Stabilization of carbocations CH$_3^+$, C$_2$H$_5^+$, i-C$_3$H$_7^+$, tert-Bu$^+$, and cyclo-pentyl$^+$ in solid phases: experimental data versus calculations$^\dagger$

Evgenii S. Stoyanov$^{a,b}$ and Anton S. Nizovtsev$^{b,c}$

Comparison of experimental infrared (IR) spectra of the simplest carbocations (with the weakest carborane counterions in terms of basicity, CHB$_2$Hal$_{-}$, Hal = F, Cl) with their calculated IR spectra revealed that they are completely inconsistent, as previously reported for the t-Bu$^+$ cation [Stoyanov E. S., et al. J. Phys. Chem. A, 2015, 119, 8619]. This means that the generally accepted explanation of hyperconjugative stabilization of the carbocations should be revised. According to the theory, one CH bond (denoted as CH$^s$) from each CH$_3$/CH$_2$ group transfers its $\sigma$-electron density to the empty 2p$_z$ orbital of the sp$^2$ C atom, whereas the $\sigma$-electron density on the other CH bonds of the CH$_2$/CH$_3$ group slightly increases. From experimental IR spectra it follows that donation of the $\sigma$-electrons from the CH$^s$ bond to the 2p$_z$ C-orbital is accompanied by equal withdrawal of the electron density from other CH bonds, that is, the electrons are supplied from each CH bond of the CH$_3$/CH$_2$ group. As a result, all CH stretches of the group are red shifted, and IR spectra show typical CH$_2$/CH$_3$ group vibrations. Experimental findings provided another clue to the electron distribution in the hydrocarbon cations and showed that the standard computational techniques do not allow researchers to explain a number of recently established features of the molecular state of hydrocarbon cations.

Most attention has been given to the tert-butyl cation, whose hyperconjugative delocalization of the positive charge has been used as a textbook explanation of its stability. As predicted by quantum chemical calculations, the most energetically stable t-Bu$^+$ cation ($C_2$ symmetry) has three CH bonds, one from each CH$_3$ group, which are aligned in parallel with the empty 2p$_z$ orbital of the central sp$^2$ carbon atom.1,16–20 This situation makes donation of its $\sigma$-electron density to this orbital possible, resulting in $\sigma$-p$_z$ hyperconjugation (Scheme 1). These three C–H bonds (one of them is marked with $\bullet$ in Scheme 1) are weakened and their $\nu$CH frequencies are significantly decreased, whereas the remaining C–H bonds (CH$'$ and CH$''$ in Scheme 1) are slightly strengthened and their $\nu$CH increases.

Thus, ab initio calculations predict a coherent picture of the mechanism underlying positive charge dispersion in the naked cations C$_2$H$_5^+$, (CH$_3$)$_2$CH$^+$ (i-Pr$^+$), and (CH$_3$)$_3$C$^+$ (t-Bu$^+$) primarily

\begin{center}
\textbf{Scheme 1} Schematic representation of the electron density redistribution in accordance with the classical understanding of the mechanism of hyperconjugation stabilization in t-Bu$^+$.\end{center}

![Scheme 1](image-url)

**Introduction**

The research on carbocation stabilization is one of the most important trends in carbocation chemistry. Experimental studies mainly deal with gas phase infrared (IR) mass spectroscopy,1–4 IR and NMR characterization in superacidic media,5–12 and X-ray structural analysis.13–17 As shown by ab initio calculations, the isolated carbocations are stabilized due to the intramolecular charge distribution under the influence of hyperconjugation$^{1,18–22}$ and polarization.23 The simplest carbocation, CH$_3^+$, is subject to only the polarization effect.23 For the gaseous C$_2$H$_5^+$ cation, the theory predicts and experiments confirm that the hyperconjugative interaction between the CH$_3$ and the empty 2p$_z$ orbital in the carbon atom of the CH$_2$ group is so strong that a bridged-proton symmetrical structure is formed.2 The isolated i-propyl (i-Pr$^+$) cation has been the subject of extensive ab initio calculations.24–27 In its lowest-energy C$_2$ conformer, two C–H bonds are aligned with the up and down lobes of the 2p$_z$ orbital of the sp$^2$ C-atom, suggesting that these C–H bonds are involved in strong hyperconjugation.

$^\dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cp06839a

$^a$ Vorozhtsov Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk 630090, Russia. E-mail: evgenii@nioch.nsc.ru

$^b$ Department of Natural Sciences, National Research University, Novosibirsk State University, Novosibirsk 630090, Russia

$^c$ Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk 630090, Russia

$^\dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cp06839a
via the hyperconjugative effect. It is clear that the polarization effect must play an important role in cation stabilization although convincing data based on calculations are actually absent.

Our recent experimental study of the t-Bu⁺ cation in condensed phases, together with interpreted IR spectra of gaseous t-Bu⁺, showed that empirical findings contradict the generally accepted hyperconjugation mechanism (Scheme 1). It follows from the experiments that all C–H bonds of the two CH₃ groups of t-Bu⁺ donate σ-electrons to the carbon's 2pₓ orbital (Scheme 2), and the third CH₃ group is mostly affected by polarization.

It should be noted that in condensed phases, there is an additional intermolecular effect of carbocation stabilization: hydrogen bonding with the immediate surroundings. It leads to the strengthening of hyperconjugation and contributes to the scattering of the positive charge to the environment.17,28

In the present work we expanded the comparison of the computational results explaining stabilization of carbocations (structurally optimized and having the lowest energy) with empirical findings in IR spectra of carbocations in the series CH₃⁺, C₂H₅⁺, i-C₃H₇⁺, t-Bu⁺, and cyclo-C₃H₅⁺, with the carbocene counterions (CHB₃t-Hal₁₁⁻, Hal = F, Cl; hereinafter abbreviated as {Hal₁₁⁻}, see Fig. 1), whose conjugated acids are the strongest pure Bronsted superacids available today.29,30 We established that IR spectra of {F₁₁⁻} or {Cl₁₁⁻} in ionic carbocation salts are not dependent on the nature of the cation and therefore are not considered here. The aims of the present study were (i) to determine whether t-Bu⁺ is a special case of a cation or a common representative of saturated carbocations and (ii) to verify the compatibility of the theoretical data with experimental results for a range of simplest carbocations. We focused on the C–H stretch vibrations because they are mostly sensitive to hyperconjugation and polarization effects. Despite the importance of intermolecular hydrogen bonding for carbocation stabilization in the condensed phase, this effect will not be examined here in detail because it does not change the hyperconjugation mechanism when going from vacuum to a condensed phase as shown previously.17,28

Experimental

All sample handling was carried out in an inert atmosphere (H₂O, O₂ < 1 ppm) in a dry box. Carbocene acids H{Hal₁₁⁻} and their CH₃{Hal₁₁⁻} salts were prepared as previously described.30–33 The salts of C₂H₅⁺ and C₃H₇⁺ cations with the {F₁₁⁻} anion were obtained by reacting CH₂F with H{F₁₁} in an IR cell-reactor with simultaneous recording of the IR spectra of the formed cations.33

The spectrum of the C₃H₅⁺{F₁₁⁻} salt was also obtained in another way: instead of the H{F₁₁} acid, Et₃Si{F₁₁} was used, synthesized as described in ref. 30. A small drop of liquid 2-Cl-propane was added to an excess of solid Et₃Si{F₁₁} placed on the surface of the diamond attenuated total reflectance (ATR) accessory. A rapid reaction takes place

\[
\text{Et}_3\text{Si}\{\text{F}_{11}\} + \text{C}_3\text{H}_7\text{Cl} \rightarrow \text{C}_3\text{H}_7\{\text{F}_{11}\} + \text{Et}_3\text{SiCl}^+, \tag{1}
\]

and gaseous Et₃SiCl is quickly removed. An ATR spectrum of the formed solid revealed strong absorption of the i-C₃H₇⁺{F₁₁⁻} salt and weak absorption of unreacted (excess) Et₃Si{F₁₁}.

Computer subtraction of the weak spectrum of residual Et₃Si{F₁₁} allowed us to obtain a high quality spectrum of the i-C₃H₇⁺{F₁₁⁻} salt.

The cyclo-C₃H₅⁺{F₁₁⁻} salt was obtained by means of direct interaction of liquid cyclo-pentane with a powder of H{F₁₁} in accordance with eqn (2):

\[
\text{cyclo-C}_3\text{H}_{10} + \text{H}\{\text{F}_{11}\} \rightarrow \text{C}_3\text{H}_7\{\text{F}_{11}\}^+ + \text{H}_2 \tag{2}
\]

It was reported that all alkanes, CₙHₙ⁺ (n ≥ 4), react with the H{F₁₁} acid in the same way. Reaction (2) proceeded under ambient conditions for 4 hours. A white powder of the C₃H₇⁺{F₁₁⁻} salt was obtained from the solution after vacuum removal of the solvent, cyclo-pentane.

IR spectra of isopropyl and cyclo-pentyl carbocations with the {Cl₁₁⁻} counterion were obtained as follows. A grain of the H{Cl₁₁} acid was placed on the top face of the diamond crystal of the attenuated total reflectance (ATR) IR accessory and was wetted with a small drop of liquid 2-chloropropane or chloro-cyclo-pentane; this amount was not sufficient for full acid utilization. This approach ensures stoppage of the reaction at the first-stage, as illustrated in eqn (3) (an example of preparation of the i-Pr⁺ salt):

\[
\text{C}_3\text{H}_7\text{Cl} + \text{H}\{\text{Cl}_{11}\} \rightarrow \text{C}_3\text{H}_7\{\text{Cl}_{11}\}^- + \text{HCl}. \tag{3}
\]

Recording the spectrum without applied pressure allowed us to obtain the spectrum of the oily byproduct covering the diamond surface as a thin film. This byproduct is formed when an excess of the chlorine hydrocarbon interacts with an acid. Recording the spectrum of the solid particles crushed under pressure, which contained mainly the carbocation salt and an excess of unreacted acid, enabled us to obtain their spectra with a minor overlap with the spectrum of byproducts. Computer-based subtraction of the spectrum of the byproducts and excess acid allowed for isolation of the carbocation spectra.

IR spectra were recorded on a Perkin Elmer Spectrum-100 spectrometer in the 4000–400 cm⁻¹ frequency range in transmission or ATR mode. The spectrometer was installed inside
the dry box. The spectra were manipulated using GRAMS/AI (7.00) software from Thermo Scientific.

**Computational details**

Geometric parameters of the species under study were optimized at the B3LYP-D3/def2-TZVPD level of theory, using ultrafine grids. Equilibrium structures of compounds R{F11} and t-Bu{Cl11} were also calculated in a dichloroethane (DCE) solution (ε = 10.125) using the SMD solvation model. All stationary points were characterized as minima by a vibrational analysis (the number of imaginary frequencies |Nimag| was equal to zero), unless stated otherwise. Zero-point energies (ZPEs) were computed from the corresponding vibrational frequencies without scaling factors. (SMD-)B3LYP-D3/def2-TZVPD optimized structures were used in all subsequent computations.

To compare calculated and experimental vibrational frequencies, (SMD-)B3LYP-D3/def2-TZVPD harmonic frequencies were scaled by a factor of 0.9674 as recommended by Kesharwani et al. To obtain more accurate relative energies of some isomers, single-point high-level CCSD(T)/def2-TZVPD coupled-cluster computations within a frozen core approximation were additionally performed.

The energy decomposition analysis (EDA) was carried out for the most stable compounds at the B3LYP-D3/TZ2P level of theory using the scalar relativistic (SR) zeroth-order regular approximation (ZORA) Hamiltonian (core potentials were not used, and the quality of the Becke numerical integration grid was set to the keyword good).

SR-ZORA-B3LYP-D3/TZ2P computations were performed using the ADF2016 software, while the remaining gas-phase calculations in the gas phase and in a DCE solution were conducted using the Gaussian09 software. The natural bond orbital (NBO) analysis was performed for the species of interest as implemented in Gaussian09, def2-TZVPD basis sets were taken from the EMSL database.

Density functional theory (DFT) calculations with periodic boundary conditions were performed using the PBE functional with D3 dispersion correction using the VASP software package. The projector augmented wave (PAW) method was used to analyze the core states along with a plane-wave energy cutoff of 400 eV. Only the 1s core orbitals were scaled by a factor of 0.9674 as recommended by Kesharwani et al.

**Results and discussion**

**Characterization of carbocations on the basis of calculations**

To obtain a unified computational view, we considered all carbocations (R') under study and their complexes with Ar and {F11} in the gas phase and in solution at the same level of theory. The lowest-energy structures were chosen for subsequent analysis (see Fig. S1–S4 in ESI† for a complete list of isomers). The results obtained for the R', R'·Ar and R{F11} species are given in Tables S1–S5 in ESI†. The stretching vibrations and some valent angles for naked and solvated carbocations are compared in Table 1.

The hyperconjugation effect is assumed to be the case starting from naked C2H5+. In this cation, the hyperconjugation strength is so significant that the H+ proton is converted to the bridge state leading to a symmetrical structure (II.1 in Fig. S1 in ESI†), which does exist in the condensed phase. Thus, we excluded the bridged structure from further analyses.

The C2H5+ structure becomes asymmetrical after solvation by the Ar atom via the C center. The CH4+ bond is oriented strictly parallel to the 2p orbital of the sp² C atom (θ = 0, see Scheme 3) and the C−C−H* angle is reduced (92.6°, Table 1); these data indicate a strong hyperconjugative interaction. The similar orientation of the CH4+ bond from each CH3 group relative to the 2p orbital of the sp² C atom has only naked t-Bu+ (Cn, θ = 2°) and t-Bu+'-Ar solvate (Cn, θ = 1°). This finding corresponds to the generally accepted mechanism of carbocation hyperconjugation stabilization (Scheme 1). Nevertheless, the θ angles of t-Bu+ (C1), despite almost the same relative energy as in t-Bu+ (C1), are increased by ca. 20°. The θ angle reaches values of 36° and 20° for the low-lying isomers of t-Pr+ (C9) and i-Pr+·Ar (C9), respectively (Fig. S2 and S3 in ESI†); which means that one C–H bond from each CH3 group is perpendicular to the vacant 2p orbital, and two other C–H bonds are equivalently affected by hyperconjugation (Scheme 4). An intermediate case takes place in c-C3H7+ and c-C3H7+·Ar species, with θ ranging from 12° to 13°. Thus, rotation of the CH3 group by angle θ has a weak influence on the carbocation hyperconjugation stabilization.

The strong hyperconjugation influence on the CH3 group in asymmetric C2H5+·Ar (Scheme 3) leads to a strong decrease in the CH4+ stretch to 2612 cm⁻¹, whereas frequencies of the other two CH and CH⁻ bonds (c-CH2) are changed much less as compared to neutral hydrocarbons (Table 1). The CH4+ and CH2 frequencies are highly characteristic and are not mixed (Fig. S5 in ESI†). Unlike C2H5+, solvation of other carbocations with Ar via the sp² C atom has a slight effect on the calculated IR spectra (Table 1). The spectra of all carbocations under study (both naked and solvated with Ar) show similar features: (i) the bands of C–H stretches affected by hyperconjugation are significantly red shifted and have increased intensity (bold faced in Table 1); (ii) frequencies of the other C–H bonds of CH2/CH2 groups are rather increased or are in the frequency region common for neutral hydrocarbons; (iii) the normal vibrations of these bonds or groups have a highly characteristic nature.

To gain insights into the bonding situation for the representative R'·Ar and R{F11} complexes, we performed the EDA (Table S1 in ESI†) and NBO analyses (Table S2 in ESI†). The results of our gas-phase calculations for the carbocations paired with the {F11} anion indicate the following: (a) in the case of R = C2H5+, the hyperconjugation effect is the weakest one because of a covalent bond between ethyl and {F11} leading to a modest energy gain corresponding to hyperconjugative stabilization (∆E_y = 9.2 kcal mol⁻¹; Table S2, ESI†) and rather weak IR intensity of
Table 1  CH stretch frequencies (scaled by a factor of 0.9674) and their IR intensities (km mol⁻¹; in parentheses) calculated at the B3LYP-D3/def2-TZVPD level of theory for the most energetically stable naked and Ar-solvated carbocations. Relevant structural parameters are also given.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C₂H₅⁺–Ar</th>
<th>i-Pr⁺</th>
<th>i-Pr⁺–Ar</th>
<th>t-Bu⁺</th>
<th>t-Bu⁺–Ar</th>
<th>c-C₅H₅⁺</th>
<th>c-C₅H₅⁺Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>Cₓ</td>
<td>C₂</td>
<td>C₂v</td>
<td>C₁</td>
<td>C₁</td>
<td>C₁</td>
<td>C₁</td>
</tr>
<tr>
<td>NImag</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Relative energy, kcal mol⁻¹</td>
<td>0</td>
<td>0.2</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dihedral angle, degrees</td>
<td>17</td>
<td>36</td>
<td>13</td>
<td>20</td>
<td>21</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Scaled CH stretches, cm⁻¹

<table>
<thead>
<tr>
<th>Compounds</th>
<th>2612</th>
<th>2764</th>
<th>2841</th>
<th>2766</th>
<th>2803</th>
<th>2835</th>
<th>2840</th>
<th>2852</th>
<th>2871</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cₓ</td>
<td>154</td>
<td>224</td>
<td>239</td>
<td>145</td>
<td>143</td>
<td>91</td>
<td>109</td>
<td>19</td>
<td>33</td>
</tr>
<tr>
<td>C₂</td>
<td>2777</td>
<td>2855</td>
<td>2799</td>
<td>2815</td>
<td>2864</td>
<td>2838</td>
<td>2843</td>
<td>2881</td>
<td>2855</td>
</tr>
<tr>
<td>C₂v</td>
<td>2985</td>
<td>3024</td>
<td>3032</td>
<td>3071</td>
<td>3058</td>
<td>3007</td>
<td>3042</td>
<td>3042</td>
<td>3042</td>
</tr>
<tr>
<td>C₁</td>
<td>3052</td>
<td>3068</td>
<td>3069</td>
<td>3059</td>
<td>3050</td>
<td>3007</td>
<td>3047</td>
<td>3042</td>
<td>3042</td>
</tr>
<tr>
<td>C₁v</td>
<td>2938</td>
<td>2960</td>
<td>2933</td>
<td>2973</td>
<td>2904</td>
<td>2973</td>
<td>2973</td>
<td>2973</td>
<td>2973</td>
</tr>
<tr>
<td>C₁</td>
<td>3292</td>
<td>3292</td>
<td>3292</td>
<td>2977</td>
<td>2981</td>
<td>2972</td>
<td>2984</td>
<td>2986</td>
<td>2986</td>
</tr>
<tr>
<td>C₁</td>
<td>3024</td>
<td>3032</td>
<td>3069</td>
<td>3059</td>
<td>3058</td>
<td>3069</td>
<td>3069</td>
<td>3069</td>
<td>3069</td>
</tr>
<tr>
<td>C₁v</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
</tr>
<tr>
<td>C₁</td>
<td>3098</td>
<td>3098</td>
<td>3098</td>
<td>3098</td>
<td>3098</td>
<td>3098</td>
<td>3098</td>
<td>3098</td>
<td>3098</td>
</tr>
<tr>
<td>C₁v</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
<td>3032</td>
</tr>
</tbody>
</table>

a E[CCSD(T)/def2-TZVPD/B3LYP-D3/def2-TZVPD] + ZPE(B3LYP-D3/def2-TZVPD). The θ angle is shown in Scheme 3. Averaged values of angle θ are presented. The characteristic frequencies of C–H bonds mostly affected by hyperconjugation are boldfaced.

The corresponding CH stretch vibration (Table S4, ESI†); (b) the spectrum of i-Pr⁺ (Table S4 in ESI†) shows only some signs of weak hyperconjugation (two slightly decreased frequencies at 2923 and 2916 cm⁻¹ with somewhat increased intensity), suggesting that the bonding between i-Pr and [F₁₁⁻] moieties is still covalent (ΔEorb = 11.7 kcal mol⁻¹; Table S2, ESI†); (c) the spectra of cyclo-pentyl¹ and t-Bu⁺ (Table S4 in ESI†) show greater resemblance to those of the corresponding Ar-solvated cations, as compared to the lighter carbocations.

NBO analysis revealed a polar covalent two-center two-electron C–F bond populated by 2.0 e⁻ at R = CH₃, C₂H₅, and i-Pr. Indeed, according to theEDA (Table S1 in ESI†), the electrostatic interaction (ΔEelstat, 52–79%) between R⁺ and {F₁₁⁻} moieties dominates over orbital (ΔEorb) and dispersion (ΔEdisp) interactions in all compounds. On the other hand, the energy of orbital interactions makes a noticeable contribution to the total attractive interactions when R = CH₃ (47%), C₂H₅ (42%), and i-Pr (34%), in line with the calculated IR spectra. Thus, a covalent contribution to the C–F bond is present in all cases and gradually decreases in the order R = CH₃ < C₂H₅ < i-Pr < cyclo-pentyl ≤ t-Bu simultaneously with the increase of hyperconjugative stabilization in the same order as can be seen from the corresponding ΔEelstat values (Table S2, ESI†).

However, as will be illustrated below, all solid R[F₁₁⁻] compounds, except for CH₃[F₁₁⁻], are characterized by ionic bonding. The reason is the bulk effect, which most clearly manifests itself in the example of alkali halides. They are ionic in the solid state, but their neutral diatomics are linked covalently in the gas phase showing stretch vibration (for example, r-Na–Cl at 364.6 cm⁻¹). So, the crystal lattice promotes ionic binding.

To model the effect of the environment taking place in the condensed phase, we performed NBO and EDA analyses of the R[F₁₁⁻] species when they are transferred from the gas phase to a DCE solution. This change of the phase is accompanied by an increase of the R–[F₁₁⁻] distance (Tables S1 and S2, ESI†), which is relatively small for R = CH₃ (Δr = 0.033 Å) and pronounced when R = C₂H₅ (Δr = 0.120 Å), making the C–F bond more polar but retaining its covalent nature (ΔEelstat, 38–48%). In the case of i-C₃H₇[F₁₁⁻], the lengthening of C–F is the most pronounced (Δr = 0.064 Å), indicating that the character of the bond changes to presumably ionic (ΔEelstat, 16%; ΔEelstat, 78%). Replacing i-C₃H₇⁺ with c-C₅H₅⁺ further increased the C–F separation to 2.584 Å, increasing the ionicity of the bond (ΔEelstat 12%). Finally, the t-C₅H₅⁺[F₁₁⁻] compound has the C–F distance typical for ionic species (>2.6 Å, ΔEelstat 11%; Table S4, ESI†). Similar results were obtained in SMD-B3LYP-D3/def2-TZVPD calculations for...
DCE solutions: the dielectric medium increased the separation between R and {Hal11} fragments (Fig. S4, ESI†), which made C–Hal bonds more ionic. The C–Cl distance in t-Bu{Cl11} became very close to that in an ionic salt (3.545 Å, Fig. S6, ESI†), resulting in a small covalent contribution—to the bonding between the ions (ΔE_{coval} 14%; Table S1, ESI†)—approaching that in the solid phase. The calculated CH stretch frequencies for both phases also correlate well (Table S5, ESI†).

Increasing the ionicity of the R{F11} compounds in the series R = C2H5 < i-Pr < cyclo-pentyl < t-Bu strengthens the effect of hyperconjugation, as followed from the corresponding ΔE_y values (Table S2, ESI†) and from the increase in the red-shift and intensity of the bands of CH stretches involved in hyperconjugation (Table S4, ESI†). It should be noted that the condensed phase enhances both ionicity and the effect of hyperconjugation in this series of R{F11} compounds gradually; this result contradicts experimental findings.

We have proved previously\textsuperscript{26} that “effective” basicity of {F11} in the solid salt, (HCO){[F11]}, is close to the basicity of the Ar atom, and the calculated spectra of the Ar–H+–CO and CO–H+–Ar solvates agree well with the experimental spectra of ionic compound (CO)H+[F11]. Therefore, the experimental IR spectra of the ionic bulk salts under study are expected to better match the calculated IR spectra of weakly bound R–Ar solvates rather than R–{F11} species with a notable covalent contribution (Table S1 in ESI†). The same conclusion follows from DFT calculations for t-Bu{Cl11}: the structure of t-Bu+ in the t-Bu{Cl11} crystal (Fig. S7 in ESI†) is similar to that in the naked or Ar-solvated carbocation rather than to the structure of molecular compound t-Bu{Cl11} with a distorted t-Bu+ moiety (Fig. S6a in ESI†). To sum up, computational results obtained for R–Ar (or naked R+) should be used for comparison with the presented experimental findings.

Experimental IR spectra and properties of the carbcations

The CH\textsuperscript{+} cation has an extremely high ability to bind to the bases. Even in the CH\textsubscript{3}{[F11]} compound with the weakest basic ion {F11}, the methyl group forms a highly polar covalent bond.\textsuperscript{33}

The CH\textsuperscript{+} cation is the most convenient object for evaluating the influence of the polarization effect on charge scattering over the methyl group in the absence of hyperconjugation.

Polarization is responsible for the transfer of some electron density from hydrogens to the central carbon. This effect leads to an increase of the CH stretch frequencies and strengthening of the force constants of CH bonds.\textsuperscript{3,24,33} For methyl carboranes, CH\textsubscript{3}{[Hal11]}, the dependence of υCH on anion basicity is linear and extrapolates to zero basicity (near CH\textsubscript{3}) at 3103 cm\textsuperscript{−1}.\textsuperscript{33} This value corresponds to the true CH\textsuperscript{+} cation in the condensed phase, and is very close to that obtained with the B3LYP-D3/def2-TZVPD approximation (3108 cm\textsuperscript{−1}, see Table S3 in ESI†).

C\textsubscript{2}H\textsubscript{5}\textsuperscript{+} and i-C\textsubscript{3}H\textsubscript{7}\textsuperscript{+} cations. An experimental IR spectrum of the C\textsubscript{2}H\textsubscript{5}\textsuperscript{+} cation in vacuum, when targeted with Ar at H+, shows three CH stretch vibrations (3114, 3032, and 2158 cm\textsuperscript{−1}) well-fitting those calculated for the non-classic bridged-proton symmetrical structure.\textsuperscript{3} Thus, the hyperconjugative interaction in the bare cation is so strong that H+ is equally shared between the two carbon atoms.

The IR spectrum of the ethyl carborane, C\textsubscript{2}H\textsubscript{5}{[Cl11]}, revealed another extreme case:\textsuperscript{33} all C–H stretch frequencies are in the region 2933–3057 cm\textsuperscript{−1} indicating covalent binding between C\textsubscript{2}H\textsubscript{5} and {Cl11} moieties, which prevents the hyperconjugation effect. The frequencies of the CH\textsubscript{2} group of C\textsubscript{2}H\textsubscript{5}{[Cl11]} (3057 and 2976 cm\textsuperscript{−1}) are slightly higher than those of the chloronium cation (C\textsubscript{2}H\textsubscript{5}+Cl\textsuperscript{−} (3038 and 2974 cm\textsuperscript{−1}), pointing to the more polar C–Cl bond in the case of C\textsubscript{2}H\textsubscript{5}{[Cl11]}.

The C\textsubscript{2}H\textsubscript{5}\textsuperscript{+} cation was obtained in the form of ionic salt C\textsubscript{2}H\textsubscript{5}{[F11]}+. Its formation through an unstable salt of fluoronium cation, (CH\textsubscript{3})\textsubscript{3}F+, is accompanied by the formation of i-Pr+.\textsuperscript{33} IR spectra showed the bands of both cations, whose intensities vary depending on the ratio of cations (Fig. 2a). Obtaining the difference between the spectra of the samples with a low and high portion of i-Pr+ (Fig. 2, red and black)—up to full compensation of the absorption from i-C\textsubscript{3}H\textsubscript{7}+—allowed us to obtain a spectrum of the C\textsubscript{2}H\textsubscript{5}\textsuperscript{+} cation (Fig. 2b). Reverse subtraction of the spectra (“black” minus “red”) did not fully remove the spectrum of the
The patterns observed in the IR spectra of the carbocations of their bands into individual components became possible. By hyperconjugation, was not distorted by impurities, and separation to be involved in hyperconjugation. All three CH bonds of isomers of i-C₃H₇+cations decomposing at room temperature. In Fig. 4, the IR bands with {F₁₁−} counterion, Fig. 5a). The third CH group (marked as CH₃*) is predominantly polarized and shows three higher-frequency bands in the gas phase. This observation is supported by important experimental evidence: the stretch vibrations of CH₃ and CH₃* groups in t-Bu* show a good correlation (Table 2), which confirms their attribution to group vibrations and indicates that both types of CH₃ groups are isoelectronic.

Table 2 The valence group vibrations (in cm⁻¹) for gaseous t-Bu+ with the proposed attribution

<table>
<thead>
<tr>
<th>Group</th>
<th>ν(CH₃)</th>
<th>ν(ν̇CH₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃*</td>
<td>3038</td>
<td>2965</td>
</tr>
<tr>
<td>CH₃</td>
<td>2880</td>
<td>2839</td>
</tr>
<tr>
<td>Ratio</td>
<td>1.055</td>
<td>1.044</td>
</tr>
</tbody>
</table>

In addition, the C–H stretch frequencies of t-Bu+ involved in hyperconjugation very well correlate with those of the isoelectronic planar trimethyl boron (CH₃)₃B(=N) (Table 3). This observation confirms that the types of local CH₃ normal vibrations for both compounds coincide, and the electron distributions in their methyl groups are identical.

Finally, a good correlation was also observed between the frequencies of the CH₃* group in t-Bu+ and those of the strongly polarized methyl group in CH₃{F₁₁−}(Table 4), confirming the above-mentioned conclusions.

In the condensed phases, t-Bu+ forms noticeable H-bonds with the nearest surroundings favoring involvement of the CH₃* group in hyperconjugation, which is, however, weaker than that formed by its other two CH₃ groups. This phenomenon is accompanied by enhanced dynamic properties of the H atoms of CH₃*, resulting in collapse of the three bands of CH₃* vibrations into one broad absorption (with an intensity of ca. 30% of that from all CH stretches) at a lower frequency (Fig. 5a).

The spectrum of i-Pr+ obtained in reaction (1) differs from that shown in Fig. 2b, but is very similar to the spectrum of t-Bu+ (Fig. 5). It shows a broad absorption pattern at 2922 cm⁻¹.
with intensity ca. 50% of the total intensity of the CH stretch vibrations of i-Pr+. The three bands at a lower frequency belong to the second CH$_3$ group involved in stronger hyperconjugation (the ratio of their intensity values may change, depending on the conditions of separation of the bands, but the number of bands is always three). Thus, the above-mentioned i-Pr$^+$ isomer is an analog of t-Bu$^+$, with similar asymmetry, and will be designated as i-Pr$_{as}$$^+$. The spectrum of the second i-Pr$^+$ isomer contains only two bands of CH$_3$ groups involved in hyperconjugation (the third band was obviously not resolved) without the broad absorption (Fig. 2c). Thus, both CH$_3$ groups equally participate in hyperconjugation. Hereinafter, we will refer to this symmetrical isomer as i-Pr$_{sym}$$^+$. The frequencies of hyperconjugated CH$_3$ groups for both i-Pr$^+$ isomers are close (Fig. 2c and 5b), which means that i-Pr$_{as}$$^+$ and i-Pr$_{sym}$$^+$ have roughly equal energy. Therefore, the efficiency of the positive charge redistribution over the CH$_3$ and CH$_3^*$ groups in carbocations is energetically equivalent.

A charged C$_3$ core of the cyclo-C$_5$H$_9^+$ cation is similar to that of i-Pr$_{sym}$$^+$. Its IR spectrum does not contain the broad absorption pattern (Fig. 3), indicating that this cation is symmetric. CH stretches of the two equivalent CH$_2$ groups involved in hyperconjugation (Scheme 5) result in two low-frequency bands at 2836 and 2765 cm$^{-1}$. The remote CH$_2$ groups yield the bands $\nu_{as}$ at 2956 and $\nu_s$ at 2904 cm$^{-1}$. Moreover, the ratio of frequencies for these bands coincides (Table 5). This finding implies identical assignment of frequencies for CH$_2^+$ and CH$_3^*$ groups and their isoelectronic character, as established for two types of CH$_3$ groups of t-Bu$^+$ (Table 2). This result leads to a major conclusion: both CH bonds of CH$_2^+$ groups equally donate $\sigma$-electrons to the 2p$_z$ orbital of the sp$^2$ C atom, in agreement with the case of t-Bu$^+$. The C$_2$H$_5^+$ spectrum shows two bands from the CH$_3$ group vibrations, which are similar to those observed in the i-Pr$_{sym}$$^+$ spectrum (Fig. 2b and c). The broad absorption pattern, of course, is absent. This finding points to some generic relation between C$_2$H$_5^+$ and i-Pr$_{sym}$$^+$. The overall picture of the generic relations between the analyzed carbocations with hyperconjugative stabilization is shown in Fig. 6.

One can see that there are two kinds of carbocations: (i) carbocations with one type of hyperconjugated CH$_3$/CH$_2$ groups...
calculated data showed that the impact of the environment i-Pr+, respectively, which are weak and located in the frequency C2H5{Cl11} and i-C3H7{Cl11}.

abrupt switch from the covalent to ionic state takes place between R = C2H5 (and larger), the compounds are purely ionic (Table S3, ESI†).

The most intense bands are boldfaced.

Table 6 IR frequencies (in cm−1) of the CH3/CH2 groups of carbocations under study affected by hyperconjugation

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>νCH3/νCH2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H5+</td>
<td>{F11}</td>
<td>2791</td>
</tr>
<tr>
<td>i-Pr+Sym</td>
<td>{F11}</td>
<td>2874</td>
</tr>
<tr>
<td>i-Pr+As</td>
<td>{F11}</td>
<td>2866</td>
</tr>
<tr>
<td>t-Bu+</td>
<td>{F11}</td>
<td>2867</td>
</tr>
<tr>
<td>Cyclo-pentyl+</td>
<td>{F11}</td>
<td>2836</td>
</tr>
<tr>
<td>i-Pr+</td>
<td>{Cl11}</td>
<td>2780</td>
</tr>
<tr>
<td>t-Bu+28</td>
<td>{Cl11}</td>
<td>2830</td>
</tr>
<tr>
<td>Cyclo-pentyl+</td>
<td>{Cl11}</td>
<td>2777</td>
</tr>
</tbody>
</table>

The most intense bands are boldfaced. *Not determined.

\( \text{(C}_{2} \text{H}_{5}^{+}, \text{i-Pr}^{+}, \text{and} \text{i-C}_{3} \text{H}_{7}^{+} \), which form a symmetrical \( C_{3} \) charged core; (ii) carbocations with an asymmetrical \( C_{3} \) or \( C_{4} \) charged core formed by two types of CH3 groups.

The frequencies of the CH3/CH2 groups mostly affected by hyperconjugation for all carbocations under study are summarized in Table 6. The decrease in the frequencies from \{F11\} to \{Cl11\} salts is due to the formation of H-bonds.17

All CH stretch vibrations of C2H5+, i-Pr+, cyclo-pentyl+, and t-Bu+ cations were observed in IR spectra with the exception of those from CH2 and CH groups at the sp² C atom in C2H5+ and i-Pr+, respectively, which are weak and located in the frequency region of the intense C–H stretches from \{F11\} or \{Cl11\} anions.

Experimental data versus calculations. Experimental and calculated data showed that the impact of the environment on the nature of the R–{F11} bond may be significant. The CH3 group is linked covalently to \{F11\}, and the calculated CH3 frequencies (both for vacuum and for the condensed phase) are in good agreement with the empirical ones for solid CH3–{F11} (Table S3, ESI†). When R is C2H5 and larger, the ionicity of the C–F bond and the hyperconjugated effect in compounds R{F11} gradually increase in the series R = C2H5, i-C3H7, cyclo-C3H7, and t-Bu. Nonetheless, the experiments showed that starting from R = C2H5 (and larger), the compounds are purely ionic (Table 7). In the case of the more basic \{Cl11\} carbocation, an abrupt switch from the covalent to ionic state takes place between C2H5{Cl11} and i-C3H7{Cl11}.

Carborane, the switch “covalent–ionic state” occurs between i-C3H7{Cl11} and t-C4H9{Cl11}. Thus, the switch from the covalent to ionic state is abrupt, without intermediates. Possibly, this happened because permittivity of carborane compounds is much higher than that of DCE, used in the calculations.

As the calculations revealed, the experimental spectra of carbocations in condensed phases must be compared with those calculated for naked carbocations or carbocations solvated by argon, taking into account that the nature of hyperconjugative stabilization of carbocations does not depend on the phase state. This comparison of cations C2H5+, i-Pr+, and t-Bu+ is shown in Fig. 7. It uncovered some similarities and some significant discrepancies, already found for t-Bu+.28

The discrepancies can be summarized as follows: (1) the calculated frequencies of hyperconjugated C–H bonds continuously increase as the number of CH3 groups in carbocations increases (C2H5+, i-Pr+, t-Bu+; Fig. 7, red), but this is not the case for the empirically determined dependence (Fig. 7, blue). (2) The calculated frequencies are notably lower than empirical ones for C2H5+ and i-Pr+ and actually coincide only for t-Bu+, which is mentioned in the literature as proof of a good match between theory and experiment.4 Judging by the above results, it is obvious that this coincidence is rather accidental. (3) According to calculations, the number of C–H stretches of hyperconjugated CH bonds is equal to the number of CH3 groups: one for C2H5+, 

\( \text{CHB}_{11} \text{Me}_{5} \text{Br}_{6} \)

Carborane, X Covalent compounds, R–X Ionic salts, R′X–

<table>
<thead>
<tr>
<th>Carborane, X</th>
<th>Covalent compounds, R–X</th>
<th>Ionic salts, R′X–</th>
</tr>
</thead>
<tbody>
<tr>
<td>{F11}</td>
<td>H–C–X</td>
<td>R = C2H5 and larger</td>
</tr>
<tr>
<td>{Cl11}</td>
<td>H–C–X, C2H5–C2H5</td>
<td>R = i-C3H7 and larger</td>
</tr>
<tr>
<td>CHB11Me5Br6</td>
<td>H–C–X, C2H5–X, i-C4H9–X</td>
<td>R = t-C4H9 and larger</td>
</tr>
</tbody>
</table>

Table 7 The covalent and ionic R–X compounds (X = carborane) identified on the basis of the presence or absence of the strong hyperconjugation effect during R stabilization

Fig. 7 Dependence of CH stretch frequencies of CH3 groups involved in hyperconjugation in ethyl+, i-Pr+, and t-Bu+ on the number of their CH3 groups. Empirical data (blue) are shown for \{F11\} salts, and the calculated data (red) are shown for cations with a similar type of normal vibrations (C2H5+–Ar, C2, i-Pr+, C3, t-Bu+, C4). The number of CH frequencies is specified. The bold and thin lines represent the most and least intense vibrations, respectively.
two for i-Pr⁺, and three for t-Bu⁺. The experiments imply that these numbers are 2(3), 3 and 3 respectively. [4] The calculated splitting of the bands is rather small (13–17 cm⁻¹) and cannot be detected in the condensed-phase IR spectra because the corresponding bands should be merged into one slightly broadened (degenerated) band. In contrast, experimental spectra show three common bands for CH₃ group vibrations separated by 96 cm⁻¹.

A comparison of the calculated frequencies for the cyclo-pentyl⁺ cation (C₂ symmetry) with the experimental spectrum of cyclo-C₅H₅⁺{F₁₁⁻} revealed [Fig. 3] that there is also a significant discrepancy between theory and experiment, as in the case of C₃H₅⁻ and i-Pr⁺ cations. From the experimental spectrum it follows that both CH bonds of the CH₃⁺ group of cyclo-pentyl⁺ are equally influenced by hyperconjugation, and CH₂ and CH₃⁺ are isoelectronic and have the same type of normal vibrations. The same is true for t-Bu⁺ (and i-Pr⁺): three C–H bonds of CH₃ are equally involved in hyperconjugation, and both CH₃ and CH₃⁺ groups are isoelectronic, with the same type of local group vibrations. Unfortunately, these results contradict computational data.

To try to reconcile the quantum-chemical calculations with the experiment, we performed PBE-D3 computations with periodic boundary conditions for the t-Bu(C₁₃) crystal lattice previously determined by X-ray crystallography. [17] No significant structural changes were found in the fully relaxed unit cell, as compared to the experiment. In contrast, the calculated vibrational frequencies of t-Bu⁺ in the crystal lattice were found to have the same features as those in gaseous t-Bu⁺ (Table S5 in ESI†), which again contradict the experimental findings. Similar results follow from the calculations when experimental atomic coordinates were used without relaxation (Table S5 in ESI†). Thus, the origin of inconsistencies in the mechanisms of carbocation hyperconjugation stabilization that follow from calculations and experiments has yet to be established.

Conclusions

According to the experiment, two sets of carbocations exist: with a symmetric and an asymmetric charged core. Our DFT calculations predict no carbocations with an asymmetrical charged core and their results in general contradict the experimental data.

The standard theoretical representation of the mechanism of hyperconjugation predicts that σ-electron density is transferred to the empty 2p₂ orbital of the sp² C atom from one preferred CH⁺ bond of each CH₃ group. At the same time, the σ-electron density on the other CH' and CH'' bonds slightly increases (Scheme 1). It looks like σ-electrons of the three C–H bonds of the CH₃ group do not merge into molecular orbitals with the generalized electrons. This phenomenon manifests itself in calculated IR spectra, including high-level CCSD(T) computations, [18] as a strong reduction in the ωCH⁺ frequency (much stronger than in the experiment) making it highly characteristic. Accordingly, vibrations of C–H' and C–H'' bonds also appear to be highly characteristic ones, which are not mixed with those of the CH⁺ bond. To the best of our knowledge, this case is unknown in the practice of vibrational spectroscopy.

From the experimental data it follows that donation of the σ-electrons from the CH⁺ bond to the empty 2p₂ orbital of the sp² C atom is accompanied by an equal withdrawal of the σ-electron density from C–H' and C–H'' bonds. That is, the electrons are supplied from each CH bond of the CH₃ group, and the C–H⁺ bond does not act as the predominant donor. Thus, all three bonds of CH₃ groups are equivalent. As a result, the CH stretches manifest themselves as typical CH₃ group vibrations with equivalent C–H bonds.

Because calculations revealed that the impact of hyperconjugation on the CH₃ group weakly depends on the dihedral θ angle (the CH₃ rotation around the C–C bond), the donation of the σ-electron density from CH₃ to the empty 2p₂ orbital of the sp² C atom may take place not only via the C–H⁺ bond, but also via CH' and CH'' bonds. This mechanism is indicated in Scheme 2 by a dashed arrow.

The aforementioned inconsistencies are valid for all quantum-chemical calculations of naked carbocations known to date. Furthermore, our DFT calculations for the t-Bu(C₁₃⁻) crystal and R{Hal₁₁} molecular compounds in a DCE solution turned out to be comparable with those for naked carbocations, leading to the generally accepted mechanism of hyperconjugative stabilization rather than the mechanism deduced from our experiments.

We can hypothesize that fine electronic structure of carbocations that has not yet been taken into account may be responsible for the observed theory-versus-experiment discrepancies. It seems that potential energy surfaces of the carbocations under study are more complicated than expected and cannot be analyzed by the standard quantum-chemical methods such as conventional DFT. This is the subject of our ongoing research.

Undoubtedly, further computational studies in this field, possibly based on the more advanced methods, will result in convergence of the theory with experiment and will allow researchers to explain a number of recently detected features of carbocations, such as the energy equivalence of the CH₃ and CH₃⁺ groups in asymmetric carbocations; why increasing the number of methyl groups from two (i-Pr⁺) to three (t-Bu⁺) does not influence the frequencies of C–H stretches; and the abrupt change in the state of the CH₃⁺ group when t-Bu⁺ is transferred from gaseous to condensed phases. [28]

Acknowledgements

This work was supported by grant # 16-13-10151 from the Russian Science Foundation and by the Ministry of Education and Science of the Russian Federation within the Project of the joint Laboratories of the Siberian Branch of the Russian Academy of Sciences and National Research Universities. Quantum chemical calculations were supported by the Russian Foundation for Basic Research (grant # 16-03-00357). The Siberian
Supercomputer Center is acknowledged for providing computational resources. The authors thank Irina S. Stoyanova for providing the carborane acids and technical support.

References