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Triangular Halogen Bond and Hydrogen Bond Supramolecular Complex Consisting of Carbon Tetrabromide, Halide, and Solvent Molecule: A Theoretical and Spectroscopic Study

Yu-je Wu†, Xiao-ran Zhao, Hai-yue Gao, Wei-jun Jin∗
College of Chemistry, Beijing Normal University, Beijing 100875, China

(Dated: Received on July 11, 2013; Accepted on May 4, 2014)

The theoretical calculation and spectroscopic experiments indicate a kind of triangular three bonding supramolecular complexes CBr₄⋯X−⋯H−C, which consist of carbon tetrabromide, halide, and protic solvent molecule (referring to dichloromethane, chloroform and acetonitrile), can be formed in solution. The strength of halogen and hydrogen bonds in the triangular complexes using halide as common acceptor obeys the order of iodide>bromide>chloride. The halogen and hydrogen bonds work weak-cooperatively. Charge transfer bands of halogen bonding complexes between CBr₄ and halide are observed in UV-Vis absorption spectroscopy in three solvents, and then the stoichiometry of 1:1, formation constants K and molar extinction coefficients ε of the halogen bonding complexes are obtained by Benesi-Hildebrand method. The K and ε show a dependence on the solvent dielectric constant and, on the whole, obey an order of iodide>bromide>chloride in the same solvents. Furthermore, the C−H vibrational frequencies of solvent molecules vary obviously with the addition of halide, which indicates the C−H⋯X− interaction. The experimental data indicate that the halogen bond and hydrogen bond coexist by sharing a common halide acceptor as predicted by calculation.

Key words: Halogen bond, Hydrogen bond, Halide, Carbon tetrabromide, Charge transfer

I. INTRODUCTION

Noncovalent interactions play an important role in the fields of chemistry, biology and physics [1]. Hydrogen bond as one of the noncovalent interactions has been widely investigated by experimental and theoretical methods [2, 3]. Halogen bond similar to hydrogen bond, a highly-directional noncovalent interaction between a covalently-bonded halogen and a negatively charged group (Lewis base, e.g., the lone pair electrons, π electrons and anion, etc.), has drawn much attention recently [4]. It is described as electrostatic interaction between the positive region, σ-hole (σₐ), of halogen atoms and negative species [5]. The covalently-bonded halogen atoms can interact with both nucleophile and electrophile due to the anisotropy of electron density distribution on them and it has been confirmed by experiments [6–8]. In fact, halogen bond is a comprehensive result from electrostatic attraction, exchange repulsion, induction, dispersion, etc. [9–11]. The absorption band of charge transfer (CT) between halogen bond donor and acceptor has prove to be an important way for monitoring halogen bond [12–15].

Resnati et al confirm that halogen bond is more competitive with hydrogen bond by experiments in some cases [16]. Meanwhile, sometimes the halogen and hydrogen bonds are collaborative, e.g., they can coexist in cocrystals, biological systems [16]. Zhou et al report by calculation and survey of crystal data base that a halogen-water-hydrogen bridge might exist in some biological systems and be contributive to stabilize biomacromolecules or to improve the interaction between biomacromolecules [17]. Li et al show by calculation the XB and HB exhibit positive cooperativity, i.e., the binding strengths of the halogen and hydrogen bond are enhanced by each other’s presence, XB at one site of a molecule can significantly enhance HB at another site [18]. The orthogonality in both energy and direction between XB and HB is possible in protein systems, too, by sharing common acceptor, carbonyl C=O, in which HB and XB act on the lone pair electrons of oxygen and π electrons of carbonyl, respectively [19]. These results show that the investigation on relationship of XB and HB has really practical significance.

It has been demonstrated by our calculation that a novel triangular bonding interaction pattern consisting of carbon tetrabromide, halide and protic solvent molecule, as shown in Fig.1, CBr₄⋯X−⋯H−C for simplification hereafter exists in gas phase [20]. In this
work, further investigation on the properties of the interaction pattern in solution has been completed. The geometries and bonding energies of the triangular bonding complexes in solution are obtained by calculation and spectroscopy. The results indicate the triangular bonding complexes can also exist in solution.

II. COMPUTATIONAL AND EXPERIMENTS DETAILS

The full geometrical optimizations of the complexes and monomers in solution were performed at MP2(full) [21] level with the basis set aug-cc-pVDZ-PP for iodine atom and aug-cc-pVDZ for all the other atoms [22]. Calculations were performed via the standard polarizable continuum model (PCM) [23]. The total interaction energy was estimated as the difference between the energy of the trimers and the sum of total energies of the three monomers ∆E\textsubscript{total} = E\textsubscript{ABC} = (E\textsubscript{A} + E\textsubscript{B} + E\textsubscript{C}). The individual halogen bond or hydrogen bond interaction energy was approximately estimated as the difference between the energy of the interactive pair with coordinates frozen in the trimers and the sum of the energies of the two monomers. The cooperative effects of the halogen bond and hydrogen bond of these trimers complexes were assessed by computing a three-body non-additive energy ∆E\textsubscript{coop} = ∆E\textsubscript{total} - (∆E\textsubscript{XB} + ∆E\textsubscript{HB} + ∆E\textsubscript{HB'}). The basis set superposition error (BSSE) was eliminated by the standard counterpoise method of Boys and Bernardi [24]. All calculations were performed using Gaussian 03 program packages [25].

Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}), chloroform (CHCl\textsubscript{3}), and acetonitrile (CH\textsubscript{3}CN) were purchased from Beijing Chemical Reagent Co. with a purity of 99.5%. Carbon tetrabromide (CBr\textsubscript{4}), and tetra-n-butylammonium chloride were obtained from TOKYO Chemical Industry Co., Ltd. with a purity of 98%. Tetra-n-butylammonium bromide and tetra-n-butylammonium iodide were obtained from Alfa Aesar with a purity of 98%, all solvents were dried by calcined 3˚A molecular sieve.

The absorption spectra of CBr\textsubscript{4}•••X\textsuperscript{−} complexes were measured by an UV-Vis spectrophotometer (GBC Corporation of Australia), in 2 mm × 10 mm quartz cells. The background line was recorded over the desired spectral region by filling both reference and sample cells with selected solvent. Then the absorption spectra of CBr\textsubscript{4} or the halide solution were recorded. Sequentially, charge transfer spectra were recorded by gradual titration of halide anion into CBr\textsubscript{4} solution.

Infrared spectra were recorded on a Nicolet 380 FT-IR spectrophotometer (Nicolet, USA) using NaCl windows and precision of wavenumber \( \leq 0.5 \) cm\(^{-1}\), the resolution was less than 0.5 cm\(^{-1}\). The concentration of carbon tetrabromide and tetrabutylammonium halide in stock solution was 0.5 and 1.0 mol/L, respectively. The liquid film was prepared by dropping the stock solution on a NaCl window.

Cyclic voltammetry (CV) was performed on a CHI660 electrochemical workstation (CH Instrument Inc, USA) with r compensation at the rate of 0.1 V/s under nitrogen atmosphere. A platinum disk, platinum gauze and a saturated calomel electrode were used as working electrode, counter electrode and reference electrode, respectively. Working solutions consisted of 4 mmol/L alkylammonium halide and 0.1 mol/L supporting electrolyte (NBu\textsubscript{4}PF\textsubscript{6}–).

All experiments were carried out under dark conditions at room temperature. Carbon tetrabromide and halide solutions must be freshly prepared before the experiment.

III. RESULTS AND DISCUSSION

A. Geometries parameters

The structures of the triangular bonding complexes CBr\textsubscript{4}•••X\textsuperscript{−}•••H–C in solution are got through the full optimization at MP2(full)/aug-cc-pVDZ(PP) level with the standard polarizable continuum model (PCM). The structures of the complexes and key geometries parameters are shown in Fig.2. All optimum Br•••X\textsuperscript{−}, H•••X\textsuperscript{−}, H•••Br distances are within the sum of van der Waals radii of corresponding atoms, which reveals the existence of the halogen bond and hydrogen bond.

The hydrogen atom of solvent molecule interacts with both bromine atom of CBr\textsubscript{4} and halide anion. The two hydrogen bonds combine with the halogen bond to form the triangular bonding systems (Fig.1).

As shown in Fig.2, the halogen bond lengths Br•••Cl\textsuperscript{−} of CBr\textsubscript{4}•••Cl\textsuperscript{−}•••H–C, vary from 3.019 Å to 3.106 Å (less than 3.600 Å, the sum of the vdW radii of chlorine and bromine). The ranges of Cl\textsuperscript{−}•••H and Br•••H distances are 2.291–2.775 and 2.860–2.969 Å, respectively. The changes of hydrogen bond length depend on the proton acidity of the solvent molecule in addition to the general solvent effects. From the data in Fig.2, the halogen bond length decreases with the decrease of the hydrogen bond in the trimers. The Br•••Cl\textsuperscript{−} distances change from 3.106 Å in CBr\textsubscript{4}•••Cl\textsuperscript{−}•••CH\textsubscript{3}CN to 3.066 Å in CBr\textsubscript{4}•••Cl\textsuperscript{−}•••CH\textsubscript{2}Cl\textsubscript{2} and 3.019 Å in CBr\textsubscript{4}•••Cl\textsuperscript{−}•••CH\textsubscript{3}Cl, while the Cl\textsuperscript{−}•••H distances change parallelly from 2.775 Å to 2.497 and 2.291 Å. Generally speaking, the shorter the bond length is, the
higher the bond strength is. That is, the halogen bond in CBr₄···Cl⁻···H−C is reinforced by the enhanced hydrogen bond strength. It indicates the cooperative effects are present between halogen bond and hydrogen bond in the trimers CBr₄···Cl⁻···H−C in solution based on the change of bond length.

The same trends are observed in CBr₄···Br⁻···H−C and CBr₄···I⁻···H−C complexes. The Br···Br⁻ distances vary from 3.127 Å to 3.239 Å (less than 3.700 Å, the sum of the vdW radii of two bromine atoms). The Br···I⁻ distances vary from 3.322 Å to 3.396 Å (less than 3.960 Å, the sum of the vdW of bromine and iodine). All Br⁻···H, I⁻···H and Br···H distances in CBr₄···Br⁻···H−C and CBr₄···I⁻···H−C complexes are also less than the sum of the vdW radii of the corresponding atoms. The halogen bond length of Br···Br⁻ in CBr₄···Br⁻···H−C and Br···I⁻ in CBr₄···I⁻···H−C becomes parallely shorter as the decrease of the hydrogen bond lengths. So, the halogen bond and hydrogen bond in the trimers CBr₄···Br⁻···H−C and CBr₄···I⁻···H−C also show cooperativity.

The halogen bond angles in the trimers range from 167.3° to 175.1°. The ranges of the hydrogen bond angles of H−C···X⁻ and H−C···Br are 158.5°−172.0° and 97.4°−121.8°. It can be seen that the angles of hydrogen bond deviate more remarkably from 180° because of semi-global positive electrostatic potential of hydrogen atom. Additionally, the mutual effect of halogen bond and hydrogen bond in the triangular bonding complexes is another factor making the corresponding angles deviated from linearity.

The halogen bond length and hydrogen bond length in solution are longer than those in gas phase [20]. The Br···Cl⁻ bond elongates by 0.367 Å in CH₃CN, 0.302 Å in CH₂Cl₂ and 0.208 Å in CHCl₃, respectively. The elongating amplitudes of the Br···Br⁻ and Br···I⁻ bonds are 0.177−0.356 Å and 0.195−0.345 Å. The hydrogen bond lengths are also elongated in solution though the variations are not so notable. The general solvent effects should result in the relaxation of the molecular structures. So the polarity of the solvents has a pronounced effect on the halogen bond distances. The varying amplitude of the distances is smaller in the solvents with lower polarity. The same conclusion was drawn in CₓFₓI···X⁻ and CₓFₓI···X⁻ reported by Lu et al. [26].
TABLE I Corrected total interaction energies, halogen bonding and hydrogen bonding energies, and cooperative energies of the trimers in solution (in kcal/mol)\textsuperscript{a}.

<table>
<thead>
<tr>
<th></th>
<th>CBr\textsubscript{4}...Cl\textsuperscript{−}...H−C</th>
<th>CBr\textsubscript{4}...Br\textsuperscript{−}...H−C</th>
<th>CBr\textsubscript{4}...I\textsuperscript{−}...H−C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{3}CN</td>
<td>(\Delta E_{\text{total}}) = −7.14 kcal/mol</td>
<td>(\Delta E_{\text{total}}) = −8.91 kcal/mol</td>
<td>(\Delta E_{\text{total}}) = −9.61 kcal/mol</td>
</tr>
<tr>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>−11.24 kcal/mol</td>
<td>−12.24 kcal/mol</td>
<td>−13.98 kcal/mol</td>
</tr>
<tr>
<td>CHCl\textsubscript{3}</td>
<td>−14.59 kcal/mol</td>
<td>−15.17 kcal/mol</td>
<td>−14.65 kcal/mol</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The BSSE-corrected interaction energies in solution are obtained in vacuum with the structural coordinates frozen in solution.

B. Interaction energies

The total interaction energies, halogen bond and hydrogen bond energies of the trimers in solution were calculated at MP2(full)/aug-cc-pVDZ-PP level and results are listed in Table I. The BSSE is eliminated through the single point energy correction in vacuum with the structural coordinates frozen in solution by the standard counterpoise method. The uncorrected interaction energies are also collected in the Table S1 (supplementary material). The BSSE should be considered for the halogen and hydrogen bond interaction energies herein due to the large BSSE-percentage of the total interaction energy (\textit{e.g.} the BSSE is 6.01 kcal/mol for CBr\textsubscript{4}...Br\textsuperscript{−}...H−C, 40.3% of the uncorrected total interaction energy).

As discussed above in term of the bond lengths, the cooperative effects occur between halogen bond and hydrogen bond in all the trimers. Here the cooperativity is further confirmed from the interaction energies. The XB/HB (Cl\textsuperscript{−}...H−C) interaction energies are −3.08/−2.11 kcal/mol for trimer CBr\textsubscript{4}...Cl\textsuperscript{−}...CH\textsubscript{3}CN, −3.75/3.54 kcal/mol for CBr\textsubscript{4}...Cl\textsuperscript{−}...CH\textsubscript{2}Cl\textsubscript{2} and −4.83/5.65 kcal/mol for CBr\textsubscript{4}...Cl−...CHCl\textsubscript{3}.

The total interaction energies, halogen bond and hydrogen bond interaction energies in solution are observed to change trends of the bond strength. A solvent cage around the complex molecule must be created in the solution. The ion-dipole, dipole-dipole and dipole-induced dipole forces will occur between the complex and solvent molecules. The molecule structures should be relaxed and the energies go down because of these interactions.

If the nature of the halogen bonding is only charge transfer (CT), the interaction energy should obey the order of iodide>bromide>chloride [27], while for electrostatic interaction dependent on surface charge density the energy order should be chloride>bromide>iodide [28–30]. Therefore, in order to insight into the nature of the triangular bonding complexes further, the UV-Vis absorption and FT-IR spectroscopy are measured.

C. UV-Vis absorption spectra of CBr\textsubscript{4}...X\textsuperscript{−} complexes and halide

The absorption spectra of halogen bond complex are examined in three representative solvents with different the dielectric constants, 37.5 (CH\textsubscript{3}CN), 10.4 (CH\textsubscript{2}Cl\textsubscript{2}), and 4.9 (CHCl\textsubscript{3}), respectively. The absorption spectra of carbon tetrabromide are characterized by the absorption peak \(\lambda_{\text{max}}\) at 225 nm in CH\textsubscript{3}CN, 230 nm in CH\textsubscript{2}Cl\textsubscript{2} and 236 nm in CHCl\textsubscript{3}. The tetrabutylammonium halide also shows different absorption bands dependent on solvents. The absorption spectra of CBr\textsubscript{4}...X\textsuperscript{−} complexes in different solvents are shown in Fig.3, with increasing halide concentration gradually. Specifically, when tetrabutylammonium iodide is added into the CBr\textsubscript{4} solution, a new absorption band emerged at 344 nm in acetonitrile, 345 nm in dichloromethane and 357 nm in chloroform (Fig.3, upper panels) and the absorption spectra grow with the increase of the tetrabutylammonium iodide concentration. Similar spectral behavior is observed as concentration of bromide or chlo-
FIG. 3 Absorption spectra of CBr₄⋯X⁻ complexes as functions of halide concentration and solvents (a) CH₃CN, (b) CH₂Cl₂, (c) CHCl₃. Upper panels for iodide, middle panels for bromide, and bottom panels for chloride. [CBr₄] is fixed at 4 mmol/L in all cases except No.0 at 0 mmol/L, which is the absorption curve of halide in selected solvent. The highest concentration used for different halide is labeled in the panels, over which the spectra produce little distortion.

The maximum absorption wavelengths of the complexes dependent on solvents are 294 nm in acetonitrile, 292 nm in dichloromethane, and 288 nm in chloroform for Br⁻ complex; 269 nm in acetonitrile, 268 nm in dichloromethane, and 264 nm in chloroform for Cl⁻ complex. The results are consistent with those reported previously as 265 nm for Cl⁻, 292 nm for Br⁻, and 345 nm for I⁻ all in dichloromethane in Ref.[31].

In brief, the absorption spectra of CBr₄⋯X⁻ complexes show the following tendencies: the maximum absorption of the complex undergoes a blue-shift with the decreasing dielectric constant of the solvent. The distance between the absorption peaks of the CBr₄ itself and CBr₄⋯X⁻ complex are significantly decreased upon declining the dielectric constant of the solvent. However, it appears that the tetrabutylammonium iodide does not obey this tendency in chloroform, presumably because the CBr₄⋯I⁻ complex is more easily oxidized in it. The maximum absorption of the complex varies with different halides in the same solvent, and displays a little difference for the same halide in different solvents and the absorption is linearly dependent on concentration of halide in a wide range in all cases.
D. Mulliken correlations

According to Mulliken [32, 33], the optical (charge-transfer) transition is related to electron promotion from the ground state to the excited state:

\[ h\nu_{CT} = E_{ES} - E_{GS} = \sqrt{(E_{D+A^-} - E_{D,A})^2 + 4H^2_{DA}} = 0.0206 \frac{\nu_{CT} \Delta \nu_1 / 2 \varepsilon_{CT}}{R_{DA}} \]  

(1)  

(2)

\[ \text{Br} \cdots X^- \text{ separation } R_{DA}, \text{ taken from calculation (see supplementary) which are longer apparently than } 3.09 \text{ Å (Br} \cdots \text{Cl}^-), 3.15 \text{ Å (Br} \cdots \text{Br}^-) \text{ and } 3.30 \text{ Å (Br} \cdots \text{I}^-) \text{ reported in crystals [31]}. \]

The changes of the absorption energy in a series of structurally related donors with the same acceptor or the same donor with various acceptors are determined mainly by differences in the energy gap \((E_{D+A^-} - E_{D,A})\) related to the donor/acceptor properties such as HOMO/LUMO energies. \(H_{DA}\) represents the electronic coupling matrix element. In solution, these donor/acceptor interactions are evaluated via reduced potentials [34]. According to Eq.(1), the absorption energy of a complex of a series of electron donors (halides) with the same electron acceptor (CBr\textsubscript{4}) must be linear with the oxidation potential of the donor, and vice versa. The oxidation waves of chloride, bromide and iodide were 1.05, 0.710, 0.378 eV in CH\textsubscript{3}CN, 1.35, 0.896, 0.441 eV in CH\textsubscript{2}Cl\textsubscript{2}, and 1.52, 1.12, 0.663 eV in CHCl\textsubscript{3}. As illustrated in Fig.4, the absorption energy of CBr\textsubscript{4}···X\textsuperscript{-} complexes \((h\nu_{CT})\) and various donors with their oxidation potentials \((E_{pa} \text{ vs. SCE})\) are linear correlations.

E. Stoichiometry, formation constants and molar extinction coefficients of CBr\textsubscript{4}···X\textsuperscript{-} complexes

The stoichiometry of halogen bonding complex can be confirmed according to the Benesi-Hildebrand methodology [35].

The complexation between CBr\textsubscript{4} and halide can be expressed as follows:

\[ \text{CBr}_4 + X^- \rightleftharpoons \text{CBr}_4 \cdot X^- \]  

(3)

The formation constant \(K\) and the molar extinction coefficient \(\varepsilon\) of the complex can be obtained by Eq.(4).

\[ \frac{c(\text{CBr}_4)}{A} = \frac{1}{c(X^-) \varepsilon K} + \frac{1}{\varepsilon} \]  

(4)

where \(A\) is the absorbance of the solution, \(l\) is the optic pathway length in cm. \(c(\text{CBr}_4)\) and \(c(X^-)\) are the concentrations of CBr\textsubscript{4} and X\textsuperscript{-} in mol/L, respectively. The plot of \(c(\text{CBr}_4)/A\) vs. \(1/c(X^-)\) is linear according to Eq.(4) if the 1:1 complex forms. The experiment data obey Eq.(4) and the correlation coefficients are all greater than 0.997, indicating the 1:1 stoichiometry of CBr\textsubscript{4} and the halide complex. The values of \(\varepsilon\) and \(K\) are calculated from the intercepts and the slopes of the fitted line, respectively, as listed in Table II.

Two conclusions could be drawn from the results in Table II. First, the molar extinction coefficients and the formation constant \(K\) values of the complexes increase with dielectric constants. The formation constant of the [CBr\textsubscript{4}, Cl\textsuperscript{-}] complex changes in similar tendency reported in Ref.[27], where the values 2.03 L/mol in dichloromethane and 4.78 L/mol in acetonitrile were determined by vibrational spectra. A similar result from the complexes between CBr\textsubscript{4} and compounds nitrogen-containing has been reported by Kochi’s group [12]. For iodide in CHCl\textsubscript{3}, the \(K\) value is an exception to the rule. Second, on the whole, extinction coefficients are apt to be greater and the complexes tend to be more stable going from iodide, bromide to chloride in the same solvent.

The electronic coupling element \((H_{DA})\) increases with the dielectric constants of solvents. For example, the \(H_{DA}\) of [CBr\textsubscript{4}, Br\textsuperscript{-}] complex are 7075 cm\textsuperscript{-1} in CH\textsubscript{3}CN, 6114 cm\textsuperscript{-1} in CH\textsubscript{2}Cl\textsubscript{2}, and 4723 cm\textsuperscript{-1} in CHCl\textsubscript{3}. It indicates CBr\textsubscript{4}···X\textsuperscript{-} complexes have a strong charge-transfer character with strongly coupled potential-energy surface (PES) [13].

F. FT-IR spectra of CBr\textsubscript{4}, CBr\textsubscript{4}···X\textsuperscript{-}, and H--C···X\textsuperscript{-} complexes

Carbon tetra bromide has a C--Br stretching vibration frequency at 676.7 cm\textsuperscript{-1} in CH\textsubscript{3}CN. With addition of halide into the CBr\textsubscript{4} solution, an apparent shift could be observed from 676.7 cm\textsuperscript{-1} to 674.7, 669.6, and 665.1 cm\textsuperscript{-1}, respectively, in the CBr\textsubscript{4}···Cl\textsuperscript{-}, CBr\textsubscript{4}···Br\textsuperscript{-}, and CBr\textsubscript{4}···I\textsuperscript{-} complexes in CH\textsubscript{3}CN. This behavior also exists when CH\textsubscript{3}CN is changed to...
TABLE II Spectroscopic and energetic characteristics of the charge-transfer complexes between CBr₄ and halide anions in different solvents.

<table>
<thead>
<tr>
<th>Halide</th>
<th>Solvent</th>
<th>λmax/μm</th>
<th>ε/10⁻⁴(L/(mol·cm))</th>
<th>K/(L/mol)</th>
<th>HDA/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>CH₂CN</td>
<td>269</td>
<td>0.54±0.13</td>
<td>6.07±1.51</td>
<td>6726</td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂</td>
<td>268</td>
<td>0.43±0.11</td>
<td>3.25±1.08</td>
<td>6056</td>
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<tr>
<td></td>
<td>CHCl₃</td>
<td>264</td>
<td>0.18±0.02</td>
<td>2.49±0.94</td>
<td>4349</td>
</tr>
<tr>
<td>Br⁻</td>
<td>CH₂CN</td>
<td>294</td>
<td>0.66±0.12</td>
<td>6.09±0.97</td>
<td>7104</td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂</td>
<td>292</td>
<td>0.48±0.06</td>
<td>4.68±0.87</td>
<td>6133</td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>288</td>
<td>0.27±0.05</td>
<td>4.11±0.89</td>
<td>4649</td>
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<tr>
<td>I⁻</td>
<td>CH₂CN</td>
<td>344</td>
<td>0.78±0.03</td>
<td>7.26±1.52</td>
<td>6528</td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂</td>
<td>345</td>
<td>0.72±0.41</td>
<td>3.24±0.44</td>
<td>6279</td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>357</td>
<td>0.41±0.12</td>
<td>8.97±2.93</td>
<td>4223</td>
</tr>
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</table>

*a In all cases, absorption of CBr₄ at interested wavelength has been deducted from total absorption of complex+CBr₄.

TABLE III Carbon-bromide stretching vibration frequency of CBr₄ in different solvents (in cm⁻¹).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>σ_CBr₄</th>
<th>σ_CBr₄Cl⁻</th>
<th>Δσc</th>
<th>σ_CBr₄Br⁻</th>
<th>Δσd</th>
<th>σ_CBr₄I⁻</th>
<th>Δσe</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CN</td>
<td>676.7</td>
<td>674.7</td>
<td>-2.0</td>
<td>669.6</td>
<td>-7.1</td>
<td>665.1</td>
<td>-11.6</td>
</tr>
<tr>
<td>Calc.</td>
<td>691.4</td>
<td>689.9</td>
<td>-1.5</td>
<td>685.3</td>
<td>-6.1</td>
<td>677.6</td>
<td>-13.8</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>672.1</td>
<td>671.7</td>
<td>-0.4</td>
<td>665.9</td>
<td>-6.2</td>
<td>664.6</td>
<td>-7.5</td>
</tr>
<tr>
<td>Calc.</td>
<td>690.0</td>
<td>689.4</td>
<td>-0.6</td>
<td>685.3</td>
<td>-4.7</td>
<td>676.3</td>
<td>-13.7</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>669.6</td>
<td>668.8</td>
<td>-0.8</td>
<td>668.7</td>
<td>-0.9</td>
<td>669.0</td>
<td>-0.6</td>
</tr>
<tr>
<td>Calc.</td>
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<td>686.3</td>
<td>-1.8</td>
<td>684.1</td>
<td>-4.0</td>
<td>673.4</td>
<td>-13.8</td>
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</tbody>
</table>

CH₂Cl₂ and CHCl₃, as listed in Table III. The magnitudes of the red-shifts, Δσ, of C–Br stretching vibration frequency are dependent on both halide and solvent. Halide affects the C–Br stretching vibration of CBr₄, on which I⁻ has the greatest influence, followed by Br⁻ and Cl⁻ in turn. This influence weakens with the decrease of the dielectric constant of solvents. The order is consistent with formation constants got from the UV-Vis absorption spectra. The computational results at MP2(full) level in Table III are in agreement with the experimental data well which indicates that the computations at MP2(full)/aug-cc-pVDZ(-PP) level are credible.

Furthermore it is noticed that C–Cl and C–H stretching vibration frequencies of solvent molecules shift when Cl⁻, Br⁻ and I⁻ is added into CHCl₃, as shown in Table IV. So it is possible that halide can bond weakly not only with CBr₄ but also with the solvent molecules. The stretching vibration frequencies of solvent molecules are also computed and listed in Table S2 (supplementary material).

As shown in Table IV, the C–H bond of CH₂CN and CH₂Cl₂ has lower stretching vibration frequencies (equivalent to a longer bond) when adding halide into them. For example, adding I⁻ makes the C–H vibration frequency shift from 2944.1 cm⁻¹ to 2941.8 cm⁻¹ in CH₂CN, and from 3054.3 cm⁻¹ to 3052.8 cm⁻¹ in CH₂Cl₂. Adding both halide and CBr₄, the frequency is almost the same as adding only halide. This indicates that hydrogen bond is formed between halide and protonic solvents CH₂CN, CH₂Cl₂. Based on the magnitude of frequency-shifts of C–H and C–Cl of CH₂Cl₂, halogen bond between solvent molecule and halide may occur in C–Cl···X⁻ pattern, but the hydrogen bond pattern C–H···X⁻ should be overwhelming. According to reports in Ref.[36], the hydrogen in CHCl₃ should be acidic with the ability to accept charge from oxygen of triethylphosphine oxide. Durov et al. reported that the dimer O···H–CCl₃ or trimer Cl₃C–H···O···H–CCl₃ patterns between chloroform and acetone might occur [37]. These previous findings indicate that the photon in chlorinated solvent can indeed act as hydrogen bond donor [37–39].

However, the C–H vibration frequencies of CHCl₃ at 1215.6 and 3018.6 cm⁻¹ do not clearly change under experimental conditions whether adding halide or not. In contrast, C–Cl vibration frequencies of CHCl₃ at 769.0 and 669.4 cm⁻¹ decrease evidently when adding halide into the solvent. For example, the addition of Cl⁻ makes the frequency shift from 769.0 cm⁻¹ to
TABLE IV Changes of vibrational frequencies relevant bonds of solvents in the presence of halides or both halide and CBr₄⁺ (in cm⁻¹).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>νᵢ-H</th>
<th>+Cl⁻</th>
<th>+CBr₄-Cl⁻</th>
<th>+Br⁻</th>
<th>+CBr₄-Br⁻</th>
<th>+I⁻</th>
<th>+CBr₄-I⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CN</td>
<td>2944.1</td>
<td>2941.7</td>
<td>2942.6</td>
<td>2941.7</td>
<td>2942.5</td>
<td>2941.8</td>
<td>2942.4</td>
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<td></td>
<td>νᵢ-N</td>
<td>2253.2</td>
<td>2252.0</td>
<td>2252.6</td>
<td>2251.8</td>
<td>2252.5</td>
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<tr>
<td></td>
<td>δᵢ-H</td>
<td>1444.1</td>
<td>1444.1</td>
<td>1445.9</td>
<td>1445.0</td>
<td>1445.0</td>
<td>1445.1</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>νᵢ-H</td>
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<td>3053.2</td>
<td>3052.8</td>
<td>3053.8</td>
<td>3052.4</td>
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</tr>
<tr>
<td></td>
<td>νᵢ-H</td>
<td>2987.0</td>
<td>3036.6</td>
<td>3035.3</td>
<td>3036.0</td>
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<td></td>
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<td>895.2</td>
<td>894.3</td>
<td>894.8</td>
<td>894.0</td>
</tr>
<tr>
<td></td>
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<td>739.8</td>
<td>739.3</td>
<td>739.3</td>
<td>740.1</td>
<td>736.6</td>
</tr>
<tr>
<td></td>
<td>νᵢ-Cl</td>
<td>705.4</td>
<td>703.4</td>
<td>704.0</td>
<td>704.0</td>
<td>703.7</td>
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<tr>
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<td>3018.5</td>
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<td></td>
<td>δᵢ-H</td>
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<td></td>
</tr>
</tbody>
</table>

* Each datum is the average of duplicate.

756.1 cm⁻¹ in CHCl₃. As shown in Table S2 (supplementary material), the hydrogen bond CHCl₃···X causes both the C−H and C−Cl vibration frequencies changes. But in fact no obvious changes for C−H vibration frequencies are observed by FTIR spectra.

The bond length of CBr₄ and solvent molecules are obtained in Table S3 (supplementary material), the formation of halogen bond between carbon tetrabromide and halide makes the C−Br bond longer. The C−Br bond length varies from 1.944 Å to 1.957 Å. The stronger halogen bond leads to more obvious elongation. The bond lengths of solvent molecules change little. The changes of bond lengths are in agreement with the changes of vibrational frequencies.

IV. CONCLUSION

The new triangular bonding complexes CBr₄···X···H−C in solution are simulated at the MP2(full)/aug-cc-pVDZ-PP and further confirmed by UV-Vis and FTIR spectrophotometer. The strength of halogen bond and hydrogen bond involved in the complexes obeys the order of iodide>bromide>chloride, which is opposite to this sequence in gas phase. Moreover, the halogen bond and hydrogen bond in the triangular bonding complexes show weak cooperative effects. The 1:1 stoichiometry, extinction coefficients and formation constants of CBr₄ and halide are confirmed according to the Benesi-Hildebrand methodology. The halogen bond strength can be estimated through the formation constants, which is in agreement with the computational results. The interaction between the halide and solvents can also be detected by the change of C−H vibrational frequency via FTIR spectroscopy. This investigation is expected to be significant in considering the solvation of reaction process in chemistry or biology, or designing new solvation model in theory chemistry involving reactants containing halogen or halide.

**Supplementary material**: The materials on the interaction energies, computed changes of vibrational frequencies relevant to bonds of solvents in the presence of halides, the covalent bond length R of carbon tetrabromide and solvents and their change with addition of halide are available on the web.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.20675009 and No. 90922023). The basis set aug-cc-pVDZ-PP for iodine atom is downloaded at the website http://bse.pnl.gov/bse/portal.


