Water-adsorption on zeolites - ab-initio interpretation of IR data

Citation for published version (APA):

DOI:
10.1021/j100143a025

Document status and date:
Published: 01/01/1993

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Water Adsorption on Zeolites: Ab-Initio Interpretation of IR Data

A. G. Pelmenschikov*†‡ and R. A. van Santen‡

Schuit Institute of Catalysis, University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, and Institute of Catalysis, Prosp. Lavrentieva 5, 630090 Novosibirsk, Russia

Received: June 8, 1993

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 band profiles of hydrogen-bonded complexes to be the so-called (A, B, C) trio, caused by resonant interactions between the ν(OH) ± ν(OH-O) combination modes and the δ(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 AOSi³⁺ 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 AOSi³⁺ 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 AOSi³⁺ 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 AOSi³⁺ 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 ν(OH) stretching vibration and the δ(OH) and γ(OH) overtones of the strongly perturbed bridging OH group (see below). This shows the adsorbed water to be in a hydrogen-bonded form, apparently like that found in ref 6. Owing to the difficulties of discriminating between the hydrogen-bonded and ion-pair structures on the basis of energy calculations (see ref 6 for more details), a theoretical support for the hydrogen-bonded structure will be based on the OH frequency calculations.

Theoretical Method

Ab-initio SCF calculations were performed with the 6-31G* basis set using the GAUSSIAN-90 package. Optimized geometries and total energies of the molecules are presented in Tables I and II, respectively.

Results and Discussion

To demonstrate the reliability of the adopted approximation, in Table III the calculated and experimental OH frequency shifts of the water trimer (1, Figure 1) are presented, with each water molecule interacting by means of two hydrogen bonds.
complex hydrogen-bonded aggregates. The vo(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

\[ \text{TABLE II} \]

<table>
<thead>
<tr>
<th>OH Frequency Shifts (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>structure</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1'</td>
</tr>
</tbody>
</table>

\(^a\) With respect to the uncoupled O–H vibrator frequency of the HOD molecule. \(^b\) Reference 13.

\[ \text{TABLE IV} \]

<table>
<thead>
<tr>
<th>6-31G* OH Frequencies (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>structure</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1'</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

\(^a\) 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 \(\nu_s\) shifts with respect to the uncoupled water O–H vibrator frequency \(\nu^0(\text{OH})\) are used, being the most appropriate of the OH vibration characteristics\(^14\) for water structure analysis in complex hydrogen-bonded aggregates. The \(\nu^0(\text{OH})\) is taken to be the HOD \(\nu(\text{OH})\), the experimental and 6-31G* values being 3687 and 4131 cm\(^{-1}\). An important feature of the interaction is that the \(\Delta
u_b = 24\) 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

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

where \(1'\) is the trimer (Figure 1) with the O–H\(_a\) vibrations replaced by the O–D\(_2\) vibrations, but also by the O–H\(_b\) bond strengthening, as \(\Delta
\nu_b(1') = 7\) cm\(^{-1}\) (Table III). The literature data (ref 15 and references therein) show such O–H\(_b\) 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)\(_4\) 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).

\[ \text{TABLE V} \]

<table>
<thead>
<tr>
<th>OH Frequency Shifts (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>structure</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

\(^a\) With respect to the uncoupled O–H vibrator frequency of the HOD molecule. \(^b\) The 3695- and 3390-cm\(^{-1}\) frequency shifts.

the case of structure 3 optimized with the \(C_3\) symmetry constraint, like that reported in ref 6, in 2 the O\(_2\)-H\(_2\) bond is strongly shifted from the O\(_1\)O\(_2\)O\(_3\) plane and slightly weakened (cf. the calculated \(R(\text{OH}^2) = 0.9482\) Å of 2, \(R(\text{OH}^4) = 0.9456\) Å of 3, and \(R(\text{OH}) = 0.9474\) Å of free molecular water). Considering the effect of O–H\(_b\) strengthening in hydrogen-bonded complexes\(^6\) (see above), this weakening has to be due to a weak H\(_2\) bond to the nearest O\(_1\) and O\(_3\) oxygens in structure 2, \(R(\text{H}^2\text{O}^1) = 3.23\) Å and \(R(\text{H}^2\text{O}^3) = 3.21\) 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 strongly and slightly shifted 3390- and 3695-cm\(^{-1}\) frequencies,\(^2-4\) with respect to the \(\nu^0(\text{OH})\).

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 \(\Delta\nu(\text{OH})\) of this group not correspond to any observable OH band maximum. The broad bands at ~2900, ~2450, and ~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 ~2600 and ~1800 cm\(^{-1}\), in the very broad \(\nu(\text{OH}) \equiv k\nu(\text{OH}–\text{B})\) superposition band of the strongly perturbed bridging OH group. These windows result from Fermi resonances of the \(\delta(\text{OH})\) in-plane overtone at ~2600 cm\(^{-1}\) and \(\gamma(\text{OH})\) out-of-plane overtone at ~1800 cm\(^{-1}\) with the \(\nu(\text{OH}) \equiv k\nu(\text{OH}–\text{B})\) 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 ~1700-cm\(^{-1}\) band, which was detected for the water
and 3695-cm⁻¹ bands belong to the water at 3695, 3390, -2900, -2450, and -1700 cm⁻¹. The 3390-water molecule complex with the bridging of the water complex. The four bands at -3390, -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 \(v(\text{OH})\) and \(\gamma(\text{OH})\) overtones of the strongly perturbed bridging OH group.

### References and Notes