Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.




# Supporting Information

for

## Chloronium ions, R-$Cl^+$-R (R = $CH_3$ or $CH_2Cl$): formation, thermal stability and interaction with chloromethanes

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## 1. Supplemental Figures

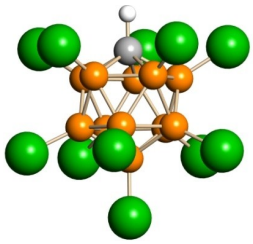

Figure S1. Icosahedral carborane anion $CHB_{11}Cl_{11}^-$ used in this work (abbrev. $\{X_{11}^-\}$.

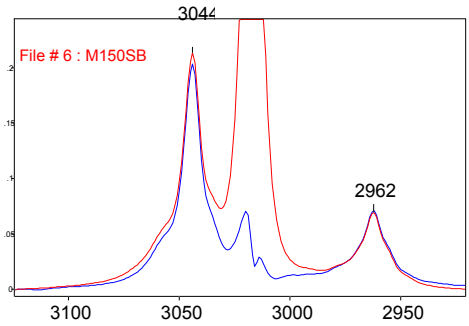


Figure S2. IR spectrum of $(CD_3\text{-}Cl^+\text{-}CH_2Cl)\{Cl_{11}^-\}$ salt in the frequency region of C-H stretches. Initial spectrum (red) and with subtraction of the νCH band at 3017 $cm^{-1}$ from $\{Cl_{11}^-\}$ anion (blue), using the spectrum of the salt $(CD_3\text{-}Cl^+\text{-}CD_2Cl)$ $\{Cl_{11}^-\}$.

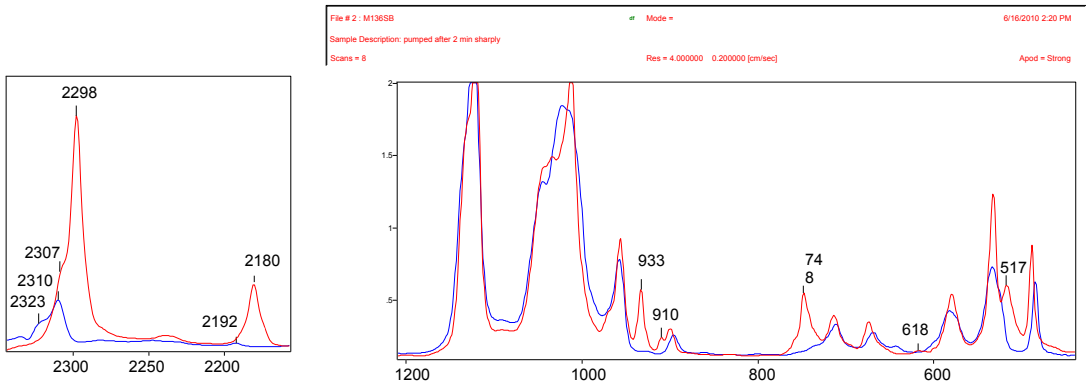


Figure S3. IR spectrum of the salt $(CD_3\text{-}Cl^+\text{-}CD_2Cl)\{Cl_{11}^-\}$ (red) compared with that of initial $CD_3\text{-}\{Cl_{11}\}$ (blue)

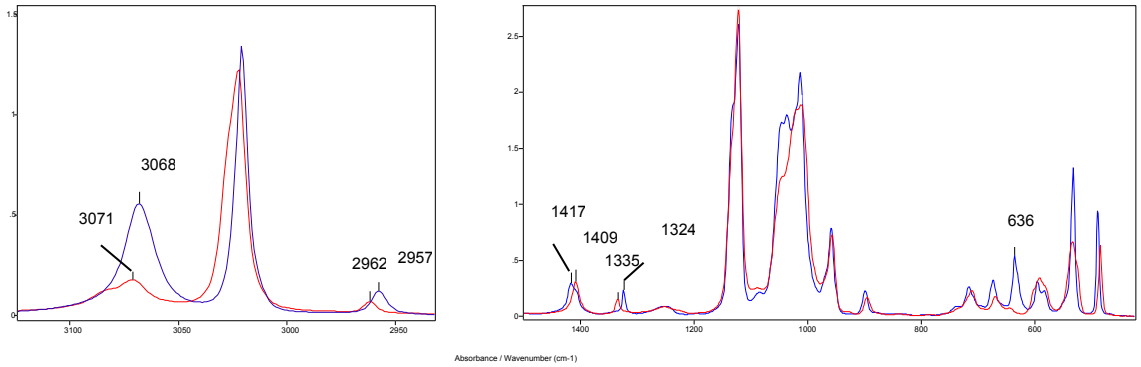


Figure S4. IR spectra of the salts $CH_3\{Cl_{11}\}$ (red) and $(CH_3)_2Cl^+\{Cl_{11}^-\}$ (blue).

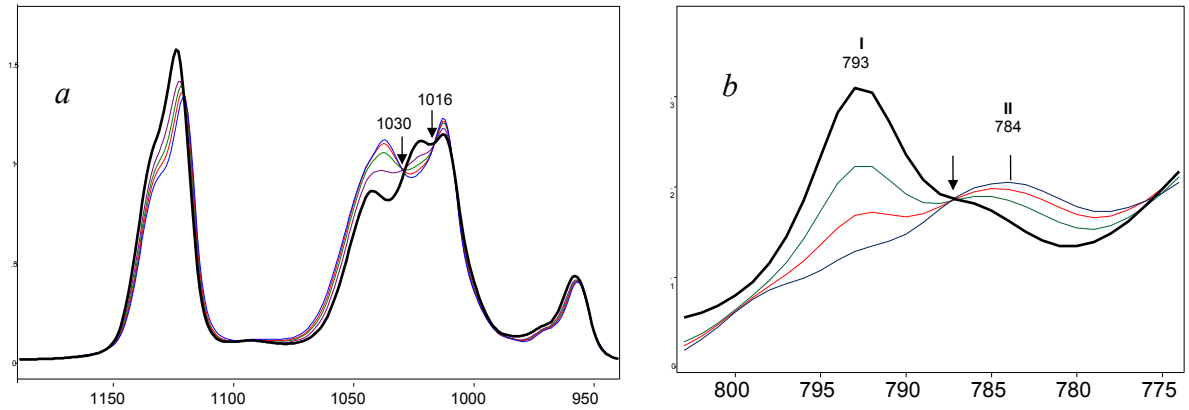


Figure S5. Change in intensity of the IR spectra of compounds $CH_2Cl\text{-}\{Cl_{11}\}$ and $CH_2Cl\text{-}Cl^+\text{-}CH_2Cl\{Cl_{11}\}$ as the reaction (5) proceeds in the frequency range of anion (*a*) and νCCl vibrations of $CH_2Cl$ groups (*b* ).

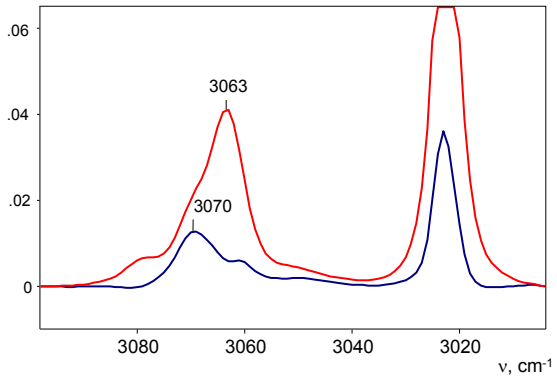


Figure S6. The initial IR spectrum of the mixture $CH_2Cl\{Cl_{11}\}$ + $CH_3\{Cl_{11}\}$ (red; point 18 in Figure 13) and after subtraction of the spectrum of $CH_2Cl\{Cl_{11}\}$ resulting in isolation of the spectrum of $CH_3\{Cl_{11}\}$ (blue).

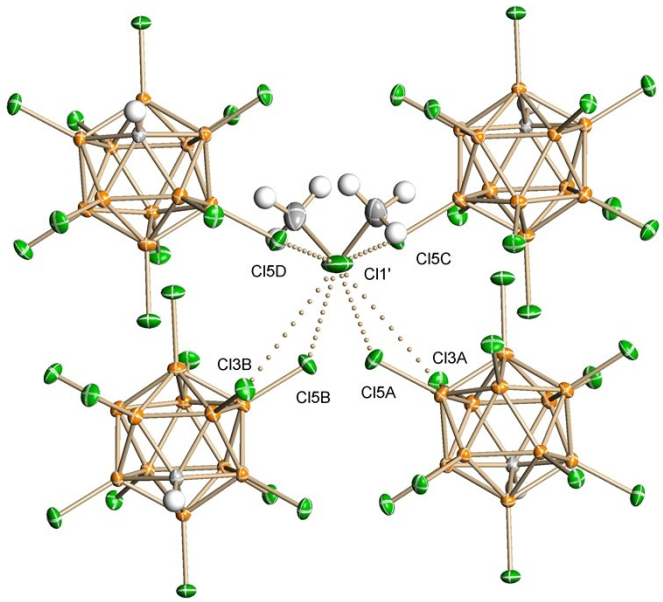


Figure S7. Crystal structure of the $(CH_3\text{-}Cl^+\text{-}CH_3)\{Cl_{11}^-\}$ salt [from the results of previous work E. S. Stoyanov, I.V. Stoyanova, F.S. Tham and C. A. Reed, *J. Am. Chem. Soc.,* 2010, 132**,** 4062], showing the shortest distances between chloronium Cl1 atom and Cl atoms of the neighboring anions.
Distances are: Cl1-Cl3A and Cl1-Cl3B 3.623 Å; Cl1-Cl5A and Cl1-Cl5B 3.837 Å; Cl1-Cl5C and Cl1-Cl5D 3.861 Å.

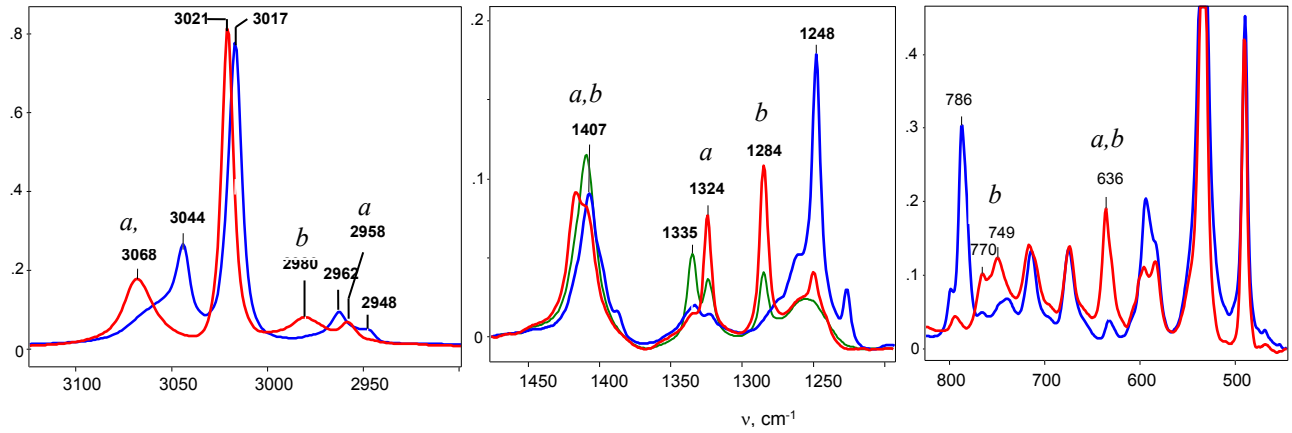


Figure S8. IR spectra of the salt $(CH_3\text{-}Cl^+\text{-}CH_2Cl)\{Cl_{11}^-\}$ before (blue) and after heating for 5 minutes at 100 °C (red) and 150 °C (green). The most characteristic frequencies of the $(CH_3)_2Cl^+$ cation are marked with (a), and of cation $(CH_2Cl)_2Cl^+$ (**IIa**) with (*b*).

## 2. Supplemental Tables

Table S1. IR frequencies of the $CD_2Cl$- and bridged C-$Cl^+$-C groups of the studied compounds in comparison with IR spectrum of $CD_2Cl_2$

| Compound | $\nu_{as}CD_2$ | $\nu_sCD_2$ | $\delta CD_2$ scissor | $\delta CD_2$ waggle | $\nu_{as}CCl_2$, $\nu CCl$ | $\nu_{as}$(CClC) |
|---|---|---|---|---|---|---|
| $CD_2Cl_2$ (liquid) [1] | 2304 | 2198 | 1052 | 955 vs | 711 vs | - |
| $CD_2Cl$-{$Cl_{11}$} | 2311 | 2188 | * | 911 vs | 755 m | - |
| $ClD_2C$-$Cl^+$-$CD_2Cl$ | 2298 | 2181 | * | 933 899 | 747 | 580 514 |
| $ClD_2C$-$Cl^+$-$CH_3$ | 2297 | 2240 2180 | * | 910 | 750 | 632 |

* Overlapped with strong absorption from {$Cl_{11}^-$} anion.

[1] B. F. E. Palma, E. A. Piotrowski, S. Sundaram and F. F. Cleveland. *J. Mol. Spectroscopy*, 1964, 13, 119.

Table S2. IR frequency comparison for most characteristic band of $CH_3$-$Cl^+$-$CH_2Cl$ and $CD_3$-$Cl^+$-$CD_2Cl$ cations

| Compound | $\nu_{as}CX_3$ | $\nu_{as}CX_2$ | $\nu_sCX_2$ | $\nu_sCX_3$ | $\delta CX_2$ waggle | | $\nu CCl$ | $\nu_{as}$(CClC) |
|---|---|---|---|---|---|---|---|---|
| **$CH_3$-$Cl^+$-$CH_2Cl$** | 3058 | 3044 | 2962 | 2948 | 1248 | 1226 | 786 | 632 |
| **$CD_3$-$Cl^+$-$CD_2Cl$** | 2307 | 2298 | 2180 | 2174 | 933 | 910 | 748 | 618w |
| H/D | 1.325 | 1.324 | 1.36 | 1.36 | 1.34 | 1.35 | 1.05 | 1.022 |