Water trapped in dibenzo-18-crown-6: Theoretical and spectroscopic (IR, Raman) studies

Marcin Dulak, Rémi Bergougnant, Katharina M. Fromm, Hans R. Hagemann, Adeline Y. Robin, Tomasz A. Wesołowski

Abstract

Experimental (IR and Raman) and theoretical (Kohn-Sham calculations) methods are used in a combined analysis aimed at refining the available structural data concerning the molecular guests in channels formed by stacked dibenzo-18-crown-6 (DB18C6) crown ether. The calculations are performed for a simplified model comprising isolated DB18C6 unit and its complexes with either H2O or H3O+ guests, which are the simplest model ingredients of a one-dimensional diluted acid chain, to get structural and energetic data concerning the formation of the complex and to assign the characteristic spectroscopic bands. The oxygen centers in the previously reported crystallographic structure are assigned to either H2O or protonated species.

Keywords: Crown ethers; One-dimensional polymer structures; Proton conductors; Spectrum assignment

1. Introduction

Low-dimensional materials with interesting physical properties are a possible solution for down-scaling dimensions in information data storage, and are therefore more than ever in the focus of current research. We are thus interested in the controlled synthesis of one-dimensional structures via a supramolecular approach, either by combining hydrogen bonding with metal ion complexation or with ligand templating and π–π interactions [1–3]. Crown ethers and their complexes with metal cations have attracted considerable attention since the pioneering work of Pedersen [4]. They are remarkably selective on metal cations, especially alkali and alkaline earth metals cations, which is a topic of fundamental interest in coordination chemistry and biochemistry. These macrocyclic ligands fascinate both because they can impose unusual coordination numbers and geometries on metal ions, and because they serve as models for metal ion transport across membranes [5]. They have also found an application as very selective separation agents on mixtures of metal ions. Especially the crown ethers with six O atoms such as 18-crown-6, dibenzo-18-crown-6 (DB18C6) and dicyclohexano-18-crown-6 are known to form stable complexes with alkali metal salts [6–8]. They are rare examples where neutral organic ligands are able to complex charged metal ions in a very efficient way.

As we are interested in the formation of new materials with functional properties, based on one-dimensional polymers [1–3,9–12] the question arose whether it was possible to stack DB18C6 ligands in such a way as to obtain one-dimensional channels. The potential capacity of DB18C6 to form π interactions upon stacking appeared to us as an interesting property in this context. As a model for biological membranes, we attempt to study these channels as proton conductors, filled with water molecules and protonated species.

We have shown before that such a one-dimensional channel compound, \( (\text{H}_2\text{O})_{\infty}((\text{DB18C6})_{\infty}(\text{pH}_2\text{O}_2)_{\infty} \)
Fig. 1. The unit cell of $\infty [(H_2O) \subset (DB18C6) (\mu_2-H_2O)_2]_2^\infty$ viewed along $c$-axis.

$\infty [(H_3O) \subset (DB18C6) (\mu_2-H_2O)_2]_2^\infty$, 1, can be obtained upon serendipity, and that such stacked DB18C6 ethers are extremely rare[13,14]. Since the single crystal data has been reported before [13,14], we will restrain ourselves to a short description of the structure in the context of comparison with the theoretical results.

1 forms dark brown rod-like single crystals of the orthorhombic space group $Pccn$ (No. 56) with two independent half molecules in the asymmetric unit (Fig. 1). The structure consists of two different channels of DB18C6. In one channel, the ligands are well stacked, containing three types of oxygen atoms (see Fig. 2). Two of them (we denote them as the oxygen atoms type A and C) are localized on the same side of the crown ether ring as the phenyl rings, and the third one (type B) in which the oxygen atoms are on the opposite side to the phenyl rings. The atom of the type C is coordinated by the oxygen atoms of the crown ether, whereas the oxygen atoms of the type A and B act as bridging atoms to the next DB18C6 unit. The attribution of the hydrogen atoms to the oxygen sites of the type A, B, and C can not be made based on the X-ray experiment. In a second channel, parallel to the first in its propagation direction, the stacking is by far less perfect. Three oxygen types of atoms, A, C, and B are also found in the center of the channel (Fig. 3), and again, the hydrogen atoms could not be attributed. It is important to notice that even though the mean O⋯O distances in the two channels are very similar, the less well stacked crown ether molecules seem to be more distorted than the other ones when looked at in detail. The distance between the oxygen sites B and C equals to 2.217 and 2.241 Å in channels 1 and 2, respectively. The corresponding distances between the C and A sites are longer and amount to 2.409 and 2.385 Å. It is noteworthy that the distance between the C and A sites matches very closely that in the $H_5O_2^+$ cation [15]. The counter ions, $I^-\infty$, are arranged parallel to the channels and fill the space left between the channels (Fig. 1).

X-ray diffraction studies allowed us to determine the detailed structure of the channel formed by stacked DB18C6 units as well as the location of the oxygen atoms of the guest molecules in the center of the channel. To get a more detailed picture, we turned to computer modeling and vibrational spectroscopy (IR and Raman). As the first step in the computational studies, we analyze the structural and vibrational properties of the simplest model of the channel, comprising just one DB18C6 unit and one guest molecule (either $H_2O$ or $H_3O^+$) by means of computer modeling. Such a model allows us to reveal some of the important properties relevant to the real system. In particular, it allows us to study the effect of the presence of the host in the center of the crown ether on its structure and vibrational properties. This simplified model is especially adequate to study properties of a neutral or protonated guest molecule well separated from other guests in the channel. It is important to underline that our model of the channel is not appropriate for studies of more complicated and probably more realistic guests such as $H_5O_2^+$ or $H_7O_3^+$ chains. In such structures, the distance between the oxygens is determined by the interactions between the corresponding hydrogens and the oxygens of different rings.

The structure of the present work is the following. In the first part, we analyze the effect of binding different guests...
on the geometry of the DB18C6 unit and identify the fragments cut out from the periodic solid corresponding to either H_2O·DB18C6 or H_3O^+·DB18C6 complex. In the second part, we compare the calculated IR and Raman spectra of the studied model systems with experimental data in order to assign the experimental bands.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1q</th>
<th>1b</th>
<th>1m</th>
<th>Isolated</th>
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</thead>
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<td>r(O-H_a)</td>
<td>0.981</td>
<td>0.979</td>
<td>0.987</td>
<td>0.974</td>
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<td>r(O-H_b)</td>
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<td>θ(O-H_a-O)</td>
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<td>103.2</td>
<td>104.7</td>
<td>104.4</td>
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</table>

Distances (r) in Ångstroms, angles (θ) in degrees.

### Table 2

<table>
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<th>1m</th>
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<th>2t'</th>
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<td>2.888</td>
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<td>r(O····O_2)</td>
<td>3.354</td>
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<td>r(O····O_3)</td>
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<td>3.367</td>
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<td>r(O····O_4)</td>
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<td>3.364</td>
<td>–</td>
<td>2.705</td>
<td>2.706</td>
</tr>
<tr>
<td>r(O····O_5)</td>
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<td>3.363</td>
<td>–</td>
<td>2.705</td>
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<td>2.856</td>
<td>2.838</td>
</tr>
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<td>r(O····O_7)</td>
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<td>172.9</td>
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<td>–</td>
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<td>r(O····O_8)</td>
<td>171.4</td>
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<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>r(O····O_9)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>172.8</td>
<td>169.6</td>
</tr>
<tr>
<td>r(O····O_10)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>172.8</td>
<td>169.6</td>
</tr>
</tbody>
</table>

Od denotes oxygen atom of H_2O or H_3O^+ molecule. Distances (r) in Ångstroms, angles (θ) in degrees.

1.1. Theoretical methods

Optimized geometries, harmonic frequencies, IR intensities and Raman scattering activities were determined using Kohn-Sham density functional theory [16]. The calculations were carried out using the semi-local exchange-correlation B88-P86 functional [17,18] and polarized double-zeta split valence (DZVP) basis set [19]. The Gaussian 03 package was used [20]. Minimum energy geometries were found imposing the tight convergence criterion on the RMS of the forces (0.00005 Hartree/Bohr or Hartree/Radian), specified by the option #IOp(1/7=50) in the input route. Pruned (99,590) grid (UltraFine) was used.

To facilitate comparisons between calculated and experimental spectra, the theoretical ones were convolved with the Gaussian-type functions with the full-width half-maximum (FWHM) equal to 12 cm^{-1}. Absolute differential Raman scattering cross sections which are proportional to the Raman intensities were calculated as described in ref. [21].

Throughout this work, the reported harmonic frequencies are not scaled.

Reported interaction energies were corrected for the basis set superposition error (BSSE) by means of the counterpoise technique of Boys and Bernardi [22].

Fig. 4. Optimized structures of DB18C6 and H_2O·DB18C6: 1q conformer.

Fig. 5. Optimized structures of H_2O·DB18C6: 1b and 1m conformers.

Fig. 6. Optimized structures of H_3O^+·DB18C6: 2t and 2t' conformers.
Table 3
Calculated geometrical parameters of the H$_3$O$^+$ molecule trapped in DB18C6 (conformers 2t and 2r) and of the isolated H$_3$O$^+$ (isol.)

<table>
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<th>Parameter</th>
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<th>2r</th>
<th>Isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(O-O$_4$)</td>
<td>1.03</td>
<td>1.04</td>
<td>0.99</td>
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<td>r(O-O$_5$)</td>
<td>1.02</td>
<td>1.01</td>
<td>0.99</td>
</tr>
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<td>r(O-O$_6$)</td>
<td>1.02</td>
<td>1.02</td>
<td>0.99</td>
</tr>
<tr>
<td>r(H$<em>2$O$</em>{20}$)</td>
<td>113.0</td>
<td>113.1</td>
<td>112.1</td>
</tr>
<tr>
<td>r(H$<em>2$O$</em>{21}$)</td>
<td>113.0</td>
<td>113.1</td>
<td>112.1</td>
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</tbody>
</table>

Distances (r) in Ångströms, angles (°) in degrees.

Table 5
Distances between oxygens of crown ether and the oxygen atoms of H$_2$O$_{18}$O$^+$ chain (ch1, ch2) in the crystal structure [13]

<table>
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<tr>
<th>Parameter</th>
<th>ch1</th>
<th>ch2</th>
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<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{13}$)</td>
<td>2.78</td>
<td>2.79</td>
</tr>
<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{14}$)</td>
<td>2.76</td>
<td>2.70</td>
</tr>
<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{15}$)</td>
<td>2.65</td>
<td>2.58</td>
</tr>
<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{16}$)</td>
<td>2.656</td>
<td>2.580</td>
</tr>
<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{17}$)</td>
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<td>2.580</td>
</tr>
<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{18}$)</td>
<td>2.650</td>
<td>2.763</td>
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<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{19}$)</td>
<td>3.819</td>
<td>3.715</td>
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<tr>
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<td>3.715</td>
</tr>
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<td>3.340</td>
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<td>3.340</td>
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<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{23}$)</td>
<td>3.502</td>
<td>3.792</td>
</tr>
<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{24}$)</td>
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<td>3.792</td>
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<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{25}$)</td>
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<td>3.578</td>
</tr>
<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{28}$)</td>
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<td>3.578</td>
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<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{29}$)</td>
<td>3.529</td>
<td>3.447</td>
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</table>

Distances (r) in Ångströms.

1.2. Experimental measurements

In a 1:1 mixture of THF and water (10 ml), the ligand DB18C6 was reacted with H$_2$ and I$_2$. After evaporation of the solvents at room temperature, 1 was obtained in quasi quantitative yield in form of dark needles of dimensions up to 2 cm x 0.2 cm x 0.2 cm. The crystals were used as such for spectroscopic analysis. The compound I appears to be stable in air, micro-Raman spectra obtained after 4 month and IR spectra obtained after 1 year on crystalline samples from the same batch (kept in screw-capped vial) were identical to the initial measurements.

Table 4
Calculated geometrical parameters of the conformers 1t, 1b, 1m, 2t, 2r, isolated DB18C6 (isol.), and experimental values (ch1, ch2) taken from [13]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1t</th>
<th>1b</th>
<th>1m</th>
<th>2t</th>
<th>2r</th>
<th>Isolated</th>
<th>ch1</th>
<th>ch2</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(O$<em>{DB18C8}$ - O$</em>{13}$)</td>
<td>5.63</td>
<td>5.58</td>
<td>5.84</td>
<td>5.37</td>
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<td>5.45</td>
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<td>r(O$<em>{DB18C8}$ - O$</em>{15}$)</td>
<td>5.49</td>
<td>5.72</td>
<td>5.58</td>
<td>5.42</td>
<td>5.45</td>
<td>5.39</td>
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<td>1.457</td>
<td>1.428</td>
<td>1.429</td>
<td>1.409</td>
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<td>1.433</td>
<td>1.428</td>
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<td>1.454</td>
<td>1.428</td>
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<td>1.516</td>
<td>1.498</td>
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</table>

Distances (r) in Ångströms, angles (°) in degrees.

Fouquet transformation infrared (FT-IR) measurement on the pure solid samples were preferred to standard nujol mull or KBr-pellet transmission measurements in order to avoid the necessity of nujol subtraction (around...
2900 cm⁻¹ or complications by potential water contaminations.

FT-IR measurements of the solid samples were performed on a Spectrum One (Perkin Elmer) instrument equipped with the Golden Gate Single Reflection Diamond (P/N 10 500 Graseby-Specac Series) ATR set-up. The spectral resolution was 2–4 cm⁻¹ and the spectral range 600–4000 cm⁻¹. Additional measurements in solution of pure DB18C6 in CH₃NO₃ and CS₂ were done using a Bio-Rad Excalibur instrument. All spectra were recorded at room temperature. Raman spectra were obtained using a Dilor Labram Raman microscope with 532 nm excitation, laser power typically 0.01 mW. Some additional measurements were done with a laboratory assembled set-up consisting of an argon ion laser (488 nm excitation wavelength) and a Kaiser Optical HoloSpec monochromator equipped with a liquid nitrogen cooled CCD camera. The spectral resolution was 3–4 cm⁻¹.

2. Results and discussions

2.1. Geometry

In this section, we analyze the influence of complexation with DB18C6 on the geometry of the guest molecules (H₂O and H₃O⁺) and the effect of the interactions on the DB18C6

Table 6

<table>
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<th>n</th>
<th>H</th>
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<th>l</th>
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<td>502 (12)</td>
<td>588 (8)</td>
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<td>H₂O, ν₁, ν₂</td>
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<tr>
<td>720 (97)</td>
<td>720 (61)</td>
<td>717 (66)</td>
<td>717 (66)</td>
<td>717 (66)</td>
<td>1.2-Disubstituted benzene ν₁, ν₂, ν₃</td>
</tr>
<tr>
<td>748 (73)</td>
<td>748 (73)</td>
<td>748 (73)</td>
<td>748 (73)</td>
<td>748 (73)</td>
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</tr>
<tr>
<td>765 (13)</td>
<td>765 (13)</td>
<td>765 (13)</td>
<td>765 (13)</td>
<td>765 (13)</td>
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<tr>
<td>831 (14)</td>
<td>831 (14)</td>
<td>831 (14)</td>
<td>831 (14)</td>
<td>831 (14)</td>
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</tr>
<tr>
<td>862 (11)</td>
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<td>862 (11)</td>
<td>862 (11)</td>
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</tr>
<tr>
<td>915 (10)</td>
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<td>915 (10)</td>
<td>915 (10)</td>
<td>915 (10)</td>
<td>1.2-Disubstituted benzene ν₁, ν₂, ν₃</td>
</tr>
<tr>
<td>918 (71)</td>
<td>918 (71)</td>
<td>918 (71)</td>
<td>918 (71)</td>
<td>918 (71)</td>
<td>1.2-Disubstituted benzene ν₁, ν₂, ν₃</td>
</tr>
<tr>
<td>919 (96)</td>
<td>919 (96)</td>
<td>919 (96)</td>
<td>919 (96)</td>
<td>919 (96)</td>
<td>1.2-Disubstituted benzene ν₁, ν₂, ν₃</td>
</tr>
</tbody>
</table>

The frequencies of intense lines are underlined. Absorption coefficients are given in parentheses (in km/mol).
Table 7
IR region 1000–1700 cm\(^{-1}\): conformers 1\(q\), 2\(t\), isolated DB18C6 (isol.), experimental (measured in crystal) frequencies of DB18C6 (exp.), and experimental (measured in crystal) frequencies of 1\(\infty\)((H\(_2\)O)\(_2\)⊂(DB18C6)\((\sim H\(_9\))\(_2\)H\(_2\)O)\(_2\)/2) 1\(\infty\)((H\(_3\)O)\(_2\)⊂(DB18C6)\((\sim H\(_9\))\(_2\)H\(_2\)O)\(_2\)/2)I 3 (1)

| \(\nu\) & 2f & Isolated & Experimental & Description |
|---|---|---|---|---|
| – & – & – & – & \(\nu_{as}C\(_{O17}\)–C, CH\(_2\), C\(_{O\text{str.}}\) |
| – & 1032 (100) & – & – & \(\nu_{as}C\(_{O17}\)–C, CH\(_2\), C\(_{O\text{str.}}\) |
| – & 1035 (77) & – & – & H\(_2\)O\(_2\) umbrella, ring (\(\sim H\(_9\)) on O\(_{14}\) side) |
| 1043 (23) & 1044.01 (40) & 1045 (22) & – & C\(_{4h}\)–H in-plane |
| 1044 (14) & 1044 (29) & 1046 (14) & – & C\(_{4h}\)–H in-plane |
| 1046 (31) & 1048 (60) & – & – & H\(_2\)O\(_2\) umbrella, ring (on O\(_{23}\) side) |
| 1048 (100) & 1049 (154) & 1049.87 (96) & – & C\(_{sym\text{str.}}\) |
| 1056 (28) & 1056 (54) & – & – & CH\(_2\) on O\(_{17}\) side |
| 1075 (22) & 1076 (12) & – & – & CH\(_2\) on O\(_{17}\) side |
| 1113 (196) & 1115 (262) & 1114 (191) & 1117 & C\(_{4h}\)–H in-plane |
| – & – & – & – & CH\(_2\) on O\(_{17}\) side, C\(_{4h}\)–H in-plane |
| 1122 (96) & – & – & – & CH\(_2\) on O\(_{17}\) side, C\(_{4h}\)–H in-plane |
| 1124 (383) & 1125 (406) & 1126 & 1127 & C\(_{4h}\)–H in-plane |
| – & 1126 (226) & – & – & CH\(_2\) on O\(_{17}\) side, C\(_{4h}\)–H in-plane |
| 1206 (13) & 1207 (117) & 1207 & 1208 & CH\(_2\) phenyl deformation |
| 1212 (292) & 1214 (28) & 1217 (22) & – & CH\(_2\) on O\(_{17}\) side |
| – & 1218 (284) & – & – & CH\(_2\) phenyl deformation |
| 1220 (28) & 1220 (25) & – & – & CH\(_2\) |
| 1222 (96) & – & – & – & CH\(_2\) on O\(_{17}\) side |
| 1223 (159) & – & – & – & CH\(_2\) C\(_{4h}\)–H in-plane |
| 1224 (122) & – & – & – & C\(_{4h}\)–O str., CH\(_2\) on O\(_{17}\) side, C\(_{4h}\)–H in-plane |
| 1225 (60) & – & – & – & CH\(_2\) on O\(_{17}\) side |
| 1252 (203) & 1253 (214) & 1256 & 1257 & C\(_{4h}\)–O str., CH\(_2\) |
| 1253 (288) & 1253 (208) & 1252 (908) & 1256 & 1257 & C\(_{4h}\)–O str., CH\(_2\) C\(_{4h}\)–H in-plane |
| 1256 (60) & 1255 (40) & 1256 & 1257 & C\(_{4h}\)–O str., CH\(_2\) C\(_{4h}\)–H in-plane |
| 1258 (170) & 1257 (111) & 1258 & 1259 & C\(_{4h}\)–O str., CH\(_2\) C\(_{4h}\)–H in-plane |
| 1261 (64) & – & 1263 (72) & – & C\(_{4h}\)–O str., CH\(_2\) |
| 1264 (8) & – & – & – & CH\(_2\) |
| – & 1323 (14) & – & – & CH\(_2\) on O\(_{17}\) side |
| 1329 (31) & 1329 (36) & – & – & CH\(_2\) on O\(_{17}\) side |
| 1329 (60) & 1329 (88) & 1330 & 1330 & CH\(_2\) |
| 1349 (13) & 1355 (16) & – & – & CH\(_2\) bend. |
| – & 1436 (57) & – & – & CH\(_2\) bend. |
| 1456 (54) & 1457 (37) & 1454 (81) & – & C\(_{4h}\)–O str., CH\(_2\) bend, C\(_{4h}\)–H in-plane |
| 1456 (92) & 1456 (29) & 1458 (28) & 1455 & 1451 & CH\(_2\) bend. |
| 1455 (31) & 1447 (29) & – & – & CH\(_2\) bend. (outside) |
| – & 1444 (31) & – & – & CH\(_2\) bend. |
| – & 1448 (20) & – & – & CH\(_2\) bend. |
| – & 1449 (14) & – & – & CH\(_2\) bend. |
| 1455 (21) & 1459 (10) & – & – & CH\(_2\) bend. |
geometry. In all geometry optimizations, the starting geometry of DB18C6 was taken from crystallographic data (channel 1 (ch1), ref. [13]). In view of our interest in the properties of guests in the crystal, conformational preferences of DB18C6 were not investigated further.

2.1.1. \( \text{H}_2\text{O} \cdot \text{DB18C6} \) complex

Three non-equivalent minimum energy structures have been found (see Figs. 4 and 5). They are denoted as conformers \( 1q \), \( 1b \), and \( 1m \), throughout this work. The binding energies amount to \(-9.1, -4.7 \) and \(-3.1 \text{ kcal/mol} \) \((-11.7, -7.1 \) and \(-4.7 \text{ kcal/mol} \) without the correction for BSSE) for the \( 1q \), \( 1b \), and \( 1m \) conformers, respectively. In the \( 1q \) conformer, the water molecule is most strongly bound to the crown ether via two bifurcated hydrogen bonds. It is also bound to the host molecule via two hydrogen bonds in the \( 1b \) conformer, but the resulting interaction is weaker. In the \( 1m \) conformer, the water molecule interacts with the ring through one hydrogen bond only and the interaction is the weakest. Moreover, this arrangement of the guest molecule is less relevant in the general context of this study because it is not observed in the solid [13]. Table 1 collects the calculated...
intramolecular geometrical parameters for the bound and the isolated water molecule.

The structure of the H$_2$O guest molecule changes upon complexation. The O–H bonds elongate due to their participation in hydrogen bonding. It is notable that the geometry of the isolated H$_2$O molecule derived from our calculation reproduces quite reasonably the experimental values [23] ($r$(O–H)$_{exp}$ = 0.957 Å versus $r$(O–H)$_{calc}$ = 0.974 Å; $\angle$(H–O–H)$_{exp}$ = 104.5° versus $\angle$(H–O–H)$_{calc}$ = 104.4°). The numbering of atoms shown in Fig. 6 is used throughout this work.

2.1.2. H$_3$O$^+$·DB18C$_6$ complex

Two non-equivalent minimum energy structures have been found (see Fig. 6). They are denoted as conformers 2t and 2t$'$ throughout this work. The interaction energies amount to $-87.6$ and $-87.2$ kcal/mol ($-89.2$ and $-89.0$ kcal/mol without the correction for BSSE). In the 2t conformer, the guest molecule and the two phenyl rings of DB18C$_6$ are on the same side of the crown ether. In the 2t$'$ conformer, which is slightly less stable, the H$_3$O$^+$ molecule and the phenyl rings are on opposite sides of the crown ether ring. In both conformers, the three hydrogen bonds are not equivalent—two are shorter and one is longer (see Table 2). All three hydrogen bonds are quasi-linear.

No minimum energy structure corresponding to the H$_2$O·DB18C$_6$H$^+$ complex, i.e., where the proton is attached not to the guest molecule but to the crown ether ring, has been found (see the discussion in the ref. [24], where the energy of the H$_2$O·18C$_6$H$^+$ complex was found to be higher than the energy of H$_2$O·18C$_6$).

Table 3 collects the calculated intramolecular geometrical parameters for the bound and the isolated H$_3$O$^+$ cation.

In the gas phase, the hydronium ion is more strongly bound to the crown than the neutral water molecule ($89.2$ versus $9.1$ kcal/mol). Obviously, gas-phase energy difference cannot be used to determine the relative populations of the charged and neutral guests in the bulk where other factors play a role: guest–guest interactions, interactions with the anions, pH, stoichiometry, etc. Without taking into account such effects the energetics derived from our gas-phase single unit model

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![Fig. 8. Calculated IR spectra of isolated DB18C6 (A), conformer 1q (B), conformer 2t (C). The 1329 cm$^{-1}$ line of (A) was used for normalization of the spectra.](image-url)
has little relevance to the energetics of the guest–channel interactions in the crystal. We recall here that the stoichiometry of the crystal material is such that only 25% of guest species are charged[13,14]. For this reasons, we turn to the analysis of vibrational properties of the considered guests.

2.1.3. The effect of interactions with guest on the DB18C6 geometry

Table 4 collects the key geometrical parameters of the isolated DB18C6 and the complexes with H$_2$O or H$_3$O$^+$ guests. At each of the five structures corresponding to the local energy minima, the geometry of DB18C6 is different. For instance, the O$_{17}$···O$_{14}$ distance which measures the overall size of the crown ether varies between 5.371 Å (conformer 2t) and 5.938 Å (conformer 1q). Binding the guest molecule affects also the angle formed by the phenyl planes and that of the crown ether. This does not change significantly the overall geometry of the whole DB18C6. For instance, the C$_{29}$···C$_{21}$ distance between two most distant carbons belonging to the opposite phenyl rings varies in a narrow

<table>
<thead>
<tr>
<th>Eq</th>
<th>2t</th>
<th>Isolated</th>
<th>Experimental</th>
<th>1</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2932 (1680)</td>
<td>--</td>
<td>--</td>
<td>H$_2$O$^+$ str.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2937.98 (46)</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ sym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2907.22 (173)</td>
<td>--</td>
<td>2904.41 (142)</td>
<td>--</td>
<td>--</td>
<td>CH$_3$ sym. str.</td>
</tr>
<tr>
<td>2907.99 (71)</td>
<td>--</td>
<td>2904.75 (37)</td>
<td>--</td>
<td>--</td>
<td>CH$_3$ sym. str.</td>
</tr>
<tr>
<td>2933 (2349)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ sym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2931 (626)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ sym. str. on O$</em>{17}$ side</td>
</tr>
<tr>
<td>2942.9 (59)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ sym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2950.20 (182)</td>
<td>--</td>
<td>2941.23 (151)</td>
<td>--</td>
<td>--</td>
<td>CH$_3$ sym. str.</td>
</tr>
<tr>
<td>2950.24 (36)</td>
<td>--</td>
<td>2942.3 (14)</td>
<td>--</td>
<td>--</td>
<td>CH$_3$ sym. str.</td>
</tr>
<tr>
<td>2951 (10)</td>
<td>--</td>
<td>2942.3 (14)</td>
<td>--</td>
<td>--</td>
<td>CH$_3$ sym. str.</td>
</tr>
<tr>
<td>2953.2 (20)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ sym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2967 (13)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ sym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2983 (34)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ sym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2996 (32)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>H$_2$O$^+$ str. CH$<em>3$ str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2995 (38)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2996 (25)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>H$_2$O$^+$ str. CH$<em>3$ str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>2992 (15)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>3005.42 (36)</td>
<td>--</td>
<td>2992.2 (110)</td>
<td>2990</td>
<td>3032</td>
<td>CH$_3$ asym. str.</td>
</tr>
<tr>
<td>3003.46 (49)</td>
<td>--</td>
<td>2992.1 (110)</td>
<td>2990</td>
<td>3032</td>
<td>CH$_3$ asym. str.</td>
</tr>
<tr>
<td>3016 (9)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ asym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>3018 (14)</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>CH$<em>3$ asym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>3026 (38)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>H$_2$O$^+$ sym. str.</td>
</tr>
<tr>
<td>3033 (41)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ asym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>3046 (91)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>CH$<em>3$ asym. str. on O$</em>{14}$ side</td>
</tr>
<tr>
<td>3139.62 (11)</td>
<td>3151.6 (11)</td>
<td>3137.95 (37)</td>
<td>--</td>
<td>--</td>
<td>C$_2$H$_4$–H str.</td>
</tr>
<tr>
<td>3139.66 (13)</td>
<td>3151.6 (11)</td>
<td>3137.95 (37)</td>
<td>--</td>
<td>--</td>
<td>C$_2$H$_4$–H str.</td>
</tr>
<tr>
<td>3153 (39)</td>
<td>3150.04 (14)</td>
<td>3151.32 (45)</td>
<td>3065</td>
<td>3066</td>
<td>C$_2$H$_4$–H str.</td>
</tr>
<tr>
<td>326 (58)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>C$_2$H$_4$–H str.</td>
</tr>
<tr>
<td>327 (326)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>C$_2$H$_4$–H str.</td>
</tr>
</tbody>
</table>

The frequencies of intense lines are underlined. Absorption coefficients are given in parentheses (in km/mol).
Table 9
Calculated IR frequencies (cm\(^{-1}\)) of the H\(_2\)O molecule trapped in DB18C6 ether (conformers 1q, 1b, 1m), isolated H\(_2\)O (isol.), experimental harmonic frequencies of H\(_2\)O (\(\omega\)), and experimental fundamentals of H\(_2\)O (\(\nu\)).

<table>
<thead>
<tr>
<th>Isolated</th>
<th>1q</th>
<th>1b</th>
<th>1m</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega)</td>
<td>(\nu)</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>120 (09)</td>
<td>H(_2)O(\rightarrow)Hb</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>153 (15)</td>
<td>H(_2)O ring</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>137 (13)</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>249 (26)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>331 (14)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>338 (52)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>367 (70)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>422 (250)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>451 (48)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>490 (80)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>519 (21)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>1642 (30)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>3626 (56)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>The frequencies of intense lines are underlined. Absorption coefficients are given in parentheses (in km/mol).</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9. Experimental IR solid phase spectrum of DB18C6 (A), calculated IR spectrum of isolated DB18C6 (B) and experimental IR spectrum of DB18C6 in CH\(_3\)NO\(_3\) (spectrum of the solvent was subtracted) (C).
range (from 10.71 Å in the 2t′ conformer to 11.02 Å in the 1b conformer).

2.1.4. The calculated structures versus solid state data

Since no coordinates of hydrogen atoms are available in the structure derived from X-ray diffraction data, each of the oxygen atoms localized in the center of the channel can be attributed to either H2O, H3O+, or a chain-like arrangement of water molecules—the Zundel cation H5O2, for instance. In a model for the channels formed by DB18C6 in which only one ligand molecule is considered to be an excerpt of the infinite structure, three oxygen sites can be identified with C being the one in the middle of the crown ether, A being the one on the side of the phenyl rings, and B the one opposite to A. Note that the oxygen sites A and B are not equivalent in our model (see Fig. 1). The ring-oxygen distance differs for the three types of oxygen. Moreover, two non-equivalent channels occur in the crystal. They will be referred to as ch1 and ch2 (see Figs. 2 and 3). The diameter O···O distances in the two channels differ by 0.258 Å (see Table 4). The relative position of the oxygens of the type A are very similar in both channels. The position of the oxygen closest to the crown ether ring (type C) was previously suggested in the literature to be attributed to H3O+ whereas the more distant ones (type A or B) to H2O [26]. Comparisons of the distances between the guest oxygen and ring oxygens in the crystal (see Table 5) with the corresponding distances in the most stable conformers of H2O·DB18C6 and H3O+·DB18C6 complexes (see Table 2) confirm the above attribution of the oxygen centers. Therefore, the two most stable intermolecular complexes of H2O·DB18C6 (1q) and H3O+·DB18C6 (2t) analyzed by means of theoretical modeling in this study can be seen as fragments cut off the solid (type B and type C, respectively). The 1b conformer does not match the type A site structure (compare Tables 2 and 5). We recall now that the crystallographic arrangement of the C and A sites matches that of the isolated H5O2 cation (not considered explicitly in our calculations).

According to our calculations, binding of H3O+ results in a significantly larger deformation of DB18C6 unit than binding of H2O. The geometry of the ring calculated in the presence of the H3O+ guest matches much closer that of the crystallographic structure than the one derived for the H2O guest (see Table 4).

2.2. Vibrational spectra

IR spectra calculated at the minimum energy structures (conformers 1q, 2t, and the isolated DB18C6 molecule) are collected in Tables 6–8. In the following sections, the effect of Fig. 10. Experimental IR solid phase spectrum of DB18C6 (A) and calculated IR spectrum of isolated DB18C6 (B).
complexation on the vibrational properties of the molecules forming the complex will be discussed.

2.2.1. H\textsubscript{2}O·DB18C\textsubscript{6} complex

Binding H\textsubscript{2}O affects negligibly the frequencies of IR bands of DB18C\textsubscript{6} (see Fig. 7). For the most stable conformer of the complex (i.e. 1q), in the spectral region 600–1700 cm\textsuperscript{-1}, the complexation induced frequency shifts of the crown ether ring frequencies do not exceed 4 cm\textsuperscript{-1} (H\textsubscript{2}O·DB18C\textsubscript{6}—1046 cm\textsuperscript{-1} versus DB18C\textsubscript{6}—1050 cm\textsuperscript{-1}, H\textsubscript{2}O·DB18C\textsubscript{6}—1220 cm\textsuperscript{-1} versus DB18C\textsubscript{6}—1216 cm\textsuperscript{-1}). Some modes change, however, their intensities (e.g. 1212 cm\textsuperscript{-1}), or modes at similar frequencies differ in H\textsubscript{2}O·DB18C\textsubscript{6} and DB18C\textsubscript{6} (e.g. H\textsubscript{2}O·DB18C\textsubscript{6}—1222 cm\textsuperscript{-1} versus DB18C\textsubscript{6}—1220 cm\textsuperscript{-1}). The largest shifts occur in the high frequency region and amount to 19 cm\textsuperscript{-1} for the CH\textsubscript{2} asymmetric stretching mode (2971 cm\textsuperscript{-1} in the complex versus 2952 cm\textsuperscript{-1} for the isolated DB18C\textsubscript{6}).

In the spectrum of the 1b conformer, the largest shifts occur for 1125 and 2904 cm\textsuperscript{-1} bands of DB18C\textsubscript{6}. They are shifted to 1114 and 2915 cm\textsuperscript{-1}, respectively, in the 1b conformer. In the case of the 1m conformer, the overall picture is similar. Some modes delocalized over the whole crown ether ring in the case of isolated DB18C\textsubscript{6} molecule become, however, localized on a fragment of the crown ether.

The spectral region between 1000 and 1300 cm\textsuperscript{-1} (see Fig. 8) corresponds mainly to C=O stretching modes. Due to the fact that ring oxygens can be involved in hydrogen bonding with the guest molecule, this spectral region can be expected to differ in the isolated DB18C\textsubscript{6} and in the complex [27,28]. Seven normal modes with significant IR intensities were found in DB18C\textsubscript{6}: one delocalized mode at 1050 cm\textsuperscript{-1}, C=O vibration in the plane of the phenyl groups at 1114 cm\textsuperscript{-1}, asymmetric stretching involving C=O(1-w-C) and C-O(1-w-C) groups of the crown at 1125 cm\textsuperscript{-1}, two modes involving CH\textsubscript{2} vibrations and deformations of phenyl groups (1212, 1220 cm\textsuperscript{-1}), and two modes characterized mainly by stretching of all C=O bonds where C is the phenyl carbon and O is the oxygen of the crown ether (1252 and 1259 cm\textsuperscript{-1}).

For the most stable conformer of H\textsubscript{2}O·DB18C\textsubscript{6} (1q), the frequencies 1048, 1113, 1224 cm\textsuperscript{-1} correspond to 1050, 1114 and 1225 cm\textsuperscript{-1} bands in the isolated DB18C\textsubscript{6}. The intensity of the 1212 cm\textsuperscript{-1} band is larger than in the isolated DB18C\textsubscript{6}, and instead of 1220 cm\textsuperscript{-1} in the isolated DB18C\textsubscript{6}, a CH\textsubscript{2} band appears at 1222 cm\textsuperscript{-1}. The 1253 and 1257 cm\textsuperscript{-1}
bands correspond to 1252 and 1259 cm\(^{-1}\) bands in the isolated DB18C6, and the band at 1259 cm\(^{-1}\) has larger intensity compared to the intensity of the weak band at 1260 cm\(^{-1}\) for isolated DB18C6 (see Fig. 11).

Table 9 collects the calculated IR frequencies corresponding to the intramolecular degrees of freedom of the isolated and complexed H\(_2\)O. Data for intermolecular modes are also included. As expected, hydrogen bonding leads to frequency redshifts of both symmetric and asymmetric stretching modes and a slight blue shift of the bending mode for all considered conformers.

2.2.2. \(\text{H}_3\text{O}^+\)DB18C6 complex

Binding of \(\text{H}_3\text{O}^+\) affects noticeably the vibrations of DB18C6 for both \(2t\) and \(2t'\) conformers. Below, we analyze the most affected modes.

The modes involving \(\text{C}═\text{O}═\text{C}\) of the ring are strongly affected by binding of \(\text{H}_3\text{O}^+\). Among six oxygen atoms, three are involved in a strong hydrogen bond in both \(2t\) and \(2t'\) conformers (see Fig. 6). As a result, instead of one \(\text{C}═\text{O}═\text{C}\) asymmetric stretching mode occurring at 1125 cm\(^{-1}\) in isolated DB18C, four new modes appear in the complex: (i) two modes involving \(\text{C}═\text{O}═\text{C}\): one strong (1032 cm\(^{-1}\)) and one weak at 1073 cm\(^{-1}\), (ii) two modes involving \(\text{C}═\text{O}═\text{C}\) and in-plane vibrations of the phenyl \(\text{C}═\text{H}\) groups at 1108 and 1122 cm\(^{-1}\). The most clearly distinct new feature appears in the spectrum of the complex, i.e. the intense 1179 cm\(^{-1}\) band in which \(\text{C}═\text{O}\) (C of the phenyl and O of the crown) stretching and in-plane stretching of the phenyl \(\text{C}═\text{H}\) are coupled. Bands in the region of 1200–1220 cm\(^{-1}\) almost disappear in the complex. Additionally two bands at 1243 and 1249 cm\(^{-1}\) appear, and the bands at 1252 and 1261 cm\(^{-1}\) change their description compared to isolated DB18C6 (see Fig. 11).

Table 10 collects the calculated IR frequencies corresponding to the intramolecular degrees of freedom of \(\text{H}_3\text{O}^+\) for the complexed and isolated guest molecule. Data for intermolecular vibrational modes are also included. As expected, hydrogen bonding leads to larger frequency redshifts of both symmetric and asymmetric \(\text{H}_3\text{O}^+\) stretching modes than those for \(\text{H}_2\text{O}\) in \(\text{H}_2\text{O}\)DB18C6.

2.2.3. Assignment of the experimental spectra

The intermolecular complexes analyzed by means of theoretical modeling can be seen as simple models of the real

![Fig. 12. Calculated IR spectrum of the conformer 1q (A), experimental IR solid phase spectrum of \(\frac{1}{2}[\text{(H}_2\text{O})_6\text{DB18C6}(\mu_2-H_2\text{O})_2\text{DB18C6}]\) (B) and calculated IR spectrum of the conformer 2t (C). The 1590 cm\(^{-1}\) line of (A) was used for normalization of the theoretical spectra.](image-url)
Their calculated IR and Raman spectra can be expected to differ from the ones measured experimentally due to two principal reasons: (i) the applied theoretical methods are not exact—we use approximated exchange-correlation functional and apply the harmonic approximation for frequencies and double-harmonic approximation for the intensities, (ii) the studied complexes are models of the real system in which the crown ethers are stacked forming a channel, the guest molecules interact with each other, and the neutralizing anions such as $I_3^-$ are used. The last three effects, present in the real system, are neglected in our theoretical model. Moreover, experimental conditions (solvent effects, crystallization) affect also the observed spectra. Nevertheless, some theoretically assigned lines can be identified with the experimental bands. The solid phase spectrum of I, together with the solid phase/solution spectrum of DB18C6 were used in the assignment.

2.2.3.1. IR spectra. All IR bands below were assigned on the basis of the calculated and solid phase/solution spectra of DB18C6 (see Figs. 9 and 10). The assigned experimental
bands are (see Tables 6–8): 738, 777, 915, 931, 1117, 1128, 1227, 1256, 1330, 1451, 1508, 1595, 2950 and 3065 cm\(^{-1}\).

The band structure of the region 1000–1300 cm\(^{-1}\) in the IR solid phase spectrum of DB18C6 is not reproduced by calculations for the isolated DB18C6 molecule. The calculated spectrum of isolated DB18C6 resembles much better the experimental spectrum of DB18C6 measured in CH$_3$NO$_3$ (see Fig. 9). This can be explained by the presence of different conformations of DB18C6 in the solution and the solid phase, as suggested in refs. [29,30].

As far as the spectrum of 1 is concerned, additional bands which can be assigned are the vibrations of H$_2$O: the stretching bands at 3547 and 3624 cm\(^{-1}\) and the bending mode at 1621 cm\(^{-1}\) in the experimental spectrum. Fig. 13 indicates also the same polarization for the totally symmetrical bending and stretching modes of the water vibrations (negative contributions in the difference trace).

Theoretical analysis of the solid phase spectrum of 1 does not provide a compelling evidence of the presence of H$_3$O$^+$ molecule. Comparison between the theoretical spectrum of 2t with the solid spectrum of 1 shows three significant differences. The foremost one is the mismatch of the relative intensities of the bands 2750–3000 cm\(^{-1}\) between the experimental and the calculated spectra (see Fig. 12). In the experimental spectrum the intensities of these bands are smaller than the intensities of the bands in the region below 1800 cm\(^{-1}\). In the calculated spectrum of the conformer 2t the intensities of the bands in the 2750–3000 cm\(^{-1}\) region are significantly larger than the intensities of the bands below 1800 cm\(^{-1}\). One of the possible reasons for this mismatch might originate from the fact that, in the real system, the vibrations of H$_3$O$^+$ might be coupled to the motions of counterions—this effect is not accounted for in our model.

Previous experimental spectra of H$_3$O$^+$ in crown ethers show a very broad band (full width more than 300 cm\(^{-1}\)) around 2850 cm\(^{-1}\), in addition to bands at about 2200 cm\(^{-1}\) (assigned to the first overtone of $\nu_2$) and the bending mode ($\nu_4$) around 1700 cm\(^{-1}\) [31]. The integrated intensity of the broad band around 2900 cm\(^{-1}\) compared to the integrated intensity of a pure C–H stretching mode (with a band width of about 10 cm\(^{-1}\)) is obviously much larger (see Fig. 1 in ref. [32] for a relevant system). The difference trace shown in Fig. 13 suggests the presence of a weak and broad band at about 2900 cm\(^{-1}\) which might indeed be associated with H$_3$O$^+$. Its relatively weak intensity may be the result of the fact that the refined crystal structure [13,14] indicates the presence of...
one cationic species for four DB18C6 molecules. However, the presence of other bands in the difference trace of Fig. 13 in conjunction with this weak band and broad band may also be associated with other protonated species.

The other difference between the theoretical spectrum of 2t and the solid spectrum of I is the presence of the 2068 cm\(^{-1}\) band in the spectrum of I, which is missing in all of the theoretical spectra. This band was assigned previously to be the first overtone of the 1048 cm\(^{-1}\) (umbrella mode) [31]. The experimental spectrum of I shows strong bands at 943, 1067 and 1128 cm\(^{-1}\) which all could contribute to this feature at 2068 cm\(^{-1}\) (943 + 1128 and 2 × 1067). The origin of the band at 2068 cm\(^{-1}\) remains thus unclear.

Turning back to the effect of stacking (point ii), one can try to identify the vibrations which could be expected to be the most affected by stacking. Such vibrational modes involve the relative motion of the phenyl groups of the DB18C6 unit with respect to their neighbors in the channel. Our calculations predict such vibrations in the 20 cm\(^{-1}\) region, which falls outside the spectral region where the measurements were made.

2.2.3.2 Raman spectra. According to refs. [29,30], the band in the experimental crystal Raman spectrum of NaBr complex of DB18C6 at 856 cm\(^{-1}\) (data in the ref. [29]) is characteristic to tG conformation of the crown (the notation used to describe conformations of the crown ethers is explained in the Appendix A). The corresponding band agrees to the spectrum of I at 845 cm\(^{-1}\) (see Fig. 14). This is in agreement with the crystallographic structure of DB18C6 units in the channel which is close to (tCttGttG)\(^\prime\) conformation. We attribute calculated band for isolated DB18C6 at 832 cm\(^{-1}\) to this vibration on the basis of intensity pattern, and the known structure of calculated molecules which is (tCGrGtGt). In the conformer 1q the corresponding band appears at 831 cm\(^{-1}\). In the case of H\(^2\)O+DB18C6 (conformer 2t), the band is split into 820 and 838 cm\(^{-1}\) because tGt are not equivalent in the two halves of the molecule (see Fig. 15). Low frequency Raman spectra confirm the presence of linear I\(^1\)−.

Similar to the IR spectra, some features in the Raman spectra measured in the solid phase are not well reproduced by our model. They include:

- The band in the solid phase spectrum of DB18C6 at 1329 cm\(^{-1}\) is missing in calculations. The bands in the solid phase spectrum of DB18C6 at about 1250 cm\(^{-1}\) are weak, however, calculated bands in this region are strong.
- The O–H stretching bands of H\(^2\)O are missing in the Raman spectrum of I.

3. Conclusions

In principle, the three non-equivalent oxygen sites (A, B, and C) in the center of the channel formed by stacked DB18C6 units can be attributed to various guests: H\(^2\)O, H\(^3\)O\(^+\) or chain-like structures (H\(^6\)O\(^2\)\(^+\), H\(^8\)O\(^4\)\(^+\), . . .). Our geometry minimization studies on a small model system comprising just one crown ether unit and one guest molecule (either H\(^2\)O or H\(^3\)O\(^+\)) allowed us to attribute the site B to H\(^2\)O. Site C, was attributed to H\(^3\)O\(^+\) or other protonated species. Geometry minimization studies indicate that the structure of the DB18C6 unit change more significantly upon binding the H\(^3\)O\(^+\) than in the H\(^2\)O case. The crown ether ring shrinks by about 0.6 Å upon H\(^3\)O\(^+\) binding. The angle between the phenyl ring planes does not change noticeably upon binding both considered guests. The applied computational method to derive the vibrational spectra of all considered complexes was shown to be adequate as evidenced by a rather good agreement between the theoretical and experimental spectra (IR and Raman) of DB18C6. In particular, the attribution of the site B to the H\(^2\)O guest based on the geometry minimization is consistent with the fact that the theoretical IR spectrum of the 1q conformer of the H\(^2\)O+.DB18C6 complex matches the experimental spectrum of I. Site C remains, therefore, the best candidate to be attributed to oxygens of protonated species. Whether it corresponds to an isolated H\(^3\)O\(^+\) molecule or a fragment of the chain-like structure H\(^6\)O\(^2\)\(^+\), H\(^8\)O\(^4\)\(^+\), etc.) remains to be clarified.
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Appendix A. The short notation to describe the conformation of crown ethers

• Small letters correspond to C=O bonds, capital letters to C–C bonds.
• \( t \) denotes dihedral angle \( A-C-O-B \) close to 180 or \(-180\) degrees.
• \( T \) denotes dihedral angle \( A-C-C-B \) close to 180 or \(-180\) degrees.
• \( G \) (gauche) denotes dihedral angle \( A-C-C-B \) close to 60 degrees.
• \( G' \) (gauche') denotes dihedral angle \( A-C-C-B \) close to \(-60\) degrees.
• \( C \) (cis) denotes dihedral angle \( A-C-C-B \) close to 0 degrees.

For instance, the structure of 18C6 (D\( _{3d} \)) in this convention is described as \( tG'\)ttGttG\( '\)ttGttG\( '\)ttGt.

Appendix B. Supplementary Data


References