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# A Theoretical Study of Intermolecular Interaction and Hydrogen Bond for Furan with HCl and $CH_{4-n}Cl_n$ ($n = 0–3$)

Daiqian Xie[1,2] and Jiang Li[2]

[1] Institute of Theoretical and Computational Chemistry, Department of Chemistry, Nanjing University, Nanjing 210093, China
[2] Department of Chemistry, Sichuan University, Chengdu 610064, China

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# A Theoretical Study of Intermolecular Interaction and Hydrogen Bond for Furan with HCl and $CH_{4-n}Cl_n$ ($n$ = 0–3)[#]

## Daiqian Xie[1,2,]* and Jiang Li[2]

[1] Institute of Theoretical and Computational Chemistry, Department of Chemistry, Nanjing University, Nanjing 210093, China
[2] Department of Chemistry, Sichuan University, Chengdu 610064, China

**Abstract**

**Motivation**. Furan has both the oxygen lone pair electrons and an aromatic π–electron. The study of the interaction between furan as a proton acceptor and a proton donor is important to understand the properties of furan and the related hydrogen bond.

**Method**. The geometries, intermolecular energies and vibrational properties of the furan–HCl and furan–$CH_{4-n}Cl_n$ ($n$ = 0–3) complexes have been performed using the second order Møller–Plesset perturbation theory. The NBO analysis of the optimized geometries has also been performed.

**Results**. The optimized geometries of furan–HCl and furan–$CH_{4-n}Cl_n$ ($n$ = 0–3) show both the C(Cl)–H…O and C(Cl)–H…π interactions. In all of the optimized geometries of furan–$CH_{4-n}Cl_n$ ($n$ = 0–3), C–H bond lengths are shorten and vibrational frequencies are blue–shifted, while for the furan–HCl complex, C–H bond length is lengthened and vibrational frequencies are red–shifted. The NBO analysis shows that, for the furan–$CH_{4-n}Cl_n$ ($n$ = 0–3) complexes, the charge transfer from the lone pairs of the O atom to both σ*(CH) antibonding MO and lone pairs of Cl atom, which is the important feature for blue–shifted hydrogen bond.

**Conclusions**. Both lone pairs and π electrons of furan can be acted as a proton acceptor interacting with a proton donor. Cl–H…O(π) is a conventional hydrogen bond , while C–H…O(π) is a blue–shifted hydrogen bond.

**Keywords**. Furan–HCl; furan–$CH_{4-n}Cl_n$ ($n$ = 0–3); hydrogen bond; *ab initio*; intermolecular interaction.

# 1 INTRODUCTION

Weak interactions of the type C–H…Y (Y = C, H, π) are currently one of the main topics on hydrogen bond in both experimental and theoretical studies. A number of C–H…O [1–5], C–H…N [6], C–H…π [7–11] complexes have been investigated, in which one of the interesting aspects is the frequency blue shift for the C–H stretching vibration. In the case of C–H…Y interaction involving $sp$ and $sp^2$ hydridization of C, a red shift of the C–H stretching vibration has been obtained, similar to the conventional hydrogen bond. However, some systems involving $sp^3$ hydridization of C show

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* Correspondence author; phone: 86–25–3596383; fax: 86–25–3596131; E–mail: dqxie@nju.edu.cn.

a contracted C–H bond and a blue–shifted vibrational frequency. In the present study, we used the furan as a proton acceptor and $CH_{4-n}Cl_n$ ($n$ = 0–3) with $sp^3$ hybridization of C as a proton donor. Furan, $C_4H_4O$, is a molecule of five–membered aromatic cycle containing a heteroatom, in which one of two lone pairs of O atom form a delocalized long $\pi$–bond with two double bonds. Therefore, the interaction of furan with $CH_{4-n}Cl_n$ ($n$ = 0–3) should involve two contacts, one is the C–H…O contact, another is the C–H…$\pi$ contact. We also studied the HCl–furan system for comparison.

## 2 METHODS

The geometries of the related monomers and dimers were fully optimized at the MP2 level of theory with the 6–31G** basis sets. For furan–HCl complexes, the 6–311+G** basis sets are also used for comparison. All optimized geometries were characterized as true minima by frequency calculations at MP2 level (all frequencies being positive). Basis set superposition error was estimated by the counterpoise method [12] for all dimers. The Gaussian94 package [13] was used for all the calculations.

## 3 RESULTS AND DISCUSSION

### 3.1 Geometry and Energy

For the furan…HCl complexes, two local minima were obtained. One local minimum has the HCl molecule lying in the plane of the furan ring (configuration A of figure 1), and another has the HCl molecule above the furan ring (configuration B).
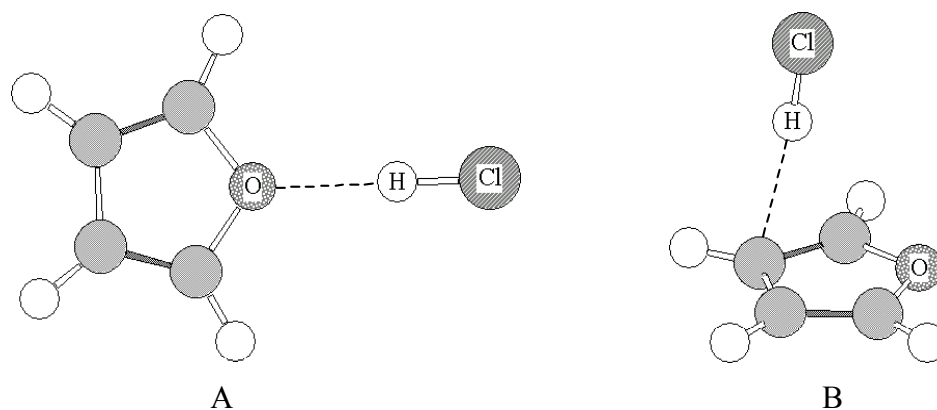


A           B

**Figure 1.** The geometries of the furan–HCl complex.

From Figure 1, one can see that the planar structure A has a linear hydrogen bond, in which furan molecule acts as a proton acceptor and the HCl molecule axis is along the bisection angle of the oxygen–carbon, which makes the complex have an symmetry of the $C_{2v}$ point group. In the case of structure B, the HCl bond is pointing towards the $\beta$ carbon atom of the furan ring, and the

optimized geometry has $C_1$ symmetry. The similar results have been for benzene–HF [14] and pyrrole–HF [15]. Table 1 presents the optimized geometry parameters and interaction energies of configurations A and B together with the harmonic vibrational frequencies of the H–Cl bond and its IR absorption intensity of monomers and dimers, computed with 6–31G** and 6–311+G** basis set at MP2 levels of theory. The distances R(O…H) of configurations A obtained from the two methods are very close to each other and in excellent agreement with the experimental data (1.98 Å) [16]. In the case of the configuration B, the distance R(C…H) at MP2/6–311+G** is slightly longer than that obtained with MP2/6–31G** method. As show in Table 1, all the changes in H–Cl bond length and stretching vibrational frequency are similar to the conventional hydrogen bond. It is well known that the formation of a conventional hydrogen bond (X–H…Y) leads to an elongation of X–H bond which is accompanied by a red shift of the X–H stretch frequency and a increase of the infrared intensity, compared to the monomer. In this way, the interaction of furan with HCl can be regarded as a conventional H–bond.

**Table 1.** Selected structural parameters,[a] interaction energies ΔE (kcal/mol )calculated with counterpoise correction of basis superposition error , shift in vibrational frequency Δυ (cm$^{-1}$) , and IR intensities (km/mol) in the monomer (m) and in the dimer (d)

|   | Method | R(O…H) | R(O…Cl) | Δ(H–Cl)[b] | α[c] | ΔE | Δυ | I(m) | I(d) |
|---|---|---|---|---|---|---|---|---|---|
| A | MP2/6–31G** | 1.997 | 3.275 | 0.0084 | 179.7 | −3.30 | −112 | 22.4 | 482 |
|   | MP2/6–311+G** | 1.990 | 3.271 | 0.0079 | 179.7 | −3.06 | −106 | 35.4 | 497 |
|   | Method | R(C…H) | R(C…Cl) | Δ(H–Cl)[b] | α | ΔE | Δυ | I(m) | I(d) |
| B | MP2/6–31G** | 2.395 | 3.668 | 0.0071 | 175.0 | −2.58 | −97 | 22.4 | 283 |
|   | MP2/6–311+G** | 2.605 | 3.688 | 0.0066 | 173.4 | −2.62 | −90 | 35.4 | 285 |

[a] Bond lengths are given in Å
[b] Change of H–Cl bond length(in Å) of the HCl upon complex function
[c] Angle α defined as O(C)…H–Cl

A comparison of the energy of geometries A and B shows that structure A which has the Cl–H…O hydrogen bond corresponds to a global minimum, while Cl–H…π contacts is less stable. It can be seen from table 1 that there is a clear correlation between the energy and the distance R(O…H) or R(C…H), since the lone pair electrons are more contracted than π electrons. The results show that the interaction of Cl–H…O is stronger than that of Cl–H…π.

The case for the complexes of furan with $CH_{4-n}Cl_n$ ($n$ = 0–3) is much more complicated. Similar to the furan–HCl complex, a planar structure having CH…O contact was obtained, which is labeled as configuration A in Figure 2. The structural parameters obtained from MP2/6–31G** calculations are given in Table 2.

In Figure 2, angle α represents the angle of C–H…O, angle β represents the direction of proton acceptor. From Table 2 and Figure 2, one can see that the configuration A involving chloromethanes show a departure from linearity. The distances between one of the chlorines in derivatives and a hydrogen atom in furan vary from 2.945 Å for $CHCl_3$, 3.078 Å for $CH_2Cl_2$, to 3.219 Å for $CHCl_3$. In the same sequence, the value of angle α deceases, while the value of angle β

increases. These results show that there is another weak interaction between one of the chlorines in derivatives and a hydrogen atom in furan leads to a six–member coplanar ring. This phenomenon has also been found in $F_3CH...OH_2$ [17] and $C_2H_2...CHCl_3$ [10]. These results demonstrate that the structure A involving chloromethanes were dominated by the combined interactions, in which one is the CH...O interaction, and another is CH...Cl interaction. In the former case, chloromethanes act as proton donor, while furan acts as a proton acceptor. In the later case, however, the CH of furan acts as a proton donor, while Cl acts as a proton acceptor. In the geometry A involving furan–$CH_4$, C–H bond of $CH_4$ is not coplanar with furan. The dihedral angle of H with the furan ring is about 54° and the angle of C–H...O show a slightly departure from linearity. This may be due to the existence of CH...Cl interaction in chloromethanes complexes, which makes the C–H bond coplanar with the furan ring.
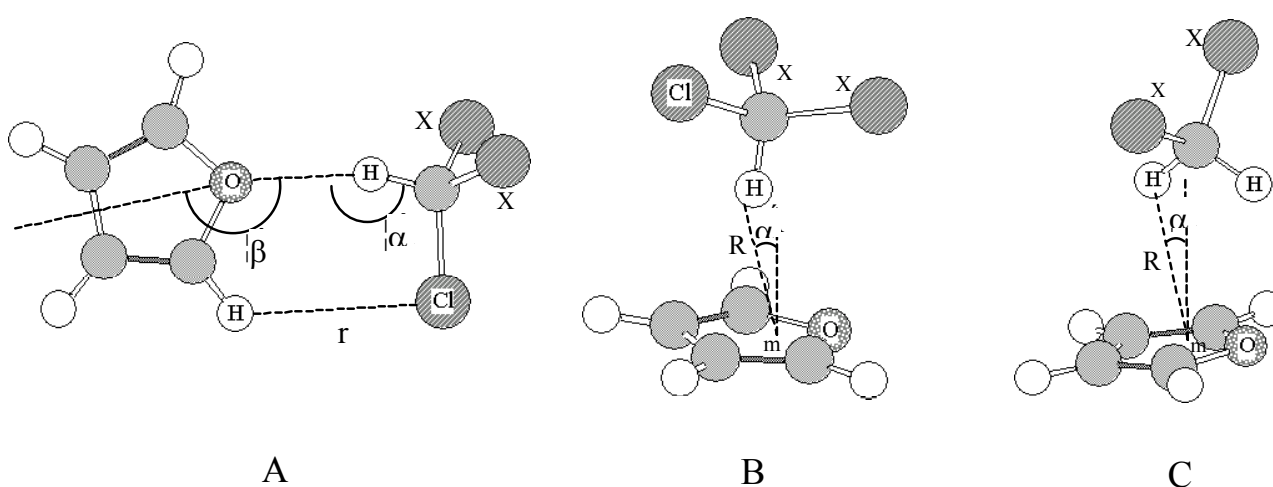


**Figure 2.** The optimized geometries of furan–$CH_{4-n}Cl_n$ ($n = 0–3$) complexes. For the structure A, $\alpha$ denotes the angle of C–H...O and $\beta$ denotes the angle of the direction of proton acceptor. For structure B and C, m denotes the center of mass, R is the distance between H atom and m, and $\alpha$ is the angle between R and the line normal to the plane of furan.

**Table 2.** Selected structural parameters for geometries A [a]

|  | R(C–H) | R(H...O) | R(C...O) | $\alpha$ | $\beta$ | $\Delta$(C–H) [b] | r |  |
|---|---|---|---|---|---|---|---|---|
| $CH_4$ A | 1.085 | 2.607 | 3.684 | 5.9 |  | 0.0002 |  | $CH_4$ A |
| $CH_3Cl$ A | 1.083 | 2.451 | 3.441 | 15.7 | 139.4 | 0.0006 | 2.945 | $CH_3Cl$ A |
| $CH_2Cl_2$ A | 1.083 | 2.289 | 3.321 | 14.5 | 131.3 | 0.0008 | 3.078 | $CH_2Cl_2$ A |
| $CHCl_3$ A | 1.082 | 2.168 | 3.223 | 10.7 | 127.2 | 0.0008 | 3.219 | $CHCl_3$ A |

[a] Bond lengths are given in Å
[b] Change of C–H bond length (in Å) of the proton donor upon formation of a complex

For the structure B of complexes involving $CH_{4-n}Cl_n$ ($n = 0–3$) with furan, similar to HCl above furan ring, $CH_{4-n}Cl_n$ ($n = 0–3$) can also be located above the furan ring forming a CH–$\pi$ contact, which shows a similar nature as benzene with $CHCl_3$ [14]. In the complex of benzene with $CHCl_3$, the donor C–H group points toward the center of the benzene ring. In Figure 2, m is the center of mass, R is the distance between H atom and m, and $\alpha$ is the angle between R and the line normal to

the plane of furan. The optimized geometry parameters are given in Table 3. One can see from this table that $\alpha$ is small and R decreases from 2.725 Å for $CH_3Cl$ to 2.539 Å for $CH_2Cl_2$ and then to 2.238 Å for $CHCl_3$. The distance of benzene…$CH_4$, benzene…$CHCl_3$ [10] and fluorobenzene…$CHCl_3$ [17] is 2.707, 2.198 and 2.424 Å, respectively. In Ref. [17], CH…$\pi$ distances of $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$ are 2.73, 2.65 and 2.38 Å, respectively. These results demonstrate that the interaction of furan with chloromethanes above the furan ring is very similar with that of benzene with chloromethanes.

In addition, we find the third geometry C, as shown in Figure 2. In this configuration, the donor lies over the ring, with one of donor H atom pointing toward the furan ring as geometry B and another H atom pointing to O atom of furan. This pattern was also found in the pyrrole($C_4H_5N$)–$H_2O$ [18] and benzene–$H_2O$ [19] complexes.

Our calculations show that for all A, B and C geometries, the distance between H atom and O atom or delocalized $\pi$–electron decreases as increasing the acidity of the C–H donor group, and the changes in the bond length of donor C–H upon complexes are positive, which represent the contractions of the C–H bond, rather than the normally expansion in the conventional hydrogen bond. This situation is similar as in Refs. [3,5]. There is a rough correlation between the shortening of CH bond length and the acidity of the CH donor group. The interaction energies with counterpoise correction of BSSE are displayed in Table 4. For the furan–$CH_{4-n}Cl_n$ ($n = 0–3$) complexes with structure A, the interaction energies increase along with the increase of acidity of proton donor, that is, $CH_4 < CH_3Cl < CH_2Cl_2 < CHCl_3$. The pattern of complexes with structures B and C is same as that in structure A.

**Table 3.** Selected structural parameters for geometries B and C [a]

|  | R | $\alpha$ | $\Delta$R(C–H) [b] |  |
| --- | --- | --- | --- | --- |
| $CH_3Cl$ B | 2.725 | 3.69 | 0.0004 | $CH_3Cl$ B |
| $CH_2Cl_2$ B | 2.539 | 2.89 | 0.0011 | $CH_2Cl_2$ B |
| $CHCl_3$ B | 2.238 | 3.07 | 0.0025 | $CHCl_3$ B |
| $CH_4$ C | 2.997 | 1.20 | 0.0001 | $CH_4$ C |
| $CH_3Cl$ C | 2.582 | 8.54 | 0.0008 | $CH_3Cl$ C |
| $CH_2Cl_2$ C | 2.357 | 1.84 | 0.0017 | $CH_2Cl_2$ C |

[a] Bond lengths are given in Å
[b] Change of C–H bond length(in Å) of the proton donor upon formation of a complex

**Table 4.** The interaction energies (kcal/mol) of furan with $CH_{4-n}Cl_n$ ($n = 0–3$)

|  | A | B | C |
| --- | --- | --- | --- |
| $CH_4$ | −0.41 |  | −0.83 |
| $CH_3Cl$ | −1.61 | −1.24 | −1.34 |
| $CH_2Cl_2$ | −2.08 | −1.92 | 2.26 |
| $CHCl_3$ | −2.61 | −2.63 |  |

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**Table 5.** Calculated shift in vibrational frequency $\Delta \upsilon$ (cm$^{-1}$) and IR intensities (km/mol) in monomer (m) and dimer (d)

| | Geometry A | | | | Geometry B | | | Geometry C | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | $CH_4$ | $CH_3Cl$ | $CH_2Cl_2$ | $CHCl_3$ | $CH_3Cl$ | $CH_2Cl_2$ | $CHCl_3$ | $CH_4$ | $CH_3Cl$ | $CH_2Cl_2$ |
| $\Delta \upsilon$ | +7 | +13 | +13 | +22 | +11 | +25 | +41 | +4 | +10 | +19 |
| I(m) | 21.3 | 6.8 | 0.7 | 0.3 | 6.8 | 0.7 | 0.3 | 21.3 | 6.8 | 0.7 |
| I(d) | 6.5 | 1.1 | 15.7 | 68.4 | 1.6 | 5.8 | 38.0 | 14.2 | 3.6 | 2.3 |

## 3.2 Vibrational Spectra

Table 5 gives the spectroscopic data that contains the frequency shift of CH and the infrared intensities of CH in the free molecule and in their corresponding complexes with furan. The results for furan–HCl complex, reported in Table 1, show that the frequencies shift has a negative value, which indicates a conventional H–bond. However, the C–H frequency shift involving $CH_4$ and its chlorinated derivatives $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$ have a positive value, which is called as blue shift in frequency. A similar result was found in a number of recent articles including CH…O interaction [3,5,17], CH–$\pi$ interaction [9,10,17], most of which involve in $CH_4$, fluoromethanes and chloromethanes with a C of $sp^3$ hybridization. The magnitude in blue shift is increased along with the decrease of C–H bond length. The blue shifts of C–H bond of $CH_{4-n}Cl_n$ ($n$ = 0–3) vary in magnitude from 4 to 41 cm$^{-1}$, which is smaller than that in the furan–HCl system (112 cm$^{-1}$, 97 cm$^{-1}$). From Table 4 it can be seen that the changes in the intensity of CH stretching are not significantly correlated to the frequency blue shifts. In the geometries A, B and C of $CH_4$ and methylchloride derivates with furan, the intensity decreases. For the $CH_2Cl_2$ and $CHCl_3$ complexes, in contrast to the above cases, the intensity increases with the acidity of the CH group. Taking the geometry C of the furan–$CH_2Cl_2$ complex as an example, the intensity varies from 0.33 for the monomer to 68.4 for the dimer. The same results were found in the furan–HCl complex, which was regard as a conventional H–bond. The same behavior was also found in the complexes of $CH_{4-n}Cl_n$ ($n$ = 0–3) with $H_2O$.

## 3.3 NBO Analysis of the Electronic Structure

One of the characteristic features of H–bond is the charge transfer from the proton acceptor molecule to the donor molecule. The charge transfer along with the changes in natural atomic charges of each atoms of proton donor is presented in Table 6. It can be seen that the intermolecular charge transfer (CT) for $CH_4$ and it derivates are about 1~11 me, while charge transfer for HCl A and B are 23.3 and 14.5, respectively. These values are consistent with the results for CH…O [5]. It can be seen that charge transfer is increased along with the acidity of the CH group. All H atoms involving CH…O or CH…$\pi$ interaction lose electronic density, except for the $CH_3Cl$ C geometry. However, in all of complexes, the change of atomic charger of donor C atom is positive, in contrast with Ref. [5]. For Cl and H atoms that involve H–bond, the changes are negative.

**Table 6.** Charge transferred from proton acceptor to donor molecule and charge in natural population atomic charge (me) of the different atoms relative to monomers

| | CT | $\Delta q_H$ | $\Delta q_C$ | $\Delta q_{Cl}$ | | | $\Delta q_H$' | | | $\Delta q_O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| HCl A | 23.3 | 8.2 | | −31.5 | | | | | | −28.1 |
| HCl C | 14.5 | 0.2 | | −14.7 | | | | | | 7.9 |
| CH4 A | 4.3 | 8.1 | 4.3 | | | | −2.6 | −2.5 | −2.1 | −3.9 |
| CH3Cl A | 1.7 | 11.8 | 1.7 | −11.6 | | | −1.8 | −1.7 | | −14.6 |
| CH2Cl2 A | 3.3 | 12.6 | 3.4 | −14.3 | −5.2 | | −2.7 | | | −19.7 |
| CHCl3 A | 11.1 | 12.5 | 5.0 | −15.8 | −6.4 | −6.4 | | | | −24.7 |
| CH3Cl B | 3.3 | 3.3 | 7.9 | −8.3 | | | −3.7 | −2.5 | | −1.7 |
| CH2Cl2 B | 5.1 | 0.5 | 13.9 | −8.7 | −7.8 | | −3.0 | | | −1.0 |
| CHCl3 B | 10.2 | −2.9 | 18.2 | −9.5 | −8.6 | −7.3 | | | | 3.4 |
| CH4 C | 3.2 | 2.6 | 3.8 | 1.4 | | | −4.1 | −4.1 | | −0.1 |
| CH3Cl C | 3.9 | 2.4 | 4.4 | 3.4 | −10.4 | | −3.7 | | | −2.4 |
| CH2Cl2 C | 8.5 | 2.3 | 4.0 | 5.3 | −10.5 | −9.6 | | | | −3.3 |

**Table 7.** Charge in the occupation of the σ*(CH'), σ*(CH) and σ* (CCl) orbital and of the lone pairs of Cl and O(me)

| | σ*(CH') | σ*(CH) | | | σ*(CCl) | | | LP(Cl) | | | LP(O) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HCl A | 22.0 | | | | | | | −1.6 | | | −17.7 | 22.5 |
| HCl C | 14.5 | | | | | | | −2.4 | | | −0.3 | −7.1 |
| CH4 A | 3.3 | 0.1 | 0.1 | 0.1 | | | | | | | −1.8 | 2.3 |
| CH3Cl A | 3.2 | −0.4 | −0.4 | | 0.1 | | | −0.6 | | | −3.6 | 8.5 |
| CH2Cl2 A | 3.6 | −0.3 | | | 1.0 | −1.1 | | 0.6 | 1.9 | | −5.5 | 12.3 |
| CHCl3 A | 3.9 | | | | 1.8 | −0.8 | −0.9 | 0.8 | 0.9 | 3.3 | −8.1 | 16.3 |
| CH3Cl B | 2.6 | 0.1 | 0.2 | | 0.1 | | | 0.4 | | | 0.0 | 1.3 |
| CH2Cl2 B | 2.0 | 0.0 | | | 0.3 | 0.0 | | 0.4 | 0.9 | | 0.0 | 0.5 |
| CHCl3 B | 2.2 | | | | 0.6 | 0.4 | 0.1 | 0.3 | 1.0 | 1.4 | −0.2 | −2.9 |
| CH4 C | 1.1 | 1.5 | 0.4 | 0.4 | | | | | | | −0.6 | 0.2 |
| CH3Cl C | 1.5 | 0.7 | 0.3 | | 0.5 | | | 1.1 | | | −0.6 | 0.8 |
| CH2Cl2 C | 1.8 | 0.5 | | | 1.0 | 1.0 | | 1.4 | 1.7 | | −0.6 | 1.1 |

The NBO analysis of several typical H bond systems [5,20] has also been performed. The former has a charge transfer from the lone pairs of the proton acceptor to the antibonding orbital of the proton donor, and the latter has a charge transfer from the lone pairs of the proton acceptor to the lone pairs of Cl atom in the proton donor. Table 7 presents the changes in occupation of orbital and of the lone pairs of Cl and O. From this table one can see that, for HCl A and B, the dominant part of the charge mainly enter into the σ*(CH') antibonding MO of proton donor, whose population increase 22.0 me for A and 14.5 me for B. This pattern is as same as the typical H bond. The recent article [5] reports another case. In $Cl_nH_{3-n}CH-H_2O$ (X = F, Cl) complexes, the charge transfer performed from the lone pairs of the proton acceptor to both σ*(CH') antibonding MO and lone pairs of F or Cl atom. Our results are very similar to this case. Although the change of the population of σ*(CH) antibonding MO is not as same as in Ref. [18] in which the values are all negative, its value is rather small. Finally, let us take a look at the lone pairs on the O atom of furan. When forming CH…O interaction, the occupation of the lone pairs that not involving delocalized π–electron obviously decreases due to the charge transfer to donor, the changes are very small. When forming CH…π interaction, the occupation of lone pairs involving π–bond increase.

# 4 CONCLUSIONS

In the present study, we have used *ab initio* calculations to study the interaction of furan–HCl and furan–$CH_{4-n}Cl_n$ ($n$ = 0–3) complexes, and found for the first time the frequency blue–shifted hydrogen bond occurring in later complexes. The geometries, interaction energies and vibrational frequencies have been obtained. The optimized geometries of furan–HCl and furan–$CH_{4-n}Cl_n$ ($n$ = 0–3) shown both C(Cl)–H…O and C(Cl)–H…π interactions. The results demonstrated that both lone pairs and π electrons of furan can act as a proton acceptor interacting with a proton donor. In all geometries of furan–$CH_{4-n}Cl_n$ ($n$ = 0–3), C–H bond length are shorten and vibrational frequency are blue–shifted, while for the furan–HCl complex, C–H bond length are lengthened and vibrational frequencies are red–shifted. The results of NBO analysis show the charge transfer from the lone pairs of the O atom to both the $\sigma^*$(CH) antibonding MO and the lone pairs of Cl atom.

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## Biographies

**Daiqian Xie** is professor of chemistry at the institute of theoretical and computational chemistry, department of chemistry, Nanjing University. After obtaining a Ph.D. degree in physical chemistry from Jilin University, Dr. Xie undertook postdoctoral research with Professor Auchin Tang at Jilin University. More recently, Dr. Xie has collaborated on potential energy surface and molecular dynamics with Professor Hua Guo at university of New Mexico, USA and Professor Donghui Zhang at National university of Singapore.

**Jiang Li** is a graduate student pursuing his Ph.D in the Department of Chemistry, Sichuan University under the supervision of Prof. Xie.