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The Nature of the H_3O^+ Hydronium Ion in Benzene and Chlorinated Hydrocarbon Solvents. Conditions of Existence and Reinterpretation of Infrared Data

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Abstract: Salts of the C_{3v} symmetric hydronium ion, H_3O^+ , have been obtained in the weakly basic solvents benzene, dichloromethane, and 1,2-dichloroethane. This is made possible by using carborane counterions of the type $\text{CHB}_{11}\text{R}_5\text{X}_6^-$ ($\text{R} = \text{H, Me, Cl}$; $\text{X} = \text{Cl, Br, I}$) because they combine the three required properties of a suitable counterion: very low basicity, low polarizability, and high chemical stability. The existence of the H_3O^+ ion requires the formation of three more-or-less equivalent, medium-to-strong H-bonds with solvent or anion bases. With the least basic anions such as $\text{CHB}_{11}\text{Cl}_{11}^-$, IR spectroscopy indicates that C_{3v} symmetric trisolvates of formulation $[\text{H}_3\text{O}^+ \cdot 3\text{Solv}]$ are formed with chlorocarbon solvents and benzene, the latter with the formation of π bonds. When the solvents and anions have comparable basicity, contact ion pairs of the type $[\text{H}_3\text{O}^+ \cdot n\text{Solv} \cdot \text{Carborane}]$ are formed and close to C_{3v} symmetry is retained. The conditions for the existence of the H_3O^+ ion are much more exacting than previously appreciated. Outside of the range of solvent basicity bounded at the lower end by dichloromethane and the upper end by tributyl phosphate, and with anions that do not meet the stringent requirements of weak basicity, low polarizability of high chemical stability, lower symmetry species are formed. One H-bond from H_3O^+ to the surrounding bases becomes stronger than the other two. The distortion from C_{3v} symmetry is minor for bases weaker than dichloromethane. For bases stronger than tributyl phosphate, $\text{H}_2\text{O}-\text{H}^+-\text{B}$ type species are formed that are more closely related to the H_5O_2^+ ion than to H_3O^+ . IR data allow criteria to be defined for the existence of the symmetric H_3O^+ ion. This includes a linear dependence between the frequencies of $\nu_{\text{max}}(\text{OH})$ and $\delta(\text{OH}_3)$ within the ranges $3010-2536 \text{ cm}^{-1}$ for $\nu_{\text{max}}(\text{OH})$ and $1597-1710 \text{ cm}^{-1}$ for $\delta(\text{OH}_3)$. This provides a simple way to assess the correctness of the formulation of the proton state in monohydrated acids. In particular, the 30-year-old citation classic of the IR spectrum believed to arise from $\text{H}_3\text{O}^+ \text{ SbCl}_6^-$ is reinterpreted in terms of $(\text{H}_2\text{O})_x \cdot \text{HSbCl}_6$ hydrates. The correctness of the hydronium ion formulation in crystalline $\text{H}_3\text{O}^+\text{A}^-$ salts ($\text{A}^- = \text{Cl}^-, \text{NO}_3^-$) is confirmed, although, when A^- is a fluoroanion, distortions from C_{3v} symmetry are suggested.

Introduction

When a chemical reaction in an organic solvent is catalyzed by a strong protic acid, the proton will typically take part as a hydrated species. Trace water is difficult to avoid in organic solvents, and, because water is both a good base and a strong participant in H-bonding, it will typically interact strongly with the acid. The exact nature of the hydrated species is frequently unknown or unspecified, often just written as $\text{H}^+(\text{soln})$, but in its simplest form will involve the H_3O^+ hydronium ion.

The H_3O^+ ion has been known since the early 1920s¹ and has been studied in crystalline acid monohydrates by vibrational spectroscopy (IR and Raman),²⁻⁷ and by X-ray³⁻¹¹ and neu-

tron^{12,13} diffraction methods. Studies of H_3O^+ and its solvates in the gas phase continue to draw interest,¹⁴⁻¹⁶ as do calculational approaches.^{17,18} However, the number of publications relating to the molecular state of H_3O^+ in nonaqueous solutions, arguably the most important medium for practical chemistry,

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is quite limited. The first IR and Raman identification of the C_{3v} symmetry H₃O⁺ ion in dichloromethane solutions of hydrated hexachloroantimonic acid, written H₃O⁺SbCl₆⁻, was published in 1974.⁵ This paper has become a classic and is widely cited in reviews and monographs.¹⁹ In the last 30 years, however, there have been practically no further studies of the C_{3v} symmetric H₃O⁺ ion in non-O-donor solvents. This is surprising and begs the question: Why? An additional question, given the lack of subsequent corroboration, is whether attribution of the published vibrational spectrum to the H₃O⁺ ion in hydrated hexachloroantimonic acid is in fact correct.

The existence of the H₃O⁺ cation in solution has been demonstrated by NMR in HF/SbF₅ superacid media^{20,21} and in certain other nonaqueous solvents such as SO₂, dimethylsulfone, and HF.^{22,23} However, NMR spectroscopy has not led to an understanding of the solvation of H₃O⁺ by solvent molecules or its interaction with counterions. The ¹H NMR spectrum of H₃O⁺ in nonaqueous media appears as a single peak in a narrow chemical shift range (10–13 ppm) with no established relationship to the nature of the counterion or solvent. Vibrational spectroscopy allows one to obtain this information, but publications based on this method are scarce. The C_{3v} symmetric H₃O⁺ ion is stabilized in low-dielectric organic media by complexation to crown ethers^{24,25} or to stronger O-atom bases such as tributyl phosphate (TBP), forming solvent-separated ion pairs.²⁶ In these situations, the H₃O⁺ ion acts as a strong H-bond donor to O atom ligands (L). Normal, linear O_w–H···O_L hydrogen bonds are formed in the [H₃O·3TBP]⁺ cation in solution, and in the H₃O⁺ complex with the unsymmetrical benzo-18-crown-6 ether in both solution and solid state. However, in the complex with the symmetrical 18-crown-6 in solution, the experimental data indicate that all six O-atoms equivalently interact with H₃O⁺.²⁵ Theory has yet to reproduce the differences in data between the symmetrical and unsymmetrical crown ethers in solution, and the differences between crystalline and liquid-state structures for [H₃O⁺·18-crown-6].²⁷ In crystalline acid monohydrates, H₃O⁺ ions are similarly stabilized by three strong H-bonds, in this case to the conjugate base anions from the lattice. For the H₃O⁺ ion to exist and have good solubility in weakly basic solvents such as benzene or chlorinated hydrocarbons, similar H-bond stabilization by solvent molecules must take place. Such investigations have been hampered by the lack of a suitable superacid.

In this paper, we present the results of our investigation into the nature of monohydration of carborane acids, H(carborane). Carborane acids are a new class of extraordinarily strong Lewis-free Brønsted acids²⁸ notable for their ability to cleanly protonate species and produce isolable salts.²⁹ They react with 1 equiv of

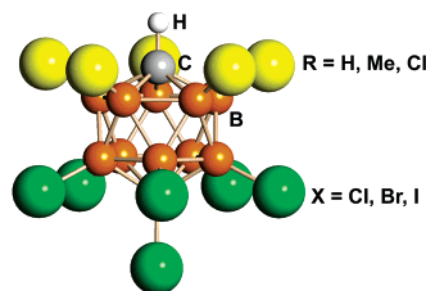


Figure 1. Icosahedral carborane anions of the type CB₁₁R₅X₆⁻, used in this work (abbreviated {R₅X₆}⁻).

water to give well-characterized [H₃O][carborane] salts that have workable solubility in benzene, dichloromethane, and 1,2-dichloroethane (DCE). The novel structure and preliminary IR analysis of the tri- π -benzene solvated H₃O⁺ ion in crystals of [H₃O·3benzene][CHB₁₁Cl₁₁]⁺·benzene was communicated earlier.³⁰ Three carborane anions (abbrev. Carb) of decreasing basicity²⁸ CHB₁₁Me₅Br₆⁻ > CHB₁₁H₅Cl₆⁻ > CHB₁₁Cl₁₁⁻ have been mainly used for the solution studies. They are shown in Figure 1 and abbreviated {Me₅Br₆}⁻, {H₅Cl₆}⁻, and {Cl₁₁}⁻. Square brackets are used throughout this paper to indicate a completed first solvation sphere of the H₃O⁺ ion, for example, [H₃O⁺·3benzene].

Experimental Section

Carborane acids and benzenium ion salts were prepared as previously described.^{28,30,31} Solvents were purified and dried according to the literature methods.³² Glassware was dried at 160 °C overnight before taking it into a glovebox. All operations were performed in a Vacuum Atmospheres Corp. glovebox under He (O₂, H₂O < 0.5 ppm). IR spectra were run on a Shimadzu-8300 FT-IR spectrometer in the 4000–450 cm⁻¹ range (32 scans, resolution 2 cm⁻¹) housed inside the glovebox. A cell with Si windows with 0.036 mm separation at the beam transmission point was used. To avoid interference effects, the cell configuration was wedge-shaped. The spectra in the 500–210 cm⁻¹ range were run on a Bruker IFS 120 HR spectrometer using 1 mm polyethylene cell. Data were manipulated using GRAMMS software, and examples of the solvent subtraction and deconvolution procedures are given in Figures S1 and S2 of the Supporting Information.

Benzene solutions of carborane acid monohydrates were prepared by taking a weighed quantity of solid acid (~0.044 mmol) and adding measured volumes of dry benzene (1.1 mL) and water-saturated benzene (0.9 mL) to obtain an acid:H₂O mole ratio of 1:0.55. After this mixture was shaken, the insoluble portion was allowed to settle and the supernatant was syringed off. The primrose colored benzene phase contained ca. 0.010–0.012 M [H₃O][carborane], close to saturation. Dichloromethane and 1,2-dichloroethane (DCE) solutions of [H₃O]-[carborane] were prepared from weighed quantities of [C₆H₇][carborane] salts to which was added a calculated volume of water-saturated solvent (0.081 M in CH₂Cl₂, 0.10 M in DCE) followed by sufficient dry solvent to obtain resulting solutions with concentrations of 0.01–0.025 M and acid:H₂O mole ratios of 1:1.

To prepare solutions of the monohydrate H₂O·HSbCl₆ in CH₂Cl₂ (0.010 M), the calculated volumes of three DCM solutions containing (a) 0.1 M SbCl₅, (b) 0.081 M H₂O, and (c) 0.12 M HCl were mixed. Solutions (a) and (b) were used to adjust the H₂O/SbCl₅ mole ratio to 1:1. Solution (c) provided the excess of HCl to shift the equilibrium to

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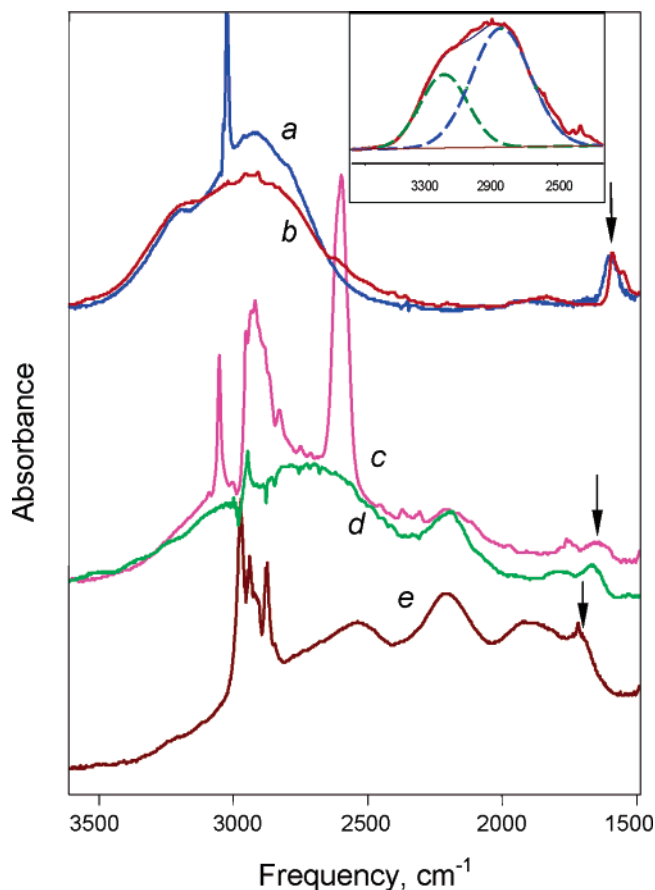


Figure 2. IR spectra of H_3O^+ cation (C_{3v}) in (a) solid $\text{H}_3\text{O}^+\{\text{Cl}_{11}\}^-$ (blue), (b) solid $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ (red), (c) DCE solution of $[\text{H}_3\text{O}^+\cdot 18\text{-crown-6}]\{\text{H}_5\text{Cl}_6\}^-$ (magenta), (d) DCE solution of $\text{H}_3\text{O}^+\text{OTf}^-$ (green), and (e) TBP solution of $[\text{H}_3\text{O}^+\cdot(\text{TBP})_3]\text{FeCl}_4^-$ (brown). Inset: Deconvolution of stretching H_3O^+ vibrations in spectrum (b) into $\nu_1(A_1)$ and $\nu_3(E)$ bands. Arrowheads identify the $\nu_4(E)$ band. The spectrum of solvent has been subtracted in (c), (d), and (e).

quantitative $\text{H}_2\text{O}\cdot\text{HSbCl}_6$ formation. To prepare solution (a), a weighed portion of SbCl_5 was dissolved in CH_2Cl_2 . Solution (b) was prepared by saturating CH_2Cl_2 with water. Solution (c) was produced by saturating dichloromethane with anhydrous HCl gas. The HCl concentration in the solution was determined by NaOH titration. Solutions of the dihydrate $(\text{H}_2\text{O})_2\cdot\text{HSbCl}_6$ (0.010 M) were prepared in the same manner, mixing calculated volumes of three solutions (a), (b), and (c) to adjust the molar ratio $\text{H}_2\text{O}/\text{SbCl}_5 = 2$ with some excess of HCl. The spectrum of excess HCl was subtracted from the spectra of the resulting solutions, using the spectrum of solution (c) as a standard. The scaling factors of these subtractions allowed determination of the concentrations of free HCl and HCl complexed to SbCl_5 . The molar ratios of complexed HCl to SbCl_5 were found to be close to 1 for all solutions under study.

X-ray Structure. Single crystals of $\text{H}_3\text{O}^+\{\text{CHB}_{11}(\text{CH}_3)_5\text{Br}_6\}\cdot 1.5\text{C}_6\text{H}_6$ were grown from a saturated benzene solution of the carborane acid monohydrate, prepared as described above, by slow evaporation of benzene under weak vacuum for several hours at room temperature. The structure was solved and refined by standard methods. Details are provided in the Supporting Information.

Results

Solid State. Infrared spectra of the H_3O^+ cation in solid H_3O^+ salts with different carborane anions are all very similar (see Figure 2a,b and Table 1). They contain a very broad, intense band in the frequency range $2800\text{--}3200\text{ cm}^{-1}$ that represents the overlapping $\nu_1(A_1)$ and $\nu_3(E)$ bands of the O–H stretching

Table 1. Vibrational Frequencies of the H_3O^+ Ion in Solid $\text{H}_3\text{O}^+\{\text{Anion}\}$ Salts

anion	$\nu_3(\text{OH}_3)$ $\nu_1(A_1)$	$\nu_{as}(\text{OH}_3)$ $\nu_3(E)$	$\nu_{max}(\text{OH}_3)$	$\delta_{as}(\text{OH}_3)^a$ $\nu_4(E)$	ref
$\text{CHB}_{11}\text{Cl}_{11}^-$	3224	2911	2921	1602 1571w	this work
$\text{CHB}_{11}\text{H}_5\text{Cl}_6^-$	3208	2900	2940	1590 1548vw	this work
$\text{CHB}_{11}\text{H}_5\text{Br}_6^-$	3143	2844	2903	~1566 br	this work
$\text{CHB}_{11}\text{Me}_5\text{Br}_6^-$	3200	2849	2930	1589 1548w	this work
$\text{CHB}_{11}\text{Me}_5\text{I}_6^-$	3164	2752	2932	1590 br /210	this work
ClO_4^- ^{b,c}	3020	2780		1625 1548	4
Cl^-	2895 ^c	2630 ^c 2525 ^c	2840 ^d	1650 ^c 1615 ^c	5
HSO_4^-		2840 (2560)	2840	1620	6
NO_3^-		2780 (2560)	2780	1680	6
SbF_5OH^-	2700		2700	no data	7

^a Italicized frequency is the most intense band. ^b Orthorhombic phase. ^c From Raman spectrum. ^d From IR spectrum.

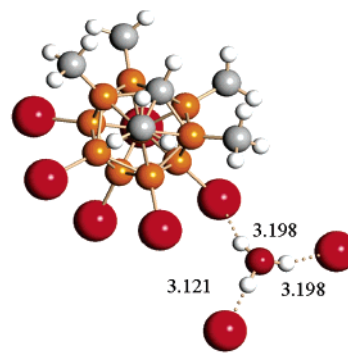


Figure 3. X-ray structure of $\text{H}_3\text{O}^+\{\text{CHB}_{11}\text{Me}_5\text{Br}_6\}^-$ showing H-bonded interactions of H_3O^+ with Br atoms of carborane anions. O...Br distances are given. Only one anion is fully represented.

vibrations. The $\nu_4(E)$ band associated with H_3O^+ bending is seen in the range $1550\text{--}1650\text{ cm}^{-1}$, but the expected $\nu_2(A_1)$ band at ca. $1000\text{--}1100\text{ cm}^{-1}$ overlaps with strong bands of the carborane anion that cannot be reliably subtracted.

The crystal structure of $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ shows that each hydrogen atom of the H_3O^+ ion is H-bonded to Br atoms from surrounding carborane anions (Figure 3). Because of site asymmetry in the crystal packing, each interaction is slightly different and the symmetry of H_3O^+ is somewhat lower than C_{3v} . This is reflected in the IR spectrum as a splitting of the doubly degenerate $\nu_4(E)$ band into two components (Figure 2b). The weak lifting of this degeneracy is also manifested in broadening of the 1590 cm^{-1} band in $\text{H}_3\text{O}^+\{\text{Me}_5\text{I}_6\}^-$ and splitting in $\text{H}_3\text{O}^+\{\text{Cl}_{11}\}^-$ (Figure 2, Table 1). The doubly degenerate $\nu_3(E)$ band of the antisymmetric OH stretching vibrations should be also split into two components. However, because the bands are very broad and strongly overlapping, both components appear as a single broad band. This is why we can separate the broad asymmetric absorption in the $2800\text{--}3200\text{ cm}^{-1}$ range into only two bands, $\nu_1(A_1)$ and $\nu_3(E)$. The deconvolution is good (see Figure 2, inset), indicating that this approximation is entirely acceptable. Thus, the symmetry of H_3O^+ in solids is close to C_{3v} and the attribution of the IR bands is made in accordance with this symmetry.

Solutions. Acid monohydrates of the type $\text{H}_3\text{O}^+\{\text{anion}\}$ dissolve in organic solvents only if the solvation energy is higher than the lattice energy. In practice, this means that reasonably effective H-bonding of the H_3O^+ ion to the solvent must occur to break up H-bonding to the surrounding anions in the solid state. As a consequence, the molecular state of the H_3O^+ ion in solution can differ significantly from that in the solid state.

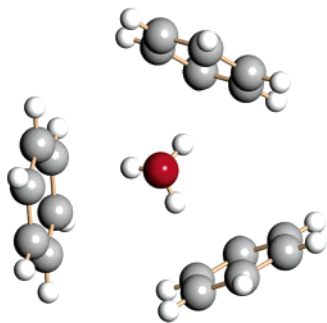


Figure 4. Perspective view of the H₃O⁺·3benzene cation in the X-ray structure of the CHB₁₁Cl₁₁[−] salt.

Related to this concept, the anhydrous carborane acids, which are believed to have polymeric structures in the solid state with proton bridges between halide substituents, do not dissolve in solvents such as saturated hydrocarbons. They are sufficiently strong acids that they react with chlorocarbon and arene solvents. In the case of arenes, reversible protonation occurs and arenium ion salts such as C₆H₇⁺{carborane}[−] have been isolated.³³

Only IR spectroscopy has proven suitable for the investigation of acid monohydrates in solution. All attempts to obtain Raman spectra failed due to the combination of high fluorescence background, low solubility, and low intrinsic band intensities.

Benzene Solutions. Benzenium ion salts of carboranes are insoluble in benzene. However, if one adds a known quantity of water (in the form of water-saturated benzene) to a suspension of C₆H₇⁺{Carb}[−](_s) in benzene, the salt begins to dissolve. The dissolution of the solid increases as the amount of added water increases. IR spectra of the solutions indicate developing concentrations of H₃O⁺ and carborane ions. The intensities of their bands are proportional to the amount of added water up to the formation of a saturated solution, ca. 0.012 M in the case of H₃O⁺{Me₅Br₆}[−]. The H₂O/carborane ratio is close to 1:1 in agreement with the H₃O⁺{Carb}[−] formulation. At higher concentrations of added water, the spectrum of the H₅O₂⁺ ion³³ develops with characteristic bands at 3380 and 1671 cm^{−1}.³⁴

The IR spectrum of the H₃O⁺ cation in benzene solution with the {Cl₁₁}[−] anion coincides with that for crystalline [H₃O⁺·3C₆H₆]{Cl₁₁}[−]·C₆H₆, which was isolated from this solution and investigated by X-ray crystallography.³⁰ This indicates that the composition and structure of [H₃O⁺·3benzene] cation are the same in both phases. The crystal structure shows fully separated [H₃O⁺·3C₆H₆] cations and {Cl₁₁}[−] carborane anions. The closest approach of the cation to the anion has an O···Cl separation of 3.48 Å, a nonbonding distance. As illustrated in Figure 4, each hydrogen atom of the H₃O⁺ ion is π-bonded to a benzene molecule. This causes the H₃O⁺ ion in benzene solution to experience a large upfield ring current effect, and its ¹H NMR resonance is shifted to 6.2 ppm as compared to 11.2 ppm in SO₂ solution.

In the case of H₃O⁺{Me₅Br₆}[−] in benzene solution, the ¹H NMR resonance is similarly upfield shifted to 5.9 ppm. The IR spectrum of H₃O⁺ in this solution is also very similar to that with the {Cl₁₁}[−] anion except for a broadening on the low energy side of the band from the OH stretching vibrations (Figure 5). This suggests a slightly stronger ion pairing perturbation of the H₃O⁺ cation from the {Me₅Br₆}[−] anion,

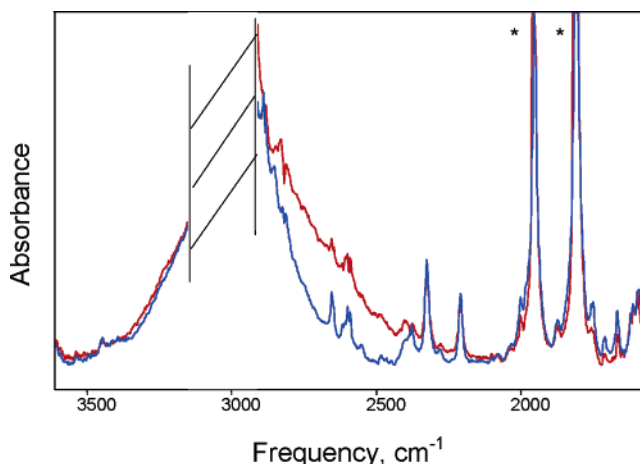


Figure 5. IR spectra of [H₃O⁺·3C₆H₆] in benzene with {Cl₁₁}[−] (blue) and {Me₅Br₆}[−] (red) anions. Spectra are standardized to unit concentration. Combination bands of π-solvated benzene molecules are marked by asterisks. The spectrum of the solvent has been subtracted.

consistent with its higher basicity and higher polarizability. These data collectively establish that the hydronium ion in benzene solution of H₃O⁺{Me₅Br₆}[−] is essentially the same as that in crystalline [H₃O⁺·3C₆H₆]{Cl₁₁}[−]·C₆H₆ (Figure 4). In crystalline [H₃O⁺·3C₆H₆]{Cl₁₁}[−]·C₆H₆, a lattice solvate molecule of benzene has a π-interaction with one of the benzene molecules in the first coordination sphere of [H₃O⁺·3C₆H₆]. This is suggestive of the nature of the second coordination sphere. Indeed, the molar intensity of the 1800–2000 cm^{−1} combination bands of benzene molecules π-bonded to H₃O⁺ is much higher in benzene solution than in the solid state, indicating the existence of a large volume outer sphere solvation shell for [H₃O⁺·3C₆H₆] in benzene solution.³⁰

At high concentrations of H₃O⁺{Carb}[−] (0.008–0.012 M), obtainable with {Cl₁₁}[−] and {Me₅Br₆}[−] counterions, a very weak spectrum of the benzenium C₆H₇⁺ cation was observed. Bands characteristic of the stretching ν_s and ν_{as} vibrations of the CH₂⁺ group at 2670–2780 cm^{−1} and ν(CC) at 1598 cm^{−1} are observed, and they coincide almost exactly with those for corresponding benzenium ion salts in the solid state.³¹ From X-ray structural data, and consistent with solid-state NMR,³¹ the structures of these benzenium ion salts are known to be contact ion pairs with both protons of the acidic CH₂ group of the C₆H₇⁺ cation H-bonded to halogen atoms of the carborane anion. As mentioned above, C₆H₇⁺{Carb}[−] salts are insoluble in pure benzene, so their ability to dissolve in the presence of relatively high concentrations of H₃O⁺{Carb}[−] salts can only be explained by the formation of mixed associates of both salts, (C₆H₇⁺{Carb}[−])_x(H₃O⁺{Carb}[−])_y. At concentrations near saturation, the polar ion pairs of H₃O⁺{Carb}[−] are expected to aggregate in a nonpolar solvent such as benzene, apparently allowing them to incorporate polar ion pairs of C₆H₇⁺{Carb}[−] within the aggregates. A related phenomenon has been observed in tributyl phosphate solutions of hydrated tetrachloroferrate acid, H⁺(H₂O)_xFeCl₄[−], which forms associates similar in structure to reverse nano-micelles with definite compositions.³⁵ These associates can incorporate HCl_(aq), resulting in significantly increased extraction of HCl from water as compared to when FeCl₄[−] is not present.

IR spectra of benzene solutions of H₃O⁺{Carb}[−] are stable with time if the solutions are kept dry and are not in contact

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(34) Stoyanov, E. S.; Reed, C. A.; Kim, K.-C., to be published.

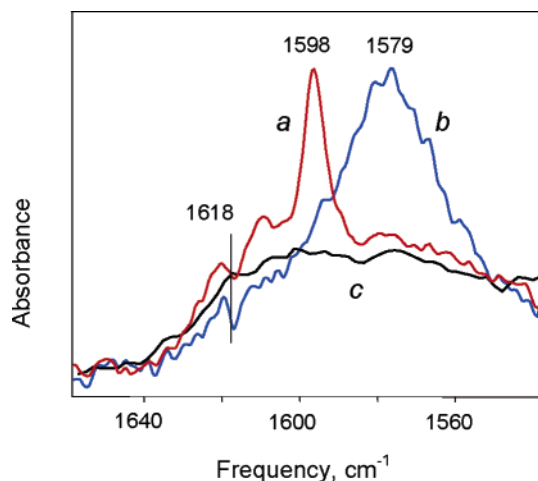
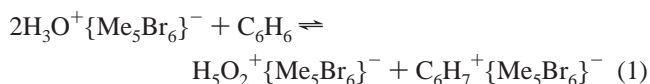


Figure 6. IR spectra of H_3O^+ in benzene solutions of $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ in the frequency range of $\nu_4(\text{E})$: (a) fresh solution with sharp band at 1598 cm^{-1} due to a small amount of C_6H_7^+ salt (red), and (b) the same solution aged 30 min (blue). The spectrum of $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ in the form of ion pairs **A** (c) is given for comparison (black). Spectra are normalized to unit $\{\text{Me}_5\text{Br}_6\}^-$ concentration. The minimum at 1618 cm^{-1} is an artifact of the subtraction process.

with solid. When kept in equilibrium with the solid phase, the spectra begin to change after about 20–30 min, developing weak bands arising from the H_5O_2^+ ion ($3380, 1671\text{ cm}^{-1}$).^{33,34} There is a concomitant change in the composition of the solid. The IR spectrum of solid that remains after freshly preparing a saturated solution of $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ contains the bands of both H_3O^+ and C_6H_7^+ cations. With time, the intensity of the bands of H_3O^+ decreases to disappearance while the spectrum of H_5O_2^+ appears and increases in intensity, overlapping with the spectrum of the C_6H_7^+ cation. Thus, in the solid phase the hydronium ion salt slowly disproportionates in accordance with the equilibrium in eq 1.



The spectrum of a benzene solution of $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ measured immediately after preparation showed intense bands from the $[\text{H}_3\text{O}^+\cdot 3\text{C}_6\text{H}_6]$ cation and a very weak spectrum of the benzenium ion in $\text{C}_6\text{H}_7^+\{\text{Me}_5\text{Br}_6\}^-$, characterized by a sharp band at 1598 cm^{-1} (Figure 6). Upon aging this solution in equilibrium with the solid phase for 30 min, new weak bands from the H_5O_2^+ cation appeared at 3380 and 1671 cm^{-1} . At the same time, the band at 1598 cm^{-1} from dissolved C_6H_7^+ ion salt disappeared (Figure 6) and the intensity of bands due to H_3O^+ decreased. This means that in solution, eq 1 is shifted to the right-hand side and the C_6H_7^+ salt is precipitated. Consistent with this shift in equilibrium, the total concentration of $\text{H}^+(\text{H}_2\text{O})_n\{\text{Me}_5\text{Br}_6\}^-$ compounds in solution, determined from the intensity of the spectrum of anion, decreased by 20%.

Unexpectedly, the $\nu_4(\text{E})$ bending frequency of the H_3O^+ cation at 1593 cm^{-1} (spectrum c) changed during this 30 min aging process. It narrowed, decreased in frequency by 15 cm^{-1} , and the molar intensity increased approximately 2-fold (spectrum b). At the same time, the intensity of benzene bands at 1959 and 1814 cm^{-1} that characterize π -solvation of H_3O^+ by benzene³⁶ decreased significantly. These observations indicate evolution from a benzene-solvated H_3O^+ cation to a contact

ion pair with direct $\text{O}-\text{H}\cdots\text{Br}$ interactions. The benzene-solvated form, $[\text{H}_3\text{O}^+\cdot 3\text{C}_6\text{H}_6]\{\text{Me}_5\text{Br}_6\}^-$ (denoted as **A**), is weakly ion-paired and is present in the freshly prepared solution. The less benzene-solvated, more tightly ion-paired form is designated as **B**. The spectrum of **B** was isolated by subtracting the weak spectrum of H_5O_2^+ from the spectrum of the aged solution. When the spectra of **A** and **B** were normalized to unit intensity of $\{\text{Me}_5\text{Br}_6\}^-$ bands, the intensities of the 1959 and 1814 cm^{-1} bands of π -bound benzene are close to an **A/B** ratio of 3:1. Thus, if in **A** all three OH groups of H_3O^+ are π -bound with benzene, in **B** there should only be one such OH group, and the other two must have direct contacts with bromine atoms of the $\{\text{Me}_5\text{Br}_6\}^-$ anion; that is, the formulation is $\text{H}_3\text{O}^+\cdot\text{C}_6\text{H}_6\cdot\{\text{Me}_5\text{Br}_6\}^-$. The conversion of **A** to **B** in the presence of a minor quantity of H_5O_2^+ cation can again be explained in terms of ion pair aggregation. Mixed associates of H_3O^+ and H_5O_2^+ salts apparently favor the transformation of **A** to **B**.

One final observation concerning benzene solutions of carborane salts of the H_3O^+ ion is the occurrence of rapid H/D exchange between hydronium ions and solvent. When $\text{C}_6\text{H}_7^+\{\text{Carb}\}^-$ is added to $0.0122\text{ M D}_2\text{O}$ in protio-benzene, complete H/D exchange occurs within the time of measurement (< 3 min). The only deuterated species observed was $\text{C}_6\text{H}_5\text{D}$, characterized by νCD at 2269 cm^{-1} and ρCD at 779 and 610 cm^{-1} .³⁷ It is likely that the π complex, $[\text{D}_3\text{O}^+\cdot 3\text{C}_6\text{H}_6]$, provides a low energy pathway to the formation of the σ complex $\text{C}_6\text{H}_7^+\cdot\text{D}_2\text{O}$, a presumed intermediate in the exchange reaction. Calculations on such an intermediate have been reported.³⁸

Dichloromethane Solutions. In CH_2Cl_2 , the spectrum of H_3O^+ with the least basic $\{\text{Cl}_{11}\}^-$ anion belongs to a C_{3v} symmetric $[\text{H}_3\text{O}^+\cdot 3\text{L}]$ type cation because it showed only one unsplit $\nu_4(\text{E})$ band at 1597 cm^{-1} (Table 2). Overlapping bands from the stretching vibrations are well deconvoluted into two components, $\nu_1(\text{A}_1)$ and $\nu_3(\text{E})$ (see Figure S1), with frequencies higher than those for $[\text{H}_3\text{O}^+\cdot 3\text{C}_6\text{H}_6]$ or solid $\text{H}_3\text{O}^+\{\text{Cl}_{11}\}^-$ (Tables 1, 2). This is in agreement with a weaker H-bonding interaction of H_3O^+ with dichloromethane than with benzene or the $\{\text{Cl}_{11}\}^-$ anion. Nevertheless, the solubility of $[\text{H}_3\text{O}^+\cdot 3\text{L}]\{\text{Cl}_{11}\}^-$ in CH_2Cl_2 is reasonably high ($> 0.015\text{ M}$).

In contrast to $\text{H}_3\text{O}^+\{\text{Cl}_{11}\}^-$, the solubility of $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ in CH_2Cl_2 is low (0.004 M), much less than in benzene (0.012 M). This indirectly indicates a type **B** structure for this anion with less than three CH_2Cl_2 molecules H-bonded to H_3O^+ . The absorption maximum of the OH stretching vibrations is shifted by $\sim 50\text{ cm}^{-1}$ to higher frequency relative to that in benzene solution or solid $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$. Thus, one or two of the OH groups of H_3O^+ are solvated with dichloromethane forming weaker H-bonds than with benzene.

1,2-Dichloroethane (DCE) Solutions. The solubility of $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ in 1,2-dichloroethane ($> 0.02\text{ M}$) is significantly higher than in benzene, indicating the important role of solvation. Indeed, the OH stretching frequencies in DCE are noticeably lower than for the tri-benzene solvate $[\text{H}_3\text{O}^+\cdot 3\text{C}_6\text{H}_6]^+$ or for solid $\text{H}_3\text{O}^+\{\text{Me}_5\text{Br}_6\}^-$ or $\text{H}_3\text{O}^+\{\text{Cl}_{11}\}^-$ (Table 2). The $\nu_4(\text{E})$ band is narrow and unsplit, indicating C_{3v} symmetry. This

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(38) Kryachko, E. S.; Nguyen, M. T. *J. Phys. Chem. A* **2001**, *105*, 153–155.

Table 2. Fundamental Vibrational Frequencies of Solvated H₃O⁺ Cation with C_{3v} Symmetry in Solution

no.	cation or H-bonded ion pair	anion	solvent	$\nu(\text{OH}_3)$	$\delta_{\text{as}}(\text{OH}_3)$
1	[H ₃ O·3CH ₂ Cl ₂] ⁺	CHB ₁₁ Cl ₁₁ ⁻	CH ₂ Cl ₂	ν_s 3244 ν_{as} 2915 3010 ^a	1597
	H ₃ O· <i>n</i> CH ₂ Cl ₂ ·Anion	CHB ₁₁ Me ₅ Br ₆ ⁻	CH ₂ Cl ₂	2982 ^a	<i>b</i>
2	[H ₃ O·3C ₆ H ₆] ⁺	CHB ₁₁ Cl ₁₁ ⁻	C ₆ H ₆	ν_s 3170 ν_{as} 2930 2932 ^a	1592
3	[H ₃ O·3C ₆ H ₆] ⁺ A	CHB ₁₁ Me ₅ Br ₆ ⁻	C ₆ H ₆	2932 ^a	1593 br
4	H ₃ O·C ₆ H ₆ ·Anion B	CHB ₁₁ Me ₅ Br ₆ ⁻	C ₆ H ₆	2932 ^a	1578 sh
5	[H ₃ O·3DCE] ⁺	CHB ₁₁ Me ₅ Br ₆ ⁻	DCE	ν_s 3143 ν_{as} 2837 2916 ^a	1593
	H ₃ O·C ₆ H ₆ ·Anion	CHB ₁₁ Me ₅ I ₆ ⁻	C ₆ H ₆	ν_s 3130 ν_{as} 2807 2932 ^a	<i>b</i>
6	[H ₃ O·(18-crown-6)] ⁺	CHB ₁₁ H ₅ Cl ₆ ⁻	DCE	2770 ^a	1640
7	H ₃ O·DCE·Anion	CF ₃ SO ₃ ⁻	DCE	2732 ^a	1667
8	[H ₃ O·3TBP] ⁺	FeCl ₄ ⁻	TBP	2536 ^a	1710

^a Maxima of the nondeconvoluted bands. ^b Not observable due to low solubility.

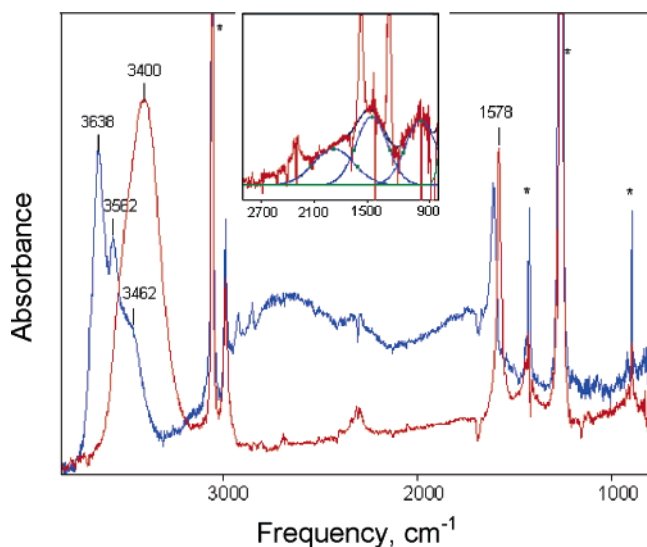
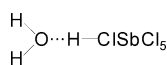


Figure 7. Solvent-subtracted IR spectra of dichloromethane solutions of H₂O·HSbCl₆ (red) and (H₂O)₂·HSbCl₆ (blue). Inset: Spectrum of H₂O·HSbCl₆ in the region of the bridging proton frequencies. Asterisks denote uncompensated bands of solvent.

leads to the conclusion that in DCE solutions, the H₃O⁺ forms a symmetrical tri-solvate, [H₃O⁺·3DCE], having stronger H-bonds to DCE than the π -bonds to benzene in [H₃O⁺·3C₆H₆]⁺.

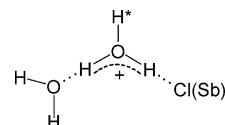
Hydrated HSbCl₆ in Dichloromethane and Benzene. The IR spectrum of the monohydrate of HSbCl₆ in dichloromethane solution (Figure 7) shows two bands from OH stretching vibrations, $\nu_s = 3520$ and $\nu_{\text{as}} = 3400$ cm⁻¹, at much higher frequencies than those for the C_{3v} [H₃O⁺·3CH₂Cl₂] cation in the same solvent. Moreover, the spectrum contains no indication of a band in the range of 815–1200 cm⁻¹, attributable to the $\nu_2(\text{A}_1)$ vibration of H₃O⁺. This band is expected to be more or less comparable in intensity and width to the $\nu_4(\text{E})$ band, seen as a strong band at 1578 cm⁻¹ with width at half-height of 21 cm⁻¹ (Figure 7). This region of the spectrum is transparent for SbCl₆⁻ salts, so even a very weak band of this nature would be detectable. These data indicate that the H₃O⁺ cation is absent. In fact, the values of the observed OH stretching frequencies, and the frequency and strong intensity of the bending vibration at 1578 cm⁻¹, are typical of H₂O molecules bound to a cation via the O atom.¹⁹ Thus, H-bonding is present in H₂O·HSbCl₆, but proton transfer from the anion to the O atom of water does not occur.



The IR spectrum has three weak and very broad bands (width in brackets) at 1870 (600), 1460 (414), and 904 (406) cm⁻¹, arising from the bridging proton vibrations in the OHCl group (inset in Figure 7). These frequencies correspond to strong or very strong H-bonding.

Without proton transfer to the O atom, the H₂O·HSbCl₆ monohydrate cannot contain a symmetrical SbCl₆⁻ anion. One of the Sb–Cl bonds should be weakened by protonation, and the symmetry of the SbCl₆⁻ anion should decrease from O_h to C_{4v}, lifting the degeneracy of the $\nu_3(\text{F}_{1u})$ mode. Thus, we sort corroboration of the structure of H₂O·HSbCl₆ by observing the Sb–Cl vibrations in the low-frequency region (200–500 cm⁻¹). Because the studied solutions showed very strong fluorescence, Raman spectroscopy could not be used and only IR spectroscopy was applicable. The $\nu_3(\text{F}_{1u})$ frequency of the O_h SbCl₆⁻ ion appears as an intense sharp band at 350 cm⁻¹ in benzene solutions of (Oct)₄N⁺SbCl₆⁻. This band is absent in the IR spectrum of a 0.02 M H₂O·HSbCl₆ solution in benzene and is replaced by an intense band at 371 cm⁻¹. This significant shift to higher frequency is consistent with protonation of the SbCl₆⁻ anion. We have been unable to definitively assign bands arising from the other $\nu\text{Sb}-\text{Cl}$ stretching frequencies expected from symmetry lowering. This is because SbCl₅ reacts with benzene to produce contaminants having peaks in the same region that evolve with time, and because in dichloromethane it is not fully IR transparent of the region.

The addition of water to H₂O·HSbCl₆ solutions in sufficient quantity for dihydrate formation results in a spectrum, which is significantly different from that of the symmetrical H₃O₂⁺ cation (Figure 7). It does not contain the very intense and broad $\nu_{\text{as}}(\text{OHO})$ band near 1000 cm⁻¹ characteristic of the symmetrical O–H⁺–O group and, in fact, is similar to that of the H₇O₃⁺ cation.³⁴ It shows a very broad and intense absorption in the range of 1400–3200 cm⁻¹ with two maxima at 1732 and 2680 cm⁻¹ assigned to bridging proton vibrations in asymmetric O–H···O and O–H···Cl³⁹ fragments. The terminal H₂O molecule gives two OH stretching vibrations ν_s and ν_{as} at high frequency (3638 and 3562 cm⁻¹) and one bending vibration. These data are consistent with the following structural representation.



(39) Stoyanov, E. S. Z. *Neorg. Khim.* **1982**, *27*, 726–731.

Table 3. IR Spectra of $(\text{H}_2\text{O})_n \cdot \text{HSbCl}_6$ Acid in Organic Solvents^a

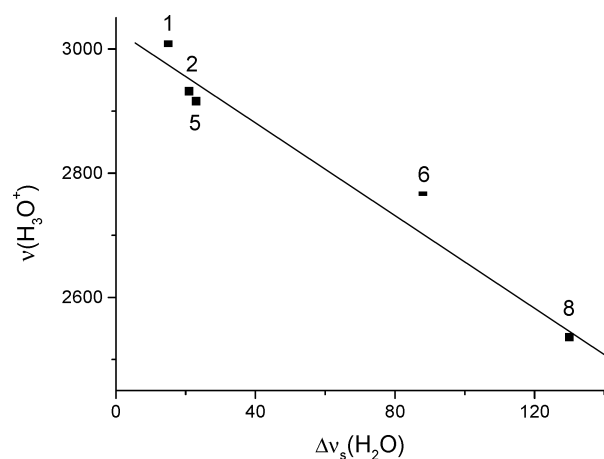
solvent	<i>n</i>	$\nu_{\text{as}}(\text{H}_2\text{O})$	$\nu_{\text{s}}(\text{H}_2\text{O})$	$\nu(\text{OH}^*)$	$\delta(\text{H}_2\text{O})$
CH_2Cl_2	1	3520	3400		1578
benzene	1	3465	3345		1569
CH_2Cl_2	2	3638	3562	3462	1606
benzene	2	3606	3528	3417	1602

^a Asterisk denotes unique OH group in dihydrate (see line drawing in text).

Table 4. Frequency Shifts (cm^{-1}) of $\nu_{\text{as}}(\text{H}_2\text{O})$ and $\nu_{\text{s}}(\text{H}_2\text{O})$ for Monomeric Water Molecules in Various Solvents

solvent	$\nu_{\text{as}}(\Delta)$	$\nu_{\text{s}}(\Delta)$
CCl_4	3707 (0)	3615 (0)
CH_2Cl_2	3685 (22)	3600 (15)
C_6H_6	3680 (27)	3595 (21)
DCE	3677 (30)	3592 (23)
SO_2^a	3665 (42)	3585 (30)
18-crown-6 ^b	3580 (127)	3527 (88)
TBP	3552 (155)	3485 (130)

^a Room temperature, 3–4 atm.⁴⁰ ^b In CCl_4 solvent.

**Figure 8.** Dependence of $\nu_{\text{max}}(\text{H}_3\text{O}^+)$ for $[\text{H}_3\text{O} \cdot n\text{Solv}]^+$ cations on $\nu_{\text{s}}(\text{H}_2\text{O})$ for monomeric water dissolved in the same solvent. The compound numbers refer to those used in Table 2.

The unique terminal $\nu(\text{OH})$ vibration (denoted H^* above) is assigned to the band at 3462 cm^{-1} (Figure 7, Table 3). These data indicate that the dihydrate has a strong interaction between the cation and the SbCl_6^- anion, preventing formation of the symmetric H_5O_2^+ cation. This result supports the conclusion that H_3O^+ does not form in the monohydrate because proton transfer from the anion to a single water molecule would be more difficult than that to a pair of water molecules.

The spectra of the mono- and dihydrates of HSbCl_6 in benzene solution are very similar to those in dichloromethane (Table 3). The only difference is that in benzene the OH frequencies are slightly lower because of the somewhat more strongly solvating properties of benzene.

Solvation of H_2O . The solvating ability of solvents with respect to proton hydrates is expected to follow the same order as that with monomeric water molecules. The strength of solvent interactions with dissolved water molecules can be evaluated from the lowering of the frequencies of the $\nu_{\text{as}}(\text{H}_2\text{O})$ and/or $\nu_{\text{s}}(\text{H}_2\text{O})$ bands relative to those in a baseline solvent such as CCl_4 . As can be seen from Table 4, the change in $\nu_{\text{as}}(\text{H}_2\text{O})$ is

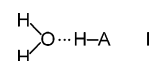
$\leq 30 \text{ cm}^{-1}$ for weakly basic solvents, is greater for weak O-donor solvents such as SO_2 , and is large (ca. 100 cm^{-1} or more) for moderate and strongly basic crown ethers and tributyl phosphate.

As revealed by Figure 8, the $\nu_{\text{max}}(\text{OH}_3)$ stretching frequencies of solvated hydronium ions, $[\text{H}_3\text{O} \cdot n\text{Solv}]^+$, are in excellent correlation with the sequence of the solvent basicity determined from solvation of water: $\text{CCl}_4 < \text{CH}_2\text{Cl}_2 < \text{C}_6\text{H}_6 < \text{DCE} \ll 18\text{-crown-6} \ll \text{TBP}$.

Discussion

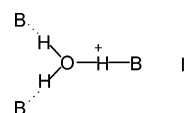
The molecular state of proton monohydrates in solid and liquid phases is determined by the energies of interaction of the hydrogen ion with anions, water, and solvent molecules. Depending on their relative basicities, three main molecular states are possible:

(i) The acidic proton interacts more strongly with the anion than with the water molecule, resulting in simple hydration of the acid.



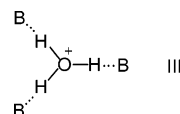
This type of compound is common in solution. The H-bond strength varies from weak to moderate and even strong. The “free” OH groups of the water molecule are weakly solvated by solvent molecules (not shown).

(ii) The acidic proton interacts more or less comparably with the O atom of water and a proton-acceptor base B. Base B can be the conjugate base anion or a neutral solvent molecule.



The core $\text{O}-\text{H}^+-\text{B}$ group has a very strong, symmetric or close-to-symmetric H-bond. In the case of $\text{B} = \text{H}_2\text{O}$, **II** is symmetric and corresponds to the H_5O_2^+ cation. When the basicity of B is close to that of H_2O , the IR spectrum of **II** (i.e., that part associated with proton vibrations) approaches that of the spectrum of the H_5O_2^+ cation and can be referred to as “ H_5O_2^+ type”. As a result of greater positive charge on the water molecule in **II** relative **I**, the terminal OH groups are more strongly solvated. Thus, they are shown as H-bonding to B in **II**, but the interaction strength is much weaker than in the core $\text{O}-\text{H}^+-\text{B}$ portion of the ion. State **II** is widespread in solution and quite possible in solids.

(iii) The proton is transferred to the water molecule resulting in the formation of the C_{3v} symmetric, or close to C_{3v} symmetric, H_3O^+ ion. All three hydrogen atoms interact more or less equivalently with neighboring atoms of the environment from bases B, which can be solvent or anion.



In this state, the $\text{O}-\text{H} \cdots \text{B}$ groups have moderate to strong H-bonds. Only in this case is the individual structural unit named a hydronium ion. State **III** is very common in solid-phase monohydrates for reasons we now discuss.

(40) Schneider, M.; Giguere, P. A. C. R. *Seances Acad. Sci., Ser. B* **1968**, *267*, 551–554.

Table 5. Vibrational Spectra of H₂O·HCl Solutions (cm⁻¹)

solvent	H ₂ O frequencies			acidic proton frequencies	ref
	ν_{as}	ν_s	(Δ) ^a		
CH ₂ Cl ₂ (IR)	3669	3586	(16)	$\nu(\text{HCl})$: 2480	this work
SO ₂ ^b (Raman)	<i>c</i>	3385	(200)	<i>c</i>	41
TBP (IR)		2810	(740)	$\nu_{as}(\text{OHCl})$: 1140	42

^a The low-frequency shift of $\nu_{as}(\text{H}_2\text{O})$ (IR) or $\nu_s(\text{H}_2\text{O})$ (Raman) as compared to those for free monomeric water in the same solvent. ^b At room temperature under 3–4 atm pressure. ^c Not available.

Solid-State Monohydrates. Even though type **III** acid monohydrates are written H₃O⁺A⁻, the hydronium ion is best considered in the form [H₃O⁺·3B], where B is a donor atom from the conjugate base anion. This arises because the H₃O⁺ ion in crystal structures is always stabilized by three more-or-less equivalent H-bonding interactions with the surrounding anions. As can be seen from Figure 2a,b for carboranes and Table 1 for other anions, the IR spectra of hydronium ion salts all take a similar form, irrespective of the nature of anion, and bands can be assigned in terms of approximate C_{3v} symmetry. The peak maximum of the νOH_3 frequencies appears in the relatively narrow range 2940–2700 cm⁻¹ as the anion varies from a carborane through oxyanions, despite their widely different basicities and proton-accepting abilities. An understanding of how this can arise is given by a comparison of the crystal structures of H₃O⁺Br⁻⁹ and H₃O⁺{Me₅Br₆}⁻. One might expect that the O–H···Br hydrogen bonds would be much stronger and shorter to the bromide ion than to the bromine substituents in the much larger, more charge-diffuse carborane anion. However, the O···Br distances in H₃O⁺Br⁻ (3.103 Å) are not much shorter than those in H₃O⁺{Me₅Br₆}⁻ (ave 3.172 Å). This is because the lattice structure of H₃O⁺Br⁻ allows the cation to have three H-bonds to a single Br atom, whereas in the carborane structure, the three H-bonds are formed at three different Br atoms of the anion. The basicity of the bromide ion is significantly reduced (on a per H-bond basis) by multiple H-bonding, whereas the B–Br bonds in the large carborane anion behave essentially independently. As a result, the H-bonding acceptor ability of the bromide anion is reduced to something approaching that of a Br atom on a carborane anion. Thus, the H₃O⁺ cation is not particularly sensitive to the nature of the H-bonding acceptor ability of the anion, and this peculiarity explains why the IR spectra of all H₃O⁺ salts are quite similar. This feature is usefully diagnostic and is important when considering the published spectra of H₃O⁺ salts having fluoroanions (see below).

Solution-State Monohydrates. When solid H₃O⁺A⁻ salts are dissolved in organic solvents, the molecular state of the cation will change depending on the ratio of the energy of solvation to the energy of interaction with anion. Let us consider the possibilities for anions of weak and strong proton affinity.

(a) Counterion has relatively strong proton affinity (Cl⁻, Br⁻, NO₃⁻, etc.), and the basicity of the solvent is changed from very weak to strong.

In weakly basic solvents (benzene, chlorocarbons), only monohydrates of **I** type are formed. For example, among the strong bands of free HCl (νHCl 2795 cm⁻¹) and of free H₂O (ν_{as} 3685 and ν_s 3600 cm⁻¹) in the IR spectrum of HCl dissolved in water-saturated dichloromethane, a weak spectrum of H₂O·HCl of **I** type is observed (Table 5). The moderate shift in νHCl upon H-bonding to water (315 cm⁻¹) corresponds to weak

H-bonding, reflecting the low stability of H₂O·HCl and the position of eq 2 to the left-hand side.



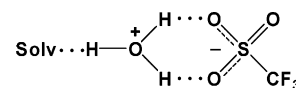
In a more basic solvent such as SO₂, the vibrational spectrum corresponds to H₂O·HCl with a structure intermediate between that of type **I** and **II**, and eq 2 is shifted to the right-hand side.⁴¹ Finally, the spectrum of H₂O·HCl in the strongly basic solvent tributyl phosphate is very similar to that of H₃O₂⁺ in the same solvent, that is, of type **II**.⁴² The distinguishing feature of this spectrum is the broad intense band at 1140 cm⁻¹ of the asymmetric vibration of O–H–Cl group with a very strong H-bond (Table 5).

Thus, as the solvent basicity increases, the interaction of the acidic proton with the Cl⁻ anion decreases, and H₂O·HCl is transformed from state **I** to state **II**. The monohydrate of this acid can form a type **III** H₃O⁺ species only in the crystal phase, because only in the solid state can the H₃O⁺ ion be stabilized by three approximately equal H-bonds from nearest neighbor Cl⁻ anions. This arrangement is not possible in solution.

(b) The counterion has a very weak proton affinity (i.e., its conjugate acid is a superacid).

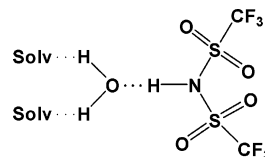
With a weakly basic anion, state **III** is more easily realized. Nevertheless, in weakly basic solvents (benzene, chlorocarbons), the monohydrates of superacids can differ significantly in their molecular states, depending on the geometry, polarizability, and stability of conjugate anion.

For example, a superacid such as triflic acid with a stable oxyanion of low polarizability, forms a type **III** H₃O⁺ salt in benzene or dichloromethane solution.³⁶ The strength of this acid is sufficient to transfer a proton to water, but the anion retains contact in an ion pair in which triflate is H-bonded to the H₃O⁺ cation in a bidentate manner:



In this case, the geometry of the O donor atoms in the anion allows the formation of two of the three H-bonds required to stabilize the H₃O⁺ cation, and all three H-bonds are roughly comparable in strength. Triflic acid is not strong enough to form solvent separated ion pairs.

By contrast, bis(trifluoromethylsulfonyl) imide, HN(SO₂CF₃)₂, is a superacid that is almost as strong as triflic acid, but does not protonate water. The monohydrate of this acid is simply a type **I** hydrate of formula H₂O·HN(SO₂CF₃)₂ in benzene or chlorinated hydrocarbon solution.³⁶



This can be understood in terms of polarizability of the anion and nonoptimal geometry of its donor atoms for bidentate stabilization of H₃O⁺. Upon ionization of the acid, the negative

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(42) Stoyanov, E. S. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2961–2966.

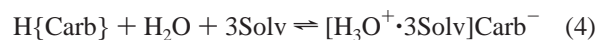
charge on the anion is delocalized into the NSO bonds, weakening the H-bonding acceptor capacity of the N atom.

Finally, superacids with anions of low chemical stability (e.g., SbCl_6^- , TlCl_4^- , FeCl_4^- , etc.) do not exist in the pure (anhydrous) state, although some monohydrates are stable. Consider the case of $\text{H}_2\text{O}\cdot\text{HSbCl}_6$, which forms a compound intermediate between type **I** and **II**. Its formation in dichloromethane or benzene can be considered as the addition of SbCl_5 as a third component to equilibrium (2) attaching to the type **I** $\text{H}_2\text{O}\cdots\text{HCl}^*$ complex via the Cl^* atom according to eq 3.

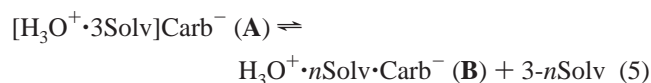


The binding of SbCl_5 weakens the $\text{H}-\text{Cl}^*$ bond but not enough for proton transfer to occur to the water molecule. The less stable FeCl_4^- anion cannot form this type of structure.

Carborane anions combine very weak proton-accepting ability with low polarizability and high chemical stability. Only with these three characteristics in combination can H_3O^+ be stabilized in benzene and chlorocarbon solvents and form type **III** trisolvates of formula $[\text{H}_3\text{O}^+\cdot 3\text{Solv}]$. Indeed, it is the same three characteristics of carborane anions that make their anhydrous acids the strongest known Brønsted acids.²⁸ Their monohydrate formation in solution is given by eq 4.



Equation 4 is a strictly accurate representation of monohydrate formation with the weakest proton-acceptor anion, $\{\text{Cl}_{11}\}^-$, in all three solvents benzene, CH_2Cl_2 , and DCE. With the somewhat more strongly proton-accepting $\{\text{Me}_5\text{Br}_6\}^-$ anion in benzene or dichloromethane, both the tri-solvated cation $[\text{H}_3\text{O}^+\cdot 3\text{Solv}]^+$ (designated form **A**) and the contact ion pair $[\text{H}_3\text{O}^+\cdot\text{Solv}\cdot\text{Anion}^-]$ ($\text{Solv} = \text{C}_6\text{H}_6$, CH_2Cl_2 ; designated form **B**) are observed (eq 5).



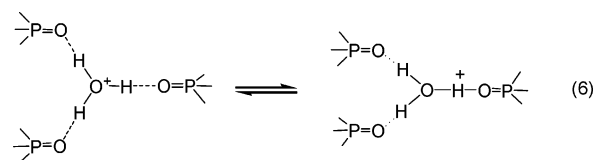
With the more strongly proton-accepting $\text{CHB}_{11}\text{Me}_5\text{I}_6^-$ anion, only contact ion pairs (form **B**) are formed, and eq 5 moves completely to the right-hand side. In DCE as solvent, the most active among the weakly basic solvents used, $\text{H}_3\text{O}^+\cdot\{\text{Me}_5\text{Br}_6\}^-$ forms only a $[\text{H}_3\text{O}^+\cdot 3\text{DCE}]$ cation and eq 5 moves completely to the left-hand side. Retention of the identity of H_3O^+ in the contact ion pairs is based on the similarity of interaction energies of the OH groups of H_3O^+ cation with both solvents and carborane anions. Approximate C_{3v} symmetry is retained as a solvent molecule in $[\text{H}_3\text{O}^+\cdot 3\text{Solv}]^+$ is replaced by a carborane anion, and the IR spectra are qualitatively very similar.

When highly basic solvents such as tributyl phosphate are used for the preparation of superacid monohydrate solutions, eq 5 is shifted to the left in favor of tri-solvate formation because of stronger H-bonding of H_3O^+ to solvent molecules than to anions. Under these conditions, it even becomes possible to use counterions with very low stability, such as FeCl_4^- or TlCl_4^- .^{26,43,44}

(43) Khramenko, S. P. Mechanistic Study of the HTlCl_4 Extraction from Chloride-Sulfate Solutions by Neutral Organophosphorus Solutions. Candidate of Chemical Science Dissertation, Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Science, Novosibirsk, 1973.

Limits of Existence of H_3O^+ in Condensed Phases. Let us trace how increasing interaction of H_3O^+ with its environment is reflected in its IR spectrum and where the limits of its existence are reached. As the indicator of increasing strength of H-bonding in the $[\text{H}_3\text{O}^+\cdot 3\text{B}]$ moiety we use the decrease of the $\nu_{\text{max}}(\text{OH}_3)$ stretching frequency.

The sensitivity of this indicator is actually quite low for H_3O^+ in the environment of carborane anions or solvent molecules such as benzene, CH_2Cl_2 , and DCE. Their IR spectra look very similar and can be almost indistinguishable without deconvolution (Figure 2). Only in the H_3O^+ complex with 18-crown-6, or in the solid-state environment of the NO_3^- anion, do the lower frequency shifts of νOH_3 stretching become visually distinct. Simultaneously, as νOH_3 decreases, it increasingly overlaps with a combination band at ca. 2200 cm^{-1} , increasing the intensity of the combination band via Fermi resonance. This evolution of the IR spectrum continues when passing to the tri-solvate $[\text{H}_3\text{O}^+\cdot 3\text{TBP}]^+$ cation formed in tributyl phosphate solvent. The base strength of this solvent is, in fact, the limit for the existence of the H_3O^+ cation of C_{3v} symmetry because it is in equilibrium with a small quantity of a cation of type **II** with one preferred OHO group whose bridging proton is more-or-less equally shared by H_2O and TBP (eq 6).²⁶



When more strongly basic solvents than tributyl phosphate, such as tributylphosphine oxide, are employed, eq 6 is shifted completely to the right-hand side.⁴³ This cation, with an isolated $(\text{H}_2\text{O})-\text{H}^+-\text{O}(=\text{P})$ group having very strong H-bonding and $\nu_{\text{as}}(\text{OHO}) = 1200\text{ cm}^{-1}$, is simply an asymmetric version of familiar proton disolvates of the type $[\text{B}-\text{H}-\text{B}]^+$, where $\text{B} = \text{H}_2\text{O}$ or O-donor solvents.^{26,42,45-47} These disolvates are quite distinct from type **III** hydronium ions.

Thus, all presently well-characterized examples of H_3O^+ salts with approximate or exact C_{3v} symmetry have similar spectra, irrespective of whether they are in an anion environment in the solid phase or a solvated environment in the solution phase (Figure 2, Tables 1 and 2). Neutral or anionic bases (**B**) bound to H_3O^+ in type **III** $[\text{H}_3\text{O}^+\cdot 3\text{B}]$ species can be arranged in accordance with increasing interaction as determined from the shift of νOH to low frequency: $\text{CH}_2\text{Cl}_2 < \{\text{Cl}_{11}\}^- < \text{benzene} \approx \{\text{Me}_5\text{Br}_6\}^- < \text{DCE} < \text{Cl}^- \approx \text{HSO}_4^- < \text{NO}_3^- \leq 18\text{-crown-6} < \text{TBP}$. As shown in Figure 8, the solvents in this ranking follow the same order of H-bonding strength to a water molecule. When using this ranking for H_3O^+ , it is important to remember that the data for small anions (Cl^- , HSO_4^- , and NO_3^-) come from solid-state data where three H-bonds to each anion decrease their basicities relative to the same anions forming a single H-bond.

Within the limits of the existence of the H_3O^+ ion, there is a linear relationship between decreasing stretching OH frequen-

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(45) Stoyanov, E. S. *J. Struct. Chim.* (a translation of *Zr. Struct. Khim.*, Russia) **1993**, *34*, 714-721.

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(47) Stasko, D.; Hoffmann, S. P.; Kim, K.-C.; Fackler, N. L. P.; Larsen, A. S.; Drovetskaya, T.; Tham, F. S.; Reed, C. A.; Rickard, C. E. F.; Boyd, P. D. W.; Stoyanov, E. S. *J. Am. Chem. Soc.* **2002**, *124*, 13869-13876.

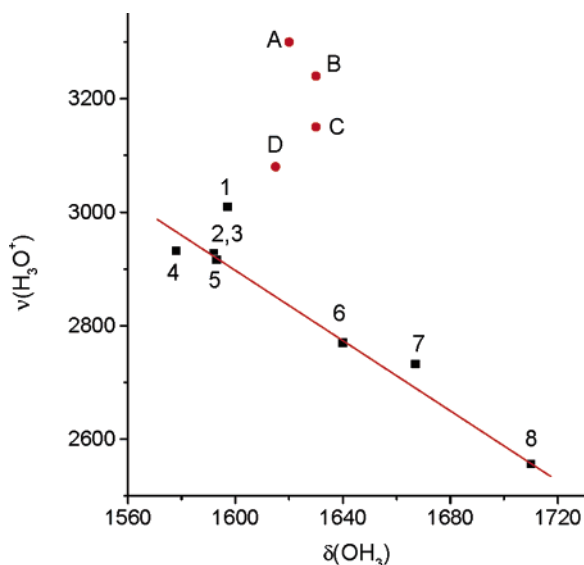


Figure 9. Dependence of the $\nu_{\max}(\text{OH}_3)$ stretch on the $\delta(\text{OH}_3)$ bending frequency. Compound numbers correspond to those used in Table 2. Points A–D are for proton monohydrates with TiF_5^- , BiF_6^- , SbF_6^- , and AsF_6^- anions, respectively.

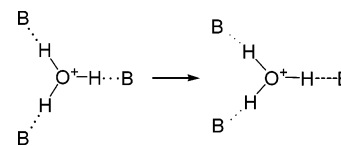
cies and increasing bending $\nu_4(\text{E})$ frequency (Figure 9). This is expected for an isostructural series of $[\text{H}_3\text{O}^+\cdot 3\text{Sol}]$ compounds with changing basicity of the solvent and serves as a criterion for existence of the hydronium ion in solvents of different nature. Outside the upper basicity limit of TBP, the H_3O^+ cation changes from state **III** to state **II**, which should be considered a proton disolvate of $[\text{H}_2\text{O}-\text{H}^+-\text{B}]$ type, where B is a strongly basic molecule or anion.

Dichloromethane is the weakest basicity solvent in which the $[\text{H}_3\text{O}^+\cdot 3\text{B}]$ cation has been obtained experimentally. The question then arises: Can a symmetrical H_3O^+ cation exist with surrounding bases weaker than dichloromethane? Fluoroanions such as PF_6^- , AsF_6^- , etc. are more weakly basic than carborane anions,³⁴ so let us consider the literature data on fluoroacid monohydrates.^{3,8,48} They have been studied by IR and Raman spectroscopy, and the IR spectra of the H_3O^+ cations show some differences from those obtained in the present work. The present work gives new insight into published data.

Observations about Prior Studies. Solids of nominal $\text{H}_3\text{O}^+\text{A}^-$ type for $\text{A}^- = \text{AsF}_6^-$, SbF_6^- ,^{3,48} BiF_6^- , and TiF_5^- have been structurally characterized by X-ray crystallography. Their IR and Raman spectra in the solid state coincide with those obtained in HF solution. The OH stretching vibrations (ν_{as} from 3080 to 3240 cm^{-1}) are considerably higher than expected from the present work. Also, the $\nu_4(\text{E})$ bending increases rather than decreases as νOH increases. As a result, when the data for these samples are plotted onto Figure 9 (points A–D), they are outliers from the linear dependence for H_3O^+ in C_{3v} symmetry.

The changes in the vibrational spectrum of $\text{H}_3\text{O}^+(\text{fluoroanion})$ species compared to $[\text{H}_3\text{O}^+\cdot 3\text{B}]$ in C_{3v} symmetry can be explained by distortion of a type **III** cation in the direction of a type **II** cation, where B is an HF solvent molecule or an F atom from the anion (Scheme 1). The greater is the asymmetry of the base interactions, the more the vibrational spectrum

Scheme 1



approaches type **II**. The νOH stretching and the $\delta(\text{H}_2\text{O})$ bending ($\nu_4(\text{E})$ in C_{3v} symmetry) vibrations increase in frequency, and the intensities of the $\delta(\text{H}_2\text{O})$ band and that at $\sim 900\text{ cm}^{-1}$ (labeled $\nu_2(\text{A}_1)$ in C_{3v} symmetry) both increase significantly. It is apparent from the data in Figure 9 that the distortion increases in the order $\text{AsF}_6^- < \text{SbF}_6^- < \text{BiF}_6^- < \text{TiF}_5^-$. These data suggest that the symmetrical H_3O^+ ion becomes unstable in the low basicity environment of fluoroanions and HF. Indeed, the distortion appears to be already occurring in CH_2Cl_2 solvent, because in Figure 9 the CH_2Cl_2 point deviates from linear dependence, in the direction of the fluoroanions. Thus, dichloromethane appears to represent the lower limit of basicity for which H_3O^+ can exist in C_{3v} symmetry. In an HF solvent environment, or in the solid state with fluoroanion interactions, the H_3O^+ moves away for C_{3v} symmetry toward a type **II** structure. This subtlety could not have been observed in the earlier ^{19}F NMR studies in HF solution because of fluxionality on the time scale of the measurement. Similarly, it would not have been evident in the solid-state structural investigations due to high thermal motion in the OH_3^+ cation and the usual difficulty of locating H atoms accurately in X-ray crystallography. The transformation from a type **III** toward a type **II** structure appears to be gradual outside the low basicity limit. Its origin may lie in ion-pairing effects that preferentially favor one of the three H-bonds.

In summary, we propose that the IR criterion for the existence of an H_3O^+ ion of approximate C_{3v} symmetry is an essentially linear dependence of $\nu_{\max}(\text{OH}_3)$ and $\delta(\text{OH}_3)$ within the ranges 3010–2536 cm^{-1} for $\nu_{\max}(\text{OH}_3)$ and 1597–1710 cm^{-1} for $\delta(\text{OH}_3)$. This provides a simple way to assess the appropriateness of the formulation of the proton state in acid monohydrates. For example, the point for SO_2 solutions of the monohydrate of HCl lies completely outside the field of Figure 9, in agreement with its formulation as a compound intermediate between types **I** and **II**. More importantly, the data reported for the monohydrate of HSbCl_6 , widely cited as the textbook example of the IR spectrum of the free $\text{H}_3\text{O}^+(C_{3v})$ ion in solution, cannot be correct. The data of Desbat et al.⁵ ($\nu_{\text{s}}\text{OH} = 3560$, $\nu_{\text{as}}\text{OH} = 3510$, and $\delta(\text{OH}_3) = 1600\text{ cm}^{-1}$ in dichloromethane) lie well outside the field of Figure 9. Our redetermination of the data for dichloromethane or benzene solutions (Table 3) also leads to points well outside the field of Figure 9, in agreement with our conclusion that the monohydrate of HSbCl_6 is, in fact, a type **I–II** compound. From a comparison of our spectra (Figure 7) with those of Desbat et al., it is likely that the previously published spectrum ascribed to $\text{H}_3\text{O}^+\text{SbCl}_6^-$ belongs to a mixture of dihydrate and trihydrates of HSbCl_6 . Our data on di- and trihydrates will be the subject of a future publication.³⁴

Conclusions

From the results of the present work, we can understand why, over a period of more than 30 years, there have been virtually no publications on the vibrational spectra of the H_3O^+ ion in organic solvents. For the H_3O^+ ion to be stable in solution, a

(48) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1975**, *14*, 2224–2230.

fairly exacting set of requirements must be met. Three more-or-less equivalent, medium-to-strong H-bonds must be formed with the solvent or counterion. Only solvents within the basicity range chlorocarbons to tributyl phosphate are suitable. The range includes benzene, which has unexpectedly strong π interactions with the O–H bonds of H_3O^+ . The H-bonds to dichloromethane are also unexpectedly strong, moving the νOH frequencies ca. 400–500 cm^{-1} lower than in the gas phase. There are three requirements of the counterion. It must have very low proton-acceptor ability, be relatively nonpolarizable, and have high chemical stability. Carborane anions fulfill these requirements but have only become recognized in more recent times.^{29,49}

Outside the framework of these requirements, the preferentially stronger interaction of one of the H-bonds of the H_3O^+ ion with a solvent or anion base (B) causes a transition toward a $[\text{H}_2\text{O}-\text{H}^+-\text{B}]$ type structure. The distortion from C_{3v} symmetry is minor for bases weaker than dichloromethane, but with

bases stronger than tributyl phosphate, the species formed is more closely related to H_5O_2^+ than H_3O^+ .

This has allowed us to provide further insight into the nature of H_3O^+ salts with fluoro counterions and show that the spectrum previously attributed to H_3O^+ in dichloromethane solution with SbCl_6^- as counterion in reality belongs to the spectrum of hydrates of the form $(\text{H}_2\text{O})_x \cdot \text{HSbCl}_6$ ($x = 2-3$).

Acknowledgment. This work was supported by NIH grant GM 23851. We thank Dr. Fook Tham for determination of the X-ray structures. We thank Professor Karl Christe for helpful discussions.

Supporting Information Available: IR spectra of $\text{H}_3\text{O}^+[\text{Carb}]$ with demonstrations of the solvent subtraction and deconvolution procedures, and details of the X-ray crystal structure determination of $\text{H}_3\text{O}^+\text{CHB}_{11}\text{Me}_5\text{Br}_6^- \cdot 1.5\text{C}_6\text{H}_6$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0551335

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