Water Adsorption on Zeolites: Ab-Initio Interpretation of IR Data

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Ab-initio 6-31G* OH frequency calculations show the water molecule complex with the bridging OH group of zeolites to be hydrogen-bonded. The experimental 3390- and 3695-cm⁻¹ frequencies of the complex are interpreted to belong to the water OH group interacting with the surface by two hydrogen bonds and to the other slightly perturbed water OH group, respectively. The broad ~2900-, ~2450-, and ~1700-cm⁻¹ bands are explained on the basis of a theory of OH bend profiles of hydrogen-bonded complexes to be the so-called (A, B, C) trio, caused by resonant interactions between the H(OH) and γ(OH) overtones of the perturbed bridging OH group.

Introduction

Adsorption of water on Bronsted sites of zeolites has been studied with IR methods by many authors (refs 1-5 and references therein). The four OH bands at 3695, 3390, ~2900, and ~2450 cm⁻¹ have been assigned to a water molecule complex with the bridging OH group in HZSM-5 zeolites. This complex was suggested by Jentys et al. to be a hydroxonium ion attached to the lattice AOSi acid residue. The sharp 3695-cm⁻¹ band was attributed to the free OH group of the H₂O⁺ ion, pointed away from the surface. The broad bands at ~2900 and ~2450 cm⁻¹ were proposed to be associated with the antisymmetric and symmetric H₂O⁺ vibrations involving the two other OH groups bonded to the AOSi bridging oxygen. The 3390-cm⁻¹ band, appearing together with the three other above-mentioned bands, was not discussed in detail.

An ab-initio study with a DZP basis set by Sauer et al. showed the water complex to be hydrogen-bonded, the one water OH group interacting both with the bridging OH group and with the nearest AOSi oxygen, as a proton acceptor and as a proton donor, respectively, and the other OH group being free. Within the DZP approximation this structure was found to be more stable, by about 18 kJ/mol, than the ion-pair structure, corresponding to the H₂O⁺ ion attached by two strong hydrogen bonds to the AOSi lattice residue. Electron-correlation contributions estimated in this study by the MP2 method led to about the same energy of the hydrogen-bonded and ion-pair structures. Due to the known uncertainty of the MP2 approximation, the authors did not come to any definite conclusion about the real nature of the adsorbed complex.

The conclusion of experimental IR studies in favor of the H₂O⁺ ion is based mainly on the assumption of the ~2900- and ~2450-cm⁻¹ doublet belonging to the antisymmetric and symmetric vibrations of the surface H₂O⁺. However, as it was shown in our recent study, these two bands, detected also in the adsorption of many other basic molecules, belong to the so-called (A, B, C) trio of OH bands, at ~2900, ~2400, and ~1700 cm⁻¹, typical for medium-strong and strong hydrogen-bonded complexes in vapors, liquids, and solids (refs 8-11 and references therein). According to a theory of OH bond profiles of hydrogen-bond complexes, they are caused by resonant interactions between the γ(OH) stretching vibration and the δ(OH) overtones of the strongly perturbed bridging OH group.

Table I: Bond Lengths, AB (Å), and Angles, ABC and ABCD (deg)

| molecule | AB | geometry
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁺</td>
<td>0.947</td>
<td>OH⁻, 0.955; H⁺OH², 106.2; HO⁻, 129.9; OH⁻, 2.9</td>
</tr>
<tr>
<td>AIO⁺</td>
<td>1.917</td>
<td>AIO⁺, 1.751; AIO⁺, 1.723; H⁺OH², 0.953; H⁺OH², 0.944; H⁺OH², 0.942; H⁺OH², 0.937; H⁺OH², 0.946</td>
</tr>
<tr>
<td>AIO⁺</td>
<td>1.908</td>
<td>AIO⁺, 1.749; AIO⁺, 1.718; H⁺OH², 0.943; H⁺OH², 0.942; H⁺OH², 0.937; H⁺OH², 0.946</td>
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</tr>
</tbody>
</table>

Table II: Total Energies (hartrees)

<table>
<thead>
<tr>
<th>structure</th>
<th>energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-228.058</td>
</tr>
<tr>
<td>2</td>
<td>-620.4764</td>
</tr>
<tr>
<td>3</td>
<td>-620.4703</td>
</tr>
</tbody>
</table>

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complex hydrogen-bonded aggregates. The \( \nu(OH) \) is taken to
vibrations to the normal OH modes in Table IV), their
vibrations to each normal mode, estimated from the normalized sums of
the squares of the eigenvectors of each atom for each mode.

TABLE II: \( \nu(OH) \) Frequencies (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>structure</th>
<th>assignment</th>
<th>calcd</th>
<th>obsd*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \nu(OH_a) )</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>1'</td>
<td>( \nu(OH_b) )</td>
<td>136</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td>( \nu(OH) )</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>

* With respect to the uncoupled O–H vibrator frequency of the HOD molecule.

Figure 1. Molecular structures.

TABLE III: OH Frequency Shifts* (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>structure</th>
<th>assignment</th>
<th>calcd</th>
<th>obsd*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \nu(OH_a) )</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>1'</td>
<td>( \nu(OH_b) )</td>
<td>136</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td>( \nu(OH) )</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>

* With respect to the uncoupled O–H vibrator frequency of the HOD molecule.

TABLE IV: 6-31G* OH Frequencies (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>structure</th>
<th>assignment*</th>
<th>freq</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \nu(OH_a) ) (90) + ( \nu(OH_b) ) (10)</td>
<td>4155</td>
</tr>
<tr>
<td></td>
<td>( \nu(OH_a) ) (13) + ( \nu(OH_b) ) (87)</td>
<td>3995</td>
</tr>
<tr>
<td>1'</td>
<td>( \nu(OH_a) ) (100)</td>
<td>4138</td>
</tr>
<tr>
<td>2</td>
<td>( \nu(OH_a) ) (97) + ( \nu(OH_b) ) (3)</td>
<td>4135</td>
</tr>
<tr>
<td>3</td>
<td>( \nu(OH_a) ) (7) + ( \nu(OH_b) ) (93)</td>
<td>3859</td>
</tr>
<tr>
<td>3</td>
<td>( \nu(OH_a) ) (96) + ( \nu(OH_b) ) (4)</td>
<td>4174</td>
</tr>
<tr>
<td>3</td>
<td>( \nu(OH_a) ) (10) + ( \nu(OH_b) ) (90)</td>
<td>3883</td>
</tr>
</tbody>
</table>

* Numbers in parentheses indicate the contribution of localized vibrations to each normal mode, estimated from the normalized sums of the squares of the eigenvectors of each atom for each mode.

like in the hydrogen-bonded structure suggested by Sauer et al.6 As
the coupling between the nonbonded and bonded O–H vibrators
in the complex is quite small (see contributions of localized
vibrations to the normal OH modes in Table IV), their \( \nu_b \) and \( \nu_p \) shifts with respect to the uncoupled water O–H vibrator
frequency \( \nu^*(OH) \) are used, being the most appropriate of
the OH vibration characteristics14 for water structure analysis in
complex hydrogen-bonded aggregates. The \( \nu^*(OH) \) is taken to
be the HOD \( \nu(OH) \), the experimental and 6-31G* values being
368713 and 4131 cm\(^{-1}\). An important feature of the interaction
is that the \( \Delta \nu_{OH} = 24 \) cm\(^{-1}\) is positive (Table III). As follows from
the calculations, this positive shift is provided not only by the
coupling effect, the contribution being

\[
\Delta \nu_{coupl} = \nu_{hs}(1) - \nu_{hs}(1') = 17 \text{ cm}^{-1}
\]

where 1' is the trimer (Figure 1) with the O–H\(_b\) vibrators replaced
by the O–D\(_b\) vibrators, but also by the O–H\(_a\) bond strengthening,
as \( \Delta \nu_{hs}(1') = 7 \) cm\(^{-1}\) (Table III). The literature data (ref 15 and
references therein) show such O–H\(_a\) strengthening to be a general
phenomenon for hydrogen-bonded complexes.

The full optimization of the water position with respect to the
H\(_2\)O–Al(OH)\(_x\) molecular analog of the bridging OH group led to structure 2 (Figure 1), which is in good agreement with the experimental OH frequency shifts (Table V).

TABLE V: OH Frequency Shifts* (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>assignment</th>
<th>calcd</th>
<th>obsd*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu(OH_a) )</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>( \nu(OH_b) )</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>( \nu(OH) )</td>
<td>-273</td>
<td></td>
</tr>
</tbody>
</table>

* With respect to the uncoupled O–H vibrator frequency of the HOD molecule.

the case of structure 3 optimized with the C\(_2\) symmetry constraint,
like that reported in ref 6, in 2 the O\(_2\)–H\(_2\) bond is strongly shifted from the O\(_1\)O\(_2\) plane and slightly weakened (cf. the calculated
\( R(OH^2) = 0.9482 \) Å of 2, \( R(OH) = 0.9456 \) Å of 3, and \( R(OH) = 0.9474 \) Å of free molecular water). Considering the effect of
O–H\(_a\) strengthening in hydrogen-bonded complexes15 (see above),
this weakening has to be due to a weak H\(_2\) bond to the nearest
O\(_1\) and O\(_2\) oxygens in structure 2, \( R(OH^1) = 3.23 \) Å and \( R(OH^2) = 3.21 \) Å. Therefore structure 3, with the O\(_2\)–H\(_2\) vibrator being
nonbonded, overestimates the highest OH frequency of the
adsorbed water significantly (Table V). We consider structure
2 to be a molecular analog for the water adsorption on the bridging
OH group of zeolites, with the O–H\(_a\) and O–H\(_b\) (weakly bonded)
vibrators being responsible for the slightly and slightly shifted
3390- and 3695-cm\(^{-1}\) frequencies,14 with respect to the \( \nu^*(OH) \).

As shown in our recent experimental and theoretical study,7 there
is a very interesting phenomenon in interactions of basic
molecules with the bridging OH group of zeolites, which makes
the \( \Delta \nu(OH) \) of this group not correspond to any observable OH
band maximum. The broad bands at \( \sim 2900, \sim 2450, \) and \( \sim 1700\)
cm\(^{-1}\), reported in the literature for more than 15 different
adsorption complexes on the bridging OH groups,7 including
the water complex, belong to the so-called (A, B, C) trio,7 well-
known for strong hydrogen-bonded complexes in vapors, liquids, and solids.8–11 In terms of the theory of OH band profiles of
hydrogen-bonded complexes,8–11 these bands, actually pseudobands,
are produced by the Evans transmission windows at \( \sim 2600\) and
\( \sim 1800\) cm\(^{-1}\), in the very broad \( \nu(OH) \neq k \nu(OH-B) \) superposition
band of the strongly perturbed bridging OH group. These
windows result from Fermi resonances of the \( \delta(OH) \) in-plane
overtones at \( \sim 2600\) cm\(^{-1}\) and \( \gamma(OH) \) out-of-plane overtone at
\( \sim 1800\) cm\(^{-1}\), with the \( \nu(OH) \pm k \nu(OH-B) \) modes in the vicinity
of these overtones. Other examples of this trio in adsorptions on
zeolites, taken from ref 16 with our assignment of the OH bands,
are presented in Table VI. According to this interpretation, the broad \( \sim 1700\) cm\(^{-1}\) band, which was detected for the water

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are presented in Table VI. According to this interpretation, the broad \( \sim 1700\) cm\(^{-1}\) band, which was detected for the water
TABLE VI: OH Pseudoband Wavenumbers* (cm⁻¹)

<table>
<thead>
<tr>
<th>adsorbed molecule</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>2900</td>
<td>2500</td>
<td></td>
</tr>
<tr>
<td>dimethyl ether</td>
<td>2950</td>
<td>2300</td>
<td>1900-1300</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>2950</td>
<td>2300</td>
<td>1900-1300</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>2900</td>
<td>2370</td>
<td>1900-1300</td>
</tr>
<tr>
<td>di-n-butyl ether</td>
<td>2900</td>
<td>2300</td>
<td>1900-1300</td>
</tr>
<tr>
<td>acetone</td>
<td>2900</td>
<td>2370</td>
<td>1800-1300</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>2820</td>
<td>2430</td>
<td></td>
</tr>
<tr>
<td>benzonitrile</td>
<td>2800</td>
<td>2360</td>
<td></td>
</tr>
<tr>
<td>formic acid</td>
<td>2900</td>
<td>2460</td>
<td>1700-1300</td>
</tr>
<tr>
<td>acetic acid</td>
<td>2900</td>
<td>2470</td>
<td>1800-1300</td>
</tr>
</tbody>
</table>

* From ref 16 with our assignment on the basis of a theory of OH band profiles of hydrogen-bonded complexes.²⁻¹¹ Apparently complicated by δ(OH) + ν(OT) modes (see ref 10).

adsorption in refs 3 and 4 and could be easily found in the spectra of ref 2, also belongs to the water complex with the bridging OH group, being the C band. As shown in a recent study by Ratajczak et al.,¹⁰ for solids the C band range can be complicated by δ(OH) + ν(OT) combination modes, δ(OT) being a lattice vibration of the bridging OH group oxygen atom.

As the methanol complex with the bridging OH group is similar to the water complex,¹⁷⁻²⁰ the hydrogen atom of the slightly perturbed water OH group being replaced by the CH₃ group, four OH bands could be expected a priori for this complex, analogous with the 3390, ~2900, ~2450, and ~1700 cm⁻¹ bands of the water complex. The four bands at ~3390, ~2900, ~2440, and ~1687 cm⁻¹, similar in shape to the above-mentioned ones for the water complex, were found in a recent IR study of the methanol adsorption on HZSM-5 zeolites by Mirth et al.²¹ (cf. Figure 5 in ref 3 and Figure 2d in ref 21).

Conclusion

In conclusion we suggest five OH bands to be attributed to the water molecule complex with the bridging OH group in zeolites, at 3695, 3390, ~2900, ~2450, and ~1700 cm⁻¹. The 3390- and 3695-cm⁻¹ bands belong to the water OH group interacting by two hydrogen bonds with the bridging OH group and with the nearest AlOSi bridging oxygen and to the other slightly perturbed water OH group, respectively. The broad pseudobands at ~2900, ~2450, and ~1700 cm⁻¹ are the well-known (A, B, C) trio, typical for strong hydrogen-bonded complexes in vapors, liquids, and solids, being due to resonant interactions between the δ(OH) ± ν(HO—O) superposition modes and the δ(OH) and γ(OH) overtones of the strongly perturbed bridging OH group.

References and Notes