



# HYDROGEN BOND BETWEEN HALOFORMS AND CHLORIDES OF SILICON AND GERMANIUM IN LOW - TEMPERATURE FILMS

I. I. Grinvald,<sup>[a]</sup> I. Yu. Kalagaev,<sup>[a]</sup> A. V. Vorotyntsev,<sup>[a]</sup> A. N. Petukhov<sup>[a]</sup>  
A. I. Grushevskaya<sup>[a]</sup> R. V. Kapustin<sup>[a]</sup> and I. V. Vorotyntsev<sup>[a]</sup>

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The FTIR study allowed to reveal that a hydrogen bond can arise in low - temperature films at 20 K between chloroform, bromoform and tetrachlorides of silicon and germanium, as well as a dihydrogen bond between chloroform and trichlorosilane. The general scheme of molecular interaction was simulated by *ab initio* calculation in terms of the DFT method. It was shown that the hydrogen atom of methane halides bound with the negatively charged chlorine atom of silicon or germanium tetrachloride, accompanied by transformation of their geometry from molecular symmetry T<sub>d</sub> to C<sub>3v</sub>.

\* Corresponding Authors

Fax: +7 (831) 436 0351

E-Mail: [grinwald@mts-nn.ru](mailto:grinwald@mts-nn.ru)

[a] R. E. Alekseev Nizhny Novgorod State Technical University, 24 Minin street, 603950 Nizhny Novgorod, Russian Federation.

tribromomethane with tetrachlorosilane, tetrachlorogermane or trichlorosilane in the 20-200K interval. *Ab initio* calculation of the modeled complexes in terms of density functional theory (DFT) was carried out as well.

## Introduction

There is a big number of experimental and theoretical works devoted to different aspects of the hydrogen bond IR manifestation in the condensed phase (see for example<sup>1-3</sup>). However, most of them consider the interaction in solution of binary systems. The investigation in solid state relates basically either to the arising of a hydrogen bond in molecular crystals or the matrix isolated at low temperatures unstable species.<sup>4-6</sup> At the same time, the complex formation of the hydrogen bond in homogeneous low-temperature films remained beyond attention. Meanwhile, similar films can simulate the structure of many intermediates arising in chemical reactions. It seems that for the study of this problem the low-temperature IR study of frozen mixture, containing interacted components, is a perspective approach.

The haloforms (trichloro- and tribromomethane) are typical proton donors at hydrogen bond formation with suitable proton acceptors.<sup>7-9</sup> The silicon and germanium chlorides have a strong charge separation on the bond between the central element and the halogen atom. That can lead to the hydrogen bond formation between the negatively charged center (halogen atom) of Si- and Ge-halides and the positively charged hydrogen atom of haloforms.<sup>10</sup> On the other hand, we might expect the arising of the hydrogen bond between SiHCl<sub>3</sub> and haloforms owing the interaction of oppositely charged hydrogen atoms in these compounds.<sup>11</sup> However, mentioned types of hydrogen bond were not studied up to date.

In the recent paper, we have presented the IR findings for hydrogen bonded structures in low-temperature films, containing binary mixtures of trichloromethane or

## Experimental

For the preparation of the low-temperature films, the closed cycle optical refrigerator Displex CSE-202A (Advanced Research System Co. Inc.) with the equipment for depositing of liquid samples vapor on the cooled optical window was used. The operating procedure includes the following steps:

-The refrigerator was vacuumed up to about 10<sup>-6</sup> Pa and the films of haloform (CHCl<sub>3</sub>, CCl<sub>4</sub> and CHBr<sub>3</sub>) were deposited on a cooled optical window (NaCl).

-The samples of silicone or germanium chlorides were injected from a sealed volume, connected to the refrigerator, and deposited on the cooled haloform films.

-The ratio of components was chosen in such a way that the obtained sample had a minimal background and optimal absorption in the recorded spectral interval.

-The film was heated up to 150 K. The optical window was cooled after heating up to 20 K again.

This procedure was repeated 3 times to exclude the IR manifestation of non-equilibrium species. The refrigerator was placed in a spectrometer and the IR spectra were recorded in the 3600 – 2000 cm<sup>-1</sup> range. The purity of samples was controlled by chromatography-mass spectrometry GCMS - QP2010 Plus (Shimadzu Co. Inc.) with a vacuum samples inlet system (Valco Instruments Co. Inc.) and was not less 99 %.

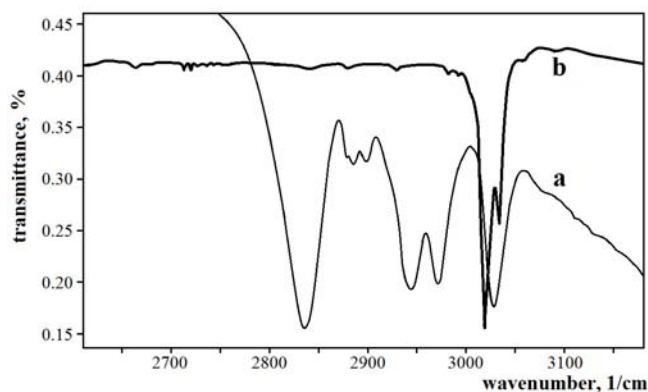
Water impurity in low-temperature films was controlled by its absorption in the 3600-3000 cm<sup>-1</sup> region and was limited to less than 5 %. The temperature of the window was operated by a computer connected supply and registered on a digital controller.

IR spectra were recorded by Fourier spectrometer FSM 1202 (Infraspec Co. Ltd.) in the case of SiCl<sub>4</sub>/CHCl<sub>3</sub>, GeCl<sub>4</sub>/CHCl<sub>3</sub>, SiCl<sub>4</sub>/CDCl<sub>3</sub>, GeCl<sub>4</sub>/CDCl<sub>3</sub> and SiHCl<sub>3</sub>/CHCl<sub>3</sub> or IR Affinity-1 (Shimadzu Co. Inc.) in the case of SiCl<sub>4</sub>/CHBr<sub>3</sub> and GeCl<sub>4</sub>/CHBr<sub>3</sub> films. Therefore the wavenumbers in the Figures presented in the text have a different order in accordance with the view in the original records of the devices. A standard installation of IR instruments was used for the spectra measurements. The resolution was 2 or 4 cm<sup>-1</sup> at 80 scans depending on the type of the spectrometer.

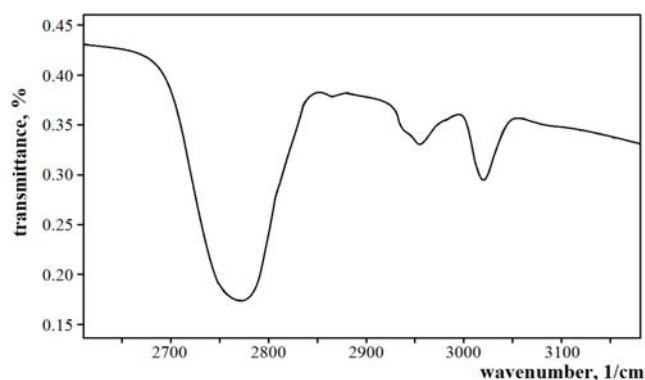
## Results and discussion

### FTIR study

Silicon and germanium tetrachloride have no IR absorption in 3600-2000 cm<sup>-1</sup> region.<sup>10</sup> In the spectra of liquid chloroform and bromoform, the band of CH stretching at about 3020 cm<sup>-1</sup> is shown. In the spectra of low-temperature films CHCl<sub>3</sub>/SiCl<sub>4</sub> recorded at 20K the new bands at 2971, 2941 cm<sup>-1</sup> (doublet), 2898, 2882 cm<sup>-1</sup> (doublet of weak bands) and a strong band at 2832 cm<sup>-1</sup> were observed (Figure 1a).



**Figure 1a.** The spectra of SiCl<sub>4</sub>/CHCl<sub>3</sub> film at 20 K (a) and pure CHCl<sub>3</sub> film at 20 K (b)

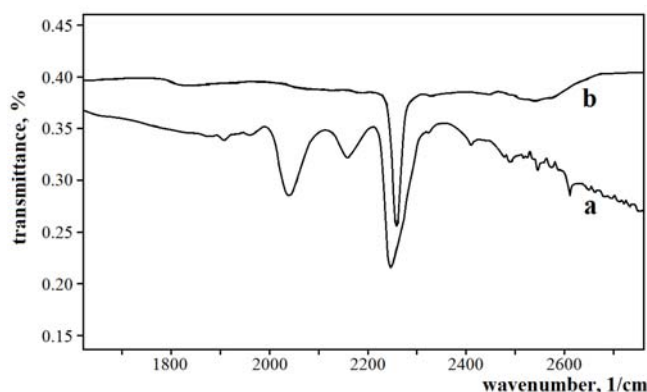


**Figure 1b.** The spectrum of GeCl<sub>4</sub>/CHCl<sub>3</sub> film at 20 K.

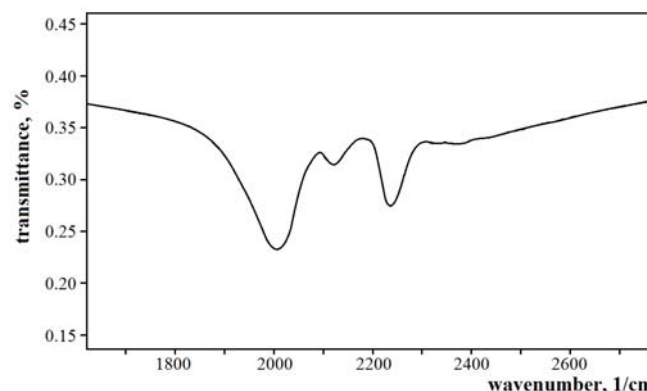
In the spectra of films, CHCl<sub>3</sub>/GeCl<sub>4</sub> recorded at the same conditions the new bands at 2954 cm<sup>-1</sup> (strong band) and 2772 cm<sup>-1</sup> (weak band) were detected (Figure 1b).

The band at 3023 cm<sup>-1</sup> in both cases belongs to CH stretching of non-bonded chloroform. These bands remained in the spectra at film heating up to 200 K, i.e. the temperature of film destruction. Besides, the spectra did not change at reversible heating of films up to 150 K and cooling to 20 K.

In the spectra of tetrachloride films deposited on the deuterated chloroform, the new bands having the expected isotopic shift were shown (Figure 2a and b). Therefore the mentioned above new bands in the spectra of SiCl<sub>4</sub>/CHCl<sub>3</sub> and GeCl<sub>4</sub>/CHCl<sub>3</sub> films were assigned to the manifestation of hydrogen bond arising between haloforms and tetrachlorides.



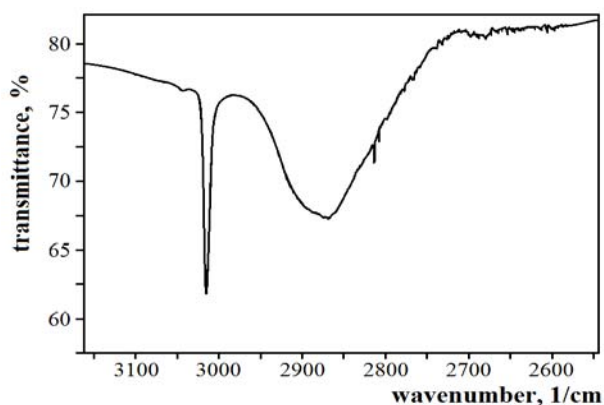
**Figure 2a.** The spectra of SiCl<sub>4</sub>/CDCl<sub>3</sub> film at 20 K (a) and pure CDCl<sub>3</sub> film at 20 K (b)



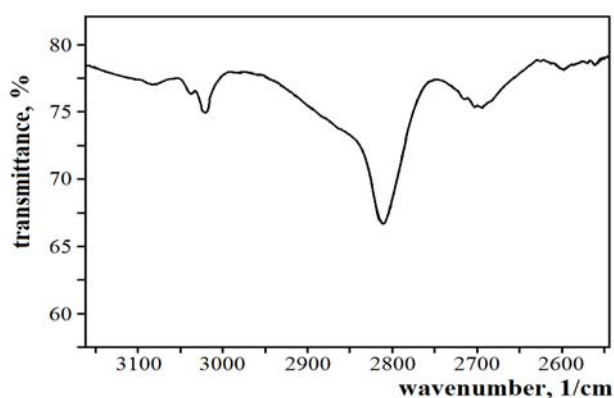
**Figure 2b.** The spectrum of GeCl<sub>4</sub>/CDCl<sub>3</sub> film at 20 K.

In the case of CHBr<sub>3</sub>/SiCl<sub>4</sub> film the typical spectral picture of hydrogen bond was observed: along with the CH stretching band of non-bonded bromoform at 3013 cm<sup>-1</sup> the wide band shifted to the lower frequencies ("red shift"<sup>22</sup>) relative to the CH stretching at 2871 cm<sup>-1</sup> was found (Figure 3a). For films CHBr<sub>3</sub>/GeCl<sub>4</sub> the similar IR manifestation of hydrogen bond was revealed, but the weak band at 2691 cm<sup>-1</sup> could be seen additionally (Figure 3b). As well as for CHCl<sub>3</sub> films the appearing bands remain in the spectra at reversible heating 20-150-20K. The band at 3013 cm<sup>-1</sup>

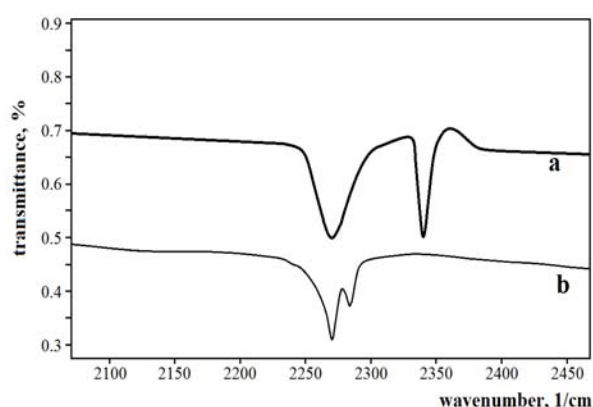
(Figure 3a) and the band at 3016 cm<sup>-1</sup> (Figure 3b) assign to CH stretching vibration of non-bonded bromoform.



**Figure 3a.** The spectrum of SiCl<sub>4</sub>/CHBr<sub>3</sub> film at 20 K.



**Figure 3b.** The spectrum of GeCl<sub>4</sub>/CHBr<sub>3</sub> film at 20 K.



**Figure 4.** The spectra of SiHCl<sub>3</sub>/CHCl<sub>3</sub> film at 20 K (a) and pure SiHCl<sub>3</sub> film at 20 K (b).

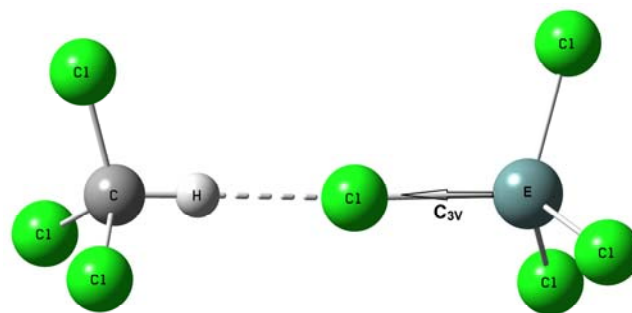
The arising of the hydrogen bond in the SiHCl<sub>3</sub>/CHCl<sub>3</sub> film causes another display in IR spectra of films deposited at 20 K (Figure 4). The new band at 2341 cm<sup>-1</sup> locates close to the SiH stretching vibration in pure SiHCl<sub>3</sub> (2271 cm<sup>-1</sup>) and has a “blue shift”<sup>2</sup> relatives to this one. In the case of interaction between tetrachlorides and haloforms, the hydrogen bond can exist between negatively charged chlorine atom of tetrachloride and the positively charged hydrogen atom of haloforms only.

The trichlorosilane has at least two acceptor centers for the hydrogen atom of the chloroform binding: the chlorine atom and the negatively charged hydrogen atom of trichlorosilane.<sup>10</sup> The position of the new band and its shift relative to SiH stretching corresponds to the mixed (CH<sup>δ+</sup>...<sup>δ-</sup>HSi) stretching vibration of the dihydrogen bond.<sup>2</sup>

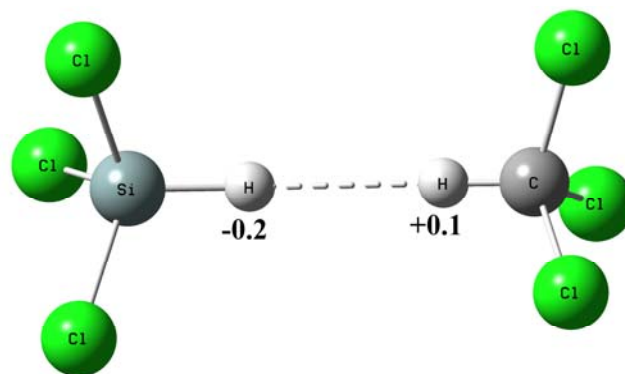
#### DFT study

*Ab initio* calculation was carried out in terms of density functional theory (DFT),<sup>12</sup> realized in the computer program GAUSSIAN 09.<sup>13</sup> The main molecular characteristics were obtained using the B3LYP functional and the 6-311++G(2d,2p) basis set.<sup>14</sup> The DFT calculation for the interacting molecules in the condensed phase should be taken as an approximate model only, in the first regard, because a single electron approximation is not suitable for similar systems.<sup>14</sup> Therefore the quantitative agreement between the calculated and experimental data can hardly be expected. It is particularly true for the theoretically predicted geometry and electronic parameters as well as for the vibration frequencies of hydrogen bonded complexes to be investigated. Hopefully, this calculation allows imagining the general scheme of hydrogen bond formation in low-temperature films.

The computational procedure predicts the light transition of tetrachlorides geometry from T<sub>d</sub> molecular symmetry to C<sub>3v</sub> shape. This transformation needs energy less than 12.5 kJ mol<sup>-1</sup>. Therefore the most stable state of intermediates in the case of tetrachlorides and haloforms interaction corresponds to the structure, presented in Figure 5a



**Figure 5a.** The calculated geometry and charges of atoms for tetrachlorides (E=Si or Ge) - chloroform complexes.



**Figure 5b** The calculated geometry and charges of atoms for trichlorosilane – chloroform hydrogen bonded complex.

In the case of SiHCl<sub>3</sub>/CHCl<sub>3</sub> system the hydrogen bond forms between oppositely charged hydrogen atoms of components. The structure of this complex, as well as the charges of the interacting hydrogen atoms, are shown in Figure 5b.

On the whole FTIR and DFT study confirm the arising of a hydrogen bond between haloforms and chlorides of silicon and germanium. The DFT calculation predicts a linear geometry of molecular coordination. The halogen atom of tetrachloride or hydrogen atom of trichlorosilane locates on the C<sub>3v</sub> axis of complexes. The few bands, which were revealed in low-temperature films of investigated species, can be considered as the manifestation of less stable hydrogen-bonded structures with another geometry.

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