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## A Theoretical Study of HF-C HCl and (HF)-CHCl Complexes

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## A Theoretical Study of HF-CH<sub>3</sub>Cl and (HF)<sub>2</sub>-CH<sub>3</sub>Cl Complexes

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### Abstract

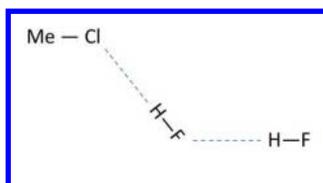
The equilibrium geometries, relative stabilities and vibrational properties (frequencies and intensities) of the HF-CH<sub>3</sub>Cl (1:1) and (HF)<sub>2</sub>-CH<sub>3</sub>Cl (1:2) complexes have been reinvestigated at the MP2/Aug-cc-pVTZ level. The results are discussed in light of the results obtained in solid argon matrices by L. Andrews and coworkers and related to the bonding analysis. The stability and cooperative effects in the hydrogen bonding of the (HF)<sub>2</sub>-CH<sub>3</sub>Cl complex in its cyclic form are outlined.

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## Introduction

It has been early recognized that the matrix-isolation technique could be applied to the study of intermolecular forces and, inasmuch as the molecular guest-cryogenic crystal interaction can be considered much weaker than the intermolecular interactions which is very often the case, in particular, for Hydrogen-bonded small molecular clusters<sup>1</sup> embedded in solid rare gas crystals. Following early studies on heavy halide dimers,<sup>2</sup> for instance, L. Andrews and coworkers initiated in the 80's a series of pioneering studies involving HF complexes with most known small polyatomic molecules, ranging from hydrogen to aromatic 18-atoms molecules.<sup>3,4</sup> Among the many systems studied, two articles tackled the HF-Chloromethane system,<sup>5,6</sup> reaching structural conclusions about the structures of the HF-CH<sub>3</sub>Cl (1:1) and (HF)<sub>2</sub>-CH<sub>3</sub>Cl (1:2) complexes based on spectroscopic observations (H-F stretching frequency shifts, number of H-F proton donor non-degenerate librational motions). These conclusions were later substantiated in a theoretical study by Del Bene and Mettee.<sup>7</sup> In substance, all studies converged in predicting a most stable configuration for the 1:1 complex with a nonlinear arrangement of the F-H --- Cl-CH<sub>3</sub> hydrogen bond. This structure can be compared with that inferred for the Cl-H --- Cl-CH<sub>3</sub> in liquefied argon or deduced in the gas phase.<sup>8,9</sup> It should be noted that the predicted binding energy in reference 7 is quite low (13.4 kJ/mol at MP2/cc-pVTZ+ level, after zero point energy correction) and thus the matrix role in the complex properties might not be completely negligible. In reference 6, Hunt and Andrews also reported a weak band near 3897 cm<sup>-1</sup>, due to another isomer of the complex, probably the so called anti-hydrogen bonded structure. Predictions for much more very weakly bound, methyl hydrogen to fluorine bonded structures were also made by Del Bene and Mettee, the most stable one with the three methyl hydrogens pointing at the fluorine atom and a head-to tail arrangement of the two molecular dipoles (with a binding enthalpy of about 4 kJ/mol around 13K). An even more weakly bonded structure was also predicted with only two methyl hydrogens pointing at the fluorine end of the H-F molecule, with an estimated binding enthalpy of only 1.2 kJ/mol at 13K.

Another conclusion from the experimental results is a strengthening of the HF to Chlorine hydrogen bond upon addition of a second HF molecule.<sup>5</sup> Again, the multiplicity of the observed HF librational modes advocated a nonlinear molecular cluster arrangement, which was, at the time, supposed to be that of an angled chain:



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3 With the progress of instrumentation and the development of free jet expansion to stabilize molecular  
4 clusters, it becomes possible to observe such weakly bound complex in the gas phase, free of potential  
5 matrix effects. Indeed, in a more recent study, Asselin and coworkers observed small HF-containing  
6 species in a free jet expansion,<sup>10</sup> some of them induced by seeding the gas with methyl chloride, also  
7 leading to a clear observation of the methyl chloride – HF complex with a prominent Q-branch near 3747  
8 cm<sup>-1</sup>. The rotational structure was not resolved in these experiments, but it is clear that the way is open  
9 for a fuller characterization of either 1:1 or 1:2 complexes in the gas phase. This contribution thus  
10 presents a reinvestigation of the 1:1 or 1:2 complexes with state-of-the-art theoretical methods, in view  
11 of facilitating future experimental characterizations.  
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### 18 **Computational Methods**

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20 All calculations have been done with the Gaussian 09 software package.<sup>11</sup> Optimization and vibrational  
21 frequency calculations have been performed using the second-order of Moller-Plesset perturbative  
22 method (MP2) with the augmented triple zeta basis set of Dunning Aug-cc-pVTZ for all atoms as  
23 implemented in Gaussian 09 software package. The anharmonic vibrational frequencies have been  
24 calculated using the second order perturbative approach PT2 as also implemented in the Gaussian 09  
25 software package. The basis set superposition error has been calculated for the complexes using the  
26 counterpoise technique (noted as CP).  
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## 34 **Results**

### 35 **1 - Structures and energetics**

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37 For the 1:1 complex, following the study of Del Bene and Mettee, we optimized their three structures at  
38 the MP2/Aug-cc-pVTZ level of theory (labelled S11-I to -III in Fig. 1). The most weakly bound structure  
39 suggested by Del Bene, S11-III, now appears to be a transition state, connecting the S11-I structure to  
40 the S11-II one. We note that the barrier height for this isomerization is, indeed, very low ( $\cong 1$  kJ/mol).  
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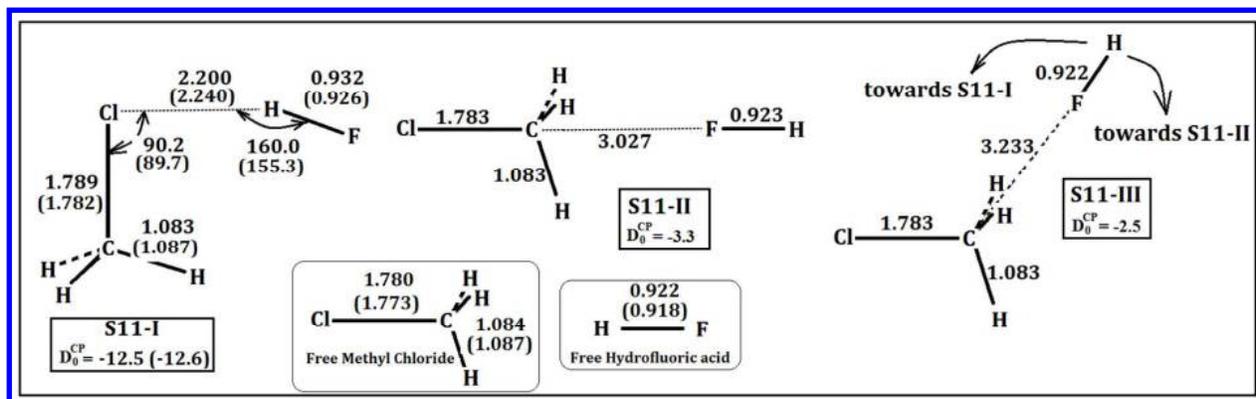
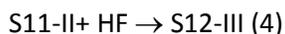
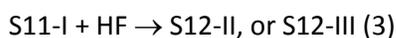
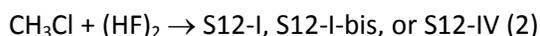
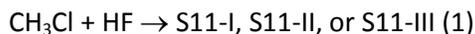


Fig. 1. Some relevant structural parameters for the studied 1:1 complexes calculated at the MP2/Aug-cc-pVTZ level. Binding energies (corrected for the zero-point-vibrational-energy and for the basis-set-superposition error) are given in kJ/mol. Data reported in parentheses are obtained at the CCSD(T)-F12/Aug-cc-pVDZ level of theory.

The binding energy corresponding to the minima found on the potential energy surfaces of both complexes are gathered in Table 1.  $D_e$  and  $D_0$  represent the binding energy and the ZPE corrected binding energy (in kJ/mol).  $D_e^{(CP)}$  and  $D_0^{(CP)}$  are the  $D_e$  and  $D_0$  corrected for the basis set superposition error. The  $C_s$  symmetry structure S11-I is by far the most likely to be observed in the gas phase. Equilibrium rotational constants are thus predicted to be 0.4338, 0.1177 and 0.09375  $\text{cm}^{-1}$ .

Concerning the 1:2 complex, energetic properties have been calculated considering the following equations:



Four stationary points are now found on the potential energy surface (labelled S12\_I to -IV Fig. 2) at the MP2/Aug-cc-pVTZ level. Table 1 presents the energetic results of these calculations. Four local minima could be considered as potentially observable in low temperature experiments as isomeric forms of the  $\text{CH}_3\text{Cl} - (\text{HF})_2$  system. The S12-I is the global minimum and is by far the most strongly bound form ( $D_0$  about -24 kJ/mol), while the structure suggested by Arlinghaus and Andrews in reference 5, labelled 12-I-bis in figure 2, corresponds to the transition state for the rotation of the second HF molecule around of the axis of the HF molecule engaged in the Cl...H-F hydrogen bond. The barrier height for this motion is calculated about 8 kJ/mol. The structure noted as S12-II in Fig. 2 represents two HF molecules in interaction with the chlorine atom in a bifid position. This form might be produced by addition of

another HF moiety to the S11-I complex, but the energy gained in adding a second HF molecule is substantially less than in the previous structure (-8 compared to -12.5 kJ/mol). The structure noted as S12-III in Fig. 2 could arise from a S11-I + HF interaction, but with an even smaller energy stabilization (-5 kJ/mol). Finally, the last minimum (noted as S12-IV in Fig. 2) could arise from a CH<sub>3</sub>Cl + (HF)<sub>2</sub> addition with a ClCH<sub>3</sub> ... F anti-hydrogen bonding interaction. It has a very weak binding energy (less than 3 kJ/mol) compared to structure S12-I and is the least likely to be observed in free jet experiments.

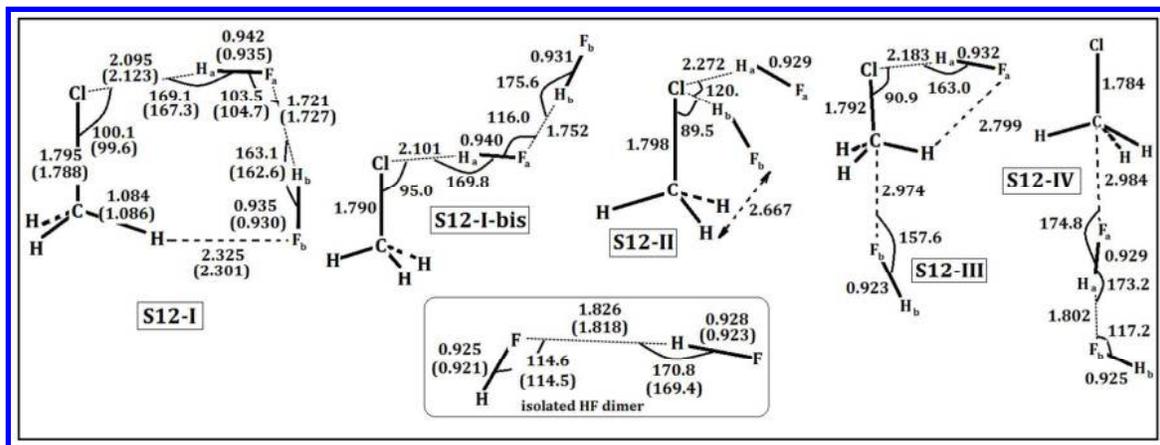


Fig. 2. Some relevant structural parameters for the calculated stationary points on the 1:2 potential energy surface at the MP2/Aug-cc-pVTZ level. Data reported in parentheses are obtained at the CCSD(T)-F12/Aug-cc-pVDZ level of theory.

Geometrical parameters, reported in figures 1 and 2, show that the so-called "anti-hydrogen bonded complex" is characterized by a small lengthening of the H-F distance (some thousandths of an angstrom or less) while a more pronounced H-F lengthening in the "H-bonded" structures (about a tenth of an angstrom).

In order to check the reliability of our theoretical geometrical and energetic results obtained at the MP2/Aug-cc-pVTZ level of theory, we optimized the three subunits (free HF and CH<sub>3</sub>Cl molecules and the (HF)<sub>2</sub> dimer) as well as both most stable 1:1 and 2:1 complexes (S11-I and S12-I) with the highly accurate theoretical method for hydrogen-bonded systems, the coupled-cluster approach. Optimization calculations have been done at the explicitly correlated CCSD(T)-F12 level with the Aug-cc-pVDZ basis set, using the MolPro package.<sup>12</sup> As shown in Fig. 1 and 2, one can note that, for both open-chain and cyclic hydrogen bonded complexes, there is a good agreement between the geometrical parameters calculated with two ab initio (MP2 and CCSD(T)-F12) techniques. Furthermore, we should underline that the complexation energy (see Table 1) calculated with MP2 method for both S11-I and S12-I structures

( $D_0^{(CP)} = -12.5$  and  $-24.1$  kJ/mol) is very close to that obtained at CCSD(T)-F12/Aug(cc-pVDZ level ( $D_0^{(CP)} = -12.6$  and  $-24.2$  kJ/mol). In line with an earlier work,<sup>13</sup> we note that the MP2/Aug-cc-pVTZ is suitable to study the hydrogen bonded complexes.

## 2 - Vibrational analysis

Our goal in this contribution is to bring out reliable predictions of the vibrational or rovibrational properties, in order to assist in the assignments of future experimental studies. Table 2 compares the available matrix data of the literature with our results at the harmonic level for the isotopic effects and anharmonic level for the main  $\text{CH}_3^{35}\text{Cl} - \text{HF}$  isotopic species.

*1:1 complex.* As observed by Andrews and collaborators, the HF stretching mode is clearly the most intense fundamental. Also, our results fully confirm Andrews' group assignment of the two HF librational modes, who relied on the larger HF/DF isotopic ratio for the out of plane motion than for the in-plane one (1.393 vs 1.305 calculated here). Also, our results reproduce the trend reported in intensities (the in-plane mode is predicted twice as strong as the out of plane). This supports our calculations and in table 2 and 3 are reported complete predictions of all fundamentals at the anharmonic level for both  $C_s$  and anti-hydrogen bonded  $C_{3v}$  minima to help in future characterizations. As stated above, a recent low resolution study has assigned an absorption near  $3747\text{ cm}^{-1}$  to the strongest mode of the  $\text{CH}_3\text{Cl} \cdots \text{H-F}$  complex in a free jet expansion, close to the band origin of  $3736\text{ cm}^{-1}$  predicted here. This latter figure can also be compared to the signal at  $3734\text{ cm}^{-1}$  by Tokhadze and Tkhorzhevskaya in liquid Xe cryosolution of HF and methyl chloride,<sup>14</sup> although the exact stoichiometry of the complex is perhaps uncertain. It is therefore relevant to compare what could be simulated at our level for the  $\nu_1$  band of the structure calculated most stable (S11-I). Considering the ground state rotational constants ( $0.4429$ ,  $0.12$  and  $0.0957\text{ cm}^{-1}$  for  $A''$ ,  $B''$  and  $C''$ , respectively) calculated here, the complex corresponds to an asymmetric rotor with an asymmetry parameter  $\kappa = -0.85$ , that is close to the symmetric rotor limit. The transition moment for the HF stretching mode is nearly parallel to the principal axis and a band contour simulation should resemble an A-type asymmetric rotor band. Figure 3 presents such a simulation ( $I_r$  representation) for the fundamental, based on our calculated parameters for a 30K temperature and in the rigid rotor approximation, using the PGOPHER software.<sup>15</sup>

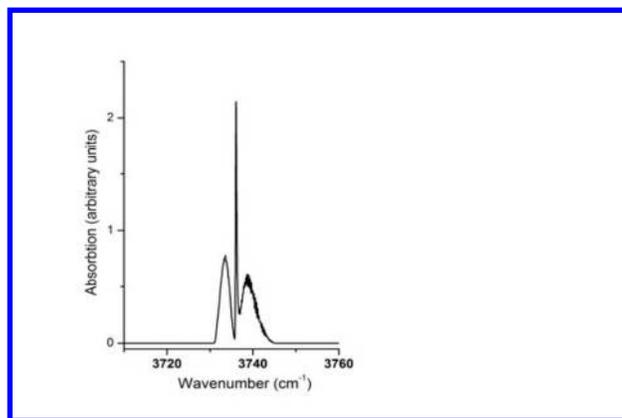


Figure 3. Simulated band contour for the  $\nu_1$  band of the S11-I structure of the  $\text{CH}_3\text{Cl} \cdots \text{H-F}$  complex, with a  $0.1 \text{ cm}^{-1}$  apparatus function, 30K rotational temperature and  $0.4429$ ,  $0.12$  and  $0.0957 \text{ cm}^{-1}$  for  $A''$ ,  $B''$  and  $C''$ ,  $0.4425$ ,  $0.1223$  and  $0.0972 \text{ cm}^{-1}$  for  $A'$ ,  $B'$  and  $C'$ , respectively.

It is interesting to note that the asymmetry in the band profile with a more rapid degradation on the high frequency side of the R branch is very sensitive to the evolution of the rotational constants between ground and excited states, but reproduces at least qualitatively the observed profile in reference 8, thus supporting strongly its assignment. The second and third most intense bands for the S11-I form are the HF in- and out-of plane librational modes, seen near  $436$  and  $378 \text{ cm}^{-1}$  in solid argon, respectively.<sup>5,6</sup> Our results suggest that these IR absorptions might be observable some  $30$  to  $20 \text{ cm}^{-1}$  higher in the gas phase, as these should have notable intensities (roughly three to six times less than the stronger HF stretching mode). The strongest mode in intensity in the  $\text{CH}_3\text{Cl}$  moiety is the C-Cl stretching mode, is predicted near  $734 \text{ cm}^{-1}$ , that is, shifted by  $-13 \text{ cm}^{-1}$  from the calculated value of  $747 \text{ cm}^{-1}$  at the same level. This is in qualitative agreement with the  $-20 \text{ cm}^{-1}$  shift observed for the same mode in solid argon. The very low values calculated for the H-bond stretching near  $49 \text{ cm}^{-1}$  or the torsional motion of the methyl group near  $15 \text{ cm}^{-1}$ , should be considered as only indicative.

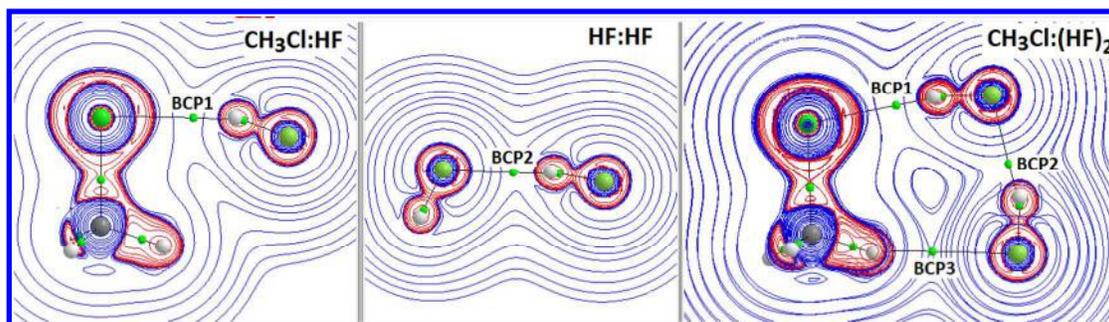
Calculations of the vibrational fundamentals at the same level are also reported for the secondary minimum S11-II in table 4. The strongest mode is the HF stretching mode, calculated four times less intense than in the first structure and whose band center is predicted  $-11 \text{ cm}^{-1}$  shifted from that of free HF at the same level. This is substantially less than the  $-63 \text{ cm}^{-1}$  shift observed in solid argon [6] and a sign that matrix effect might strongly affect the position of the band center for such a weakly bound species. The next strongest IR absorption is calculated near  $85 \text{ cm}^{-1}$  for the HF librational mode. This suggests that an identification in the gas phase will be more difficult and the best chance of observation might be in combined jet-microwave experiments, which have revealed unexpected structure for F-H hydrogen bonded complexes.<sup>16,17</sup>

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3 *1:2 complex*. The results concerning the  $(\text{HF})_2\text{-CH}_3\text{Cl}$  (1:2) complex in table 5-and 6 are the first  
4 predictions of observable spectroscopic properties for this species. In table 5 are reported the predicted  
5 frequencies and intensities for the most stable conformation (S12-I on figure 2). The match of the two H-  
6 F stretching modes, predicted most intense at 3707 and 3520  $\text{cm}^{-1}$  at the anharmonic level with the 3665  
7 and 3521  $\text{cm}^{-1}$  bands observed in solid argon is reasonable. Two H-F librational modes ( $A''$  and  $A'$   
8 symmetries) are predicted near 545 and 493  $\text{cm}^{-1}$ , relatively close to the observed bands at 508 and 475  
9  $\text{cm}^{-1}$  observed by Andrews and coworkers.<sup>5,6</sup> A third librational mode is however, predicted with a  
10 comparable intensity at 706  $\text{cm}^{-1}$ , but has not been observed. Note that this band should fall in the  
11 region of the intense  $\nu_2$  C-Cl  $\text{CH}_3\text{Cl}$  precursor band and is likely to be obscured in matrix isolation  
12 experiments. We thus feel confident that these predictions can constitute a good guide for future  
13 experimental characterizations, except perhaps the very low frequency modes below 100  $\text{cm}^{-1}$  for which  
14 the perturbative treatment of the anharmonicity is probably not sufficient.

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24 Table 6 gathers results obtained at the harmonic and anharmonic levels for the S12-II to IV  
25 conformations. As noted above, the perturbative treatment of anharmonic effects limit the scope of the  
26 predictions for the low frequency intermolecular modes, but these might serve as a guide for possible  
27 experimental characterization in conditions of very strong adiabatic expansions capable of freezing out  
28 rapidly the complex in a metastable configuration.

### 3- Bonding and conclusive remarks.

34  
35 It is interesting to compare the results for the bonding in the cyclic  $\text{CH}_3\text{Cl}\cdots(\text{HF})_2$  most stable, S12-I  
36 structure to that in the  $\text{CH}_3\text{Cl}\cdots\text{H-F}$  complex or in the  $(\text{HF})_2$  dimer itself. The bonding analysis has been  
37 done in the framework of QTAIM (Quantum Theory of Atoms In Molecules<sup>18</sup>) using the AIMALL  
38 software.<sup>19</sup> For three compounds, the bonding critical points on the 2D Laplacian of the charge are  
39 displayed in Figure 4.



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55 Figure 4. Bond critical points of the Laplacian of the electron density for three complexes.

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3 An important point is the existence of three bond critical points in the electronic structure: one in  
4 between the chlorine and first HF, one in between the two HF moieties, but also one between the in-  
5 plane C-H bond and the Fluorine atom of the second HF. The electron densities at the first two bond  
6 critical points (0.031 and 0.035) can be compared to those in the CH<sub>3</sub>Cl---H-F complex (0.024) and the  
7 (HF)<sub>2</sub> dimer (0.025). It shows a strengthening of the two H-bonds in a cooperative mechanism with  
8 respect to the binary complexes. This is in line with the slight shortening in the H to chlorine distance  
9 (2.095 in the ternary vs 2.200 Å in the binary complex) or in the inter HF hydrogen bond (1.721 vs 1.826 Å  
10 in (HF)<sub>2</sub>), or in the evolution of the corresponding vibrational modes. In conclusion, the present results  
11 point out at a surprising stability of the “ring” structure for the CH<sub>3</sub>Cl---(HF)<sub>2</sub>, first observed by Andrews  
12 using the matrix isolation technique and thus likely to be characterized in free jet expansion conditions  
13 as well as the CH<sub>3</sub>Cl---H-F complex.  
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#### 22 **4- Acknowledgements**

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26 competing financial interest.  
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## Tables

	E(ZPE)	$D_e$	$D_e^{(CP)}$	$D_0$	$D_0^{(CP)}$	Remark
<b>S11-I</b>	-599.828201 (-599.890502)	-21.6 (-21.3)	-18.8 (-18.5)	-15.3 (-15.4)	-12.5 (-12.6)	with respect to CH <sub>3</sub> Cl + HF
<b>S11-II</b>	-599.823949	-5.9	-5.1	-4.1	-3.3	with respect to CH <sub>3</sub> Cl + HF
<b>S11-III</b>	-599.8720026	-4.9	-4.1	-3.3	-2.5	with respect to CH <sub>3</sub> Cl + HF One imaginary frequency $\omega = 16i$
<b>S12-I</b>	-700.169324 (-700.255573)	-36.2 (-35.7)	-31.9 (-31.7)	-28.4 (-28.2)	-24.1 (-24.2)	with respect to CH <sub>3</sub> Cl + (HF) <sub>2</sub>
<b>S12-I-bis</b>	-700.163670	-28.0	-24.8	-22.0	-18.8	with respect to CH <sub>3</sub> Cl + (HF) <sub>2</sub> One imaginary frequency $\omega = 8i$
<b>S12-II</b>	-700.163670	-15.5	-12.9	-10.4	-7.8	with respect to S11-I + HF
<b>S12-III</b>	-700.161925	-7.8 -23.5	-6.8 -20.6	-5.8 -17.0	-4.8 -14.1	with respect to S11-I + HF with respect to S11-II + HF
<b>S12-IV</b>	-700.161032	-5.9	-4.8	-3.5	-2.4	with respect to CH <sub>3</sub> Cl + (HF) <sub>2</sub>
<b>HF</b>	-100.331498 (-100.355021)					
<b>(HF)<sub>2</sub></b>	-200.667628 (-200.715218)	-19.7 -21.0)	-17.7 (-18.4)	-12.2 (-13.6)	-10.2 (-11.0)	with respect to HF + HF
<b>CH<sub>3</sub>Cl</b>	-499.490880 (-499.529612)					

Table 1. Energetic properties of the studied species obtained using the MP2/Aug-cc-pVTZ method and (in parentheses) at the CCSD(T)-F12/Aug-cc-pVDZ level of theory. E(ZPE) is the total energy corrected for the ZPE contribution (in Hartree).  $D_e$  and  $D_0$  are respectively the binding and the ZPE corrected binding energies (in kJ/mol).  $D_e^{(CP)}$ ,  $D_0^{(CP)}$  are the  $D_e$  and  $D_0$  values corrected for the basis set superposition error.

	Mode	Exp.			Calc. MP2/aVTZ			
		HF	DF	$\Delta\nu$	Structure	HF $\omega_e(\text{IR Int}) / \nu$	DF $\omega_e(\text{IR Int})$	$\Delta\omega_e$
<b>1:1 species</b>	$\nu_s$	3726,3716 (site)	2738	<b>988</b>	<b>S11-I</b>	3904(564)/3736	2831(291)	<b>1073</b>
	$\nu_s^a$	3897	2858	<b>1039</b>	<b>S11-II</b>	4111(144)/3945	2815(5)	<b>1296</b>
	$\nu_l$	436	331	<b>105</b>	<b>S11-I</b>	538(159)/462	412(80)	<b>126</b>
	$\nu_l$	378	283	<b>95</b>	<b>S11-I</b>	447(87)/398	321(47)	<b>126</b>
<b>1:2 species</b>	$\nu_{sa}$	3521	2595	<b>926</b>	<b>S12-I</b>	3696(943)/3520	2577(451)	<b>1119</b>
	$\nu_{sb}$	3665	2699	<b>966</b>	<b>S12-I</b>	3861(532)/3707	2784(248)	<b>1077</b>
	$\nu_l$	508			<b>S12-I</b>	615(182)/545	589(74)	<b>26</b>
	$\nu_l$	475			<b>S12-I</b>	573(159)/493	411(80)	<b>162</b>
<b>1:1 species</b>		Exp.			Calc. MP2/aVTZ			
		$\text{C-}^{35}\text{C}$	$\text{C-}^{37}\text{Cl}$	$\Delta\nu$	Structure	$\text{C-}^{35}\text{Cl}$	$\text{C-}^{37}\text{Cl}$	$\Delta\omega_e$
	$\nu_{\text{C-Cl}}$	708	702	<b>6</b>	<b>S11-I</b>	748(22)/734	742(20)	<b>6</b>

Table 2. Experimentally observed vibrational frequencies ( $\text{cm}^{-1}$ ) in solid Ar compared to the calculated harmonic vibrational frequencies and intensities ( $\text{km/mol}$ ) as well as the HF/DF and  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopic shifts ( $\Delta$ ).

a-HF stretching anti hydrogen bonded form.

Mode	E(harm) ( $\text{cm}^{-1}$ )	IR Int (km/mole)	E(anharm) ( $\text{cm}^{-1}$ )	Exp.	Approx. description
1	3904	564.1	<b>3736</b>	<b>3726</b>	( A' ) HF stretch
2	3232	0.1	<b>3095</b>		( A' ) CH stretch
3	3116	13.8	<b>3014</b>		( A' ) CH stretch in phase
4	1509	6.4	<b>1464</b>		( A' ) CH <sub>3</sub> bend
5	1405	9.9	<b>1372</b>		( A' ) CH <sub>3</sub> bend in phase
6	1062	1.8	<b>1034</b>		( A' ) CH <sub>3</sub> bend
7	748	21.7	<b>734</b>		( A' ) CCl stretch
8	538	159.3	<b>462</b>	<b>436</b>	( A' ) FH lib in-plane
9	155	7	<b>139</b>		( A' ) FH--ClC CH <sub>3</sub> stretch
10	68	11.2	<b>49</b>		( A' ) FH--Cl CH <sub>3</sub> bend
11	3235	0.7	<b>3096</b>		( A'' ) CH stretch
12	1511	6.3	<b>1464</b>		( A'' ) CH <sub>3</sub> bend
13	1053	2	<b>1033</b>		( A'' ) CH <sub>3</sub> bend
14	447	87.2	<b>398</b>	<b>378</b>	( A'' ) FH lib out-of-plane
15	34	0	<b>15</b>		( A'' ) CH <sub>3</sub> torsion

Table 3. Predicted vibrational fundamental bands of 1:1 H-bonded complex ( $C_s$ , S11-I in Fig. 1) at the MP2/aVTZ level. Frequencies are given in  $\text{cm}^{-1}$  and IR intensity in km/mole.

Mode	E(harm) ( $\text{cm}^{-1}$ )	IR Int (km/mole)	E(anharm) ( $\text{cm}^{-1}$ )	Exp.	Assignment
1	4111	144.1	<b>3945</b>	<b>3897</b>	( A <sub>1</sub> ) HF stretch
6	3231	3.4	<b>3092</b>		( E ) CH stretch
2	3119	20.8	<b>3014</b>		( A <sub>1</sub> ) CH stretch in-phase
7	1508	10.6	<b>1464</b>		( E ) CH <sub>3</sub> bend
3	1396	9.8	<b>1362</b>		( A <sub>1</sub> ) CH <sub>3</sub> bend in phase
8	1045	4	<b>1025</b>		( E ) CH <sub>3</sub> bend
4	759	31.3	<b>743</b>		( A <sub>1</sub> ) CCl stretch
5	67	0.1	<b>53</b>		( A <sub>1</sub> ) F-- CH <sub>3</sub> stretch
9	33	8	<b>80</b>		( E ) HF--Cl CH <sub>3</sub> bend
10	83	328	<b>84</b>		( E ) HF lib

Table 4. Predicted vibrational fundamental bands of 1:1 anti-H-bonded complex ( $C_{3v}$ , S11-II in Fig. 1) at the MP2/aVTZ level. Frequencies are given in  $\text{cm}^{-1}$  and IR intensity in km/mole.

Mode(Quanta)	E(harm) ( $\text{cm}^{-1}$ )	IR Int (km/mole)	E(anharm) ( $\text{cm}^{-1}$ )	Exp.	Assignment
1	3861	532.3	<b>3707</b>	<b>3665</b>	( A' ) HF stretch out-of-phase
2	3696	942.7	<b>3520</b>	<b>3521</b>	( A' ) HF stretch in phase
3	3241	7.4	<b>3108</b>		( A' ) CH stretch
4	3238	0.4	<b>3098</b>		( A'' ) CH stretch
5	3119	13.9	<b>3017</b>		( A' ) CH stretch in phase
6	1516	6.5	<b>1466</b>		( A' ) $\text{CH}_3$ bend
7	1511	6.5	<b>1465</b>		( A'' ) $\text{CH}_3$ bend
8	1412	11.4	<b>1375</b>		( A' ) $\text{CH}_3$ bend in phase
9	1070	1.2	<b>1045</b>		( A' ) $\text{CH}_3$ bend
10	1057	2.1	<b>1035</b>		( A'' ) $\text{CH}_3$ bend
11	819	145.8	<b>706</b>		( A' ) lib HF in-plane opp phase
12	733	35.6	<b>719</b>		( A' ) CCl stretch
13	615	181.9	<b>545</b>	<b>508</b>	( A'' ) lib HF out-of-plane in phase
14	573	158.9	<b>493</b>	<b>475</b>	( A' ) lib HF in-plane opp phase
15	512	9.5	<b>466</b>		( A'' ) lib HF out-of-plane opp phase
16	221	8.2	<b>194</b>		( A' ) FH--FH stretch
17	177	21.5	<b>156</b>		( A' ) FH--Cl $\text{CH}_3$ stretch
18	126	6.8	<b>99</b>		( A' ) FH--FH--Cl $\text{CH}_3$ bend
19	77	0.6	<b>62</b>		( A'' ) $\text{CH}_3$ torsion
20	67	2.1	<b>62</b>		( A' ) FH--FH--Cl $\text{CH}_3$ bend
21	11	2.9	<b>57</b>		( A'' ) Cl $\text{CH}_3$ lib

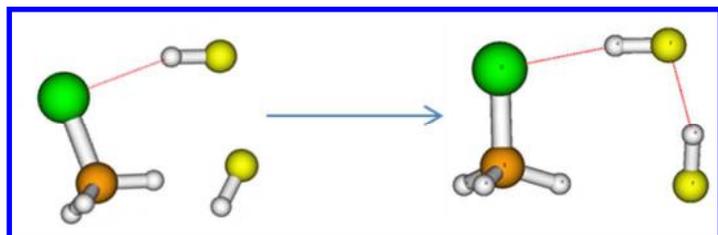
Table 5. Predicted vibrational fundamental bands of cyclic 1:2 complex (S12-I in Fig. 2) at the MP2/aVTZ level. Frequencies are given in  $\text{cm}^{-1}$  and IR intensity in km/mole.

S12-II		S12-III		S12-IV	
$\omega$ (IR Int)/ $\nu$	Assignment	$\omega_e$ (IR Int)/ $\nu$	Assignment	$\omega_e$ (IR Int) / $\nu$	Assignment
3959(655)/3794	( A'' ) HF stretch out-of-phase	4108(150)/3939	anti-H-bonded HF stretch	4078(137)/3909	free HF stretch
3239(1)/3103	( A'' ) CH stretch	3886(616)/3720	H-bonded HF stretch	3964(610)/3823	C-bonded HF stretch
1508(7)/1463	( A'' ) CH <sub>3</sub> bend	3244(0) /3105	CH stretch	3235(2)/3100	CH stretch
1071(2)/1044	( A'' ) CH <sub>3</sub> bend	3242(0)/3105	CH stretch	3234(2)/3100	CH stretch
441(154)/350	( A'' ) lib in-plane out-of-phase	3124(13)/3019	Sym. CH stretch	3122(20)/3016	CH stretch
363(47)/304	( A'' ) lib out-of-plane out-of-phase	1507(6)/1462	CH <sub>3</sub> bend	1508(5)/1463	CH <sub>3</sub> bend
145(11)/122	( A'' ) HF-Cl stretch out-of-phase	1507(6)/1461	CH <sub>3</sub> bend	1507(5)/1462	CH <sub>3</sub> bend
78(18)/44	( A'' ) HF-Cl bend out-of-phase	1398(9)/1365	symm CH <sub>3</sub> bend	1394(9)/1366	CH <sub>3</sub> bend (in phase)
57(0)/21	( A'' ) CH <sub>3</sub> torsion	1058(2)/1034	CH <sub>3</sub> bend	1044(2)/1022	CH <sub>3</sub> bend
3973(200)/3804	( A' ) HF stretch in- phase	1049(2)/1028	CH <sub>3</sub> bend	1043(2)/1023	CH <sub>3</sub> bend
3242(0)/3104	( A' ) CH stretch	742(30)/727	C-Cl stretch	756(34)/747	C-Cl stretch
3118(9)/3016	( A' ) CH stretch in- phase	555(145)/472	lib (in) H <sub>a</sub> F <sub>a</sub>	591(157)/139	lib (in) H <sub>a</sub> F <sub>a</sub>
1511(7)/1463	( A' ) CH <sub>3</sub> bend	466(87)/400	lib (out) H <sub>a</sub> F <sub>a</sub>	493(158)/485	lib (out) H <sub>a</sub> F <sub>a</sub>
1408(8)/1373	( A' ) CH <sub>3</sub> bend	159(7)/139	FH---Cl stretch	237(146)/191	lib (in) H <sub>b</sub> F <sub>b</sub>
1061(2)/1037	( A' ) CH <sub>3</sub> bend	94(154)/104	lib (out) H <sub>b</sub> F <sub>b</sub>	174(6)/ 98	HF--HF bend
731(21)/718	( A' ) C-Cl stretch	93(134)/104	lib (in) H <sub>b</sub> F <sub>b</sub>	57(0)/ 38	HF--CH <sub>3</sub> stretch
478(245)/384	( A' ) lib. in-plane in phase	74(47)/75	intermol bend	38(19)/-202	Intermol bend
397(119)/317	( A' ) lib. out-of-plane in-phase	67(1)/75	intermol bend	36(6)/ 108	Intermol bend
128(1)/108	( A' ) HF-Cl stretch in phase	38(1)/40	intermol bend	13(4)/ 191	intermol bend
63(10)/108	( A' ) HF-Cl bend in phase	33(0)/5	CH <sub>3</sub> torsion	13(5)/ 403	H <sub>b</sub> F <sub>b</sub> torsion
14(2)/-34	( A' ) HF-Cl-HF bending	18(2)/-13	intermol bend	5(96)/-5644	lib (out) H <sub>b</sub> F <sub>b</sub>

Table 6. Vibrational fundamental bands of the S12-II, S12-III, and S12-IV complexes. Frequencies are given in cm<sup>-1</sup> and IR intensity in km/mole. Note that the lowest vibrational frequency were found

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3 negative when calculated with the anharmonicity correction using the second perturbative approach. It  
4 shows that PT2 is not reliable enough for the low frequency modes (particularly  $< 100 \text{ cm}^{-1}$ ).  
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9 **TOC Graphic**



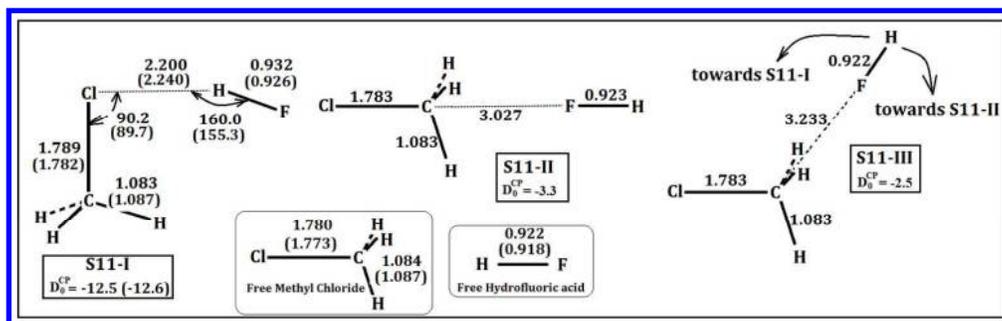


Fig. 1. Some relevant structural parameters for the studied 1:1 complexes calculated at the MP2/Aug-cc-pVTZ level. Binding energies (corrected for the zero-point-vibrational-energy and for the basis-set-superposition error) are given in kJ/mol. Data reported in parentheses are obtained at the CCSD(T)-F12/Aug-cc-pVDZ level of theory

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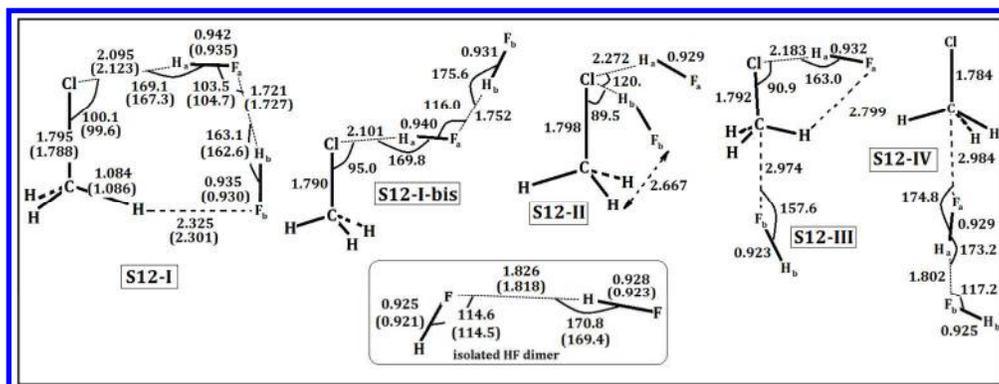


Fig. 2. Some relevant structural parameters for the calculated stationary points on the 1:2 potential energy surface at the MP2/Aug-cc-pVTZ level. Data reported in parentheses are obtained at the CCSD(T)-F12/Aug-cc-pVDZ level of theory.

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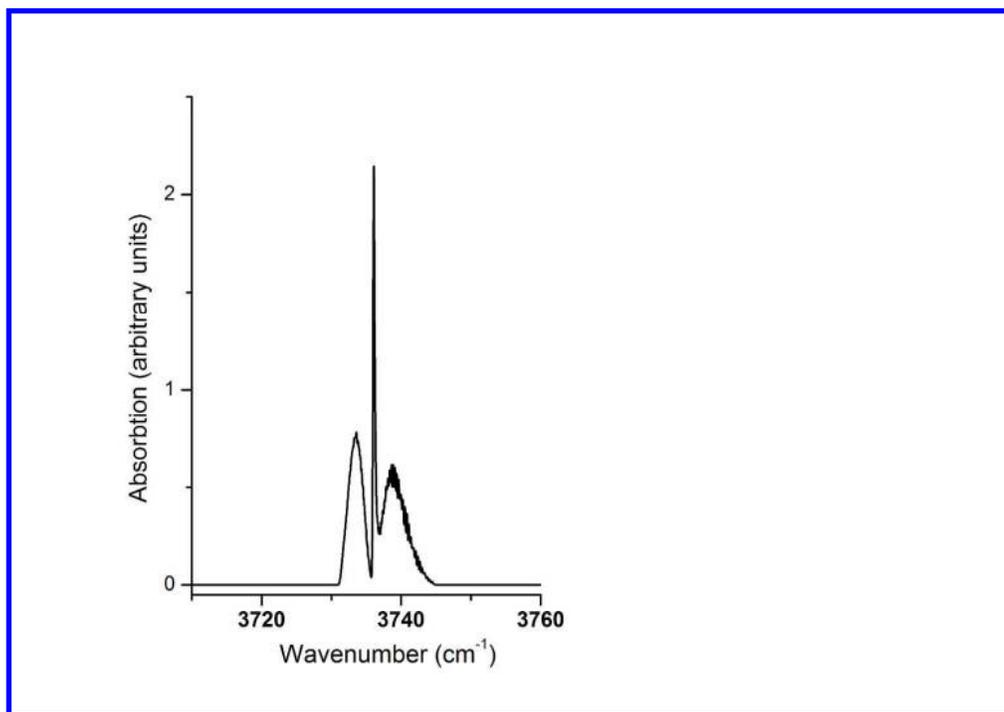


Figure 3. Simulated band contour for the v1 band of the S11-I structure of the CH<sub>3</sub>Cl --- H-F complex, with a 0.1 cm<sup>-1</sup> apparatus function, 30K rotational temperature and 0.4429, 0.12 and 0.0957 cm<sup>-1</sup> for A'', B'' and C'', 0.4425, 0.1223 and 0.0972 cm<sup>-1</sup> for A', B' and C', respectively

288x201mm (300 x 300 DPI)

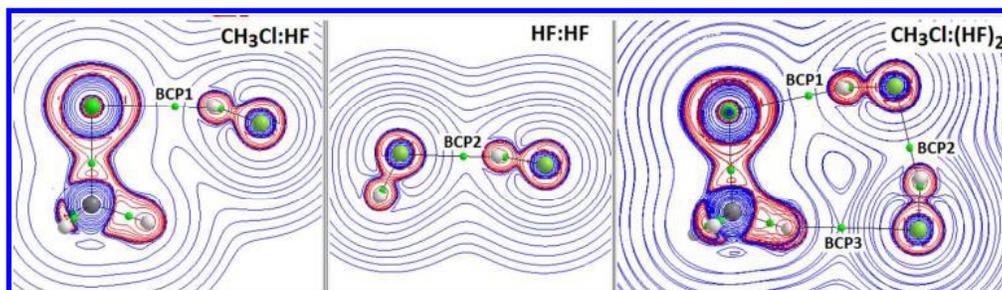
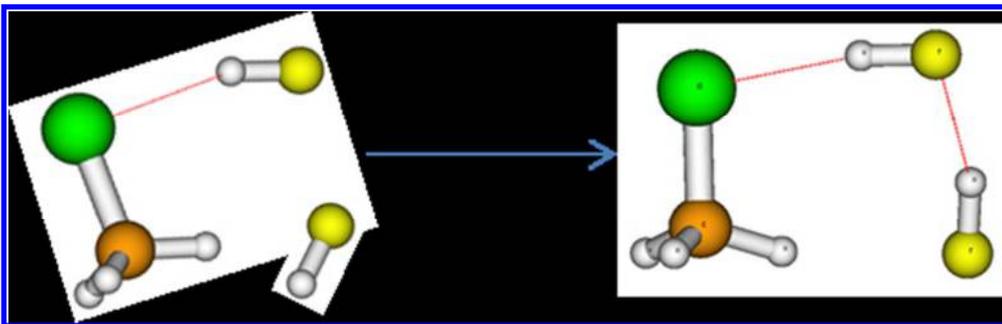


Figure 4. Bond critical points of the Laplacian of the electron density for three complexes.

354x98mm (96 x 96 DPI)



TOC Graphic

93x29mm (150 x 150 DPI)