

CD3CN as a probe of Lewis and Bronsted acidity of zeolites

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CD₃CN as a Probe of Lewis and Bronsted Acidity of Zeolites

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The well-known trio of IR bands (A, B, C) at ~ 2800 , ~ 2400 , and ~ 1700 cm⁻¹, typical for strong H complexes in vapors, liquids, and solids, is also found in CD₃CN adsorption on Bronsted sites of HZSM-5 and HY zeolites. The observed CN frequencies in interaction with different Bronsted and Lewis sites of these zeolites are quantitatively reproduced by ab initio 3-21g calculations combined with the frequency scaling procedure.

Introduction

Acetonitrile appears an attractive probe for zeolite acidity, since it will allow for two kinds of vibrational studies. When interacting with zeolite acid sites, both the zeolite OH frequencies and the acetonitrile $\nu(\text{CN})$ frequency will shift. This makes acetonitrile an interesting probe for Lewis as well as Bronsted acidity. CD₃CN is more appropriate for these studies than CH₃CN, as the CH₃CN CN spectral region is strongly complicated by Fermi resonance between the $\nu(\text{CN})$ and the combination $\delta_s(\text{CH}_3) + \nu(\text{CC})$ frequencies.¹⁻³ Here we will present results of an IR study on CD₃CN adsorption on HZSM-5 and HY zeolites. The analysis of the data will be supported by a comparison with literature data and results of ab initio calculations.

A very broad complex OH band, consisting of three subbands at ~ 2800 , ~ 2400 , and ~ 1700 cm⁻¹, was found^{2,4-12} in adsorption of many basic molecules on zeolites. The nature of this spectral trio was not unambiguously interpreted in the literature^{2,4-12} until now. In the present paper, we will apply a resonance theory of OH band profiles of molecular H complexes to hydrogen bonding in zeolites. These subbands, actually pseudobands, appear to be due to resonant interactions between the OH stretching and overtone bending modes of perturbed bridging OH groups.

Experimental Section

Zeolites. ZSM-5 was synthesized hydrothermally at 440 K for 48 h with TPA Br as a templating agent. Si/Al = 52 for this sample was estimated on the basis of adsorption calorimetric measurements, taking an amount of adsorbed ammonia at 423 K as a measure of the NH₄⁺ ion-exchange capacity (see ref 13 for more details). NH₄Y zeolite was prepared from a commercial product (AKZO PA 42611B) by a moderate dealumination with SiCl₄ followed by exchange with an excess of NH₄NO₃.¹⁴ The Si/Al = 5.1 ratio was evaluated from ²⁹Si MAS NMR measurements, as described in ref 15, using a Bruker MSL 400 spectrometer. Before gas dosage, the samples were calcinated in high vacuum at 723 K for 1 h.

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/cm² disks. The spectral resolution was 1 cm⁻¹.

Computational Method

Ab initio calculations were performed at the SCF level with the 3-21g basis set using the GAUSSIAN-90 package.¹⁶

Optimized geometries of the molecules are reported in Table I. To eliminate a systematic error in ab initio 3-21g $\nu(\text{CN})$ frequencies of CD₃CN complexes, the scaling procedure was used (see, for example, refs 20 and 21) with the scale factor $k_{\text{CN}} = 0.8758$, chosen to fit the 3-21g $\nu(\text{CN})$ frequency of CD₃CN (2594 cm⁻¹) to the observed one (2272 cm⁻¹).²²

Results and Discussion

The fundamental $\nu_s(\text{CD}_3)$ and $\nu_{\text{as}}(\text{CD}_3)$ frequencies of adsorbed CD₃CN are equal to 2114 and 2250 cm⁻¹ on all the samples (Figure 1), being shifted to lower wavenumbers by 12 and 7 cm⁻¹, respectively, in comparison with gaseous CD₃CN.²² According to an ab initio study,²³ electron density perturbation in the CD₃ group, caused by CD₃CN interaction with an electron-acceptor site, leads to insignificant upward shifts of the CD stretching frequencies. Therefore, as the small widths of the $\nu_{\text{as}}(\text{CD}_3)$ and $\nu_s(\text{CD}_3)$ bands and the $\nu_{\text{as}}(\text{CD}_3)$ degeneracy³ imply the absence of any specific interaction of the CD₃ group, the downward shift has to be due to a weak interaction with the zeolite channel wall. Such small shifts of CH and CD stretching frequencies by 10-15 cm⁻¹ are usual for organic molecules perturbed by dispersion interactions in going from gas to liquid.²⁴

Five bands appear in the CN spectral region at 2332-2323, 2300, 2284, 2278, and 2265 cm⁻¹ in the adsorption (Figure 1). The sequences of their appearance in increasing the pressure and their disappearance in outgassing the samples (Figure 1) are in agreement with the established dependence^{2,3,23,25} of the $\nu(\text{CN})$ on the strength of CD₃CN electron-donor interaction through the nitrogen electron lone pair: a strengthening of the interaction leads to an upward shift of the frequency.

According to literature data, the bands at 2332-2323, 2300, 2278, and 2265 cm⁻¹ can be tentatively attributed to the adsorption on Lewis alumina sites,^{3,26} bridging OH groups,²⁷ terminal SiOH groups,²⁸ and liquid CD₃CN,³ respectively. The $\nu(\text{CN})$ in interaction with Lewis sites in HZSM-5 being larger than those in HY (Figure 1) can be explained by a lower coordination number of extralattice alumina atoms in HZSM-5 than in HY zeolites, as suggested in ref 29. The calculated $\nu(\text{CN})$ frequencies (Table II) of CD₃CN in interaction with Si(OH)₄, (HO)₃SiOAl(OH)₃ (model 1b), Al(OH)₃, and Al(OH)₃·2H₂O, molecular analogs of Bronsted and Lewis sites of zeolites (Figure 2), support this assignment. The nature of Bronsted sites responsible for the 2284-cm⁻¹ CN band of adsorbed CD₃CN will be discussed below.

As to the Bronsted sites, at low coverage the adsorption occurs mainly on the bridging OH groups adsorbing at 3610 and 3630 cm⁻¹ in HZSM-5 and HY zeolites, respectively (spectrum 4 in Figure 3a and spectrum 3 in Figure 3b). The so-called (A, B, C) trio of bands appears at ~ 2890 , ~ 2400 , and ~ 1700 cm⁻¹, typical for medium-strong and strong H complexes in vapors, liquids, and solids.³⁰⁻³⁴ According to experimental and theoretical

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

molecule	geometry ^a
1a ^b	SiO ₁ , 1.629; O ₁ H, 0.965; HN, 1.920; NC, 1.137; CC, 1.457; CH, 1.083; SiOH, 130.8; CCH, 110.0
1b	SiO ₁ , 1.672; SiO ₂ , 1.650; SiO ₃ , 1.631; AlO ₁ , 1.839; AlO ₄ , 1.703; O ₁ H, 0.998; HN, 1.700; NC, 1.136; CC, 1.457; CH, 1.082; SiO ₁ Al, 128.9; SiO ₁ H, 119.0; CCH, 109.9; O ₁ SiO ₂ , 99.9; O ₁ SiO ₃ , 113.5; AlO ₁ SiO ₃ , 61.3; O ₁ AlO ₄ , 100.6
1b' ^c	SiO ₂ , 1.644; SiO ₃ , 1.630; SiO ₁ , 1.663; AlO ₄ , 1.695; AlO ₅ , 1.701; O ₁ H, 0.993; HN, 1.716; NC, 1.136; CC, 1.457; CH, 1.082; O ₂ SiO ₁ , 96.3; SiO ₁ H, 120.3; CCH, 110.0
1b'' ^c	SiO ₂ , 1.654; SiO ₃ , 1.641; SiO ₁ , 1.684; AlO ₄ , 1.718; AlO ₅ , 1.707; O ₁ H, 1.001; HN, 1.705; NC, 1.136; CC, 1.457; CH, 1.082; O ₂ SiO ₁ , 97.7; SiO ₁ H, 115.4; CCH, 110.0
1c	AlO, 1.695; AlN, 1.993; NC, 1.132; CC, 1.455; CH, 1.082; OAlN, 99.6; CCH, 109.7
1d ^d	AlO ₁ , 1.784; AlO ₂ , 1.940; AlN, 2.083; NC, 1.133; CC, 1.456; CH, 1.082; CCH, 109.8
2a ^e	Si ₁ H, 1.484; Si ₁ O ₂ , 1.669; Si ₂ O ₂ , 1.644; Si ₂ O ₃ , 1.638; Si ₂ O ₁ , 1.660; O ₁ H, 0.993; AlO ₄ , 1.692; AlO ₅ , 1.700; HN, 1.720; NC, 1.136; CC, 1.457; CH, 1.082; O ₂ Si ₁ H, 110.3; O ₂ Si ₂ O ₁ , 97.3; Si ₂ O ₁ H, 119.7; CCH, 110.0
2b ^e	AlH, 1.594; AlO ₂ , 1.699; SiO ₂ , 1.639; SiO ₃ , 1.645; SiO ₁ , 1.660; O ₁ H, 0.991; AlO ₄ , 1.692; AlO ₅ , 1.699; HN, 1.736; NC, 1.136; CC, 1.457; CH, 1.082; O ₂ Si ₁ H, 110.3; O ₂ SiO ₁ , 98.0; SiO ₁ H, 119.7; CCH, 110.0
(HO) ₃ SiOHAl(OH) ₃ ^f	SiO ₁ , 1.684; SiO ₂ , 1.649; SiO ₃ , 1.627; AlO ₁ , 1.850; AlO ₄ (AlO ₅), 1.699; OH ₁ , 0.971; O ₁ SiO ₂ , 97.2; O ₂ SiO ₃ , 113.1; O ₃ SiO ₂ Al, 61.5; O ₂ AlO ₄ , 98.7; SiO ₂ H, 118.2

^a O-H bond lengths and TOH angles (T = Si, Al) of the terminal OH groups not involved in the modeled interactions are equal to those optimized for Si(OH)₄¹⁷ (*D*_{2d} point group symmetry) and H₂O-Al(OH)₃¹⁸ molecules. ^b R(SiO) are equal to those for Si(OH)₄.¹⁷ ^c O₂, O₃, O₄, and O₅ atoms in 1b are fixed to model steric constraint of the Si-(OH)···Al fragment in the lattice (see refs 18 and 19 for more details): their positions correspond to those of (HO)₃SiOHAl(OH)₃ molecule (see the table), shifted from the optimal positions by ΔR(SiO₁) = ΔR(AlO₁) = 0.05 Å and Δ∠SiO₁Al = 5° for 1b' and by ΔR(SiO₁) = ΔR(AlO₁) = -0.05 Å and Δ∠SiO₁Al = -5° for 1b''. ^d For H₂O molecule, its gas-phase geometry was adopted: R(OH) = 0.96 Å and ∠HOH = 104°. ∠O₁AlO₁ = ∠O₁AlO₂ = 90°. ^e O₂, O₃, O₄, and O₅ positions as in model 1b'. ^f Designation of geometry parameters as in model 1b.

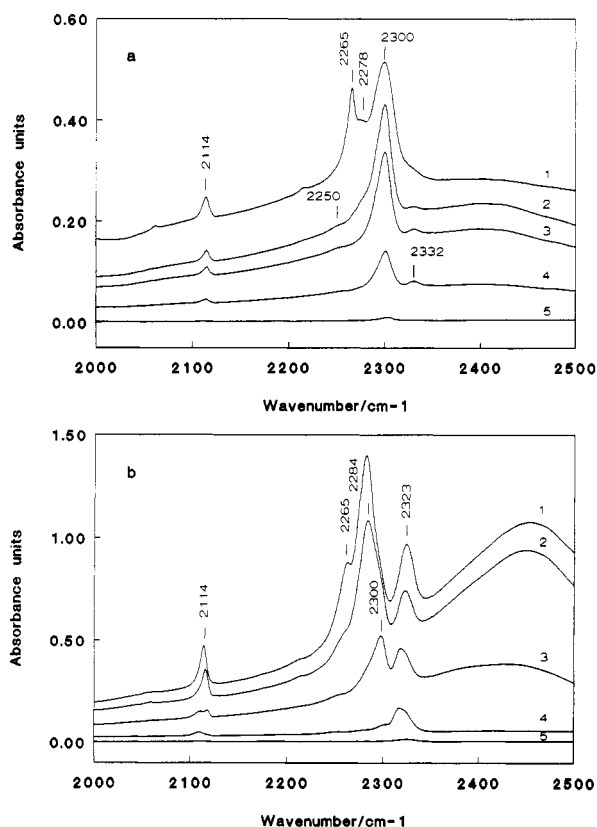


Figure 1. Changes in 2500–2000-cm⁻¹ spectral region. (a) Activated HZSM-5, induced by CD₃CN adsorption: (1) at 295 K and 1.14 mbar; (2) at 295 K and 0.05 mbar; by the adsorption at 295 K and 1.14 mbar followed by outgassing (3) at 295 K for 15 min; (4) at 353 K; and (5) at 573 K for 1 h. (b) Activated HY, induced by CD₃CN adsorption: (1) at 295 K and 0.8 mbar; (2) at 295 K and 0.05 mbar; by the adsorption at 295 K and 0.8 mbar followed by outgassing (3) at 295 K; (4) at 353 K; and (5) at 573 K for 15 min.

studies (refs 30–34 and references therein), in vapors and liquids these pseudobands are caused by Evans transmission windows at ~2600 and ~1900 cm⁻¹, in the broad ν(OH) ± kν(OH···B) superposition band (ν_{1/2} ≥ 800 cm⁻¹) of the H complexes. These windows result from Fermi resonances of the δ(OH) in-plane overtone at ~2600 cm⁻¹ and γ(OH) out-of-plane overtone at ~1900 cm⁻¹ with the ν(OH) ± kν(OH···B) modes in the vicinity of these two frequencies. For solids, the C band range can be

TABLE II: CN Stretching Frequencies (cm⁻¹)

molecule	calcd ^a	obsd ^b	molecule	calcd ^a	obsd ^b
1a	2283	2278	1c	2330	2332
1b	2298	2300	1d	2322	2323

^a Scaled 3-21g frequencies. ^b Figure 1.

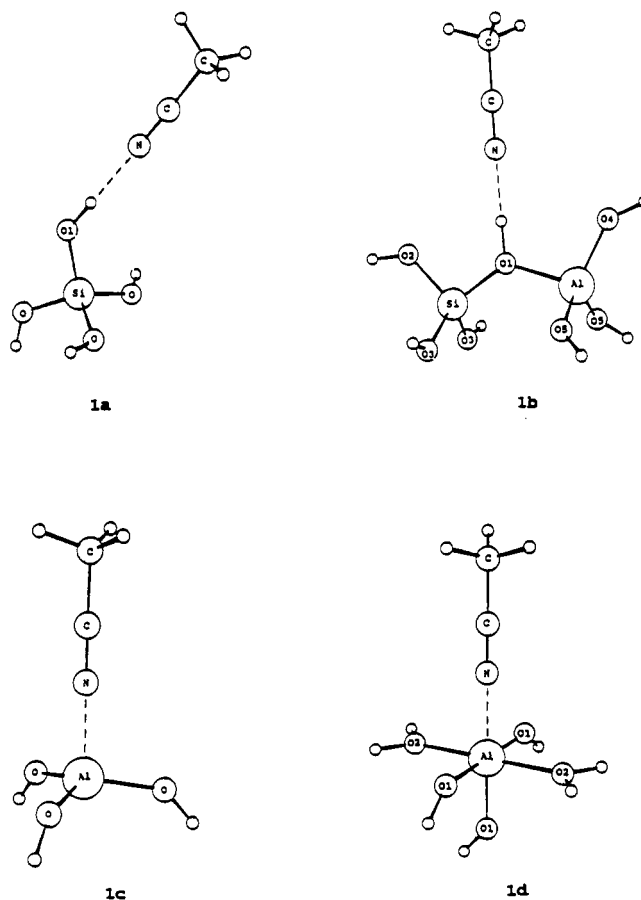


Figure 2. Molecular models.

complicated³² by δ(OH) + ν(TO) combination modes, ν(TO) being a lattice vibration of the OH group oxygen atom. IR data by Parker et al.⁴ on adsorption of a wide range of basic molecules on HZSM-5 can be used for a further demonstration of the validity

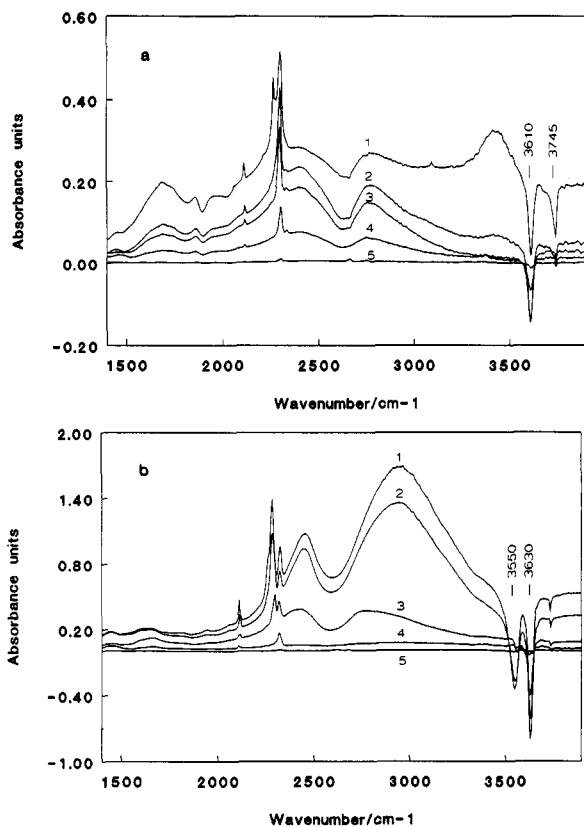


Figure 3. Changes in 4000–1400-cm⁻¹ spectral region of (a) activated HZSM-5, spectra 1–5 correspond to spectra 1–5 of Figure 1a, and of (b) activated HY, spectra 1–5 correspond to spectra 1–5 of Figure 1b.

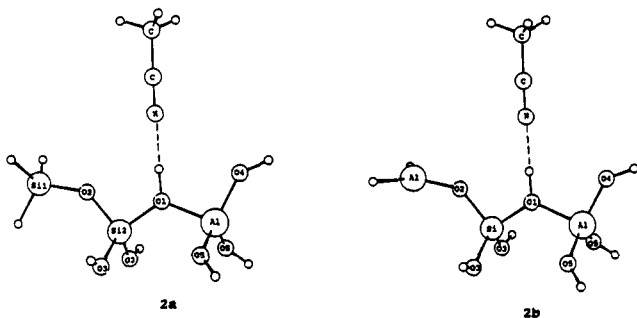


Figure 4. Molecular models.

TABLE III: Pseudoband Wavenumbers^a (cm⁻¹)

adsorbed molecule	assignment		
	A	B	C ^b
water	2900	2500	
dimethyl ether	2950	2500	1900–1300
diethyl ether	2950	2300	1900–1300
tetrahydrofuran		2370	1900–1300
di- <i>n</i> -butyl ether	2900	2300	1900–1300
acetone	2900	2370	1800–1300
<i>n</i> -butyraldehyde	2900	2400	1700–1300
acetonitrile	2820	2430	
benzonitrile	2800	2360	
formic acid	2900	2460	1700–1300
acetic acid	2900	2470	1800–1300

^a From ref 23 with our assignment. ^b Apparently complicated by $\delta(\text{OH}) + \nu(\text{TO})$ modes (see text).

of this theory for surface H complexes (see Table III with our assignment of OH bands from ref 4): all the OH band maxima detected in the adsorption of strong bases can be explained in terms of the OH band profiles.

When the $\nu(\text{OH})$ of the medium-strong AOH...B molecular complex falls in the 2500–2600-cm⁻¹ range (see, for example, the

TABLE IV: CN Stretching Frequencies (cm⁻¹)

molecule	calcd ^a	obsd ^b	molecule	calcd ^a	obsd ^b
1b'	2296		2a	2298	2300
1b''	2298		2b	2295	

^a Scaled 3-21g frequencies. ^b Observed for the adsorption on bridging OH groups.

IR spectrum of phenylphosphonic acid in ref 30), the C band is absent as the $\nu(\text{OH}) \pm k\nu(\text{OH}\cdots\text{B})$ band is not spread enough to low frequencies (see about $\nu_{1/2}$ below) for a significant Fermi resonance with $2\gamma(\text{OH}) \sim 1900 \text{ cm}^{-1}$ to occur. Therefore, on the basis of recent theoretical study by Ratajczak et al.³² and by analogy with the similar spectrum for CsHSeO₄ crystal,³² we suppose the C band in the obtained spectra for HZSM-5 and HY ($\nu(\text{OH}) \sim 2500 \text{ cm}^{-1}$, Figure 3) to be due to $\delta(\text{OH}) + \nu(\text{TO})$ modes, apparently enhanced by the weak resonance with the $\nu(\text{OH}) \pm k\nu(\text{OH}\cdots\text{NCCD}_3)$.³² In zeolites, $\nu(\text{TO})$ should correspond to TO stretching modes (T = Si, Al) from the 800–1200-cm⁻¹ spectral range.³⁵

As shown by Odinkov et al.,³¹ the known empirical relations (refs 36 and 37 and references therein) between $\Delta\nu(\text{OH})$ and other measured characteristics of moderate hydrogen bonds (with only the A OH band in the spectra)

$$(\Delta\nu(\text{OH}) - 40)^{1/2} = 9.0\Delta A^{1/2} \quad (1)$$

$$\Delta A^{1/2} = 0.41\Delta\delta' \quad (2)$$

$$-\Delta H = 2.91\Delta A^{1/2} \quad (3)$$

(A , δ' , and H being the OH band intensity, the proton chemical shift corrected for the base anisotropy, and the enthalpy, respectively) are valid also for medium-strong hydrogen bonds, with $\nu(\text{OH})$ taken to be the center of gravity of the (A, B) doublet³⁸ on the ν axis.³¹ Therefore, that these $\nu(\text{OH})$ values are approximately the same for both the zeolites at low coverage ($\sim 2500 \text{ cm}^{-1}$, Figure 3; the A band in the spectrum of HY zeolite is slightly increased by a contribution from the perturbed 3550-cm⁻¹ OH groups) indicates equal absolute acidity of the most acidic 3630-cm⁻¹ OH groups in HY and bridging OH groups in HZSM-5. The $\Delta\nu(\text{OH}) \approx 1100 \text{ cm}^{-1}$ and $\nu_{1/2} \approx 800 \text{ cm}^{-1}$ of these (A, B) doublets are also in good agreement with the empirical relation³⁹

$$\nu_{1/2} = 0.72\Delta\nu(\text{OH}) \quad (4)$$

for H complexes, implying homogeneity of these strongly acidic bridging OH groups in both the zeolites.

Increasing the coverage on both the zeolites causes new bands to grow on the high-frequency side of the A band, showing an existence of other, weaker Bronsted sites. For HZSM-5, these are mainly the terminal SiOH groups: a decrease of the 3745-cm⁻¹ band intensity is accompanied by a growth of the 3440-cm⁻¹ band (Figure 3a), characteristic of acetonitrile interaction with the SiOH group.³ On HY, the growth of a new band at $\sim 3000 \text{ cm}^{-1}$ occurs in parallel with the 3550-cm⁻¹ band intensity decrease (Figure 3b). The corresponding $\Delta\nu(\text{OH}) \approx 550 \text{ cm}^{-1}$ frequency shift shows the 3550-cm⁻¹ OH groups to be considerably less acidic than the 3630-cm⁻¹ OH groups ($\Delta\nu(\text{OH}) \approx 1100 \text{ cm}^{-1}$). Also, the 2284-cm⁻¹ CN band, growing in parallel with the $\sim 3000\text{-cm}^{-1}$ band, is close to the 2278-cm⁻¹ CN band in the interaction with nonacidic SiOH groups. As follows from the calculations (Table IV), structural (models 1b' and 1b'') and chemical (models 2a and 2b, Figure 4) differences in the lattice can lead only to a 2–3-cm⁻¹ $\nu(\text{CN})$ difference in the adsorption on the bridging OH groups ($\nu(\text{CN}) = 2300 \text{ cm}^{-1}$). Considering the 3550-cm⁻¹ OH group to be bridging one, these facts can be explained by some structural hindrance for the interaction with acetonitrile. This agrees with the generally accepted assignment

of the 3550-cm⁻¹ band to the O3-H group located in the cubooctahedra,^{40,41} which is hardly accessible for adsorption interactions. Obviously, the OH frequency shift does not characterize the absolute acidity in this case.

At high coverage, a decrease occurs of the 3630-cm⁻¹ OH band intensity but without a parallel increase of the C band intensity, as at low coverage (cf. the C band changes in going from spectrum 4 to 3 and from spectrum 2 to 1 in Figure 3b). In agreement with ref 42, this indicates an inhomogeneity of the 3630-cm⁻¹ OH groups in HY zeolite: at the high coverage the adsorption takes place on OH groups that are less acidic than those at the low coverage, with the $\nu(\text{OH})$ being shifted too far to high frequencies for the $\delta(\text{OH}) + \nu(\text{TO})$ band to be enhanced by Fermi resonance with the $\nu(\text{OH}) \pm k\nu(\text{OH} \cdots \text{NCCD}_3)$ modes.³² Therefore, the C band intensity in the acetonitrile adsorption might be suggested as a measure of the strongest Bronsted site concentration in zeolites.

Conclusion

The well-known (A, B, C) trio of IR bands, typical for medium-strong and strong H complexes in vapors, liquids, and solids, is also found in CD₃CN adsorption on HZSM-5 and HY zeolites. The theory of OH band profiles of H complexes in these media is shown to be valid for surface H complexes in zeolites.

The CN stretching frequency of CD₃CN is shown to be efficient in distinguishing different adsorbing sites of zeolites. Tentative attributions of the CN bands at 2332, 2323, 2300, and 2278 cm⁻¹ to the adsorption on strong and weak Lewis alumina sites, bridging OH groups, and terminal SiOH groups, respectively, are supported by ab-initio calculations: the observed frequencies are quantitatively reproduced by 3-21g calculations of the corresponding molecular models, combined with the frequency scaling procedure.

The IR spectra show approximately equal absolute acidity of the most acidic bridging OH groups in HY, adsorbing at 3630 cm⁻¹, and bridging OH groups in HZSM-5. This supports the theoretical and experimental studies^{18,19} which show that the absolute acidity of SiOHAl groups in zeolites is mainly defined by the chemical nature of their neighboring T atoms: (SiO)₃Si-OHAl lattice fragments in HY zeolites should possess the highest absolute acidity for the bridging OH groups in zeolites (see also refs 43 and 44 and references therein), corresponding to that in HZSM-5. It is to be noted that the acidity measured by adsorption calorimetry or temperature-programmed desorption of strong bases can be different for bridging OH groups of equal absolute acidity in different zeolites, due to a difference in the energy of the protonated bases' solvation by the zeolite lattices.⁴⁵⁻⁴⁷

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