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(A,B,C) Triplet of Infrared OH Bands of Zeolitic H-Complexes

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The phenomenon of the (A,B,C) triplet of infrared OH bands at ~2800, ~2400 and ~1700 cm⁻¹, well-known for strong X—OH—Y molecular H-complexes in solutions, liquids, and solids, is studied for the first time for surface H-complexes using CD₂CN and CCl₃CN adsorption on deuterated H-ZSM5 and H-FeS₅₄ zeolites. A direct experimental proof is given that the minimum between the A and B bands of D-complexes occurs at nearly exactly the 2Δ(OD) in-plane bending overtone frequency of the perturbed OD group. This verifies the resonance theory of the (A,B) doublet by Claydon and Sheppard. In reference to zeolites this means that the ~2800 and ~2400 cm⁻¹ OH bands recently found in adsorption of many basic molecules on zeolitic OH groups are actually pseudobands, caused by the subdivision of the very broad v(OH) ± k·v(OH—Y) superposition band of the perturbed OH groups by Evans transmission window at the 2Δ(OD) ~2600 cm⁻¹ frequency.

TABLE 1: Wavenumbers (cm⁻¹) of the Three Main OH Bands of Some Hydrogen-Bonded Complexes in the 1500–3000 cm⁻¹ Region (the A, B, and C Bands)

<table>
<thead>
<tr>
<th>Adsorbed Molecule</th>
<th>A (cm⁻¹)</th>
<th>B (cm⁻¹)</th>
<th>C (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution in CCl₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>monochloroacetic acid</td>
<td>2900</td>
<td>2545</td>
<td>1900</td>
</tr>
<tr>
<td>+ dimethyl sulfoxide</td>
<td>2800</td>
<td>2540</td>
<td>1900</td>
</tr>
<tr>
<td>dichloroacetic acid</td>
<td>2880</td>
<td>2440</td>
<td>1875</td>
</tr>
<tr>
<td>+ dimethyl sulfoxide</td>
<td>2750</td>
<td>2430</td>
<td>1900</td>
</tr>
<tr>
<td>trichloroacetic acid</td>
<td>2750</td>
<td>2430</td>
<td>1880</td>
</tr>
<tr>
<td>+ dimethyl sulfoxide</td>
<td>2720</td>
<td>2400</td>
<td>1900</td>
</tr>
<tr>
<td>Solids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dibutylphosphinic acid</td>
<td>2600</td>
<td>2240</td>
<td>1650</td>
</tr>
<tr>
<td>toleneseleninic acid</td>
<td>2720</td>
<td>2270</td>
<td>1660</td>
</tr>
<tr>
<td>dimethyarsinic acid</td>
<td>2700</td>
<td>2350</td>
<td>1740</td>
</tr>
<tr>
<td>KH₃PO₄</td>
<td>2750</td>
<td>2400</td>
<td>1500</td>
</tr>
<tr>
<td>NaH₃(SeO₃)₂</td>
<td>2750</td>
<td>2350</td>
<td>1600</td>
</tr>
<tr>
<td>Zeolitic OH Group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ dimethyl ether</td>
<td>2900</td>
<td>2500</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>2300</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>2300</td>
<td>1900–1300</td>
</tr>
<tr>
<td>+ n-butylaldehyde</td>
<td>2800</td>
<td>2430</td>
<td>1700</td>
</tr>
<tr>
<td>+ acetonitrile</td>
<td>2820</td>
<td>2430</td>
<td>1700</td>
</tr>
<tr>
<td>+ benzonitrile</td>
<td>2800</td>
<td>2360</td>
<td>1700</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>
<tr>
<td>+ diethyl ketone</td>
<td>2850</td>
<td>2400</td>
<td>1700–1300</td>
</tr>
<tr>
<td>+ mesityl ketone</td>
<td>2850</td>
<td>2400</td>
<td>1700–1300</td>
</tr>
<tr>
<td>+ water</td>
<td>2900</td>
<td>2450</td>
<td>1700</td>
</tr>
<tr>
<td>+ methanol</td>
<td>2900</td>
<td>2450</td>
<td>1700</td>
</tr>
</tbody>
</table>


However, unlike the original theory, in ref 23 the C band was associated with a δ(OH) + v(SeO) combination band enhanced by the resonance with the v(OH) ± k·v(OH—Y) band, v(SeO) corresponding to an intermolecular vibration of the OH group oxygen.

Also another theory has been suggested19,24–26 which supposes the (A,B,C) triplet to originate from Fermi resonance of the v(OH) with 2δ(OD) and 2γ(OD) levels. As distinct from the theory by Claydon and Sheppard, it considers the A, B, and

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C bands of X\(\rightarrow\)OH\(\rightarrow\)Y complexes to be individual IR bands corresponding to the \(\delta(OH), \nu(OH), \) and \(\gamma(OH)\) frequencies, respectively, with the A and C bands being strongly enhanced and shifted by the \(\delta(OH) \leftrightarrow \nu(OH) \leftrightarrow \gamma(OH)\) resonance interactions with respect to the unperturbed \(\delta(OH)\) and \(\gamma(OH)\) frequencies. In this interpretation two "holes" between the A, B, and C bands are not taken to be Evans windows. A semiempirical model developed by Odinokov et al.25,26 was successfully applied for predicting the C band maximum and the A + B band "center of gravity" wavenumbers25 for a wide range of H-complexes of benzoic, acetic, monoacetic, and triacetate acids. As to the application of this theory to surfaces, it was used by Angeli and Howell3 to explain an unexpected experimental result that acetonitrile complex with the structural OH group of HY zeolite, which should have only one OH stretching mode, generates two OH bands at 2800 and 2400 cm\(^{-1}\).

The third theory, the double-minimum theory,19,32–35 postulates that the (A,B,C) infrared structure of strong H-complexes is produced by a pair of quasigenerate vibrational levels of an asymmetric double-minimum proton potential, corresponding to the "neutral" X\(\rightarrow\)OH\(\rightarrow\)Y and "ionic" X\(\rightarrow\)O\(\rightarrow\)HY\(^+\) states of these complexes. Considering the proton tunneling through the potential barrier between two minima, the selection rules for transitions amongst the lowest levels in such a potential permit four of the infrared active modes. As the separation between the corresponding OH bands and their intensity depend on the exact shape of the potential, only three or fewer bands may be found under certain circumstances. So far, no quantitative agreement has been obtained between spectral characteristics of an observed (A,B,C) triplet and the results of their calculations using a suitable double-minimum potential. As Hadzi noticed,19 the chances of such agreement are very small. It is necessary either to have a very good model to start from or to carry out an immense number of calculations in view of the large number of physically possible double-minimum situations and the lack of initial data. Nevertheless, this model of strong H bonding is in wide use now. In an experimental study by Kubelkova et al.4 it was utilized for the interpretation of IR spectra of acetone, diethyl ketone, and mesityl ketone adsorption on Bronsted sites of H-ZSM5 zeolite: the \(\sim\)2800 and \(\sim\)2400 cm\(^{-1}\) bands were associated with the "neutral" and "ionic" states of the adsorption H-complexes. Also, in an IR study by Parker et al.5 these OH bands found in adsorption of many other basic sorbants on H-ZSM5 were explained in terms of the double-minimum model.

In our recent studies1,2 the \(\sim\)2800, \(\sim\)2400, and \(\sim\)1700 cm\(^{-1}\) OH bands of zeolitic H-complexes were supposed to conform to the resonance theory by Claydon and Sheppard. The main change in the interpretation of IR spectra of surface H-complexes, caused by the extension of this theory to surfaces, results from the fact that the \(\sim\)2800, \(\sim\)2400, and \(\sim\)1700 cm\(^{-1}\) bands should be associated not with three different OH modes of these complexes, as generally accepted in the literature now,3–18 but with the \(\nu(OH)\) mode of the perturbed OH group only. For example, in previous experimental IR studies9,10,12,14,17,18 of water and methanol complexes with the zeolitic OH group the 2900, 2450, and 1700 cm\(^{-1}\) bands were assigned to the antisymmetric, symmetric, and deformation OH vibrations of H\(_2\)O and CH\(_3\)OH\(^+\) ions, respectively. As shown in ref 2, the resonance theory suggests a substantially new assignment of OH bands for these complexes and leads to the conclusion that they are "neutral". Considering numerous IR studies devoted to surface H-complexes during the last 50 years, a modern reconsideration of their IR data on the basis of the resonance theory can lead to a significant revision of many other previously accepted interpretations. To justify such utilization of the resonance theory, its experimental proof becomes very topical, in view of the fact that at present this theory can be regarded as only a fairly reasonable one, for it has not been rigorously proved for a concrete case of the (A,B,C) triplet. As follows from above, this has a direct bearing also on discriminating between the single-minimum model of strong H bonding, tacitly assumed by the resonance theory, and the double-minimum model. Also an experimental validation of the analogy between the (A,B,C) triplet of molecular H-complexes and the \(\sim\)2800, \(\sim\)2400, and \(\sim\)1700 cm\(^{-1}\) OH bands of surface H-complexes is very important, considering that the phenomenon of the (A,B,C) triplet has never been specially studied for surface H-complexes.

Here the (A,B,C) triplet is investigated for surface H-complexes using CD\(_3\)CN and CCl\(_3\)CN adsorptions on deuterated H-ZSM5 and H-FeSil zeolites. A direct experimental proof will be given for the first time in the study of this phenomenon that the wavenumber of the minimum between the A and B bands of D-complexes is nearly equal to the \(\delta(OD)\) overtone frequency of the perturbed OD group. This verifies the hypotheses by Claydon and Sheppard about the nature of the A and B bands.

**Experimental Section**

**Zeolites.** ZSM-5 was synthesized hydrothermally at 443 K for 48 h with TPABr as a templating agent. A Si/Al = 52 ratio for this zeolite was estimated on the basis of adsorption calorimetric measurements, taking an amount of the adsorbed ammonia at 423 K as a measure of the SiOHAl lattice sites.56

MFI ferrosilicate FeSil was prepared using iron sulfate and silicate solution as described in detail in ref 37. A Si/Fe = 32 ratio was determined by adsorption calorimetric measurements (see above).

Deuteriation was performed by reacting the activated samples for 1.5 h at 623 K with 100 mbar of D\(_2\).

**IR Measurements.** IR spectra were recorded at room temperature using a Bruker IFS 113v FTIR spectrometer with a heatable vacuum cell. The samples were pressed into 7.5 mg/cm\(^2\) disks. Before gas dosage the samples were activated for 1 h at 723 K under 10\(^{-6}\) mbar pressure.

**Results and Discussion**

In agreement with recent experimental studies by Jacobs et al.38,39 H → D exchange of H-ZSM5 and H-FeSil zeolites gives rise to the \(\delta(OD)\) bands of the bridging SiODAl and SiODFe groups at 894 and 865 cm\(^{-1}\), respectively, between the very intense bands of symmetric (600–800 cm\(^{-1}\)) and antisymmetric (1000–1300 cm\(^{-1}\)) lattice stretching vibrations40,41 of these zeolites. Figure 1 and Table 2 show the changes of these bands caused by the CD\(_3\)CN and CCl\(_3\)CN adsorptions. According to our IR and ab initio studies of CD\(_3\)CN interaction with zeolitic OH groups,1 these adsorptions should result in the formation of four different medium-strong D-complexes.
This also agrees with IR studies of the OH(0D) bending mode (Figure 1). Changes of the δ(OD) bands of (a) H-ZSM5 induced by CD3CN (1) and CCl3CN (2) adsorption at 295 K and 0.05 mbar (in different arbitrary absorbance units); (b) H-FeSil induced by CD3CN adsorption at 295 K and 0.05 mbar (1) and CCl3CN adsorption at 295 K and 1.36 mbar (2) (in different arbitrary absorbance units).

**TABLE 2: δ(OD) Band and Transmission Window Minimum Wavenumbers (cm⁻¹)**

<table>
<thead>
<tr>
<th>Bronsted site</th>
<th>CD3CN adsorption</th>
<th>CCl3CN adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiODAI</td>
<td>894</td>
<td>898</td>
</tr>
<tr>
<td>SiODFe</td>
<td>865</td>
<td>950</td>
</tr>
</tbody>
</table>

*Twice the δ(OH) frequency of the perturbed OH group.

Both the small Δδ(OD) = 65–95 cm⁻¹ upward frequency shift and the insignificant change of the δ(OD) band intensity in these interactions (Figure 1 and Table 2) are in good agreement with previous experimental studies of the OH(OD) bending mode for molecular H(D)-complexes.⁴² The Δδ(OD) shift increases upon replacing CCl3CN with CD3CN (by ~20 cm⁻¹) and upon replacing SiODFe with SiODAI (by ~10 cm⁻¹) in structure 1 due to the strengthening of the acid-base interaction by these replacements, CD3CN being more basic compared with CCl3CN and SiODAI being more acidic compared with SiODFe.⁴¹ This also agrees with IR studies of the OH(OD) bending mode for molecular H(D)-complexes.⁴²

It is to be noted that in previous experimental studies of the (A,B,C) triplet, performed mainly for H-complexes of organic acids in solutions and liquids, the δ(OD) band fell into the heavily populated “fingerprint” spectral region of these compounds at 500–1500 cm⁻¹.¹⁹,²⁰,⁴² The identification of the δ(OD) band is known to be very difficult in this case.²⁰ In an experimental study by Claydon and Sheppard²⁰ H→D exchange combined with low-temperature IR techniques was used in order to locate accurately the δ(OD) fundamental for H-complexes of liquid phenylphosphonic and dibutylarsinic acids. As a result of this investigation, the conclusion was made that the 2δ(OD) frequency of these two complexes corresponds approximately not with the A band maximum, as one could expect according to a previously proposed¹⁹,²⁴ interpretation of the (A,B,C) triplet, but with the minimum between the A and B bands. However, the found difference between the minimum wavenumber and the 2δ(OD) frequency (~100 cm⁻¹ for dibutylarsinic acid) was too large for this result to be regarded as an experimental proof of the resonance theory.²⁰ Therefore, an alternative theoretical interpretation was suggested later²⁵,²⁶ for the (A,B,C) infrared structure by Odinokov et al. (see the Introduction). In the present study an attempt is undertaken to prove the resonance theory of the (A,B) doublet by comparing the 2×δ(OD) frequency with the wavenumber of the minimum between the A and B OD bands for the above-mentioned zeolitic D-complexes. According to refs 20, 25, and 26, this transmission window should be significantly narrower for D-complexes as compared with H-complexes. This is accounted for²⁰ by a strong weakening of the Fermi coupling between the stretching fundamental and the bending overtone due to the anharmonicity decrease by H→D exchange.²⁵,²⁶ As follows from theoretical constructions of the window for cases of a comparatively weak Fermi resonance,²¹ we can expect the wavenumber of the minimum between the A and B OD bands to be equal to the 2×δ(OD) frequency within a few cm⁻¹ if the resonance theory is correct. Assuming 2δ(OD) ≈ 2×δ(OD), the anharmonicity of the δ(OD) vibration is thus neglected. This is not believed to be a serious error, as the Xδδ anharmonic constant of δ(XH) bending modes is known to be very small²⁵ (see also below). As an example, the wavenumber of a narrow Evans window in the OD stretching band of OD₂ complexes with Na⁺ and Ag⁺ cations in Na,Ag,A zeolites (the OD groups are nonbonded in this case) was found by Baumann et al.⁴³ to be equal to the 2×δ(OD) frequency to an accuracy of a few cm⁻¹.

Figure 2 shows the changes in the 1300–4000 cm⁻¹ spectral region for CD3CN and CCl3CN adsorptions on H-ZSM5, H-FeSil, H/D-ZSM5, and H/D-FeSil zeolites. Two broad OH bands appear at ~2800 and ~2400 cm⁻¹ in the adsorptions on the H-zeolites, typical for medium-strong X-OH-Y molecular complexes in solutions, liquids, and solids.¹⁹,²⁰,²⁵,²⁶,²⁹ the so-called A and B bands. For molecular H-complexes they are usually accompanied by another broad OH band at ~1700 cm⁻¹, the C band.¹⁹,²⁰,²⁵,²⁶ In Figure 2 the C band can be found only for the CD3CN complex with the SiODAl group, being the strongest of the four H-complexes involved. This fact agrees with an IR spectroscopic regularity for molecular H-complexes in solutions:¹⁹,²⁶ in a series of closely related X-OH-Y complexes the C band intensity increases on strengthening the acid-base interaction. On going from the H- to H/D-zeolites (Figure 2), the intensity of the A and B OH bands decreases and broad, complex OD bands appear in the 1700–2300 cm⁻¹ region due to the frequency isotopic shift. As shown for H-complexes of organic acids,¹⁹,²⁶ H→D exchange causes the A and B bands to shift to ~2000 and ~1750 cm⁻¹. The corresponding C OD band has not been definitively resolved in the very complex 500–1500 cm⁻¹ spectral region of these complexes.²² Also for zeolites the C OD band should be obscured in the 1000–1300 cm⁻¹ region of the antisymmetric lattice vibrations.
Neither the OH nor the OD bands (Figures 1 and 2) can be directly used to check whether the transmission window position between the A and B bands corresponds to the in-plane bending overtone. For the perturbed SiOHAl and SiOHFe groups this window is well-pronounced in the spectra at \( \sim 2600 \text{ cm}^{-1} \) (Figure 2 as an example), but the corresponding \( \delta(\text{OH}) \) in-plane bending band falls in the 1000–1300 cm\(^{-1}\) region of lattice vibrations (see Figure 3). This makes the zeolitic OH groups...
useless for the following consideration. For the perturbed SiODAl and SiODFe groups the δ(OD) band is well-defined (Figure 1), but the 1800-2000 cm⁻¹ region, where the corresponding Evans window is expected to appear, according to the 2×δ(OD) frequencies (Table 2), is strongly complicated by two intense lattice bands at 1880 and 2007 cm⁻¹ (Figure 3). Also in the difference spectra this region remains too complex for a definitive interpretation as the subtraction of the 1880 and 2007 cm⁻¹ bands of the unloaded zeolites from these slightly shifted by the adsorption produces "imaginary" positive and negative bands here (Figure 2 and the inset in Figure 3). This complication of difference spectra through the 1880 and 2007 cm⁻¹ bands is usual for IR experimental studies of adsorption on zeolites. A unique procedure of separation of the (A,B) OD doublet of interest from these two bands is suggested below.

The spectra recorded after the adsorption on the deuterated and hydrogen forms of zeolites in the 1800-2000 cm⁻¹ region (Figure 2) can be written, respectively, as

\[ S^d = S^d_{OD} + S^d_L + S^d_{OH} \] (2)

and

\[ S^h = S^h_{OH} + S^h_L \] (3)

\[ S^d_{OD}, S^h_{OH}, \text{and } S^h_L \text{ designating the OD, OH, and lattice 1880 and 2007 cm⁻¹ bands. Assuming the lattice vibrations to be independent of the H-D exchange, that means } \]

\[ S^d_L = S^h_L \] (4)

\[ S^d_{OD} \text{ can be written as } \]

\[ S^d_{OD} = (S^d - S^h) - (S^d_{OH} - S^h_{OH}) \] (5)

As \( S^h_{OH} \text{ and } S^h_{OH} \text{ are smooth low-frequency tails of the OH bands in the 1800-2000 cm⁻¹ region (see Figures 2 and 3), the term } (S^d_{OH} - S^h_{OH}) \text{ can be neglected in (5), being capable of changing only a base line of the } S^d_{OD} \text{ spectra. In Figure 4 the } S^d_{OD} \text{ curves are presented for the CD₃CN adsorptions on H-ZSM5 and H/D-FeSil, constructed as } \]

\[ S^d_{OD} = (S^d - S^h) \] (6)

The transmission windows become clearly observable in these spectra at 1977 and 2002 cm⁻¹, very close to their expected values of 2×988 = 1976 and 2×950 = 1900 cm⁻¹ (see Table 2) according to the resonance theory. This verifies the hypotheses by Claydon and Sheppard about the nature of the (A,B) doublet. The negligibly small difference between the window positions and the 2×δ(OD) values is an indication of a very small value of the anharmonicity constant,

\[ \chi_{55}^{OD} = 2\delta(OD) - 2\times\delta(OH)) / 2 \] (7)

for the hydrogen-bonded OD groups. In an ab initio study by Mix et al., the \( \chi_{55}^{OD} \) of the free zetilic OH groups was found to be equal to -4 cm⁻¹. This shows the contribution to the potential curve of the bending vibration from the H bonding to be harmonic with high precision. In agreement with ref 20, the transmission windows between the A and B bands are significantly narrower for the D-complexes compared with the H-complexes (cf. Figures 2 and 4).

The same procedure of the \( S^d_{OD} \) construction for the CCl₃CN adsorption on H/D-ZSM5 and H/D-FeSil (the spectra are not presented) shows that this molecule is not basic enough to provide the shift of the \( v(OD) + 2v(OD-B) \) band to the 1800-2000 cm⁻¹ region of the 2δ(OD) overtone.

Conclusion

The IR study of CD₃CN and CCl₃CN adsorption on H/D-ZSM5 and H/D-FeSil zeolites shows the ~2800 and ~2400 cm⁻¹ OH bands found in adsorption of many basic molecules on zeolites to be analogous to the so-called A and B OH bands of strong molecular H-complexes in solutions, liquids, and solids. A direct experimental proof of the resonance theory of these bands by Claydon and Sheppard is suggested. According to this theory the A and B bands of medium-strong X-OH-Y complexes are actually pseudobands caused by the subdivision of the very broad OH stretching band by Evans transmission window at the 2δ(OH) bending overtone frequency.

Acknowledgment. We thank Dr. G. Vorbeck (Eindhoven University of Technology) for preparation of the samples.

References and Notes

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(44) This can be inferred also from an experimental finding by Odinokov et al. that in series of closely related X-OH-Y complexes the "center of gravity" of the A + B + C band shifts to lower frequencies on strengthening the H bond. The "center of gravity" is defined as the crossing point of the ν axis and the vertical line dividing the A and B area into two subareas with equal integral intensity. It should approximately correspond to the wavenumber of the maximum of the ν(OH) + kν(OH-Y) band in the absence of the resonance interactions generating the Evans window.


(47) The subtraction of spectra of the unloaded H-zeolites from spectra of the corresponding H/D-zeolites produces the "zero-intensity" line in the 1800-2000 cm⁻¹ region, which shows the lattice 1880 and 2007 cm⁻¹ bands of these zeolites to be independent of the H -> D exchange.


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