $\Delta\nu^a$ | $\Delta R_{XF}$ |
| $H_2O-ClF$ | 29.9 | 0.016 | 65.6 | 0.030 | 41.5 | 0.018 | 44.8 | 0.018 |
| $C_2H_4-ClF$ | 86.9 | 0.032 | 153.3 | 0.066 | 143.3 | 0.051 | 159.9 | 0.055 |
| $H_3C-ClF$ | −195.3 | −0.002 | *b* | *b* | −239.8 | −0.002 | −144.3 | 0.010 |
| $H_2-ClF$ | 1.8 | 0.001 | 11.5 | 0.004 | 7.7 | 0.003 | 5.8 | 0.002 |
| $H_2O-LiF$ | −11.1 | 0.022 | −1.1 | 0.026 | 2.3 | 0.029 | −20.1 | 0.019 |
| $C_2H_4-LiF$ | −3.2 | 0.010 | 13.8 | 0.014 | −23.4 | 0.008 | 0.7 | 0.008 |
| $H_3C-LiF$ | 3.2 | 0.008 | 9.8 | 0.010 | −19.6 | 0.006 | −1.2 | 0.004 |
| $H_2-LiF$ | −2.8 | 0.003 | −0.7 | 0.004 | −23.4 | 0.005 | −8.9 | 0.001 |
| $H_2O-HF$ | 346.8 | 0.015 | 422.3 | 0.019 | 412.6 | 0.018 | 415.4 | 0.018 |
| $C_2H_4-HF$ | 183.0 | 0.008 | 254.1 | 0.011 | 244.1 | 0.010 | 254.5 | 0.010 |
| $H_3C-HF$ | 141.6 | 0.006 | 289.9 | 0.012 | 179.0 | 0.007 | 203.2 | 0.008 |
| $H_2-HF$ | 23.9 | 0.001 | 58.5 | 0.002 | 47.6 | 0.002 | 39.4 | 0.001 |

[a] $\Delta\nu$ is the frequency shift in cm$^{-1}$. Positive values represent a red shift, and negative values represent a blue shift compared to the monomer frequencies. [b] Optimization of $H_3C\cdots ClF$ at this level was not successful and led to the reaction forming $H_3CCl$ and F.

**III.2. Frequency Shifts and Change in $R_{DX}$.** Historically, after the distance criterion, the most important criterion of the H-bonding interactions involving HF is the shift in HF frequency upon complex formation and a concomitant decrease in $R_{HF}$. Table 2 compares the frequency shift in the X−F stretching mode, $\Delta\nu$, with the change in $R_{XF}$, $\Delta R_{XF}$, following the complex formation for X = H/Li/Cl. Not surprisingly, hydrogen-bonded complexes with HF as donor show positive $\Delta R_{XF}$ and a significant red shift in stretching frequencies. It has been observed in all the HF complexes reported here. The calculated red shifts in frequencies at the MP2/aug-cc-pVTZ level are 415, 255, 203, and 39 cm$^{-1}$ for the HF complexes with $H_2O$, $C_2H_4$, $CH_3$, and $H_2$, respectively. These are in reasonable agreement with the experimental shifts observed in these complexes (i.e., 364 cm$^{-1}$ for $H_2O\cdots HF$,[44] 230 cm$^{-1}$ in $C_2H_4\cdots HF$,[45] and 162 cm$^{-1}$ in $H_3C\cdots HF$).[46] Compared to these values, the $H_2\cdots HF$ complex appears to show a very small frequency shift of only 39 cm$^{-1}$. The frequency shifts observed for LiF complexes are significantly smaller, and they are either red (3−14 cm$^{-1}$) or blue (1−20 cm$^{-1}$) shifted compared to the LiF monomer value. Moreover, there is no obvious correlation with $\Delta R_{LiF}$. This has been noted in the earlier report on blue-shifting Li bonds as well.[31]

The frequency shifts observed for ClF complexes sprang a few surprises. At all levels of calculations, the $\pi$ Cl-bonded complexes ($C_2H_4\cdots ClF$) showed a significantly larger red shift than the lone pair Cl-bonded complex ($H_2O\cdots ClF$). This trend is the opposite of what has been observed for HF complexes and also does not follow the trend observed in binding energy of these two complexes (section III.3). However, it is consistent with the experimental red shifts reported for these complexes. For example, the red shift observed in the $\pi$ Cl-bonded complexes[47] varies from 60 to 200 cm$^{-1}$, whereas the shift is only 50−100 cm$^{-1}$ for the lone pair Cl-bonded complexes.[48] The red shifts, however, do correlate with the ClF bond lengthening observed in these complexes. For example, the increase in ClF bond distance in $C_2H_4\cdots ClF$ complex formation is 2−3 times that following the formation of $H_2O\cdots ClF$ complex. The $H_2\cdots ClF$ complex shows significantly smaller red shift and also smaller bond lengthening. Even this distance correlation is not found for the one-electron chlorine-bonded complex that has been studied for the first time. It showed a large blue shift of 144 to 240 cm$^{-1}$ depending on the basis set at the MP2 level of calculations. It appears to be the largest blue shift estimated for any weakly bound complex. Unlike the consistent blue shift predicted by the different level of calculations, the Cl−F bond distance varies with level of calculations. With the lower basis sets (aug-cc-pVDZ and 6-311++G**), the Cl−F bond shortens by 0.0015 Å on complex formation, but with the aug-cc-pVTZ basis set, it lengthens more signifi-

**TABLE 3: Displacement of the Atoms in the Nominal X−F Stretching Mode for the $H_3C\cdots XF$ Complexes Calculated at MP2(FULL)/6-311++G** and MP2(FULL)/aug-cc-pVTZ Levels**

MP2(FULL)/6-311++G**

| | $H_3C\cdots HF$ | | | | $H_3C\cdots LiF$ | | | | $H_3C\cdots ClF$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | X | Y | Z | A | X | Y | Z | A | X | Y | Z |
| C | −0.00 | −0.00 | 0.00 | C | −0.03 | 0.00 | −0.00 | C | −0.04 | 0.00 | 0.00 |
| F | 0.05 | −0.00 | −0.00 | Li | 0.94 | 0.00 | −0.00 | Cl | 0.48 | 0.00 | 0.00 |
| H | 0.00 | 0.00 | −0.00 | F | −0.33 | −0.00 | 0.00 | F | −0.87 | −0.00 | −0.00 |
| H | 0.00 | −0.00 | 0.00 | H | 0.00 | 0.00 | 0.00 | H | 0.04 | 0.00 | −0.00 |
| H | 0.00 | 0.00 | 0.00 | H | 0.00 | 0.00 | −0.00 | H | 0.04 | −0.00 | 0.00 |
| H | −1.00 | 0.00 | 0.03 | H | 0.00 | −0.00 | 0.00 | H | 0.04 | −0.00 | −0.00 |

MP2(FULL)/aug-cc-pVTZ

| | $H_3C\cdots HF$ | | | | $H_3C\cdots LiF$ | | | | $H_3C\cdots ClF$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | X | Y | Z | A | X | Y | Z | A | X | Y | Z |
| C | 0.00 | 0.00 | 0.00 | C | −0.02 | 0.00 | 0.00 | C | −0.01 | 0.00 | −0.00 |
| F | 0.05 | 0.00 | 0.00 | Li | 0.94 | 0.00 | 0.00 | Cl | 0.48 | 0.00 | −0.00 |
| H | 0.00 | 0.00 | 0.00 | F | −0.33 | 0.00 | 0.00 | F | −0.88 | −0.00 | 0.00 |
| H | 0.00 | 0.00 | 0.00 | H | −0.02 | 0.00 | 0.00 | H | 0.04 | −0.00 | −0.00 |
| H | 0.00 | 0.00 | 0.00 | H | −0.02 | 0.00 | 0.00 | H | 0.04 | 0.00 | −0.00 |
| H | −1.00 | 0.00 | 0.00 | H | −0.02 | 0.00 | 0.00 | H | 0.04 | −0.00 | 0.00 |

**TABLE 4: Interaction Energy, $\Delta E$, Basis Set Superposition Error, $E_B$, and BSSE Corrected Interaction Energy, $\Delta E_B$, in Kilocalories per Mole for All the Complexes Calculated at Various Levels of Theory**

| | MP2(FULL)/6-311++G** | | | B3LYP/6-311++G** | | | QCISD/6-311++G** | | | MP2(FULL)/aug-cc-pVDZ | | | MP2(FULL)/aug-cc-pVTZ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| dimers | $\Delta E$ | $E_B$ | $\Delta E_B$ | $\Delta E$ | $E_B$ | $\Delta E_B$ | $\Delta E$ | $E_B$ | $\Delta E_B$ | $\Delta E$ | $E_B$ | $\Delta E_B$ | $\Delta E$ | $E_B$ | $\Delta E_B$ |
| $H_2OClF$ | −6.2 | 0.1 | −6.1 | −7.2 | 0.3 | −6.9 | −5.4 | 0.0 | −5.3 | −6.1 | 0.1 | −6.0 | −6.0 | 0.1 | −5.9 |
| $C_2H_4ClF$ | −5.0 | 0.3 | −4.7 | −6.3 | 1.3 | −5.0 | −3.1 | 0.0 | −3.0 | −7.7 | 0.8 | −6.9 | −8.0 | 1.0 | −6.9 |
| $CH_3ClF$ | −2.2 | 0.1 | −2.1 | | | | −1.9 | 0.1 | −1.8 | −3.6 | 0.1 | −3.5 | −4.2 | 0.2 | −4.0 |
| $H_2ClF$ | −0.6 | 0.0 | −0.6 | −0.6 | 0.0 | −0.6 | −0.5 | 0.0 | −0.5 | −1.2 | 0.0 | −1.2 | −1.2 | 0.0 | −1.2 |
| $H_2OLiF$ | −19.3 | 0.1 | −19.2 | −18.4 | 0.2 | −18.2 | −19.0 | 0.1 | −18.9 | −19.7 | 0.2 | −19.5 | −18.4 | 0.1 | −18.3 |
| $C_2H_4LiF$ | −10.6 | 0.1 | −10.5 | −8.9 | 0.1 | −8.8 | −10.1 | 0.1 | −10.0 | −11.8 | 0.1 | −11.7 | −10.8 | 0.0 | −10.8 |
| $CH_3LiF$ | −6.6 | 0.2 | −6.4 | −5.8 | 0.3 | −5.5 | −6.4 | 0.2 | −6.2 | −7.9 | 0.2 | −7.7 | −7.1 | 0.2 | −6.9 |
| $H_2LiF$ | −2.7 | 0.0 | −2.7 | −2.4 | 0.0 | −2.4 | −2.7 | 0.0 | −2.7 | −4.5 | 0.0 | −4.5 | −3.3 | 0.0 | −3.3 |
| $H_2OHF$ | −9.8 | 0.2 | −9.6 | −10.1 | 0.3 | −9.8 | −9.3 | 0.1 | −9.2 | −9.1 | 0.2 | −8.9 | −9.4 | 0.2 | −9.2 |
| $C_2H_4HF$ | −4.5 | 0.1 | −4.4 | −4.5 | 0.1 | −4.4 | −3.9 | 0.0 | −3.9 | −5.5 | 0.1 | −5.4 | −5.7 | 0.1 | −5.6 |
| $CH_3HF$ | −2.6 | 0.2 | −2.5 | −3.3 | 0.2 | −3.0 | −2.4 | 0.1 | −2.3 | −3.3 | 0.2 | −3.1 | −3.6 | 0.1 | −3.5 |
| $H_2HF$ | −0.8 | 0.0 | −0.8 | −0.9 | 0.0 | −0.9 | −0.8 | 0. 0 | −0.8 | −1.3 | 0.0 | −1.3 | −1.2 | 0.0 | −1.2 |

cantly by 0.0099 Å. Thus, the largest blue shift estimated for any weakly bound complex is not due to the bond length variation. Hence, this shift must be the result of mode mixing. The displacements of all the atoms corresponding to the nominal X−F stretching modes in $DX\cdots CH_3$ complexes are shown in Table 3. Clearly, the Cl−F stretching mode is coupled to the $CH_3$ out-of-plane bending mode in this normal mode, leading to an anomalous large frequency shift. The displacements of Cl and F atoms in this normal mode are virtually identical to those observed in the ClF monomer stretching mode (not shown here) at the same level of calculation. The H−F complex retains the essentially local mode H−F stretching vibrational motion, whereas the Cl−F stretching is coupled to the $CH_3$ out-of-plane bending vibration in the normal mode. Similar mode mixing is also seen (not shown here) for the ClF complexes with $C_2H_4$ and $H_2O$. Not surprisingly, the frequency shifts for the ClF complexes do not show any correlation with the binding energy of the complex or bond length variation on complex formation. The fact that H−X stretching frequencies are far removed from other vibrational modes contributes significantly to the excellent correlation observed between the frequency shifts and binding energy[11] of the H-bonded complex.

As mentioned earlier, the large blue shift observed in $CH_3\cdots ClF$ is independent of the basis set used in these calculations. The good agreement between the calculated and experimental frequency shifts for all the HF and the other ClF complexes convinces us that the blue shift predicted for $H_3C\cdots ClF$ should be realistic. We hope that these results would stimulate experimental research on one-electron chlorine-bonded complexes. These complexes could play a crucial role in the reaction dynamics of radical-molecule reactions. The $H_3C\cdots HF$ complex has been described as the exit-channel complex,[46] referring to the H abstraction reaction $F + CH_4 \rightarrow HF + CH_3$.

The red and blue shifts observed for the one-electron Li bonds are very small, and they depend on the level of calculations. This type of contradictory predictions were observed earlier and reported for a H-bonded complex by Lu et al.[49] They observed a blue shift at the MP2 level and a red shift in DFT(B3LYP) calculations for $F_2N{-}H\cdots FH$ complex. Also, infrared studies on the $CF_3H\cdots NH_3$ complex show that the blue shift observed for this complex is not caused by a strengthening of the CH bond during the complexation. It is due to the changes in the Fermi resonance interactions.[50]

**III.3. Interaction Energies for DX$\cdots$A Complexes.** Interaction energies with and without BSSE correction are presented in Table 4 for all the complexes. The BSSE corrections are fairly small ($<$0.2 kcal mol$^{-1}$) for all complexes except that of $C_2H_4\cdots ClF$, indicating that the basis sets used are sufficiently large in our calculations. Even for the $C_2H_4\cdots ClF$ complex, the BSSE is less than 1 kcal mol$^{-1}$, which is typically 10−15% of the binding energy. Interaction energies for Li bonds are invariably higher than those for the H and Cl bonds, both of which have very similar binding energies. From the early days of Li bonding, it was recognized that it is stronger than analogous H bonding.[29−32] From the values of the interaction energies in Table 4, it is clear that the accepting abilities of lone pair, $\pi$ bond, unpaired, and $\sigma$ bond electrons decrease in the order $H_2O > C_2H_4 > CH_3 > H_2$ for Li and H bonds at all levels of calculations reported in this work. The frequency shifts reported earlier show a very similar trend for H-bonded complexes. However, the results for Cl-bonded complexes change with the level and basis set of calculations. With the 6-311++G** basis set, all levels of calculations (MP2, DFT(B3LYP), and QCISD) show the same trend as that of H/Li-bonding interaction. Using Dunning's augmented correlation consistent basis sets[51] (i.e., aug-cc-pVDZ and aug-cc-pVTZ) changes the trend, and the interaction energies decrease in the order $C_2H_4 > H_2O > CH_3 > H_2$ for the Cl-bonded complexes. Though it is consistent with the observed decrease in the frequency shift, $C_2H_4 > H_2O > H_2$, it should be remembered that, for the ClF complexes, mode mixing with the acceptor affects the normal-mode frequencies. In any case, as Dunning and co-workers pointed out, it is not enough to use highly correlated methods if the basis set is small.[52] For the ClF complexes, the commonly used triple-$\zeta$ 6-311++G** basis set makes a prediction different from that of Dunning's correlation consistent basis sets.

Interaction energies of $H_2\cdots HF$ and $H_2\cdots ClF$ are about 1 kcal mol$^{-1}$ at all levels of theory, and that of $H_2\cdots LiF$ varies from 2−4.5 kcal mol$^{-1}$. Clearly, even with the weakest acceptor, the Li bonding is stronger than H/Cl-bonding interactions. It is reassuring to note that, for $H_2\cdots HF$, the interaction energies reported here are in very good agreement with the results reported by Grabowski and co-workers at the same level of calculations.[17]

**III.4. AIM Theoretical Analysis.** Bader pointed out that the presence of (3, −1) critical point, denoted as a bond critical point (BCP), along the bond path of the interacting atoms is the necessary and sufficient condition for the two atoms to be bonded in a usual chemical sense.[36] It is applicable for covalent, ionic, van der Waals, hydrogen, chlorine, or lithium bonds. Koch and Popelier presented[43] eight criteria for the presence of a hydrogen bond including the presence of the BCP along the bond path. According to them, mutual penetration of H and the acceptor atom A is the necessary and sufficient criterion. All the other criteria were satisfied when mutual penetration was found. Mutual penetration is determined by comparing the

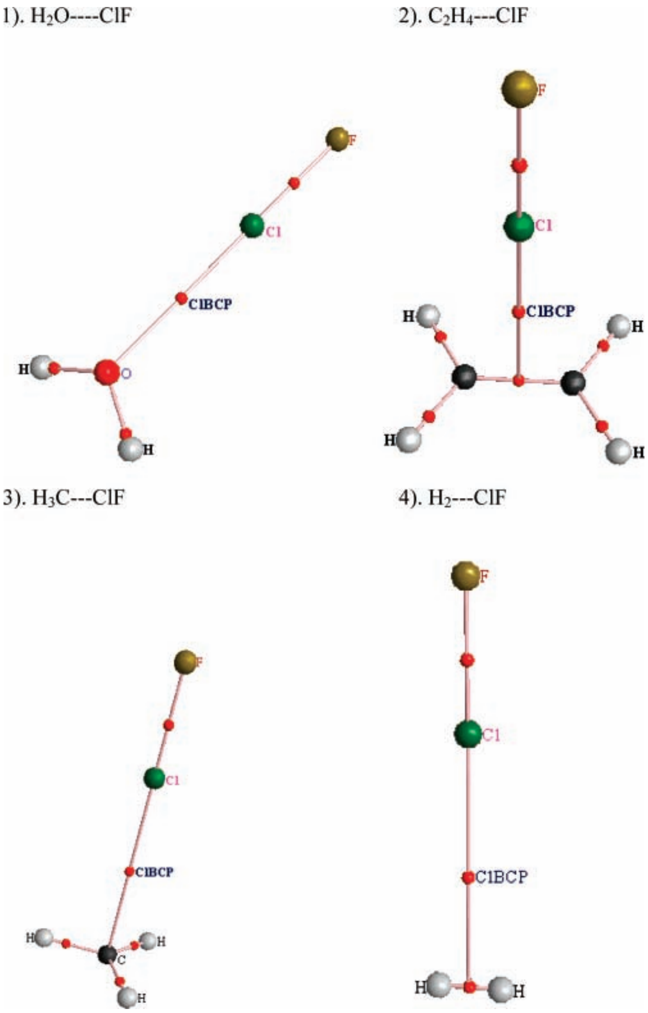

**Figure 1.** Structures of $H_2O\cdots ClF$, $C_2H_4\cdots ClF$, $H_3C\cdots ClF$, and $H_2\cdots ClF$ with bond critical points at the MP2(FULL)/aug-cc-pVTZ level of calculation. ClBCP stands for the Cl bond critical point. The H- and Li-bonded complexes have similar structures and are not shown in the figure. Detailed structural parameters can be found in Tables 1, 2, and 6.

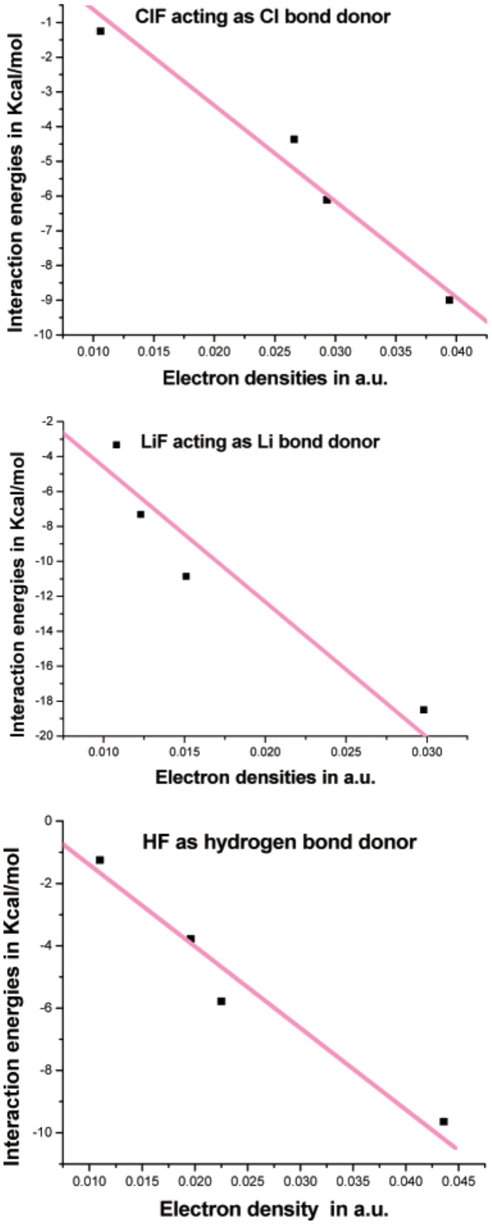

**Figure 2.** Plot of the binding energy as a function of electron density at the X-bond critical point for H-, Cl-, and Li-bonded complexes.

bonded and nonbonded radii of the two atoms. In our view, Bader's criterion is objective while that of Koch and Popelier is subjective. A detailed AIM theoretical analysis was carried out on all the complexes under investigation, and the results are discussed next.

All 12 complexes show (3, −1) bond critical points corresponding to the covalent as well as H/Cl/Li bonds where expected. Representative molecular graphs of all the ClF complexes are shown in Figure 1. Geometries of the Li- and H-bonded complexes are similar to that of Cl-bonded complexes. According to the Bader criterion, they are all bonded. Koch and Popelier pointed out that there is a strong correlation between the electron density as well as the Laplacian at the BCP and the binding energy for the complex. Electron densities and the Laplacian of the electron densities, calculated with MP2/aug-cc-pVTZ wave functions, at the BCPs of Cl-, Li-, and H-bonded complexes are presented in Table 5. It should be noted that the Laplacian reported in Table 5 is $-{}^1/_4\nabla^2\rho$, as defined in the AIM2000 package.[37] These values are given in atomic units. Figure 2 shows the correlation between the electron density at the BCP and the binding energy for H-, Cl-, and Li-bonded complexes. The correlation coefficients are quite remarkable at 0.98, 0.98, and 0.96, respectively, considering the fact that the four acceptors are quite different. Koch and Popelier showed earlier that the correlation is better when the same acceptor atom is used in a series of complexes.[43] On the other hand, Parthasarathi et al.[53] showed that such a linear relationship is observed for a wide range of interaction energies for a series of complexes. From the linear fit of electron density versus interaction energy, the latter can be calculated for a given electron density for H, Cl, and Li bonds as follows:

$$\Delta E = (-263.2)^{*}\rho + 1.22 \quad \text{(for H bond)}$$

$$\Delta E = (-277.8)^{*}\rho + 2.14 \quad \text{(for Cl bond)}$$

$$\Delta E = (-769.2)^{*}\rho + 3.13 \quad \text{(for Li bond)}$$

For the Li-bonded complexes, the slope of this plot is significantly larger than that for H/Cl-bonded complexes (i.e., the electron density at the BCP is significantly smaller for the Li bond compared to that of H/Cl bonds of similar strength). This indicates that the contribution to the interaction energy for Li bond comes largely from electrostatic interactions and that the H bond is more covalent than Li bond (i.e., there is

**TABLE 5: Electron Densities ($\rho$) and the Laplacian ($L$) Values Calculated at the Covalent Bond and X-Bond CPs of the Free Monomers and the Complexes at MP2(FULL)/aug-cc-pVTZ[a] (Note: The Laplacian Values Reported in This Table Are Defined as $-{}^{1}/_{4}\nabla^2\rho$)[37]**

| | $\rho$ | | | | | L | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Y−Z | | X−F | | Y⋯X | Y−Z | | X−F | | Y⋯X |
| systems | mono | comp | mono | comp | | mono | comp | mono | comp | |
| $H_2OClF$ | 0.3662 | 0.3637 | 0.2136 | 0.2051 | 0.0293 | 0.6670 | 0.6689 | 0.0467 | 0.0343 | −0.0303 |
| $C_2H_4ClF$ | 0.3583 | 0.3504 | 0.2136 | 0.1903 | 0.0394 | 0.3215 | 0.3097 | 0.0467 | 0.0084 | −0.0230 |
| $H_3CClF$ | 0.2964 | 0.2973 | 0.2136 | 0.2086 | 0.0266 | 0.2999 | 0.3028 | 0.0467 | 0.0395 | −0.0160 |
| $H_2ClF$ | 0.2724 | 0.2708 | 0.2136 | 0.2130 | 0.0106 | 0.3096 | 0.3062 | 0.0467 | 0.0458 | −0.0108 |
| $H_2OLiF$ | 0.3662 | 0.3631 | 0.0742 | 0.0703 | 0.0298 | 0.6670 | 0.6814 | −0.1759 | −0.1636 | −0.0588 |
| $C_2H_4LiF$ | 0.3583 | 0.3546 | 0.0742 | 0.0726 | 0.0151 | 0.3215 | 0.3144 | −0.1759 | −0.1704 | −0.0179 |
| $H_3CLiF$ | 0.2964 | 0.2954 | 0.0742 | 0.0734 | 0.0123 | 0.2999 | 0.2989 | −0.1759 | −0.1725 | −0.0142 |
| $H_2LiF$ | 0.2724 | 0.2715 | 0.0742 | 0.0741 | 0.0108 | 0.3096 | 0.3064 | −0.1759 | −0.1749 | −0.0150 |
| $H_2OHF$ | 0.3662 | 0.3637 | 0.3676 | 0.3412 | 0.0436 | 0.6670 | 0.6735 | 0.7816 | 0.7346 | −0.0262 |
| $C_2H_4HF$ | 0.3583 | 0.3554 | 0.3676 | 0.3526 | 0.0225 | 0.3215 | 0.3159 | 0.7816 | 0.7483 | −0.0114 |
| $H_3CHF$ | 0.2964 | 0.2961 | 0.3676 | 0.3563 | 0.0196 | 0.2999 | 0.2999 | 0.7816 | 0.7523 | −0.0096 |
| $H_2HF$ | 0.2724 | 0.2713 | 0.3676 | 0.3655 | 0.0110 | 0.3096 | 0.3069 | 0.7816 | 0.7823 | −0.0087 |

[a] X−F stands for HF, LiF, or ClF as given in the row heading. Y−Z stands for the OH, C═C, C−H, and H−H covalent bonds in the acceptors $H_2O$, $C_2H_4$, $CH_3$, and $H_2$, respectively. Mono stands for the monomer and comp stands for the complex. Note that the electron density of the X−F bond is significantly altered on X-bond formation. Y⋯X represents X bond, where X is H, Li, or Cl.

more accumulation of electron density between the X and A atoms for H/Cl bonds than that for Li bonds). This in turn would affect the electron density in the monomer bonds (vide infra). The large frequency shifts of H and Cl bonds, relative to those of Li bonds, substantiate this fact. Berski and Latajka showed earlier that the Li bond has a more electrostatic nature than the H bond, using electron localization function.[54]

The electron density and Laplacian of the electron density are in the range of (0.0110−0.0436) and (−0.0262 to −0.0087) for the H-bonded complexes in this study. These values are well within the range given by Koch and Popelier for characterization as a H bond, except for the fact that Table 5 has $L = -{}^{1}/_{4}\nabla^2\rho$, whereas Koch and Popelier have reported $L$ as $\nabla^2\rho$.[43] Even for the $H_2$⋯HF complex, the electron density at hydrogen bond critical point (HBCP) is 0.0110 au. The electron densities for Li and Cl bonds are in the range of (0.0108−0.0298) and (0.0106−0.0394), respectively, while the Laplacian values are (−0.0150 to −0.0588) and (−0.0108 to −0.0303). At the lower limit of interaction energy, the electron densities at BCP for H, Cl, and Li bonds are more or less same, and at the upper limit of interaction energy, electron densities differ considerably. All the Laplacian values are negative as expected for these "closed shell" interactions.[55]

Table 5 lists the electron density and the Laplacian values at the X−F and Y−Z covalent BCPs in the monomer and complex as well. The Y−Z is O−H, C═C, C−H, and H−H in the four acceptors $H_2O$, $C_2H_4$, $CH_3$, and $H_2$, respectively. The electron density at the X−F covalent bond decreases upon complex formation in all these complexes. The corresponding decrease in the acceptor Y−Z covalent bond is relatively smaller. For $H_2$ acceptor, the decrease in electron density upon complex formation at the covalent BCP of H−H bond is only 0.001 au for all $H_2$⋯XF complexes. The electron density at the Cl−F BCP for $H_3C$⋯ClF complex is 0.005 au smaller than that of the monomer ClF. The Cl−F bond distance does show a concomitant increase. As noted earlier, MP2 calculations with the 6-311++G** basis set predict a small decrease in Cl−F bond distance upon complex formation. The electron density calculated for the Cl−F BCP (0.1816 au) does show a corresponding increase compared to the value for the ClF monomer (0.1809 au).

**TABLE 6: Bonded ($r^b$) and Nonbonded ($r^\circ$) Radii (in Angstroms) of Acceptor (A) and Donor (X) Atoms and Penetration, $\Delta r$, Defined as the Sum of the Differences in Bonded and Nonbonded Radii of A and X (X = Cl, Li, or H)**

| systems | $r^\circ$ (A) | $r^b$ (A) | $r^\circ - r^b$ (A) | $r^\circ$ (X) | $r^b$ (X) | $r^\circ - r^b$ (X) | $\Delta r$ |
|---|---|---|---|---|---|---|---|
| $H_2O$−ClF | 2.04 | 1.29 | 0.75 | 1.95 | 1.30 | 0.65 | 1.40 |
| $C_2H_4$−ClF* | 2.33 | 1.36 | 0.97 | 2.00 | 1.38 | 0.62 | 1.59 |
| $H_3C$−ClF | 2.25 | 1.53 | 0.72 | 2.00 | 1.52 | 0.48 | 1.20 |
| $H_2$−ClF* | 1.70 | 1.34 | 0.36 | 1.98 | 1.64 | 0.34 | 0.70 |
| $H_2O$−LiF | 1.99 | 1.20 | 0.79 | 1.15 | 0.75 | 0.4 | 1.19 |
| $C_2H_4$−LiF* | 2.41 | 1.50 | 0.91 | 1.20 | 0.86 | 0.34 | 1.25 |
| $H_3C$−LiF | 2.32 | 1.53 | 0.79 | 1.20 | 0.88 | 0.32 | 1.11 |
| $H_2$−LiF* | 1.76 | 1.23 | 0.53 | 1.18 | 0.89 | 0.29 | 0.82 |
| $H_2O$−HF | 2.02 | 1.12 | 0.9 | 1.27 | 0.56 | 0.71 | 1.61 |
| $C_2H_4$−HF* | 2.34 | 1.44 | 0.9 | 1.32 | 0.76 | 0.56 | 1.46 |
| $H_3C$−HF | 2.25 | 1.47 | 0.78 | 1.33 | 0.78 | 0.55 | 1.33 |
| $H_2$−HF* | 1.72 | 1.25 | 0.47 | 1.29 | 0.86 | 0.43 | 0.90 |

Another important criterion used for predicting the existence of H bond is mutual penetration of hydrogen and acceptor atom.[43] This analysis is extended here to Cl and Li bonds. Distance from the nucleus to the critical point of electron density 0.001 au along the bond path is defined as the nonbonded radius, $r^\circ$, and the distance from the nucleus to the bond critical point is called bonded radius, $r^b$. The difference between nonbonded and bonded radii gives the extent of penetration, $\Delta r$. A positive $\Delta r$ indicates that the two atoms are mutually penetrating the electron cloud of the other atom, resulting in "bonding". The values of $r^\circ$, $r^b$, and $\Delta r$ ($r^\circ + r^b$) are presented in Table 6 for all complexes. All of them have positive $\Delta r$, indicating the presence of bonding. Interestingly, for H-, Cl-, and Li-bonded complexes with lone pair, $\pi$ bonded pair, and unpaired electrons, $\Delta r$ is more than 1 Å. However, it is of the order of 0.7−0.9 Å for these complexes with $\sigma$ bond electrons as acceptor.

A closer scrutiny of Table 6 reveals some important points. The nonbonded radii for the $H_2$⋯HF complex are 1.72 and 1.29 Å, for the acceptor and donor, respectively. In this complex, both acceptor and donor atoms are H, though to be more precise the acceptor is the $\sigma$ bonding orbital of the $H_2$ molecule and the donor is the H atom in the HF molecule. In $H_2$, it is the point at which the electron density of the $\sigma$ bonding orbital reduces to 0.001 au in the direction perpendicular to the H−H bond. In HF, it is the point at which the electron density is reduced to 0.001 au along the F−H bond axis, away from the H and the $\sigma$ bonding orbital of HF. Clearly, the distance at which the electron density becomes 0.001 along the bond path should be different in these two cases. That they differ by about 0.4 Å should be noted.

The nonbonded radii given in Table 6 are higher than the van der Waals radii of atoms used in section III.1. Nonbonded acceptor radii for C atoms in both $CH_3$ and $C_2H_4$ are very close (2.25 and 2.34 Å, respectively), and they are nearly the same for HF and ClF donors. They are about 0.1 Å larger in the LiF complex. Clearly, the nonbonded acceptor radii are different for different donors. Moreover, these radii are significantly higher than the van der Waals radii of C atom used in section III.1, 1.7 Å. Hence, using a single set of van der Waals radii for various atoms to confirm or rule out H/Cl/Li bonding could lead to erroneous conclusions. This has clearly been demonstrated in our recent work on H bond radii[39,40] and chlorine bond radii.[41] Independently, Klein[42] pointed out that the radii used for C−H···O and O−H···O interactions should be different. Though Koch and Popelier explicitly defined the nonbonded radii as mentioned earlier, use of a single set of van der Waals radii is continuing. For example, Munshi and Guru Row[56] recently reported experimental electron densities in a series of substituted coumarins and identified several C−H···O and C−H···$\pi$ contacts. While the bonded radii were experimentally determined, nonbonded radii were assumed to be the same as common van der Waals radii of atoms. Such an analysis shows a clear distinction between "H bond" and "van der Waals" interactions. They concluded that C−H···O interaction is H-bonded and C−H···$\pi$ interaction is van der Waals. Interestingly, analyses of the other criteria suggested by Koch and Popelier show that there is a continuous change in these interactions and the distinction between "H bond" and "van der Waals" interaction is indeed arbitrary.

## IV. Conclusion

The Cl, Li, and H bonds with lone pair, $\pi$ bond, unpaired, and $\sigma$ bond electrons were studied. It is seen that Cl- and Li-bonded complexes can be formed with all acceptors that form H bonds. Geometrical parameters show the similarities in all these interactions. Energetically, Li bond is invariably more stable than H and Cl bonds. Analysis of the electron density topology using AIM theory highlights the similarities and differences in these interactions. Low electron densities at the BCP and low-frequency shifts indicate that Li bond is more electrostatic than H bond. The frequency shift has a strong correlation with binding energy only for the H-bonded complexes, and such a correlation is not found for Cl- or Li-bonded complexes. However, the calculated electron densities at the BCP show a strong correlation with the binding energy for H-, Cl-, and Li-bonded complexes. This correlation can be seen for the complexes with a wide range of acceptors from lone pair to $\pi$ bonded pair to unpaired electron to $\sigma$ bonded pair electrons. To the best of our knowledge, this is the first report on one-electron chlorine-bonded complex, $H_3C$···ClF, which shows an anomalous and the largest blue shift predicted for any weakly bound complex.

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