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IR Spectrum of the $H_5O_2^+$ Cation in the Context of Proton Disolvates $L-H^+-L$

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The $H_5O_2^+$ ion has been studied in chlorocarbon, benzene, and weakly coordinating anion environments to bridge the gap between the gas-phase and traditional condensed-phase investigations. Symmetrical cations of the type [$H_5O_2^+\cdot$4Solv] are formed via H-bonding with the terminal O−H groups. In the infrared spectrum, the ν_sOH and ν_{as}OH vibrations behave in a manner similar to those of common water molecules: the stronger is the H-bonding interaction with the surroundings, the lower is the frequency shift. A consistent pattern of IR bands from the central $O-H^+-O$ group is identified, regardless of the strength of the interaction of $H_5O_2^+$ with its environment. Three intense bands develop: ***a*** (860−995 cm^{-1}), ***b*** (1045−1101 cm^{-1}), and ***c*** (1672−1700 cm^{-1}), as well as two weak bands, ***d*** (∼1300 cm^{-1}) and ***e*** (∼1400−1500 cm^{-1}). These fingerprint bands are highly characteristic for vibrations of O−H−O group irrespective of formal charge. They are seen in symmetrical proton disolvates of the type $L-H^+-L$, where L is an O-atom donor (alcohol, ether, ketone, phosphate, etc.), and in $[A-H-A]^-$ acid salts ($A^- =$ oxyanion). The commonality is equivalency of the two O-atoms, a short O···O distance (ca. 2.40 Å), and a flat-bottomed potential well for the bridging proton, that is, a short, strong, low-barrier H-bond. Assignments for bands ***a***−***e*** are suggested in an attempt to resolve inconsistencies between experimental and calculated data.

Introduction

One of the oldest unsolved problems of chemistry is developing an accurate molecular description of the aquated proton H_{aq}^+. The problem can be reduced to a discussion of the relative importance of H_3O^+ and $H_5O_2^+$ as primary ions, but this avoids the complexity introduced by the inevitable network of H-bonding in immediate and higher solvation shells. There has been considerable progress in describing the nature of $H(H_2O)_n^+$ clusters in the gas phase via combined experimental and theoretical approaches,[1,2] but, arguably, understanding the nature of H_{aq}^+ in condensed media is where advances are needed to improve our description of the proton in water and in acid-catalyzed processes. Understanding the anomalously high mobility of H^+ in water,[3] elucidating the role of low-barrier H-bonds in enzymatic catalysis,[4] and describing the mechanisms of biological proton pumping[5−8] remain considerable challenges.

Our approach is to study the simplest hydrates of the proton (H_3O^+, $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$, etc.) in organic solvents, and in solids, with weakly coordinating anions. The intention is to provide a bridge between gas-phase studies and bulk aqueous media. Because of recent advances in instrumentation, the vibrational spectra of proton hydrates in the gas phase have become available with reasonable resolution and increasingly wide frequency range. Replacing the vacuum around gas-phase $H(H_2O)_n^+$ ions with condensed-phase environments of increasing H-bond accepting ability provides an opportunity to follow how the structure and vibrational spectra of the simple ions react to an increasingly interactive environment. The ultimate goal is to arrive at a confident interpretation of the broad and complex IR spectrum of H_{aq}^+ in terms of the molecular species present.

To date, a detailed study of this type has only been carried out for the simplest ion, the C_{3v} symmetric H_3O^+ ion.[9] Conditions for its existence in condensed media are surprisingly exacting. Only solvents in the basicity range of chlorocarbons to trialkyl phosphates can form the three medium-to-strong, near-equivalent, H-bonds necessary to stabilize the trisolvated [$H_3O^+\cdot$3L] ion (L = solvent and/or anion). For the lowest basicity solvents, it is necessary to use anions that are not only weakly basic but that have low polarizability and high chemical stability. Outside of these conditions, the H_3O^+ ion easily distorts away from C_{3v} symmetry, forming unsymmetrical disolvates of type H_2O-H^+-L.[9] The $H_5O_2^+$ ion is prototypical of a large class of symmetrical disolvates, $L-H^+-L$, and the ease of disolvate formation begs the question of under what conditions so-called Zundel-type[10] [$H_5O_2^+\cdot$4L] ions are favored over Eigen-type[11] [$H_3O^+\cdot$3L] ions.

Proton disolvates such as the $H_5O_2^+$ ion are stabilized by short, strong, low-barrier (SSLB) H-bonds.[10,12,13] The gas-phase bond dissociation enthalpy of $H_5O_2^+$ into H_3O^+ and H_2O is ca. 32 kcal mol^{-1}, double or triple that of a typical H-bond.[14] The proton resides in a nearly flat-bottomed, double-well potential such that its position becomes essentially indeterminate within an interval between the O····O bond.

$$\mathbf{O}\cdots|\leftarrow \mathbf{H}^+\rightarrow|\cdots\mathbf{O}$$

Unlike a typical O−H···O hydrogen bond, which is unsymmetrical, there is a symmetrical distribution of the proton within this interval, and nuclear motion is comparable to the IR time scale. The consequences for IR spectroscopy are dramatic and distinctive. Instead of νOH at 3000 ± 500 cm^{-1}, as seen with typical H-bonded O−H···L groups, ν_{as}OHO moves to very low energy (ca. 1000 cm^{-1}). Moreover, this ν_{as}OHO stretching vibration is believed to have lower energy than the associated bending vibrations.[15,16] This contradicts a norm of IR spectroscopy where stretching vibrations always have higher frequencies than the associated bending vibrations. In addition, an unusual broadening, diminishment, and even disappearance of IR bands

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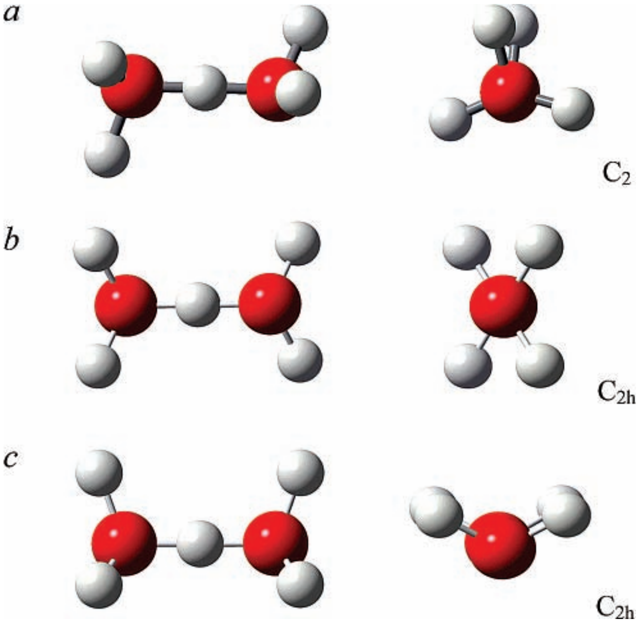


Figure 1. Three possible molecular group symmetries of the $H_5O_2^+$ cation: (a) the C_2 structure calculated to have the lowest energy in the gas phase, (*b*) the trans configuration common in the crystal state, and (c) the cis configuration that may be present in solutions.

closely associated with the OH^+O unit may occur, for example, the C−O−C stretch in the diethyl ether $(Et_2O)_2H^+$ disolvate.[17,18] This phenomenon is poorly understood.

The study of the $H_5O_2^+$ cation in condensed phases has centered on defining its existence in crystal structures of acid dihydrates, $HA{\cdot}2H_2O$. The $H_5O_2^+$ cation is always found to have H-bonding contacts with anions via the four peripheral O−H groups, and the O····O distances are short (2.41−2.42 Å).[19−21] Theory supports a C_2 minimum energy structure for the gas phase (Figure 1a), but trans C_{2h} symmetry structures are not much higher in energy[15,22] and predominate in the crystalline state (Figure 1b). In organic solvents where ion pairing takes place, a cis C_{2h} symmetry structure (Figure 1c) must be considered.

Studies on the state of the $H_5O_2^+$ cation in aprotic solvents are very limited, mainly concerning IR spectroscopic investigations of tetrasolvates $[H_5O_2^+{\cdot}4L]$ with relatively strong bases such as L = tributyl phosphate[23] or phosphine oxides.[24] Experimental IR studies of the $H_5O_2^+$ cation in surroundings of weakly basic solvent molecules are unknown, although there is one NMR investigation of octanesulfuric acid dihydrate in a mixed Freon solvent.[25] Exactly such investigations are needed to make a connection between the free $H_5O_2^+$ cation in the gas phase and its state in condensed phases surrounded by strongly interacting neighbors.

IR spectroscopy is the best method to study the $H_5O_2^+$ cation because it can be applied to all phases: gas, liquid/solutions, and solid. Remarkably, a consensus interpretation of the IR spectrum of the $H_5O_2^+$ cation has yet to be reached in any phase. Not only are there discrepancies between the published experimental spectrum of the free $H_5O_2^+$ ion in the gas phase, but authors differ considerably in their assignments of bands to particular vibrational modes. Theory is still evolving in its application to the IR spectrum of $H_5O_2^+$, and experiments that show the response of the fundamental modes in $[H_5O_2^+{\cdot}4L]$ ions to increasing interaction strength of L are necessary to develop a consistent set of assignments.

In the present work, we report the results of an IR spectroscopic investigation of the $H_5O_2^+$ cation in weakly basic solvents (benzene, dichloromethane, and dichloroethane) as well as in solids with weakly coordinating counterions, chiefly the carborane anions $CHB_{11}Cl_{11}^-$ and $CHB_{11}Me_5Br_6^-$. They are shown in Figure 2 and are abbreviated $\{Cl_{11}\}^-$ and $\{Me_5Br_6\}^-$. Square brackets are used throughout this paper to indicate a completed first solvation sphere of the $H_5O_2^+$ ion, for example, $[H_5O_2^+{\cdot}4Solv]$.

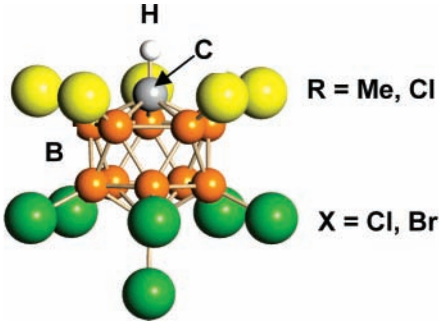


Figure 2. The $CHB_{11}R_5X_6^-$ carborane anions used in this study, abbreviated $\{R_5X_6\}^-$.

Icosahedral carboranes are among the most weakly basic anions presently known, and their conjugate acids have recently been shown to be the strongest known protic acids.[26,27] They provide the weakest perturbing counterion influence on the $H_5O_2^+$ cation in condensed phases, comparable to solvents such as benzene and chlorocarbons. The gradual change of the IR spectrum of $H_5O_2^+$ passing from the gas phase to condensed phases with weakly basic solvents and anions, and then to stronger bases, leads to new insight into the structural properties of this ion and points to how a consensus might be reached regarding the assignment of its IR spectrum.

Experimental Section

Carborane acids, $H(CHB_{11}Cl_{11})$ and $H(CHB_{11}Me_5Br_6)$, as well as their benzenium and hexamethylbenzenium ion salts, were prepared as previously described.[28,29] Solvents were purified and dried according to the literature methods.[30] All operations were performed in a Vacuum Atmospheres Corp. glovebox under He (O_2, H_2O < 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 were manipulated using GRAMMS software.

Benzene, dichloromethane (DCM), and 1,2-dichloroethane (DCE) solutions of $[H_5O_2][carborane]$ were prepared from weighed quantities of $C_6H_7^+Carb^-$ (benzene) or $HC_6Me_6^+Carb^-$ salts (DCM and DCE) to which was added a calculated volume of water-saturated solvent followed by sufficient dry solvent to obtain resulting solutions with acid:H_2O mole ratios from 1:1 to 1:2.

A thin film of solid $H\{Cl_{11}\}$ acid was obtained by direct sublimation onto Si windows in the evacuated IR cell at 160 °C and 10^{-5} Torr.[31] Exposure to moist air with simultaneous recording of IR spectra resulted in the detection of the sequential hydration of $H\{Cl_{11}\}$ acid with water.

Spectra of $H_5O_2^+$ and $[L{-}H^+{-}L]$ cations with the $FeCl_4^-$ counterion (L = ethanol, diethyl ether, acetone, and tributyl phosphate) were obtained as previously described.[18,23]

Results and Discussion

The gradual adsorption of water vapor into a film of solid $H\{Cl_{11}\}$ acid results first in the appearance of the known IR

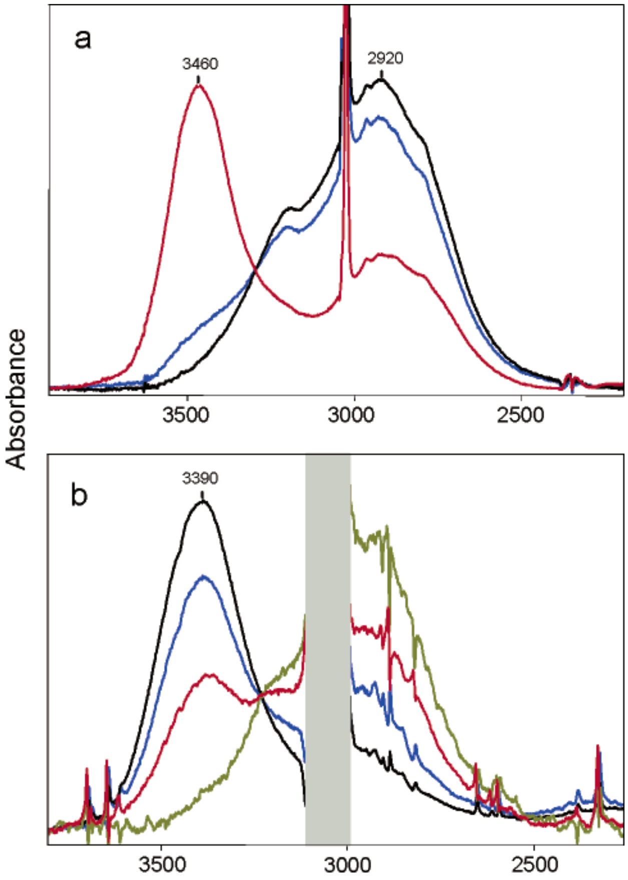


Figure 3. (a) Evolution of the IR spectrum during absorption of water vapor by solid H{Cl_{11}} acid, showing sequential formation of H_3O^+ and $H_5O_2^+$ (black→blue→red). (b) IR spectra of titration of benzene solutions of H_3O^+{Cl_{11}}$^-$ with 1 equiv of H_2O, forming $H_5O_2^+$ (khaki→red→blue→black). The spectra are normalized to unit intensity of the anion absorptions.

spectrum of the H_3O^+ cation[9] followed by the spectrum of the next higher hydrate, the $H_5O_2^+$ ion. As shown in Figure 3a for the region of the OH stretching bands, the intensities of the νOH bands of the H_3O^+ cation ($\nu_{max} \approx 2920$ cm^{-1}) decrease while those for $H_5O_2^+$ at 3460 cm^{-1} increase with increasing hydration. The overlaid sharp band at 3024 cm^{-1} arises from νCH in the {Cl_{11}}$^-$ carborane anion. Similar spectra are observed for benzene solutions of H_3O^+Carb$^-$ (Carb = {Cl_{11}}$^-$ or {Me_5Br_6}$^-$) when titrated with 1 equiv of H_2O (Figure 3b). The appearance of isosbestic points in the spectra of both the solid state and the benzene solutions indicates that H_3O^+ and $H_5O_2^+$ are the sole species formed. Similarly, spectra for the $H_5O_2^+$ cation were obtained in dichloromethane and dichloroethane (DCE) by the addition of the necessary amounts of water to corresponding solutions of hexamethylbenzenium ion salts, $HC_6Me_6^+$Carb$^-$.

A representative spectrum of a $H_5O_2^+$ carborane salt in the solid state is shown in Figure 4. The sharp bands arise from the carborane anion, while the broad bands are associated with the $H_5O_2^+$ cation.

Regardless of the symmetry of the $H_5O_2^+$ cation, it has 15 fundamental vibrational modes that can be subdivided into three groups:[32−34] (i) the primary vibrations of the two terminal H_2O molecules, four O−H stretches above 3000 cm^{-1} and two bending modes in the range 1600−1700 cm^{-1}, which, in the case of equivalency of the four peripheral OH groups, will appear in the IR spectrum as two stretching modes, $\nu_s(H_2O)$ and $\nu_{as}(H_2O)$, and one bending mode, $\delta(H_2O)$; (ii) four vibrations of the central OH^+O group, an asymmetric stretch ν_{as}(OHO), an in-plane bend δ(OHO), an out-of-plane bend γ(OHO) with regard to the approximate molecular plane, and a non-IR-active symmetric stretch ν_s(O•••O); and (iii) five low-frequency modes (below 800 cm^{-1}) that predominantly involve rock, wag, and twist vibrations of the terminal water molecules.[35,36] These five modes are not considered in the present work because they are weak and largely masked by anion and solvent bands.

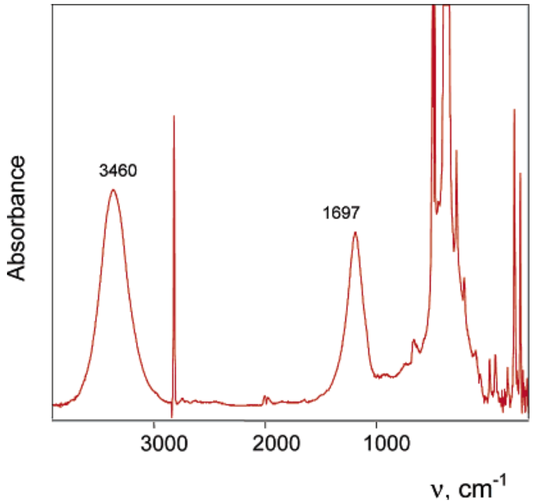
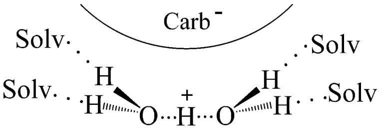


Figure 4. The IR spectrum of solid $H_5O_2^+${Cl_{11}} formed by controlled hydration of H{Cl_{11}}. The sharp bands arise from the carborane anion; the broad bands arise from the $H_5O_2^+$ cation.

Trends in νOH Stretch of the Terminal H_2O Molecule. The frequencies and contours of the νOH bands reflect the strength and symmetry of H-bonding of the $H_5O_2^+$ cation to neighboring molecules in its environment. For example, the spectrum of solid $H_5O_2^+${Cl_{11}}$^-$ obtained by hydration of the solid benzenium ion salt, $C_6H_7^+${Cl_{11}}$^-$, shows only a single, slightly unsymmetrical and relatively narrow νOH band at 3460 cm^{-1} (width at half-height 148 cm^{-1}). This indicates close overlap of the ν_s and ν_{as} OH stretches and essentially equivalent interactions of the four O−H groups with Cl atoms of the surrounding {Cl_{11}}$^-$ anions. On the other hand, the same salt produced by hydration of bare H{Cl_{11}} acid shows nearly double the bandwidth for νOH, indicating a less symmetrical local environment for the $H_5O_2^+$ ion. Nevertheless, it was not possible to obtain a reliable deconvolution of νOH into ν_s and ν_{as} under any condensed-phase conditions.

As shown in Table 1, in benzene solution the frequency maximum for νOH in various $H_5O_2^+$Carb$^-$ salts does not depend on the nature of anion for {Cl_{11}}$^-$ or {Me_5Br_6}$^-$. Similarly, ν_{max}OH is the same in dichloroethane solution irrespective of the nature of three different anions: {Cl_{11}}$^-$, {Me_5Br_6}$^-$, and {H_5Br_6}$^-$. This indicates that solvated ion pairs of the type [$H_5O_2^+$•4L]Carb$^-$ are formed in both solvents (L = solvent). Because trisolvated ion pairs are formed in dichloromethane with the monohydrated acid, [H_3O^+•3CH_2Cl_2]{Cl_{11}}$^-$, where the cation charge-to-size ratio is larger,[9] it is reasonable to assume that the data for the dihydrate $H_5O_2^+${Cl_{11}}$^-$ in CH_2Cl_2 also refer to a symmetrically solvated cation, [$H_5O_2^+$•4CH_2Cl_2].

As will be detailed later, the intensities, and to a smaller extent the frequencies, of some of the bands from the central O−H$^+$−O group vibrations were found to be sensitive to the nature of the anion in solution. This indicates that the anion faces the central OH^+O moiety of $H_5O_2^+$ cation without disrupting the O−H•••Solv hydrogen bonding:



Such an interaction would force the $H_5O_2^+$ ion to adopt a cis configuration, which is consistent with that deduced from low-temperature ^{1}H NMR for $H_5O_2^+$ in Freon solutions of octane sulfonic acid dehydrate.[25] The same type of interaction between the OH^+O group and the $Zr(NO_3)_5^-$ anion has been established for the tributyl phosphate proton disolvate ion pair [TBP$-H^+-$TBP]$Zr(NO_3)_5^-$ in TBP solution.[38]

The degree of red shifting of the νOH frequencies in the condensed-phase salts as compared to the gas-phase $H_5O_2^+$ ion gives a measure of the relative strength of the H-bonding interaction with anions and/or solvent molecules. Thus, Table 1 ranks the basicities of anions and solvents in the order $\{Cl_{11}\}^-_{solid} < CH_2Cl_2 <$ DCE $\leq \{Me_5Br_6\}^-_{solid} \leq$ benzene $< \{H_5Br_6\}^-_{solid}$. This order is similar but not identical to that obtained with H_3O^+ salts: $CH_2Cl_2 < \{Cl_{11}\}^-_{solid} < \{Me_5Br_6\}^-_{solid} \approx$ benzene $<$ DCE.[9] The somewhat different ordering may arise from mixing solid-state data with solution data and from the differing sensitivities of the $H_5O_2^+$ and H_3O^+ ions to the polarizability of the base. The $H_5O_2^+$ ion forms much weaker H-bonds than H_3O^+ and is therefore less able to polarize a base. A dramatic example of the effects of different polarizability on acid/base interactions is provided by the example of a strong acid that does not protonate water.[39] The weaker H-bonding of $H_5O_2^+$ is reflected in the smaller decrease in ν_{max}OH (187 cm^{-1}) when moving from the gas phase (average of ν_s and ν_{as}) to $\{Cl_{11}\}^-$ in the condensed phase, relative to the much larger decrease (601 cm^{-1}) for the corresponding change with the H_3O^+ ion.[9,40] This is consistent with the positive charge in the $H_5O_2^+$ ion being localized on the bridging proton as opposed to being extensively delocalized over the four terminal O$-$H groups.

Further information about the interactions of the $H_5O_2^+$ ion with solvents and anions comes from ^{1}H NMR and X-ray structure data. Although ν_{max}OH values of $H_5O_2^+$ in benzene and DCE solutions are very close (Table 1), and therefore the solvation energies of $H_5O_2^+$ in these two solvents are relatively similar, the average ^{1}H signal in the NMR spectrum of $H_5O_2^+$ in benzene solution (6.19 ppm) is considerably upfield of that in DCE solution (8.86 ppm). We ascribe this to a significant ring current effect from solvating benzene molecules in the tetrasolvated [$H_5O_2^+$·4benzene] cation. The same situation has been observed in the trisolvated hydroxonium ion, [H_3O^+·3L], where the chemical shifts are 6.86 and 10.34 ppm for L = benzene and DCE, respectively.[9] The π-solvation of benzene in the [$H_3O^+ \cdot 3C_6H_6$] cation was confirmed by X-ray crystallography.[41]

When $H_5O_2^+\{Cl_{11}\}^-$ is recrystallized from benzene solution, single crystals of a mono-benzene solvate of formula $[H_5O_2][CHB_{11}Cl_{11}] \cdot C_6H_6$ are isolated.[41] The crystal structure shows that one of the four OH groups of the $H_5O_2^+$ cation is π-bonded to a C_6H_6 molecule rather than being ion paired to Cl atoms of the counterion. The H atom of the interacting O$-$H group is located at a position nearly normal to a C atom, the likely site of maximum electron density (Figure 5). The closest O···C distance is 3.20 Å, longer than the range of nearest approaches established in the $H_3O^+ \cdot 3C_6H_6$ cation (3.06$-$3.15 Å).[41] The H···plane normal distance is 2.26 Å, which is at the long end of the range 2.13$-$2.26 Å observed for the $H_3O^+ \cdot 3C_6H_6$ cation. These dimensions reflect a weaker interaction of benzene with the $H_5O_2^+$ ion than the H_3O^+ ion.

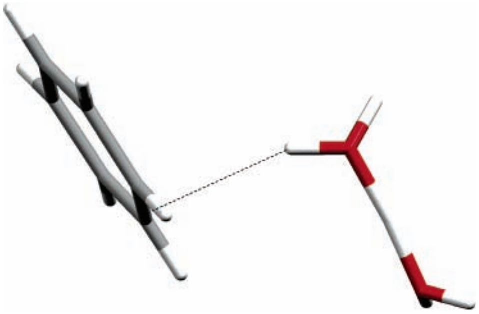


Figure 5. Fragment of the X-ray structure of $[H_5O_2][CHB_{11}Cl_{11}] \cdot C_6H_6$ showing the interaction of an OH bond of the $H_5O_2^+$ cation with the π-face of benzene.

TABLE 1: ν_{max}(OH) for [$H_5O_2^+ \cdot 4X$] (X = Anion in Solid Phase or Solvent in Solution)

anion	phase	ν_{max}OH (cm^{-1})
none[37]	gas	3684, 3609
$\{Cl_{11}\}^-$	solid	3460
$\{Cl_{11}\}^-$	CH_2Cl_2	3435
$\{Cl_{11}\}^-$	DCE	3417
$\{Me_5Br_6\}^-$	DCE	3417
$\{H_5Br_6\}^-$	DCE	3417
$\{Me_5Br_6\}^-$	solid	3405
$\{Cl_{11}\}^-$	C_6H_6	3390
$\{Me_5Br_6\}^-$	C_6H_6	3390

Bands Associated with the O$-$H$^+-$O Group Vibrations. Representative IR spectra for $H_5O_2^+$ salts in the frequency range of the central O$-$H$^+-$O group vibrations (1700$-$800 cm^{-1}) are given in Figure 6. The spectrum of the cation can typically be curve-fitted to reveal five broad bands (green), which in summation give the final spectrum (blue). The differences between the summations (blue) and the experimental spectra (red) are due to bands of the anion and occasionally to imperfect subtraction of the solvent. The anion bands are considerably sharper than the bands of $H_5O_2^+$. Typically, there are three intense bands and two weak bands. The intense bands, whose frequency maxima vary over quite small ranges, are designated ***a*** (860$-$995 cm^{-1}), ***b*** (1045$-$1101 cm^{-1}), and ***c*** (1672$-$1700 cm^{-1}). Band ***b*** is usually the most intense, band ***a*** varies considerably in intensity, and ***c*** is the best-defined band because it is well isolated from the others. The two weaker bands, which cannot always be uniquely defined by deconvolution, are designated ***d*** (1292$-$1312 cm^{-1}) and ***e*** (1403$-$1481 cm^{-1}). Data for all of the $H_5O_2^+$ carborane salts studied, in the solid state and in solution, are gathered in Table 2. The maxima are specified to ca. ±7 cm^{-1}, an error limit typically consistent with our experience in reproducing the deconvolution of these types of spectra,[9] except for band ***c***, which, because it is better isolated, is defined ±1 cm^{-1}. Perhaps the most important observation to be made from these spectra is their overall consistency. They must therefore have a uniform interpretation.

We next compare the present IR spectra of the $H_5O_2^+$ ion in the 900$-$1700 cm^{-1} region to those measured in a vacuum (Table 3). This is not as straightforward as might be expected because there are unexplained discrepancies between the published gas-phase spectra of the $H_5O_2^+$ ion.[42$-$44] Nevertheless, recognizable patterns are evident. Most of the reported gas-phase spectra of the symmetrical $H_5O_2^+$ ion show two intense bands at low energy that correlate with bands ***a*** and ***b*** in our spectra and a well-separated band near 1700 cm^{-1} that correlates with our band ***c***. Some gas-phase spectra show middle-frequency bands of variable intensity that correlate with bands ***d*** and ***e*** in the present work. The recognition of these overall similarities between gas and condensed-phase spectra allows a new ap-

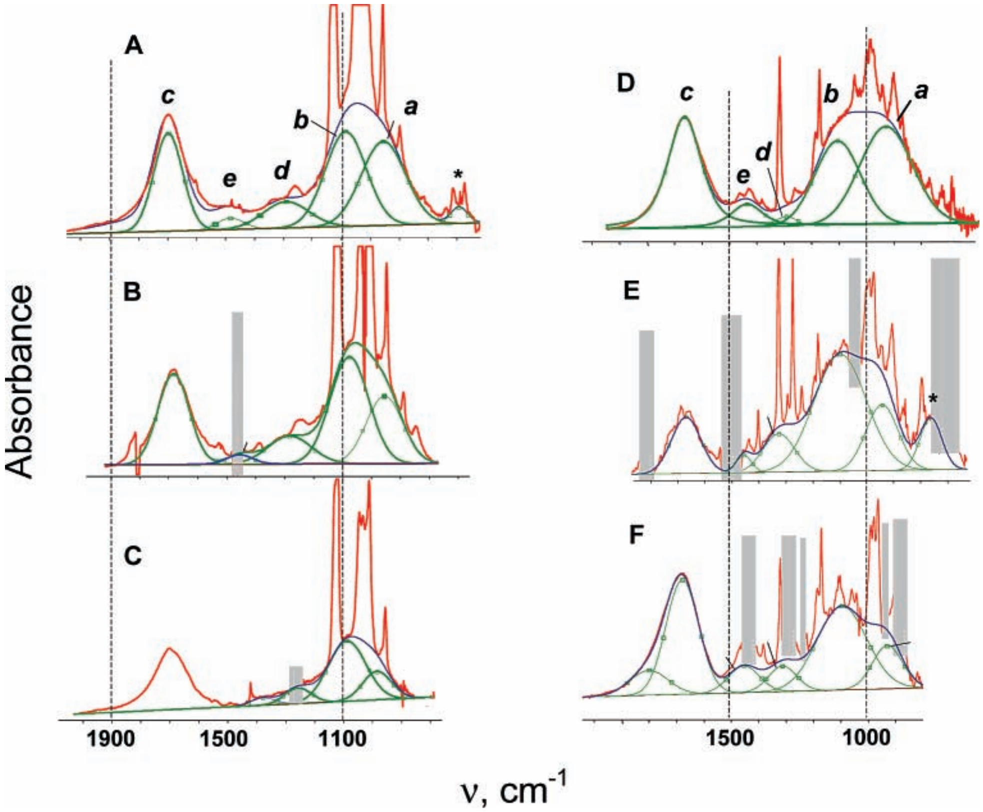


Figure 6. Representative IR spectra (red) of $H_5O_2^+\{Cl_{11}^-\}$ (A−C) and $H_5O_2^+\{Me_5Br_6^-\}$ salts (D−F): solid (A,D) and solutions in benzene (B,E), dichloromethane (C), and DCE (F). The fitted spectrum is shown in green, and the summation of the deconvolution is in blue (except for band ***c*** in spectrum C). Fitting the ~1000 cm^{-1} absorption to a single band was satisfactory only for (F) and is possible only because the band lies near regions of solvent nontransparency (shaded). Bands marked by asterisk in (A) and (E) arise from torsional vibrations that are outside the fingerprint region of the O−H−O group and are not discussed.

TABLE 2: Band Maxima (±7 cm^{-1} and ±1 cm^{-1} for *c*) Associated with Vibrations of the Central OH$^+$O Group of $H_5O_2^+$ Cation with Different Carborane Counterions in Solid Phase and Solution

anion	phase	*a*	*b*	*c*	*d*	*e*
$\{Cl_{11}\}^-$	solid	954	1084	1697	1290	1482
$\{Cl_{11}\}^-$	CH_2Cl_2	984	1087	1700	—[a]	—[a]
$\{Cl_{11}\}^-$	DCE	960	1091	1696	1314	1452
$\{Cl_{11}\}^-$	benzene	964	1085	1691	1291	1463
$\{Me_5Br_6\}^-$	solid	921	1101	1672	1292	1439
$\{Me_5Br_6\}^-$	DCE	931	1097	1678	1313	1454
$\{Me_5Br_6\}^-$	benzene	934	1089	1662	1317	1446

[a] Band positions cannot be determined accurately.

TABLE 3: Frequencies of *a*, *b*, and *c* Bands in IR Spectra of [$H_5O_2^+\cdot 4L$] with Increasing Basicity of L

	nature of L in $H_5O_2^+\cdot 4L$	phase/ solvent	νOH	*a*	*b*	*c*	ref
1	bare	gas	3609 ν_{as} 3684 ν_s	921	~1070[a]	1741	37, 42
2	single Ne[b]	gas	3603 ν_{as} 3683 ν_s	928	1047	1763 1878	44
3	Ar	gas	3600 ν_{as} 3535 ν_s	995	1100	*c*	44
4	$\{Me_5Br_6\}^-$	solid	3402	921	1101	1673	present work
5	C_6H_6	C_6H_6	3390	964	1085	1691	present work
6	Et_2O	C_6H_6	3230−3100	1027	1113	1708	present work
7	TBP	CCl_4	3150−2730	*d*	1140	1727	23
8	tetraphenylmethyl diphosphinedioxide	DCE	2900−2500	1090	1160	1720	24

[a] The center of intense triplet ***b***. [b] Solvation by a single Ne atom does not significantly distort the symmetry of the $H_5O_2^+$ ion. [c] No data. [d] Weak intensity and masked by $(n\text{-BuO})_3PO$ absorption.

preciation of the IR spectrum of the $H_5O_2^+$ cation. Contrary to expectations from recent theoretical studies,[45] bands associated with the central O−H−O bridge do not appear to be particularly sensitive to the solvation environment.

This assertion is supported by the IR spectra of tetrasolvates $H_5O_2^+\cdot 4L$ having L of greater basicity than the carborane anions, chlorocarbon solvents, or benzene used in the present study. Table 3 lists data for L = Et_2O, tri-*n*-butylphosophate (TBP), and tetraphenylmethyl diphosphine dioxide whose increasing basicity is reflected in decreasing νOH of the peripheral OH groups. Despite large changes in νOH, bands ***a***, ***b***, and ***c*** change very little. Thus, the vibrational signature of the central OH$^+$O

TABLE 4: Comparison of IR Spectra of $H_5O_2^+$ in Condensed Phases, Gas Phase, and Calculations

		OHO bands (cm^{-1}) with authors' assignments in parentheses				
study[ref]	phase	*a*	*b*	*c*	*d*	*e*
present work	soln/solid	860−995	1045−1101 (ν_{as})	1672−1700	1292−1312	1403−1481
bare $H_5O_2^+$ [42]	gas	921 (γ)	1043 (δ)	1741 (δ_{H_2O})	1317 (ν_{as})	
bare $H_5O_2^+$ [43]	gas	990 (ν_{as})	1163 (ν_{as}+H_2O_{rot})	1756 (δ_{H_2O})	1337 (ν_{as}+2H_2O_{rot})	
$H_5O_2^+$·Ne[44]	gas	928	1047 (ν_{as})	1763 (δ_{H_2O})	∼1325	∼1475
$H_5O_2^+$·Ar[44]	gas	975	1089 (ν_{as})	1768 (δ_{H_2O})		
$H_5O_2^+$·4Ar[44]	gas	995 (ν_{as})	∼1100	no data		
bare $H_5O_2^+$ [16]	calc gas		1071 (ν_{as})	1734 (ν_{as}+ν_s)	1354 (δ)	1372 (γ)
bare $H_5O_2^+$ [35]	calc gas	968 (δ) 1026 (γ)	1158 (ν_{as})	1671 (ν_{as}+ν_s)1781 (δ_{H_2O})	[a]	[a]
bare $H_5O_2^+$ [47]	calc gas	861 (ν_{as})	1000 (ν_{as})	1780[c]		1480
$H_5O_2^+ClO_4^-$ [45]	calc solid		1059 (ν_{as})	1708 (δ_{H_2O})	[b]	[b]
$H_5O_2^+ClO_4^-$ (IR)[46]	solid		1080 (ν_{as})	1680 (δ_{H_2O})	1270 (γ)	1490 (δ)
$H_5O_2^+ClO_4^-$ (IINS)[46]	solid	832 (ω,ρ)	1120 (ν_{as})	1720 (δ_{H_2O})	1320 (γ)	1560 (δ)
$H_5O_2^+Fe(SO_4)_2^-$ (IINS)[46]		994 (ω,ρ)	1150 (ν_{as})	1634 (δ_{H_2O})		1468 (δ)
$H_5O_2^+In(SO_4)_2^-$ (IINS)[46]	solid	1005 (ω,ρ)	1138 (ν_{as})	1622 (δ_{H_2O})	1371 (γ)	1518 (δ)

[a] Several combination bands are calculated in the 1543−2107 range. [b] Two OHO bending modes are calculated at 1422 and 1499 cm^{-1}. [c] Fermi-like resonance between (δ_{H_2O}) and 2ν_{as} from 861 cm^{-1}.

group in the $H_5O_2^+$ cation is relatively constant regardless of the strength of $H_5O_2^+$ ion interaction with surrounding bases.

Interpretation of Bands a−e. There is wide consensus that the ν_{as}(OHO) mode should appear as the most consistently intense band in the IR spectrum of the $H_5O_2^+$ ion and that its frequency should be near 1000 cm^{-1}.[16,22,35,44] This indicates that band ***b*** should be assigned to this fundamental. The out-of- and in-plane deformations γ(OHO) and δ(OHO) appear in condensed-phase IR spectra as weaker bands at ∼1300 and ∼1450 cm^{-1}, respectively (i.e., bands ***d*** and ***e***).[46] In the gas-phase spectra, as follows from 15D 4-mode VCI calculations, they are expected in the same frequency range, but with much less splitting (ca. 34 cm^{-1}).[16] Band ***c*** at ca. ∼1700 cm^{-1} is always well separated from the other bands, so these designations allow us to tabulate data in the form of Table 4, revealing consistency in the designation of the remaining band ***a*** in the range 830−1000 cm^{-1}. Also shown in this table (in parentheses) are the band assignments given by various authors. They reveal a surprising lack of consensus. The difficulty arises because a different theoretical basis has been used in each case to make the assignments.

The main differences in the theoretical basis of the calculations are (i) whether anharmonicity was taken into account, (ii) whether coupling between vibrations of the core O−H$^+$−O group and the terminal water molecules is significant, and (iii) the extent to which the condensed-phase medium influences the OH$^+$O group vibrations. Does it play a decisive role in the vibrational spectrum of the OH$^+$O group relative to the gas phase?

The vibrations of the bridged proton in the O−H$^+$−O fragment are close to harmonic only at very low temperatures. At 1 K the proton is on average displaced from its equilibrium position by only about 0.01 Å.[35] With increasing temperature, the proton displacements along the flat bottom of the potential well increase significantly, reaching up to 0.2 Å at 360 K.[35] As a result, the proton coordinates are subject to a large fluctuation that results in substantial mechanical and electrooptic anharmonicity. This is expected to significantly complicate the calculated IR spectrum. The most recent calculations (4D) of Vener et al.[35] take anharmonicity into account and show coupling between all four frequencies of the shared proton. At this level of theory, the fundamental bending frequencies γ(OHO) and δ(OHO) for the free $H_5O_2^+$ ion are ca. 500 cm^{-1} lower than in a harmonic calculation, specifically at 968 and 1026 cm^{-1}, respectively, bringing them into a frequency range where bands are observed experimentally. However, three bands are predicted in a region where only two are observed, because this is also the region for ν_{as}(OHO). Anharmonicity has a smaller effect on ν_{as}(OHO), increasing it by ca. 100 cm^{-1} to 1158 cm^{-1}, somewhat above the experimental position (band ***b***). While this theory places the stretching frequency higher than the associated bending frequencies, a feature in concert with basic theory of molecular vibrations, it is believed that the $H_5O_2^+$ ion is an exception in this regard.[16] Another feature predicted by anharmonic calculations is significant broadening of most absorption bands and the development of a large number of intense combination bands and overtones. Unfortunately, there are no experimental IR spectra of the $H_5O_2^+$ cation at liquid helium temperatures to test all of these predictions. We conclude that, while the most recent calculations are beginning to address the difficulties posed by anharmonicity, they are not yet overcome.

It follows from the consistency of the IR spectra of the $H_5O_2^+$ cation in different phases and environments (Tables 2−4) that the coupling between vibrations of central O−H$^+$−O group and the terminal water molecules is small. This is in contradiction with calculations that compare the gas-phase $H_5O_2^+$ ion with the crystalline state in $H_5O_2^+ClO_4^-$, where significant H-bonding occurs from each terminal O−H to a perchlorate O atom. The out-of-plane γ(OHO) frequency is calculated to increase from 1499 to 1700−1740 cm^{-1}, overlapping ***c*** with δ(H_2O) of the terminal water molecules, and the in-plane δ(OHO) frequency decreases from 1411 to 1037−1198 cm^{-1}, overlapping with ν_{as}(OHO). Such divergent splitting of the two bending modes of the central O−H$^+$−O group is inconsistent with the experimental assignments for bands ***d*** and ***e*** (Table 4).

Summarizing, band ***b*** is attributed by almost all authors to ν_{as}(OHO), and this is consistent with our experiments. Similarly, experimental data favor the assignment of bands ***d*** and ***e*** to out-of- and in-plane deformations, γ(OHO) and δ(OHO). The origin of band ***a*** is uncertain, although some authors attribute it to ν_{as}(OHO) (Table 4). Concerning band ***c***, we now show that its attribution by the majority of authors to the δ(H_2O) bending vibration of the terminal water molecules is, for condensed phases, in conflict with the experiment.

Important information about the nature of bands ***a***, ***b***, and ***c*** can be extracted from their frequency dependencies on the strength of interaction of the $H_5O_2^+$ ion with solvating molecules in [$H_5O_2^+$·4L] cations. The greater is the basicity of L, the lower is the frequency of νOH of the four peripheral OH groups (Table 3). Figure 7 shows the frequency dependencies of bands ***a*** and ***b*** on νOH. In the case of band ***b***, the asymmetric stretch, the frequency increases as the base strength of L increases. The

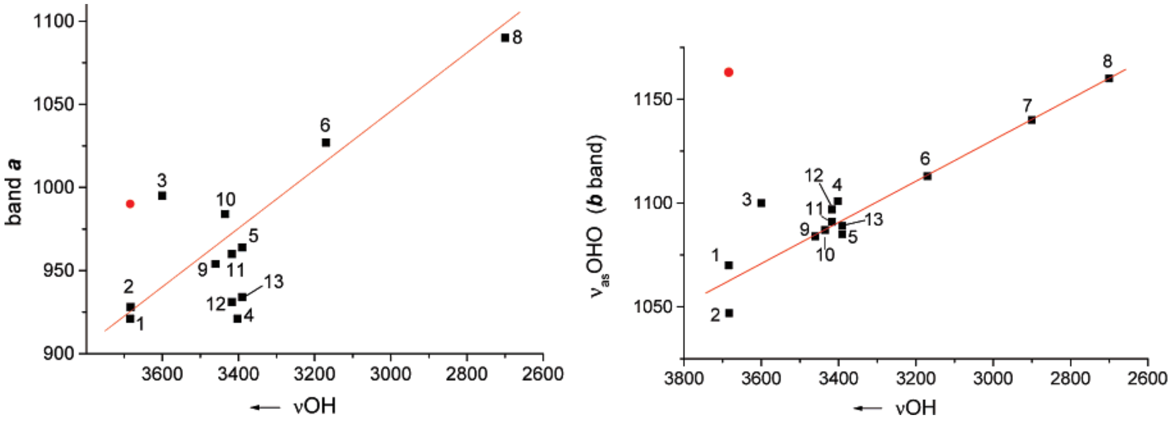


Figure 7. The frequency dependence of bands ***b*** (left) and ***a*** (right) on νOH in [$H_5O_2^+$•4L] cations as the basicity of L increases. The numeration **1**−**8** refers to compound numbers in Table 3. Points **9**−**13** are from data in Tables 1 and 2: that is, solid [$H_5O_2^+$]{Cl_{11}^-} (**9**) and [$H_5O_2^+$•4L]{Cl_{11}^-} solutions in CH_2Cl_2 (**10**) and DCE (**11**) and [$H_5O_2^+$•4L]{$Me_5Br_6^-$} solutions in DCE (**12**) and benzene (**13**). Red points are for gas-phase data from Fridgen et al. (ref 43), which differ significantly from other experimental data[42,44] (points 1, 2) and from the most recent calculations.[47]

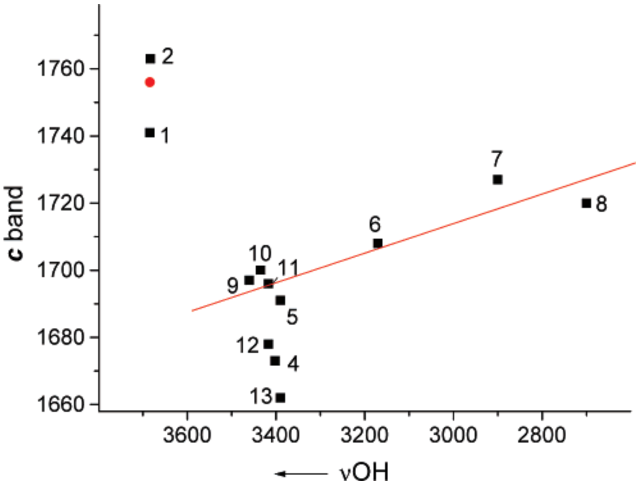


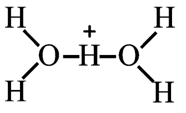
Figure 8. The frequency dependence of band ***c*** on νOH of the [$H_5O_2^+$•4L] cation as the basicity of L increases. The numeration refers to compound numbers in Figure 7.

dependence is reasonably linear with a slope of 10:100; that is, the ***b*** frequency increases 10 cm^{-1} for every 100 cm^{-1} decrease in νOH. The frequency dependence of band ***a*** on νOH shows a similar trend with slope 16:100. The correlations confirm the consistency of the designations, and the similarity of slopes indicates that the assignment of band ***a*** has a strong relationship with the asymmetric stretch.

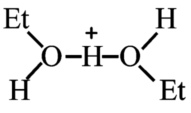
The behavior of band ***c*** is abnormal (Figure 8). The approach to a linear dependence of the frequency of ***c*** upon νOH appears to exist only for condensed-phase data (points 4−13), and even then, data from the most basic anion, {$Me_5Br_6^-$} (points 4, 12, and 13), lie somewhat below the line. The slope is low (ca. 7:100). The gas-phase data points (1, 2, and red point) are far away from this dependence, suggesting that the nature of the ***c*** band for the bare $H_5O_2^+$ cation is different from that in condensed phase.

Band ***c*** has been assigned by most authors to the $\delta(H_2O)$ bending vibration of the peripheral water molecules (Table 4), and this is consistently reproduced by theory for the bare $H_5O_2^+$ cation except in the calculations of Dai et al.[16] and Kaledin et al.[47] who attribute ***c*** to $\nu_{as}+\nu_s$ combinations or to Fermi-like 2:1 resonance between $\delta(H_2O)$ and the 2ν_{as} mode at 861 cm^{-1}, respectively. When $H_5O_2^+$ is transferred from a vacuum to a condensed phase, forming a tetrasolvate [$H_5O_2^+$•4L], this $\delta(H_2O)$ mode should always increase in frequency. The higher is the basicity of L, the stronger will be the OH•••L interaction, and the more significant will be these frequency shifts. This trend is actually seen in the condensed-phase data as L increases base strength from benzene to phosphine oxide (points 4−8). The frequency change is small (ca. 37 cm^{-1}). However, on going from the gas phase to the weakest bases, that is, L = dichloromethane, {Cl_{11}}$^-$, or benzene, the ***c*** band frequency decreases, not increases, and does so by a large magnitude (ca. 70 cm^{-1}). Indeed, all condensed-phase values are lower than the gas-phase values. This means that band ***c*** in the condensed-phase data cannot have the same assignment as in the gas phase. We conclude that the weak band at ca. 1700 cm^{-1} in gas-phase spectra is correctly assigned to $\delta(H_2O)$, but in condensed phases, a new, typically much more intense band appears in the same frequency region. That the condensed-phase band ***c*** data show the same positive slope as bands ***a*** and ***b*** suggests that band ***c*** may involve the asymmetric stretch.

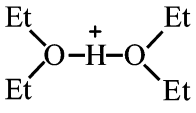
The strongest support that there is no relation between ***c*** band and $\delta(H_2O)$ follows from the progressive substitution of the terminal H atoms of $H_5O_2^+$ by ethyl groups in the ethanol and diethyl ether proton disolvates:



$H_5O_2^+$



$(EtOH)_2H^+$



$(Et_2O)_2H^+$

IR spectra of $(EtOH)_2H^+$ and $(Et_2O)_2H^+$, which cannot have a band arising from $\delta(H_2O)$, nevertheless develop intense ***c*** bands at ca. 1500−1600 cm^{-1} (Table 5). Moreover, as noted by Moore et al.,[48] in the gas phase, and as we have shown for the condensed phase, these spectra retain the same fingerprint features of the O−H$^+$−O group seen with the $H_5O_2^+$ cation, the three intense bands ***a***, ***b***, and ***c*** (Figure 9). While the pattern is the same, bands ***a*** and ***b*** for the gas phase are noticeably red shifted as compared to the condensed phase, whereas band ***c*** is insensitive to phase (Table 5). The same ***a***, ***b***, and ***c*** bands are seen in the entire range of L−H$^+$−L proton disolvates, from L = Et_2O to stronger bases such as acetone and TBP (Table 5). Even in M(AHA)$_n$ salts of carboxylic, dialkylphosphoric, and other acids, which also contain SSLB H-bonds and short O•••O distances such as $H_5O_2^+$, bands readily assigned to ***a***, ***b***, and ***c*** are observed (Table 6). This confirms that the vibrations of the central O−H$^+$−O unit can be understood in a uniform

TABLE 5: Frequencies of the OH^+O Group of Proton Disolvates in Solutions and in the Gas Phase (in Parentheses)

disolvate	solvent	*a*	*b*	*c*
$H_5O_2^+\cdot 4L$	L = DCE, C_6H_6	931−964	1085−1091	*1662−1696*[a]
$(EtOH)_2H^+$	CCl_4	929	1141	*1507* 1683 1808 1925 2042
	(gas phase[49])	(760)	(956)	(1200−1700, max ∼1450)
$(Et_2O)_2H^+$	CCl_4	921	1110	*1512* 1668 1769 1920 2084
	(gas phase[48])	(∼750)	(∼900)	(1530−1580)
$(acetone)_2H^+$	CCl_4	926	1137	*1603* 1785 1959 2154
$(TBP)_2H^+$	CCl_4	890	1042	*1461* 1632 1749 1890 2069

[a] The most intense band is in italics.

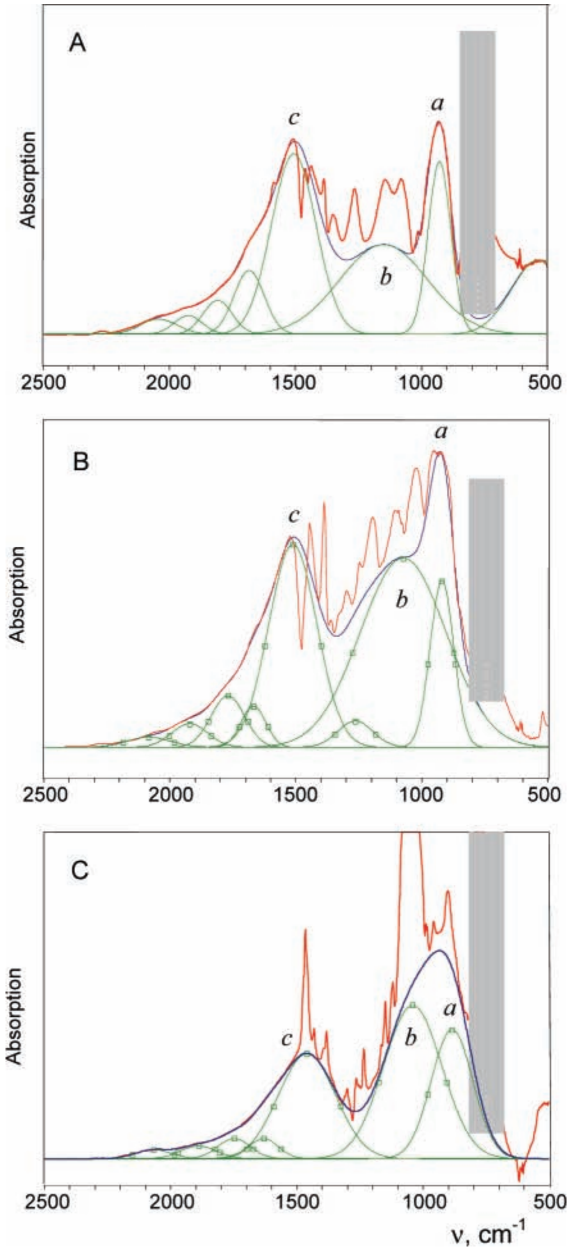


Figure 9. IR spectra of $[L-H^+-L]FeCl_4^-$ in CCl_4 solutions. L = ethanol (A), diethyl ether (B), and tributyl phosphate (C). The fitted spectrum is shown in green, and the summation of the deconvolution is in blue. The regions of solvent nontransparency are shaded. The frequencies are given in Table 5.

manner across different classes of compounds, including $H_5O_2^+$, and that they are not strongly coupled modes of the peripheral water molecules.

Additional support for the similarity of the shared proton in the $O-H^+-O$ group across compound classes comes from NMR spectra. The ^1H signal from the bridging proton of $H_5O_2^+$ in Freon solution appears at 21.3 ppm,[25] practically coincident with the corresponding signal in proton disolvates of type $L-H^+-L$ (Table 7). The chemical shift is essentially the same with a weak base such as SO_2 as with a strong base such as a trialkylphosphine oxide, indicating that the chemical shift is rather independent of the basicity of L. When pyridine is one of the bases in a hetero $N-H^+-O$-type complex with organic acids, the ^1H signal from bridging proton has a smaller downfield chemical shift but reaches a maximum value of 21.5 ppm when the base strength of the oxyanion matches that of pyridine; that is, the proton is equivalently shared by the N and O atoms.[55] Thus, the value of ∼21 ppm appears to be as good criterion of symmetry in the $O-H^+-O$ group of proton disolvates, including $H_5O_2^+$.

Let us now consider the frequency dependencies of bands ***a***, ***b***, and ***c*** on the basicity of the O-atoms in the $O-H^+-O$ group. For the class of proton disolvates $L-H^+-L$ with basicity order $H_2O < EtOH < Et_2O <$ acetone < TBP for L (Table 5), the frequency of band ***a*** appears to decrease, band ***b*** shows no definite trend, and band ***c*** decreases significantly. For the very strong base OH^- in the $H_3O_2^-$ ion, the $\nu_{as}OHO$ stretching frequency for the bare anion is 697 cm^{-1}.[57] This suggests that the stronger is the base, the lower should be $\nu_{as}OHO$. However, as shown earlier in Figures 6 and 7, the reverse trend is observed for increasing basicity of L in the class of $[H_5O_2^+\cdot 4L]$ solvates where increasing the basicity of L should increase the basicity of the O atoms in the $O-H^+-O$ group.

To understand this apparent contradiction, we return to the effect of structural asymmetry in $H_5O_2^+$ ion on the $\nu_{as}OHO$ frequency. When a single Ar atom in the gas phase is bound to one end of the $H_5O_2^+$ ion, $\nu_{as}OHO$ (i.e., band ***b***) increases by 42 cm^{-1}.[44] Band ***a***, which we will propose is due to splitting of $\nu_{as}OHO$, also increases by 47 cm^{-1}. This confirms that static asymmetry in the $H_5O_2^+$ ion should lead to a blue shifting of any band associated with $\nu_{as}OHO$.

Let us now consider the effect of dynamic fluctuations in $[H_5O_2^+\cdot 4L]$ solvates that lead to asymmetry in $O-H^+-O$ group. The greater is the instantaneous departure from symmetry of the $O-H^+-O$ group due to thermal motion of the surrounding environment, the greater will be the blue shift of $\nu_{as}OHO$. The stronger is the base L, the greater its thermal motion will influence the symmetry of the $O-H^+-O$ group. We propose that the blue shift of bands ***a*** and ***b*** in $[H_5O_2^+\cdot 4L]$ as a function of increasing L basicity is due to this effect. Formally, the symmetry of the $H_5O_2^+$ cation is not changed by complexation to four L bases, but on the time scale of stochastic thermal motion of the base donor atoms, the $O-H^+-O$ group will experience asymmetric fluctuations of charge distribution. The stronger is the base interaction, the greater is the effect. The same factors can explain the frequency increase of bands ***a*** and ***b*** when $(EtOH)_2H^+$ and $(EtO)_2H^+$ disolvates are transferred from the gas phase to solution.

TABLE 6: Vibrational Frequencies of OHO Group in Some M(AHA)$_n$ Acid Salts with O···O < 2.45 Å[a]

compound	ν_{as}(OHO)[b]/***a,b***	γ(OHO)/***d***	δ(OHO)/***c***	O···O/Å	ref
$NaH(SO_4)_2$	~900	1390−1430	1560−1620	2.432	50
$NH_4H(CH_2ClCOO)_2$	880−970	1255	1590	2.432	51
$KH(CHBr_2COO)_2$	870 ± 30	1218	1390	2.44	52
$KH(CF_3COO)_2$	800	1353	1480	no data	53
$NaH(CH_3COO)_2$	720	1285	1540	2.44	54

[a] Assignments are given as in the original work; designations ***a*−*d*** from the present work. [b] Broad band is overlapped with strong bands of anions so it cannot be separated into two components.

TABLE 7: ^{1}H NMR Signals of the Bridged Proton of $H_5O_2^+$ Cation and Other Proton Disolvates L−H$^+$−L

L	solvent	ppm	ref
H_2O (i.e., $H_5O_2^+$)	Freon	21.3	25
$R_3P{=}O$	Freon	21.4	56
SO_2	SO_2	20.4	41

Interestingly, proton disolvates of the type L−H$^+$−L do not show the same trend. Instead of the blue shifting of bands ***a*−*c*** with increasing L base strength seen with [$H_5O_2^+$·4L] ions (Figures 6 and 7), proton disolvates of the L−H$^+$−L type tend to show corresponding red shifts (Table 5). This can be explained by a smaller influence of thermal asymmetry on band ***a*−*c*** frequencies. In L−H$^+$−L proton disolvates, the environment of the donor atom is more firmly held by a greater multiplicity of adjacent covalent bonds and the amplitude of thermal motion will be lower. There appears to be two opposing influences: a blue shift from increasing thermal motion of the surroundings, and a red shift due to increasing O−H$^+$−O bond strength. The thermal motion effect is dominant in the [$H_5O_2^+$·4L] solvates, whereas the two effects more nearly compensate for each other in L−H$^+$−L complexes.

An important new observation arising from the present work is the interconnected behavior of bands ***a*** and ***b***, particularly in the [$H_5O_2^+$·4L] solvates (Figure 7). This leads us to propose that bands ***a*** and ***b*** originate from the same ν_{as}OHO vibration, split by a presently unknown mechanism. Regarding the ***c*** band (ca. 1600−1700 cm^{-1}), which also shows some connectedness to ν_{as}OHO, we note an intriguing property. On the high frequency side, there are often additional components. They are barely perceptible in some of the spectra of [$H_5O_2^+$·4L] cations, but are very obvious in the spectra of L−H$^+$−L compounds (Figure 9). They appear to be a set of harmonics with approximately constant increment within the error of position determination (see Table 5). Similar harmonics are also observed in IR spectra of acidic salts M(AHA)$_n$.[58] This peculiarity, as well as the frequency dependence on the O atom basicity in the O−H$^+$−O group (Figure 9, Table 5), suggests that band ***c*** and its harmonics belong to a combination band which includes $\nu_{as}+\nu_s$. This is in accord with the recent calculations of Vener.[35]

The remaining question is why the $\delta(H_2O)$ band, observed in the gas-phase spectrum of $H_5O_2^+$ near 1700 cm^{-1}, is not observed (or is very weak) in the condensed phase. The answer may lie in a peculiarity of the IR spectra of symmetrical proton disolvates. It has frequently been observed in L−H$^+$−L species that when an IR active chromophore (e.g., C−OH, C−O−C, P═O, etc.) from L is bound directly to H$^+$, the normally strong, sharp, stretching bands associated with these groups broaden, diminish in intensity, or even disappear into the baseline.[17,18,24,59−61] The effect is seen only in symmetrical proton disolvates. For example, both ν_{as}POO and ν_sPOO bands of crystalline di(methylphenyl)phosphoric or di(chlorophenyl)phosphoric acid dimers, where the equivalency of the O-atoms in the OHO bridges has been established by X-ray crystallography, disappear in the IR spectra.[59,60,62] The phenomenon is not dependent on O···O distance because they differ significantly in these two acid dimers, 2.512[60] and 2.398 Å, respectively.[63] By contrast, in the IR spectra of dimeric dialkylphosphorus or dialkylphosphinic acids, where asymmetric OHO groups with nonequivalent O-atoms have been established,[59,60] strong bands from POO stretch are observed. The phenomenon appears to be frequency dependent.[18] When the frequencies of chromophore are lower than ca. 1600 cm^{-1}, such as the C−O(H) and COC stretches in $(EtOH)_2H^+$ and $(Et_2O)_2H^+$, respectively, bands are not discernible in the IR spectra. In case of the carbonyl group in (acetone)$_2$H$^+$ with ν(C═O) near 1600 cm^{-1}, the band is weak and broad. On the other hand, the phenomenon does not appear to have much influence on the high-frequency OH stretch at ~3400 cm^{-1} in the spectrum of $(EtOH)_2H^+$.

For the $H_5O_2^+$ ion (i.e., L = H_2O), the postulate that high-frequency modes are not as susceptible to broadening and disappearance as low-frequency modes is in keeping with the observed spectra. The higher energy ν(OH) bands of the peripheral water molecules at ~3400 cm^{-1} have normal intensities, while the $\delta(H_2O)$ band, expected in the 1600−1700 cm^{-1} range, is weak or absent in condensed phases. Band ***c*** in condensed phases accidentally coincides with this region and has been mistakenly assigned to $\delta(H_2O)$.

The broadening or disappearance of bands in symmetrical L−H$^+$−L complexes can be understood in terms of the indeterminate position (i.e., distribution) of the bridging proton in a flat-bottomed potential well.[18] In a static description, this is equivalent to an extreme case of inhomogeneous broadening where neighboring chromophores are subject to a highly varied charge distribution and their absorption bands lose their definition. In a kinetic description, motion of the proton in the O−H$^+$−O moiety is fast on the vibrational time scale and produces rapid modulation of the force constants in neighboring vibrations. When the proton potential becomes double-welled, localizing the proton nearer to one O atom, the effect disappears. This is the case in $H_7O_3^+$, where the $\delta(H_2O)$ frequency appears as a normal band at 1610 cm^{-1} along with band ***c***.[64]

The phenomenon of band disappearance arising from the peculiarities of the low-barrier, symmetrical H-bond raises the question of how the “disappearing” bands are coupled to the vibrations of the O−H$^+$−O group. This is poorly understood, but it appears that mixing causes reciprocal broadening rather than frequency change.

Conclusions

The $H_5O_2^+$ proton dihydrate has been shown to exist in weakly basic organic solvents such as chlorocarbons and benzene when weakly coordinating carboranes are used as counterions. It is equivalently solvated by four solvent molecules as a constituent of an ion pair of type [$H_5O_2^+$·4Solv]Carb$^-$. In the solid phase, the more or less symmetrical $H_5O_2^+$ ion is stabilized by halogen atoms from the carborane anions.

Two groups of IR bands are characteristic of the $H_5O_2^+$ cation: those from of the two water molecules and those from the central O−H$^+$−O group. The ν_sOH and ν_{as}OH vibrations of the water molecules behave in a way similar to those of common water molecules: the stronger is the H-bonding interaction with the surroundings, the lower is the frequency shift. The $\delta(H_2O)$ band, although present in gas-phase spectra, is absent in condensed-phase spectra of the $H_5O_2^+$ cation. Vibrations of the central O−H$^+$−O group develop three intense bands ***a*** (860−995 cm^{-1}), ***b*** (1045−1101 cm^{-1}), and ***c*** (1672−1700 cm^{-1}), and two weak bands ***d*** (∼1300 cm^{-1}) and ***e*** (∼1400−1500 cm^{-1}). Bands ***a*** and ***b*** belong to the ν_{as}OHO vibration, and ***a*** usually has lower intensity than ***b***. Band ***c*** probably originates from an overtone of $\nu_{as}+\nu_s$ in the condensed-phase spectra. The weak band that appears in the same frequency region in the gas-phase spectrum of the bare ion is due to the δH_2O bending of the peripheral H_2O molecules. The two weak bands ***d*** and ***e*** belong to in-plane δ(OHO) and out-of-plane γ-(OHO) bending and have higher frequencies than ν_{as}OHO.

The frequencies of bands ***a*** and ***b***, and to a lesser extent ***d*** and ***e***, are relatively stable, irrespective of whether the $H_5O_2^+$ cation is bare in a vacuum or symmetrically solvated in condensed phases. In condensed phases, band ***c*** is characteristically strong, and stable in frequency. Most importantly, these fingerprint bands are highly characteristic for vibrations of O−H−O group in all type of compounds with symmetrical SSLB hydrogen bonds. This appears to be true regardless of charge or the nature of the base. The characteristic spectrum is seen in L−H$^+$−L complexes for L = a neutral O-atom base containing O−H, O−R, O═P, O═C groups, etc., in AHA$^-$ where A is an oxyanion, and in [$H_5O_2^+$·4L] with varying basicity of L. The conditions for the appearance of this characteristic spectrum are equivalency of the two O-atoms, a short O···O distance (2.40−2.44 Å), and a flat-bottomed potential well for the bridging proton.

The disappearance of the $\delta(H_2O)$ band of $H_5O_2^+$ in condensed-phase spectra appears to be related to the disappearance of stretching vibrations of O−C−O, COO, POO, P═O, etc., groups in L−H$^+$−L complexes. This phenomenon is poorly understood but may to be related to the way these vibrations are modulated by the stochastic motion of the bridging proton.

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References and Notes

(1) Zwier, T. S. *Science* **2004**, *304*, 1119.

(2) Headrick, L. M.; Diken, E. G.; Walters, R. S.; Hammer, N. I.; Christie, R. A.; Cui, J.; Myshakin, E. M.; Duncan, M. A.; Johnson, M. A.; Jordan, K. D. *Science* **2005**, *308*, 1765.

(3) Eigen, M.; Maeyer, L. D. *Proc. R. Soc. London* **1958**, *247*, 505.

(4) Gerlt, L. A.; Kreevoy, M. M.; Cleland, W. W.; Frey, P. A. *Chem. Biol.* **1997**, *4*, 259.

(5) Saraste, M. *Science* **1999**, *283*, 1488.

(6) Smondyrev, A. M.; Voth, G. A. *Biophys. J.* **2002**, *83*, 1987.

(7) Rousseau, R.; Kleinschmidt, V.; Schmitt, U. W.; Marx, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 4804.

(8) Chourasia, M.; Sastry, G. M.; Sastry, G. N. *Biochem. Biophys. Res. Commun.* **2005**, *336*, 961.

(9) Stoyanov, E. S.; Kim, K.-C.; Reed, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 1948.

(10) Zundel, G. In *The Hydrogen Bond − Recent Developments in Theory and Experiments*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Vol. II.

(11) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(12) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(13) Perrin, C. L.; Nielson, J. B. *Annu. Rev. Phys. Chem.* **1997**, *48*, 511.

(14) Dalleska, N. F.; Honma, K.; Armentrout, P. B. *J. Am. Chem. Soc.* **1993**, *115*, 12125.

(15) Chaban, G. M.; Jung, J. O.; Gerber, R. B. *J. Phys. Chem. A* **2000**, *104*, 2772.

(16) Dai, J.; Baèiæ, Z.; Huang, X.; Carter, S.; Bowman, J. M. *J. Chem. Phys*. **2003**, *119*, 6571.

(17) Stoyanov, E. S. *Mendeleev Commun.* **1999**, 190.

(18) Stoyanov, E. S. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1137.

(19) Lundgren, J. O.; Olovsson, I. *Acta Crystallogr.* **1967**, *23*, 966.

(20) Ortwein, R.; Schmidt, A. Z. *Z. Anorg. Allg. Chem.* **1976**, *425*, 10.

(21) Jones, D. J.; Roziere, J. *J. Mol. Struct.* **1989**, *195*, 283.

(22) Valeev, E. F.; Schaefer, H. F. *J. Chem. Phys.* **1998**, *108*, 7197.

(23) Stoyanov, E. S. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 4165.

(24) Stoyanov, E. S.; Smirnov, I. V. *J. Mol. Struct.* **2005**, *740*, 9.

(25) Golubev, N. S. *Khim. Fiz.* **1983**, *1*, 42.

(26) Reed, C. A. *Chem. Commun.* **2005**, 1669.

(27) Stoyanov, E. S.; Kim, K.-C.; Reed, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 8500.

(28) Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K.-C.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5352.

(29) Reed, C. A.; Kim, K.-C.; Stoyanov, E. S.; Stasko, D.; Tham, F. S.; Mueller, L. J.; Boyd, P. D. W. *J. Am. Chem. Soc*. **2003**, *125*, 1796.

(30) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Educational and Professional Publishing Ltd.: Oxford, 1996.

(31) Stoyanov, E. S.; Hoffmann, S. P.; Juhasz, M.; Reed, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 3160.

(32) Roziere, I.; Potier, I. *J. Mol. Struct.* **1972**, *13*, 91.

(33) Pavia, A. C.; Giguere, P. A. *J. Chem. Phys.* **1970**, *52*, 3551.

(34) Picotin, G.; Roziere, I.; Potiere, A. *Adv. Mol. Relax. Proc.* **1975**, *7*, 177.

(35) Vener, M. V.; Kuhn, O.; Sauer, J. *J. Chem. Phys.* **2001**, *114*, 240.

(36) Ojamäe, L.; Shavitt, I.; Singer, S. J. *Int. J. Quantum Chem. Symp.* **1995**, *29*, 657.

(37) Yen, L. I.; Okumura, M.; Myers, J. D.; Price, J. M.; Lee, Y. T. *J. Chem. Phys.* **1989**, *91*, 7319.

(38) Stoyanov, E. S.; Chizhevskaya, S. V.; Chekmarev, A. M. *J. Struct. Chem.* (translation of *Zh. Struct. Khim.*, Russia) **1993**, *34*, 722.

(39) Stoyanov, E. S.; Kim, K.-Ch.; Reed, C. A. *J. Phys. Chem. A* **2004**, *108*, 9310.

(40) Begemann, M. H.; Gudeman, C. S.; Pfaff, J.; Saykally, R. J. *Phys. Rev. Lett.* **1983**, *51*, 554.

(41) Stoyanov, E. S.; Hoffmann, S. P.; Kim, K.-Ch.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 7664.

(42) Asmis, K. N.; Pivonka, N. L.; Santambrogio, G.; Brummer, M.; Kaposta, C.; Neumark, D. M.; Woste, L. *Science* **2003**, *299*, 1375.

(43) Fridgen, T. D.; McMahon, T. B.; MacAleese, L.; Lemaire, J.; Maitre, P. *J. Phys. Chem. A* **2004**, *108*, 9008.

(44) Hammer, N. I.; Diken, E. G.; Roscioli, J. R.; Johnson, M. A.; Myshakin, E. M.; Jordan, K. D.; McCoy, A. B.; Huang, X.; Bowman, J. M.; Carter, S. *J. Chem. Phys.* **2005**, *122*, 244301.

(45) Vener, M. V.; Sauer, J. *Phys. Chem. Chem. Phys.* **2005**, *7*, 258.

(46) Jones, D. J.; Roziere, J. *J. Mol. Struct.* **1989**, *195*, 283.

(47) Kaledin, M.; Kaledin, A. L.; Bowman, J. M. *J. Phys. Chem. A* **2006**, *110*, 2933.

(48) Moore, D. T.; Oomens, J.; Meer, L.; Helden, G.; Meijer, G.; Valle, J.; Marshall, A. G.; Eyler, J. R. *ChemPhysChem* **2004**, *5*, 740.

(49) Fridgen, T. D.; MacAleese, L.; McMahon, T. B.; Lemaire, J.; Maitre, P. *PCCP* **2006**, *8*, 955.

(50) Videnova-Adrabinska, V. *J. Mol. Struct*. **1990**, *237*, 367.

(51) Baran, J.; Ilczyszyn, M. M.; Jakubas, R.; Ratajczak, H. *J. Mol. Struct*. **1991**, 246, 1.

(52) Videnova-Adrabinska, V.; Baran, J.; Ratajczak, H. *Spectrochim. Acta* **1986**, *42A*, 641.

(53) Hadzi, D.; Orel, B.; Novak, A. *Spectrochim. Acta* **1973**, *29A*, 1745.

(54) Novak, A.; Bellor, J.; Foglizzo, E.; Romain, F. *J. Chim. Phys*. **1972**, *69*, 1615.

(55) Smirnov, S. N.; Golubev, N. S.; Denisov, G. S.; Benedict, H.; Mohammedi, P. S.; Limbach, H. H. *J. Am. Chem. Soc*. **1996**, *118*, 4094.

(56) Golubev, N. S.; Denisov, G. S.; Matrosov, E. I.; Kabachnik, M. I. *Dokl. Akad. Nauk SSSR* **1981**, *260*, 907.

(57) Diken, E. G.; Headrick, J. M.; Roscioli, J. R.; Bopp, J. C.; Johnson, M. A.; McCoy, A. B. *J. Phys. Chem. A* **2005**, *109*, 1487.

(58) Stoyanov, E. S.; Chesalov, Yu. A. *J. Struct. Chem.* (translation of *Zh. Struct. Khim.*, Russia) **1996**, *37*, 270.

(59) Katzin, L. I.; Mason, G. W.; Peppard, D. F. *Spectrochim. Acta* **1978**, *34A*, 51.

(60) Gebert, E.; Reis, A. H.; Peterson, S. W.; Katzin, L. I.; Mason, G. W.; Peppard, D. F. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1451.

(61) 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.

(62) Hadzi, D.; Novak, A. *Proc. Chem. Soc., London* **1960**, 241.

(63) Callery, M.; Speakman, J. C. *Acta Crystallogr.* **1964**, *17*, 1097.

(64) Stoyanov, E. S.; Reed, C. A., manuscript in preparation.