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Interaction of Methanol with Brønsted Acid Sites of Zeolite Catalysts: An ab Initio Study

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Abstract: The adsorption of methanol on cluster models of Brønsted acid sites of zeolite catalysts has been investigated by ab initio quantum chemical methods at the Hartree–Fock self-consistent field (SCF) and at the second-order Møller–Plesset perturbation theory (MP2) levels. Among the two possible structures of the adsorption complex, the neutral methanol H-bonded to the zeolite OH group and the methoxonium cation attached to the zeolite surface (ion-pair), only the former is a minimum. The ion-pair structure is a transition structure for the proton transfer from one lattice oxygen to a neighboring one via the adsorbed methanol. However, the energy difference between both structures is only a few kJ/mol. There is a broad and shallow potential well which accommodates two symmetry-equivalent neutral complexes with the Brønsted proton attached to different O-sites of the lattice and the ion-pair structure connecting them. For the complex of methanol with the largest zeolite model optimized at the MP2 level, ^1H NMR chemical shifts of 10.8 and 17.4 ppm are predicted for the neutral and the ion-pair structure, respectively. The former value agrees well with the observed shift and therefore explains the observed signal as caused by fast exchange of the zeolite and methanol hydroxyl protons of the neutral structure. The vibrational frequencies calculated for the ion-pair structure do not permit an interpretation of the observed infrared spectrum. For the neutral structure, we predict frequencies of 1353 and 1015 cm^{-1} for the zeolitic in-plane and out-of-plane modes, respectively, while a range of 2300–2600 cm^{-1} is estimated for the zeolitic OH stretching mode. These data support a recent interpretation of the IR spectrum which explains the observed triplet of bands as a result of Fermi resonance between the strongly perturbed zeolitic OH stretch and the OH bending overtones. The required large frequency shifts are only predicted when electron correlation is included. For the methanol OH stretching frequency, we predict a range of 3260–3360 cm^{-1}. This is too low compared to the observed frequency at about 3500 cm^{-1} and leaves the question open whether the observed band can be explained by a weakly perturbed methanol OH stretch or whether another surface species is responsible for that band. We conclude that a nonconventional treatment of the dynamics may be necessary to understand the observed vibrational transitions.

Introduction

Though zeolite catalysts are extensively used in many important industrial processes, the understanding of the mechanisms of the chemical reactions which proceed on the catalyst surface is still poor. A very important step in improving our knowledge on surface reactions is the identification of surface intermediates. Besides the classical IR techniques, in recent years high-resolution NMR methods became more and more important because NMR chemical shifts are very structure-sensitive parameters. However, intuitive arguments cannot easily be applied to species with unusual structures or bonding, and therefore, the unequivocal assignment of the measured signals to postulated surface species is difficult. In this situation, quantum chemical ab initio techniques can be extremely helpful. Recent progress in computational techniques[1,2] makes it possible to predict chemical shifts with high accuracy. We present an example for the synergetic effect in identifying surface species that arises from the combined use of experimental techniques (by other groups[3–28]) and quantum chemical ab initio calculations (presented in this study). We report ab initio results on the adsorption of methanol on Brønsted sites of acidic zeolite catalysts. This is the initial step of the methanol-to-gasoline (MTG) process[29] which, as such, was the subject of numerous experimental studies. The interpretations of the results of IR and NMR investigations by the different authors, however, are in conflict. The observed spectra have been assigned to two types of surface species, a weakly perturbed methanol molecule attached via hydrogen bonds to the Brønsted site (neutral complex structure, NC; see top of Figure 1) and a methoxonium

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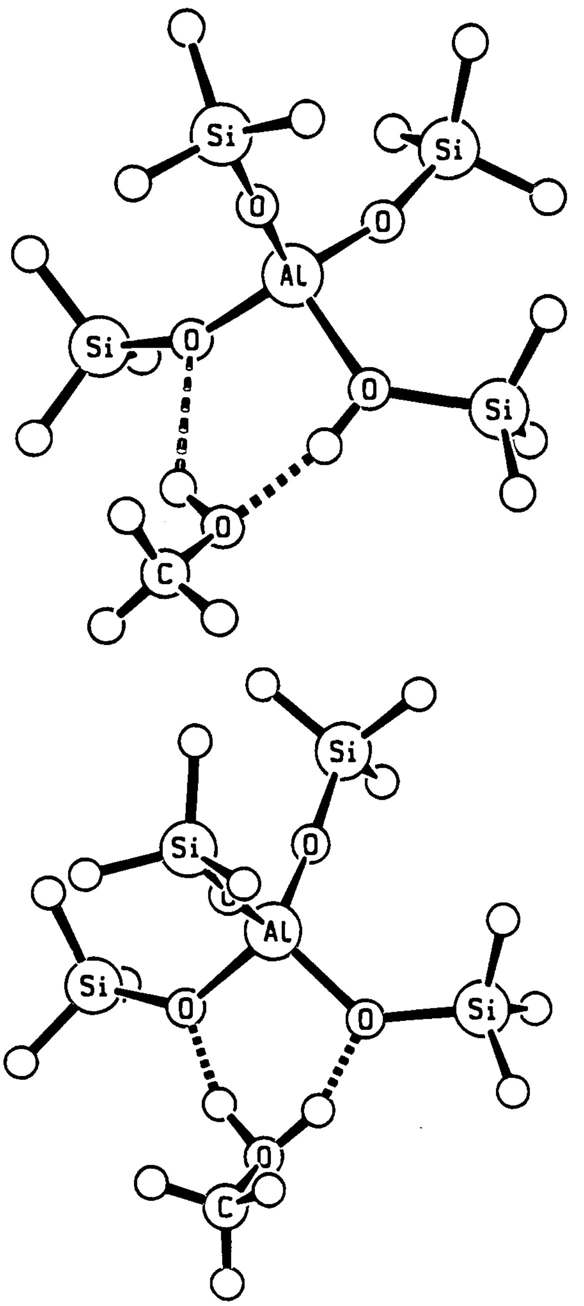

Figure 1. Equilibrium structures of the NC (top) and IP (bottom) complexes of methanol with the shell-2 model.

cation which also interacts by H-bonds with the negatively charged surface site (ion pair structure, IP; see bottom of Figure 1). While some authors claim that either one or the other type of species is present, others assume that both exist in an equilibrium.[3-6] A similar problem with the nature of the surface species formed upon adsorption on zeolitic Brønsted sites exists for other molecules, such as water[7] and acetonitrile.[8-10]

The present ab initio study includes a systematic investigation of the adsorption structures and energies of methanol with zeolite models of increasing size. All structures involved, i.e., the methanol molecule and methoxonium ion, the zeolite clusters, and the two types of surface complexes, are fully optimized. The equilibrium structures of the surface complexes were then used to evaluate the binding energies, the vibrational spectra, and the ^1H NMR chemical shifts. While all previous calculations used models of the acidic site which are not typical of any particular zeolite framework, for the first time we report also on a fully ab initio SCF-optimized structure of a surface complex between methanol and a specific model which is typical of the faujasite framework.

The standard approximation of ab initio quantum chemistry, the self-consistent field (SCF) method, is known to yield sound structures for molecules. However, bond lengths are systematically too short and, consequently, harmonic vibrational frequencies systematically too large.[30] These shortcomings are largely rectified on inclusion of electron correlation, already within the simplest approach, the second-order Møller–Plesset perturbation theory (MP2).[30] Moreover, the MP2 method is superior to SCF in describing H-bonds[31] which are the dominating feature of the surface complexes studied. The reason is that the former improves the description of electrostatic forces and takes dispersion effects into account. In a previous study, we mainly determined the structures and relative stabilities of the two possible types of the adsorption complex, the NC and IP structures, within the SCF approximation.[32] Electron correlation was included by single point calculations, and the zero point energies were taken into account. Evaluation of the MP2 energies at these SCF equilibrium structures indicated that electron correlation has a significant effect on the relative stability of the NC and IP structures. Thus, the present study goes beyond previous work in that it determines the structures within the MP2 approximation. In fact, it turned out that inclusion of electron correlation is necessary for obtaining reference structures which are accurate enough to yield realistic predictions of vibrational spectra and NMR chemical shifts. Since the computational effort involved in MP2 calculations is about 1 order of magnitude larger than that of SCF computations, an efficient code for analytical derivatives of MP2 energies was vital for the completion of this project.

Previous quantum chemical ab initio studies[33-35] were limited to the SCF approximation and, frequently, adopted zeolite cluster models with rigid or only partially relaxed structures. The only study which previously included correlation effects for obtaining vibrational frequencies was a density functional theory (DFT) study by Gale et al.[36] But as distinct from MP2, DFT methods show weaknesses in describing OH bonds (too low frequencies and too large frequency shifts on H-bond formation) even if gradient-corrected functionals are used.[37]

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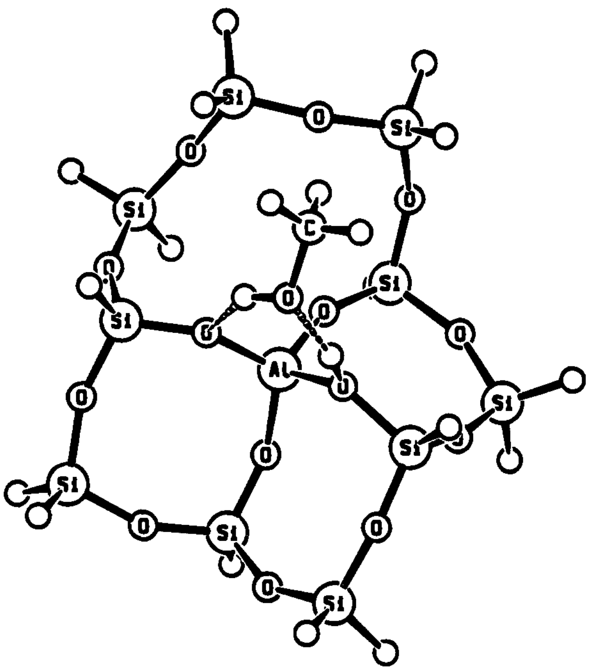

Figure 2. Equilibrium structure of the NC complex of methanol with the faujasite model.

Models

Three models of increasing size were adopted for the bridging hydroxyl site. The first and smallest—$HO(H)Al(OH)_3$ (shell-1)—consists simply of an AlO_4 tetrahedron saturated with hydrogen atoms and of the bridging hydroxyl proton. In the second model—$H_3SiO(H)Al(OH)_2OSiH_3$ (shell-1.5)—the two oxygen atoms acting as adsorption sites are bound to SiH_3 groups, i.e., there is a partial (half) second coordination sphere. The third and largest model—$H_3SiO(H)Al(OSiH_3)_3$ (shell-2)—contains a complete second coordination sphere of four silicon atoms.

While all previous calculations used models of the acidic site which are not typical of any particular zeolite framework, for the first time we report also on a fully ab initio SCF-optimized structure of a surface complex between methanol and a specific model which is typical of the faujasite framework (Figure 2). The complex comprises a cluster model which was cut out from the zeolite faujasite and consists of four condensed silicate rings. Two 4-rings of TO_4 units belong to the hexagonal prism, and one 4-ring and one 6-ring of TO_4 units belong to the sodalite cage. The aluminum is the central atom and is part of all four rings. The dangling bonds of the silicon atoms are saturated with hydrogen atoms.

Calculations

All structure optimizations were performed with the TURBOMOLE program package.[38] For the SCF calculations on the large faujasite model, the parallel algorithm[39] implemented in TURBOMOLE was used on two workstation clusters. In all calculations except those on the faujasite model, a double-ζ+ polarization basis set (DZP) was employed on all atoms except oxygen, which was described by a triple-ζ+ polarization basis set (TZP). The SCF calculations on the faujasite model used a split-valence polarization set (SVP) on all non-hydrogen atoms and an SV basis[40] set on hydrogen.

The semidirect implementation of the coupled Hartree–Fock method using gauge including atomic orbitals (CHF-GIAO) at the SCF level (SHEILA module[2] of TURBOMOLE) was employed for the calculation of the nuclear shielding constants. It uses explicitly field-dependent basis functions as suggested by Ditchfield.[41] A TZP basis derived from Huzinagas 9s5p sets by full analytical reoptimization was applied to all atoms.[40] For the conversion from the calculated isotropic absolute shielding constants σ to the relative shifts δ_{TMS}, we used the following formula:

$$\delta_{TMS}(\text{complex}) = \delta_{TMS}(CH_3OH) + \sigma(CH_3OH) - \sigma(\text{complex})$$

The methanol molecule served as an internal reference in the calculations. The calculated absolute SCF shielding constant $\sigma(CH_3OH)$ was 32.7 and 32.0 ppm at the SCF- and MP2-optimized structure, respectively, while the experimental gas phase value $\delta_{TMS}(CH_3OH)$ was measured to be 0.02 ppm.[42]

The calculation of the harmonic force constants used analytical second derivatives at the SCF level, but at the MP2 level a numerical differentiation of analytical MP2 gradients was performed. As a driver for these calculations, a slightly modified module of the ACES II program system[43] was used, and the MP2 gradient calculation was done by the MPGRAD[44] module of the TURBOMOLE program system. According to the observation that harmonic vibrational frequencies calculated at the SCF level are systematically larger than observed transition frequencies by about 10%, the theoretically predicted SCF frequencies were scaled by a factor of 0.9. To scale the frequencies evaluated at the MP2 level, we used a value of 0.954 which is the average ratio of all observed vibrational frequencies of methanol[45] and the respective MP2 values. This crude scaling procedure accounts for both systematic errors of the calculated harmonic force constants and neglected anharmonicity effects.

Results

Structure of Adsorption Complexes. The structure optimizations for the methanol complexes were done applying the following strategy: First, the structure of the ion-pair complex was optimized enforcing C_s symmetry. Then the mirror plane was abandoned and the optimization was continued within the C_1 point group. In no case was a stable ion-pair complex with C_1 symmetry found. The proton was detracted from the methoxonium ion and was transferred to the bridging oxygen of the zeolite cluster, yielding the neutral H-bonded complex in C_1 symmetry. A subsequent diagonalization of the harmonic force constant matrix of the IP structures revealed that the structures obtained are saddle points of first order but in the case of the shell-2 model complex, only a saddle point of third order. We tried to obtain a first-order saddle point by distorting the complex along the modes belonging to the imaginary frequencies after the mirror plane was abandoned. However, we only managed to remove one imaginary frequency connected with a rotation of a SiH_3 group. When distortions along the other modes were made, the complex collapsed to the NC structure as explained above. To find the first-order saddle point for this model, it is obviously necessary to apply methods which are much more sensitive to the curvature of the PES than the steepest descent which is usually used in geometry optimizations. The optimized complexes of the shell-2 model with methanol are shown in Figure 1. A similar approach was applied to find a stable IP structure for the large faujasite model. Because no symmetry can be exploited, the structure optimiza-

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Table 1. SCF and MP2 Total Energies of the Equilibrium Structures of the NC and IP Model Complexes, Zeolite Models, and Methanol (hartrees) for the DZP/TZP Basis Sets

	point group	SCF optimized		MP2 optimized
		E^{SCF}	$E^{MP2\ a}$	$E^{SCF+MP2\ b}$
NC faujasite[c]	C_1	−4303.83026	−3.63747	–
NC shell-1	C_1	−659.63871	−1.25411	−661.12417
IP shell-1	C_s	−659.62021	−1.26746	−661.11841
NC shell-1.5	C_1	−1239.87196	−1.44189	−1241.76339
IP shell-1.5	C_s	−1239.85350	−1.45703	−1241.75863
NC shell-2	C_1	−1820.12490	−1.62606	−1822.41838
IP shell-2	C_s[d]	−1820.10841	−1.64022	−1822.41393
free faufasite[c]	C_1	−4188.86812	−3.31749	
free shell-1	C_1	−544.55255	−0.89257	−545.64062
free shell-1.5	C_1	−1124.79109	−1.07952	−1126.28333
free shell-2	C_1	−1705.04196	−1.26345	−1706.93521
free MeOH	C_s	−115.06207	−0.35442	−115.44992
free MeOH[c]	C_s	−114.93505	−0.30744	

[a] Single point MP2 energy using the frozen core approximation. [b] Full correlation of all electrons. [c] SVP/SV(on H) basis set employed. [d] At the SCF level an IP structure with C_1 symmetry was found which represents a saddle point of second order as explained in text.

Table 2. Selected Optimized Bond Lengths[a] (pm) and Angles (degrees) of the Neutral H-Bonded (NC) and the Ion-Pair (IP) Structures of the Complexes of Methanol with the Models of Zeolitic Brønsted Sites Investigated

	NC structure				IP structure		
SCF	sh-1	sh-1.5	sh-2	fau	sh-1	sh-1.5	sh-2
$r(O_Z\text{-}H_M)$	188.5	216.6	223.8	202.5	139.6	144.4	146.9
$r(O_M\text{-}H_Z)$	170.4	173.4	168.5	165.8			
$r(O_ZH_Z)$	97.5	97.1	97.7	98.7			
$r(O_MH_M)$	96.1	95.3	95.3	95.7	105.2	103.4	102.6
$r(AlO_1)$	174.6	173.7	172.8	173.8	181.5	181.9	180.8
$r(AlO_2)$	192.5	190.4	190.5	190.5	181.5	181.9	180.8
$r(CO_M)$	140.0	140.4	140.6	140.4	141.9	142.5	143.5
$\angle(O_1AlO_2)$	94.9	100.5	100.6	100.2	92.7	97.6	99.1
MP2	sh-1	sh-1.5	sh-2		sh-1	sh-1.5	sh-2
$r(OZ\text{-}H_M)$	166.9	173.7	176.2		130.6	134.4	136.6
$r(O_M\text{-}H_Z)$	151.2	149.9	145.3				
$r(O_ZH_Z)$	103.0	103.3	104.9				
$r(O_MH_M)$	99.9	99.3	99.3		112.0	109.8	108.6
$r(AlO_1)$	177.9	178.2	177.0		183.9	183.9	182.4
$r(AlO_2)$	191.8	189.6	188.4		183.9	183.9	182.4
$r(CO_M)$	142.2	142.5	143.1		142.9	143.5	144.4
$\angle(O_1AlO_2)$	92.7	96.9	98.0		91.3	95.1	96.8

[a] Subscript M refers to methanol or methoxonium, Z to the zeolite cluster; subscripts 1 and 2 on the oxygen adsorption sites indicate the Al−O−Si and the Al−O−H oxygen, respectively, of the NC structure.

tion started from an ion-pair structure with fixed OH distances of the methoxonium moiety while all other degrees of freedom were optimized. Once the minimum was found, the constraints were lifted, and as in the former optimizations of the nonspecific Brønsted site models, the proton migrated to the zeolite framework oxygen. The resulting NC structure is shown in Figure 2. The general features of the NC structure can be characterized by one strong H-bond between the Brønsted proton and the methanol oxygen and a rather long and weak H-bond involving one oxygen of the AlO_4 tetrahedron and the methanol proton. The total energies and point groups of the equilibrium structures obtained are summarized in Table 1.

Table 2 shows the most important parameters of the optimized structures of the NC and IP complexes of methanol with models shell-1 to shell-2 and the faujasite model. There are two observations concerning the influence of the computational level and the size of the model. (i) Inclusion of the correlation energy yields a stronger interaction by accounting for dispersion effects between the adsorbed molecule and the zeolite model and diminishes the intermolecular H-bond distances. For the two intermolecular H-bonds of the NC structure, a substantial decrease compared to the SCF data by 19 and 22 pm (shell-1), 24 and 42 pm (shell-1.5), and 23 and 48 pm (shell-2) is observed. In the IP structures, the intermolecular H-bonds become only marginally shorter, by 10 pm, on inclusion of correlation effects. That the dispersion energy has a larger effect on the NC structures than on the IP structures is expected, since for the latter, electrostatic effects dominate the binding and are already accounted for at the SCF level. Correlation effects elongate the intramolecular O−H bonds by 4−6 pm.

(ii) The second effect depends on the size of the models and can be observed on both computational levels. With increasing size of the zeolite models (shell-1 to shell-2) for both NC and IP structure, the (OAlO) angle which involves the two oxygen atoms acting as adsorption sites opens up. For the IP structure, the intermolecular H-bonds between the adsorbed methoxonium ion and these two oxygens increase simultaneously. In the NC structure these two H-bonds are differently affected when passing from the shell-1 to the shell-2 model. The short H-bond between the Brønsted proton and the methanol oxygen decreases (with the exception of the SCF result for the shell-1.5 model) while the longer H-bond between the oxygen atom of the zeolite model and the methanol proton increases. For the complex of methanol with the faujasite model (optimized only on the SCF level), the length of these two bonds is 166 pm for the short bond, which is its smallest value, and 202 pm for the long H-bond, which is in between the data of the shell-1 and shell-1.5 model complexes.

Adsorption and Proton Transfer Energy. Table 3 gives the SCF and MP2 adsorption energies defined as the energy of the reaction of the neutral methanol molecule with the shell-1 to shell-2 models, i.e., negative values indicate stabilization. The total adsorption energy, comprising the SCF interaction energy corrected for the zero point vibrational energy and the single point MP2 energy at the SCF-optimized structures, shows the same trend for the NC and IP structures. For both structure types, when going from the shell-1 model over shell-1.5 to the shell-2 model, the total adsorption energy first increases by about 10 kJ/mol and then decreases to give −68 kJ/mol. Accounting for the correlation energy is critical to getting the relative stability of both structure types right. It stabilizes the NC structures by about 20 kJ/mol but the IP structures by nearly 60 kJ/mol. However, because the latter structure is less stable by about 40 kJ/mol on the SCF level, the total adsorption energies are virtually identical.

The proton transfer energy (Table 3) is defined as the difference between the energy of the IP complex and that of the NC complex. If corrections for the zero point vibrational energy are made and the MP2 single point energies are added, the energy difference between the two structures virtually disappears. As in the case of the adsorption energy, this is due to the marked contribution of the correlation energy which nearly compensates for the unfavorable SCF contribution. The zero point vibrational energy further reduces the proton transfer energy. On the MP2 PES, a small barrier of about 12 kJ/mol is predicted for the largest model (shell-2). However, adding the zero point vibrational energies calculated for the shell-1 and shell-1.5 model complexes has the same effect as that observed for the SCF PES. It decreases the barrier to about 5 kJ/mol for the former model and nearly cancels the barrier for the latter model.

To assess how strongly our calculated interaction energies are affected by the basis set superposition error (BSSE), we carried out counterpoise calculations. For the adsorption energy of the shell-1.5 model complex, we obtained values of 24 and

Table 3. Adsorption Energies ΔE_{Ad} of the NC and IP Complexes with Respect to the Methanol Molecule and the Free Brønsted Site Models and Proton Transfer Energies ΔE_{PT} in kJ/mol

	ΔE_{Ad}(NC)				ΔE_{Ad}(IP)			ΔE_{PT}		
method[a]	shell-1	shell-1.5	shell-2	fau	shell-1	shell-1.5	shell-2	shell-1	shell-1.5	shell-2
SCF//SCF	−63.3	−49.4	−54.8	−71.1	−14.7	−0.9	−11.5	48.6	48.5	43.3
SCF+MP2[b]//SCF	−82.0	−70.3	−76.3	−104.0	−68.5	−61.6	−70.2	13.5	8.7	6.1
SCF+MP2[b]+ZP//SCF	−73.1	−63.1	−68.7		−71.7	−61.4	−68.4	1.4	1.7	0.3
SCF+MP2//MP2[c]	−88.3	−79.0	−87.3		−73.2	−66.6	−75.6	15.1	12.4	11.7
SCF+MP2+ZP//MP2[c]								5.2	0.3	
BSSE//MP2[c]		24.2				31.6			7.4	

[a] On the left-hand side of // the computational level is designated while on the right-hand side the level of geometry optimization is specified. [b] Single point MP2 energy using the frozen core approximation. [c] MP2 energy with full correlation.

Table 4. OH Vibrational Frequencies[a] Calculated at the SCF Level for the Free Brønsted Site Models and for the NC and IP Structures of Their Complexes with Methanol (cm^{-1})

	n(i)[b]	ν(MeOH)	δ(MeOH)	ν(ZOH)	δ(ZOH)	γ(ZOH)
free MeOH	0	3731	1326			
free shell-1	0			3709	1562	650
free shell-1.5	0			3707	1045	297
free shell-2	0			3688	1043	299
NC shell-1	0	3501	1394	3235	1591	
NC shell-1.5	0	3636	1350	3298	1213	706
NC shell-2	0	3653	1350	3188	1250	784

	n(i)[b]	ν(symm)	ν(asymm)	δ
free MeOH$_2^+$	0	3522	3596	1624
IP shell-1	1	2257	1900	1652
IP shell-1.5	1	2457	2161	1665
IP shell-2	2	2459	2263	1673

[a] All frequencies scaled with 0.9. [b] Number of modes with imaginary frequency.

Table 5. OH Vibrational Frequencies[a] Evaluated at the MP2 Level for the NC and IP Complexes of Methanol with Cluster Models Shell-1 and Shell-1.5 (cm^{-1})

	n(i)[b]	ν(MeOH)	δ(MeOH)	ν(ZOH)	δ(ZOH)	γ(ZOH)
free MeOH	0	3693	1318			
NC shell-1	0	3165	1435	2600	1594	
NC shell-1.5	0	3276	1421	2548	1353	1015

	n(i)[b]	ν(symm)	ν(asymm)	δ
free MeOH$_2^+$	0	3570	3482	1601
IP shell-1	1	1628	1579	1998
IP shell-1.5	1	2131	1689	1634

[a] All frequencies scaled with 0.954. [b] Number of imaginary frequencies.

Table 6. CH and CO Frequencies[a] at the MP2 Level of the NC and IP Complexes with Clusters Shell-1 and Shell-1.5 (cm^{-1})

mode	NC sh-1	NC sh-1.5	MeOH	IP sh-1	IP sh-1.5	MeOH$_2^+$
ν_{CH}	3066	3084	3072	3084	3104	3173
	3037	3043	3000	3070	3081	3164
	2940	2948	2924	2962	2973	3016
δ_{CH}	1467	1465	1465	1453	1454	1442
	1450	1452	1451	1448	1451	1438
	1430	1443	1441	1389	1432	1421
ν_{CO}	1027	1049	1064	1043	1041	829

[a] All frequencies scaled with 0.954.

32 kJ/mol for the NC and IP structure, respectively, and about 7 kJ/mol for the proton exchange barrier.

Vibrational Frequencies. The purpose of the calculation of the harmonic vibrational frequencies was 2-fold. First, the number of imaginary frequencies obtained allows one to decide whether the stationary points located on the PES are minima (0), transition structures (1), or saddle points of higher order (larger than 1). Second, the discussion of the calculated vibrational frequencies may lead to an interpretation of the observed spectra either in terms of the neutral H-bonded or ion-pair structure.

A. SCF Frequencies. Table 4 summarizes the results of the SCF vibrational mode analysis of the neutral and ion-pair complex of methanol with the shell-1 to shell-2 models. The C_s IP structure proved to be not a local minimum but a transition structure (one imaginary frequency of the smallest cluster and the shell-1.5 model) or a saddle point of higher order (two imaginary frequencies for the shell-2 model). In all cases, the vibrational mode belonging to the imaginary frequency represents an asymmetric OH stretch of the two *intermolecular* H-bonds connected with a "rocking" of the whole $CH_3OH_2^+$ species between the two adsorption sites. It is evident that this system is a transition structure for the proton exchange between neighboring basic O-sites via the oxonium species. In the case of the shell-2 model, there is one additional imaginary frequency which belongs to the torsion of the methyl group of the methoxonium ion about the CO bond. The NC complexes of all the models possess no imaginary frequencies and hence represent minima on the potential energy surface.

The upper part of Table 4 contains the SCF results for methanol, the free zeolite models, and the NC complexes. For the OH stretching frequencies of the methanol complex with the shell-2 model, values of about 3650 and 3200 cm^{-1}, are predicted for the methanol and zeolite OH groups, respectively. Compared with the frequencies of the free species, red shifts of 80 and 500 cm^{-1}, respectively, are calculated. While the methanol OH bending frequency is virtually not affected by complex formation, the zeolitic in-plane OH bend and the out-of-plane bend are blue-shifted by 200 and 480 cm^{-1}, respectively.

For the IP structure (lower part of Table 4), the value of the symmetric and asymmetric OH stretch continuously increases with increasing model size. For the largest model, shell-2, the predicted values are 2550 and 2260 cm^{-1}. Compared with the free $CH_3OH_2^+$ species, this means a red shift by about 1000 and 1340 cm^{-1}, respectively. The OH bending frequency of this model complex is slightly blue-shifted by about 50 cm^{-1}.

B. MP2 Frequencies. Tables 5 and 6 show the calculated MP2 frequencies of the NC and IP complexes of methanol with the shell-1 and shell-1.5 models. While the two NC complexes proved to be local minima, the respective IP structures represent transition structures with one imaginary frequency (Table 5).

For the NC complexes, we found significant changes of the intermolecular OH bond lengths as well as rather moderate changes of the intramolecular OH bond distances when going from SCF- to MP2-optimized structures. Clearly, the vibrational frequencies of the involved OH groups should reflect these structure changes. In fact, the calculated frequency shifts are considerably larger than the corresponding SCF results. For the NC structure of the shell-1.5 model complex (Table 5), the methanol OH stretch is red-shifted by about 400 cm^{-1}, i.e., five times the SCF frequency shift. Although no MP2 frequencies are calculated for the free zeolite models, a comparison of the calculated zeolite OH stretch of 2550 cm^{-1} (shell-1.5) with the observed value for free zeolitic Brønsted sites of about 3600 cm^{-1} indicates a red shift as large as 1050 cm^{-1}, which is twice that predicted at the SCF level.

Because for the shell-2 model complexes the calculation of MP2 frequencies is computationally prohibitive, we employed the well-known correlation between the OH force constants and OH bond distances originally proposed by Badger[46]

$$k_e(r_e - d_{ij})^3 = C$$

to estimate the ν(OH) frequencies of the NC complex of this model. Here k_e and r_e are the harmonic force constant and the equilibrium OH bond distance while d_{ij} and C are constants. For the methanol OH group four MP2 frequencies (free methanol, NC-shell-1, NC-shell-1.5, and methanol–silanol complex) and for the zeolitic OH group only two values (NC-shell-1 and NC-shell-1.5) were correlated with the respective OH bond lengths. The extrapolated frequencies for the methanol and zeolitic OH groups are 3260 and 2300 cm^{-1}, respectively, which correspond to OH bond lengths of 99.3 and 104.9 pm (Table 2).

Besides the fact that the MP2 method overestimates frequency shifts in complexes with medium strong H-bonds as was shown recently for the water dimer,[47] another source of error is the BSSE. The BSSE leads to an overestimation of the binding of the adsorbed species and therefore weakens the methanol and zeolitic OH bond too much, resulting in a spuriously large frequency shift. To estimate the size of the BSSE in our MP2 OH stretching frequencies, we applied the counterpoise correction[48] as the most commonly used approach. We therefore performed an MP2 calculation of a BSSE-corrected potential curve by varying simultaneously both intermolecular H-bond distances while fixing the coordinates of methanol and the zeolite model. The calculated minima of the two BSSE-corrected intermolecular H-bonds of the shell-1.5 model complex are 158.0 and 182.4 pm, about 8 pm larger than the fully optimized MP2 equilibrium distances. In a second step, these H-bonds were fixed and the remaining degrees of freedom were fully relaxed by an MP2 optimization. The resulting OH bond distances of the zeolitic and methanol OH group of 101.6 and 96.4 pm were used to estimate the corresponding frequencies as in the case of the shell-2 model complex. The calculated blue shifts due to the BSSE are about 300 cm^{-1} for the zeolitic OH stretch and 100 cm^{-1} for the methanol OH stretch. With these error estimates and the predictions for the shell-2 model system, we estimate the zeolitic OH stretching frequency to appear at 2300–2600 cm^{-1} and that of the methanol OH stretch at about 3260–3360 cm^{-1}.

For the IP complex (Table 5) the OH stretch frequencies are lower by 326 and 472 cm^{-1} than the SCF values (shell-1.5 model). In contrast, the predicted MP2 frequency of the HOH bending mode of 1630 cm^{-1} nearly equals the SCF value of 1660 cm^{-1}.

^{1}H NMR Chemical Shifts. The ^{1}H chemical shifts were calculated for both the SCF- and MP2-optimized adsorption structures and are presented in Table 7. The chemical shifts predicted for the MP2-optimized structures are generally larger. While for the IP complexes, for which the shifts calculated for the SCF structures are already large, a further increase by about 2 ppm occurs; the values of the NC complexes increase by as much as 4–5 ppm. The best available shifts (shell-2 model) are 10.8 and 17.4 ppm for the NC and IP structures, respectively.

Table 7. SCF ^{1}H NMR Chemical Shifts δ (ppm) on SCF- and MP2-Optimized Structures of the Active Site Models and the NC and IP Complexes with Methanol

	ZOH	NC			
	SiO(*H*)Al	*H*OCH$_3$	SiO(*H*)Al	av	IP
SCF optimized[a]					
shell-1	3.8	5.3	9.1	7.2	17.5
shell-1.5	2.7	2.8	7.9	5.4	15.9
shell-2	2.8	2.6	8.8	5.7	15.3
faujasite[b]	4.2	3.5	10.8	7.2	
MP2 optimized					
shell-1	4.0	8.6	13.5	11.1	19.2
shell-1.5	2.8	7.1	13.0	10.1	17.8
shell-2	2.9	7.0	14.6	10.8	17.4

[a] See ref 50. [b] Chemical shift calculation using a DZP basis set on all atoms. The respective absolute shift of methanol for this basis set is 33.0 ppm.

Table 8. Assignment of Observed OH Stretch and Deformation Frequencies Assuming the Formation of Either an IP or NC structure of the Adsorption Complex (cm^{-1})

	observed			
IP complex	2900 ν_{OH}(symm)	2440 ν_{OH}(asymm)	1690 δ_{OH}	3545 ?
SCF/shell-2	2549	2263	1673	no explanation
SCF/shell-1.5	2457	2161	1665	no explanation
MP2/shell-1.5	2131	1689	1634	no explanation

	observed			
NC complex	3545 ?	(2600–2400)[a] ν_{OH}(ZOH···M)	(1340)[a] δ_{OH}(ZOH)	(1030)[a] γ_{OH}(ZOH)
SCF/shell-2	3653	3188	1250	784
SCF/shell-1.5	3636	3298	1214	706
MP2/shell-1.5	3276	2548	1353	1015
MP2/shell-2	(3260)[b]	(2300)[b]		
MP2^{BSSE}/shell-1.5	(+100)	(+300)		

[a] Estimated from observed frequencies as explained in text. [b] Extrapolated employing Badger's rule.[46]

In addition, we calculated the chemical shifts of the Brønsted proton of the free zeolite models which are also shown in Table 7. The same trends can be observed as for the methanol complexes. When one moves from the shell-1.5 to shell-2 models, the calculated shift of the Brønsted proton remains virtually constant. The predicted chemical shift for the largest model optimized at the MP2 level, shell-2, is 2.9 ppm. The chemical shift of the largest model optimized at the SCF level, the faujasite model, amounts to 4.2 ppm.

To assess the influence of the BSSE which affects the calculated shifts via the structures, we evaluated the shifts of the above-mentioned BSSE-corrected structures for the shell-1.5 model complexes. As expected, the calculated shifts are smaller by only a fraction of a ppm for the IP and by 1 ppm for the NC structure.

Discussion

Adsorption and Proton Transfer Energies. Let us take the adsorption energy of the SCF-optimized NC faujasite model complex, the largest model complex of this study, as the basis for an estimate. The SCF plus single point MP2 adsorption energy amounts to −104 kJ/mol. From the MP2-optimized shell-2 model complex, we deduce a further increase of this value by −11 kJ/mol and a decrease by the zero point energy correction of 7.6 kJ/mol. This, together with a BSSE correction

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[46] Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128; **1935**, *3*, 710.

[47] van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *J. Comput. Chem.* **1991**, *13*, 399.

[48] Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

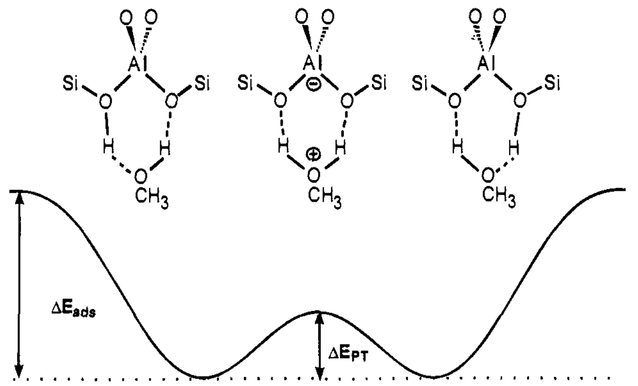

Figure 3. Sketch of the PES for the proton transfer from the Brønsted acid site onto adsorbed methanol. The H/D exchange between different O-sites of the lattice via an adsorbed methanol molecule can also be described by this PES.

of 24.2 kJ/mol, yields an estimate of −83 kJ/mol. With an estimated error related to the choice of the quantum chemical method and the finite models of about 20 kJ/mol, we arrive at a prediction of −83 ± 20 kJ/mol for the adsorption energy.

Recently Gorte et al.[28] have studied the adsorption of methanol on H-ZSM-5 and measured the heat of adsorption to be in the range of −110 to −120 kJ/mol. Taking into account the error bars, our theoretical prediction approaches the experimental range. However, the estimate of −83 kJ/mol is still too small. This may have several reasons. (i) Certainly larger basis sets are necessary to get an even larger amount of dispersion interaction. (ii) There are indications that the choice of a larger zeolite model will strengthen the interaction. The SCF plus single point MP2 adsorption energy increases by as much as 33.7 kJ/mol when one moves from the NC complex of the shell-1.5 to that of the faujasite model. In these complexes, the short intermolecular H-bond also continuously decreases with increasing model size (Table 2). The result that the gas phase acidities calculated for even the largest models of this study are slightly smaller than the values inferred from the OH frequency shifts points in the same direction.[37]

For the proton transfer energy, defined as the difference between the energies of the NC and IP structures, a value of about 12 kJ/mol is predicted if the zero point energy is not considered. However, if the zero point energy is taken into account, the barrier for the proton exchange almost disappears. We therefore characterize the PES for the adsorption of methanol as a broad and shallow potential well which accommodates two symmetry-equivalent neutral complexes with the Brønsted proton attached to different O-sites of the lattice and the ion-pair structure connecting them (Figure 3). This is consistent with the observed easy H/D exchange between methanol and zeolite catalysts at room temperature.[49]

IR Spectra. The IR spectra of methanol adsorbed on bridging OH groups of various zeolite catalysts like H-ZSM-5,[6,11,12] H-MOR,[11] and H-Y[6,11] show a characteristic triplet of bands in the ranges of 2900−2800, 2550−2400, and 1740−1610 cm^{-1} and an additional band in the range of 3576−3480 cm^{-1}. While most authors agree on these main features of the spectra, conflicting interpretations have been offered. The most common one suggests that methanol is protonated upon adsorption and forms an ion-pair adsorption complex.[11−14] The characteristic triplet of bands is assigned to the antisymmetric and symmetric OH stretching vibrations and the HOH bending vibration of the oxonium group.

The PES we calculate does not show a minimum for such a structure. Nevertheless, it may be useful to discuss whether the vibrational properties of a hypothetical IP structure could explain the observed spectra. Since the energy difference between the IP and NC structure is small, one might argue that small changes of the catalyst and/or a better quantum chemical description could create a minimum for the IP structure. Let us check if the calculated vibrational frequencies support the interpretation of the observed spectra in terms of the IP structure. We first look at the SCF results (Table 4). (i) The range of observed bands of 1740−1610 cm^{-1} fits the calculated band at 1670 cm^{-1} and can be attributed to the HOH deformation of the OH_2^+ group of the methoxonium ion. (ii) As the size of the models increases, the frequencies of the symmetric and asymmetric stretching vibrations of the OH_2^+ moiety increase and get closer to the observed ranges of 2900−2800 and 2550−2400 cm^{-1}. However, even the frequencies predicted for the largest model are still too low by about 400 and 200 cm^{-1}, respectively. Furthermore, the predicted splitting of 300 cm^{-1} is smaller than the observed splitting of 460 cm^{-1}. (iii) No vibrations are calculated to lie in the region of about 3500 cm^{-1}, which could explain the band observed at 3576−3480 cm^{-1}. The agreement even deteriorates when the MP2 level results are considered (Table 5). While points i and iii also apply to the calculated MP2 frequencies, at this level the OH stretch frequencies predicted at 2131 and 1689 cm^{-1} deviate by about 700−800 cm^{-1} from the bands observed at 2900−2800 and 2550−2400 cm^{-1}, respectively.

In a recent study, a second possible interpretation of the observed IR spectrum is presented which explains the triplet of bands in terms of the so-called A−B−C pattern known for strong H-bonded complexes.[7,15] According to this interpretation, the zeolitic OH band engaged in an H-bond interaction is shifted to lower wavenumbers and significantly broadened by superposition with the intermolecular OH stretch. The in-plane and out-of-plane SiOH deformation modes are shifted to higher wavenumbers simultaneously (see upper part of Table 4), and the overtones of these modes fall into the region of the broad strongly perturbed OH stretch. Fermi resonance occurs and creates two transmission windows at about the position of these overtones by redistributing the intensity into absorption regions on both sides of the window. Finally, three pseudo bands appear, the typical A−B−C pattern. If this reasoning were true, the overtones of the δ(ZOH) and γ(ZOH) bending modes must correspond to the approximate position of the two transmission windows which we estimate as the middle between the maxima of the A and B and the B and C bands, respectively (Figure 4). These estimates are 2675 and 2050 cm^{-1}, which means that the fundamentals can be assumed at 1340 and 1030 cm^{-1}, respectively. Moreover, this interpretation requires the zeolitic OH stretch to be red-shifted by about 1000−1200 cm^{-1}.

If we adopt this spectroscopic model, the calculated SCF vibrational frequencies of the NC complex (Table 4) give rise to the following conclusions: (i) The theoretically predicted frequency shift of the zeolitic OH stretching mode of 500 cm^{-1} is in marked contrast to the value of 1000−1200 cm^{-1}, which is required to allow a Fermi resonance with the zeolitic OH bending overtones. (ii) For the δ(ZOH) and γ(ZOH) bending fundamentals, we predict values of 1250 and 784 cm^{-1}, which are too low by 130 and 250 cm^{-1}. (iii) The observed band at 3576−3480 cm^{-1}, the only one not belonging to the A−B−C triplet, can be assigned to the OH stretch of methanol weakly interacting with a lattice oxygen atom, although calculated to be 100 cm^{-1} higher.

When the calculated MP2 frequencies of the NC complex (Table 5) are considered, the situation takes a favorable turn. For the shell-1.5 model complex, the frequencies of the δ(ZOH)

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(49) Lercher, J. Personal communication.

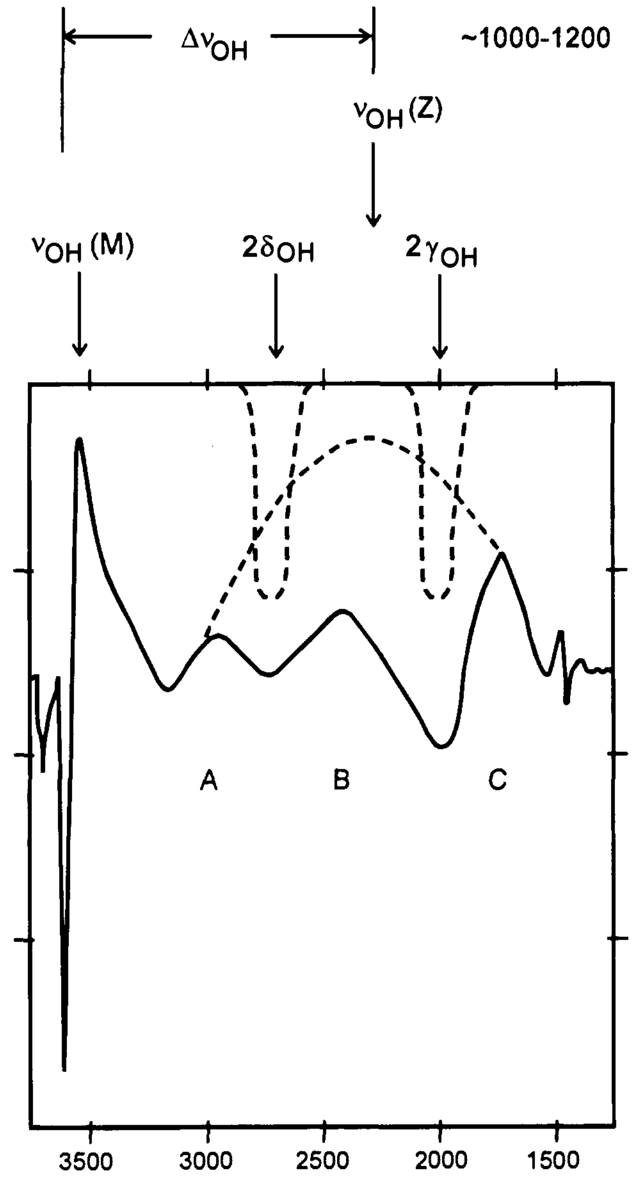

Figure 4. Sketch of an IR spectrum of adsorbed methanol showing the typical A−B−C triplet of bands (solid lines) and the approximate positions of the zeolite OH bending overtones (the transmission windows) and the strong red-shifted and broadened zeolitic OH stretching mode (dotted lines).

and γ(ZOH) modes are predicted to have values of 1353 and 1015 cm^{-1}, respectively, which are very close to the above estimated values of 1340 and 1030 cm^{-1}. Furthermore, the zeolitic OH stretch experiences a dramatic red shift down to 2548 cm^{-1} (the SCF value was 3200 cm^{-1}). This is expected, though not necessarily to that extent, because the length of the zeolitic OH bond of the shell-1.5 model complex increases from 97.1 pm (SCF) to 103.3 pm (MP2) on inclusion of correlation. Since this bond length further increases to 104.8 pm for the shell-2 model complex, the ν(ZOH) frequency decreases to about 2300 cm^{-1}. However, because the BSSE affects the frequency in the opposite direction, we arrive at a final estimate of 2300−2600 cm^{-1} for the zeolitic OH stretch. This fits well into the range of about 2400−2600 cm^{-1} which is required to allow an interaction with the δ(ZOH) and γ(ZOH) overtones.

To give a complete interpretation of the observed spectrum, it remains to explain the band at 3500 cm^{-1}, not belonging to the A−B−C triplet. On the basis of the estimate for the shell-2 model complex of 3260 cm^{-1} and taking into account that the BSSE correction causes a shift of +100 cm^{-1}, we predict this frequency in the range of 3260−3360 cm^{-1}. Though the upper limit of the estimate approaches the range of observed frequencies of 3480−3576 cm^{-1}, a remaining deviation of 100−200 cm^{-1} leaves the question open of whether the observed band can be explained by a weakly perturbed methanol OH stretch or whether another surface species is responsible for this band.

So far, only vibrations involving the OH groups were discussed. While, for these, sizable shifts upon adsorption are observed, for the CH stretch frequencies of the CH_3OH methyl group this is not necessarily expected. In fact, Kubelkova et al.[6] and Mirth et al.[12] report only small CH frequency shifts between −6 and +12 cm^{-1}, which are not very specific. From our calculated MP2 frequencies of the shell-1.5 model complex (Table 6) we deduce CH stretch frequency shifts of +12, +43, and +24 cm^{-1} and +32, +81, and +49 cm^{-1} for the NC and IP structure, respectively. The predicted values of the IP structure are about twice as large as those of the NC structure. If the IP structure were present, its CH frequency shifts should be detectable in the IR spectra.

^{1}H NMR Chemical Shifts. High-resolution solid state ^{1}H NMR spectroscopy was mainly applied to zeolite catalysts loaded with more than one methanol molecule per bridging OH group.[12,21,22] To our knowledge, the only study which explicitly reports a chemical shift for a loading of one methanol per site is the multinuclear study of Luz et al. for the adsorption on zeolite H-rho.[23] It reports a shift of 10−12 ppm and explains the broad signal by chemical exchange between different proton positions at the acidic site. No information about the structure of the hydroxyl part of the adsorption complex is provided, however. For higher loadings, the observed ^{1}H NMR chemical shifts can be divided into two groups, 4.8−5.9 ppm for zeolites H-Y and H-L and different SAPOs[22] and 9.4 and 10.5 ppm for loadings of six and two methanol molecules per acid site in H-ZSM-5, respectively.[12,22] In the case of the adsorption on H-ZSM-5, the authors favored the interpretation in terms of a methoxonium ion because the very large high-frequency shift of the hydroxyl resonance compared to that in the neat methanol liquid indicates a very strong H-bond interaction.[12,21,22]

In a recent study, we reported the ^{1}H chemical shifts of the IP and NC complexes which were optimized at the SCF level.[50] In the upper part of Table 7 the data of this study are shown. When making comparisons with observed chemical shifts, it is very important to make sure that the data refer to a loading of one molecule per acid site; this is the situation modeled in our calculations. For methanol adsorbed on H-rho at this loading, a hydroxyl shift in the range of 10 to 12 ppm was measured.[23] The calculated chemical shift of the IP complex of the largest model of 15.3 ppm exceeds the observed one by 3−5 ppm, while the value obtained for the NC complex of the shell-2 model of 5.7 ppm is also far off the observed value. However, because the observed shift is in between the calculated shifts for the neutral and ion-pair complexes, agreement between calculated and observed data can always be established by assuming that an equilibrium between these two structures exists and that both structures contribute to the observed shift. Our calculations do not support this assumption since no local minimum on the PES was found for the IP structure.

As in the case of the calculation of vibrational frequencies, the calculation of the ^{1}H NMR shifts at MP2-optimized structures lead to significant changes even for the neutral structures. This is another illustration of the general observation that chemical shifts are structure sensitive and, therefore,

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(50) Haase, F.; Sauer, J. *J. Phys. Chem.* **1994**, *98*, 3083.

comparison of calculated and observed shifts is a powerful means of assessing structure proposals. The predicted values of the NC structures of all three models between 10.8 and 11.1 ppm are in good agreement with the observed shift of 10−12 ppm for methanol adsorbed on H-rho.[23] This is an independent argument against an equilibrium (see above). Now the observed chemical shift can be explained by the chemical shift of a single structure—the NC structure. The chemical shifts of 19.1−17.4 ppm predicted for the hydroxyl protons in the IP complexes exceed the observed shift by about 7 ppm.

We also calculated the chemical shifts of the free zeolite models (first column of Table 7). These shifts are virtually identical for both SCF- and MP2-optimized structures. While the chemical shift predicted for the shell-2 model is smaller than the experimental shifts of bridging hydroxyl groups (3.6−4.3 ppm[23,51]), the value calculated for the faujasite model of 4.2 ppm agrees well with the shifts observed for the more acidic faujasites (3.9−4.0 ppm for HY[51]).

Luz et al.[23] assign a sharp peak at 3.7 ppm to the methyl protons. Our calculations predict values of 3.9 and 4.0 ppm for the methyl protons in the NC and IP structure, respectively, of the shell-2 model complex. Thus, the methyl proton shifts cannot give clues on which structure is present. However, the agreement between the calculated and observed values lends further credit to the reliability of the calculated chemical shifts.

General Aspects. The results reported above were obtained for a bridging OH group in an abstract model of a zeolite catalyst. Moreover, they refer to a loading of one methanol molecule per active site. When comparison is made with experimental results of the adsorption of methanol, it should be kept in mind that the acidity of the active site in a real catalyst may be affected by both its composition and its framework structure and that the basicity of a methanol cluster is larger than that of a single methanol molecule. These factors will directly affect the proton transfer energy, ΔE_{PT}, as is obvious from the following hypothetical decomposition.

$$\text{Z-OH}\cdots\text{M} \rightarrow \text{ZO}^-\cdots\text{HM}^+$$

$$\text{Z-OH} \rightarrow \text{ZO}^- + \text{H}^+ \qquad (1)$$

$$\text{M} + \text{H}^+ \rightarrow \text{HM}^+ \qquad (2)$$

$$\text{Z-OH}\cdots\text{M} \rightarrow \text{Z-OH} + \text{M} \qquad (3)$$

$$\text{ZO}^- + \text{HM}^+ \rightarrow \text{ZO}^-\cdots\text{HM}^+ \qquad (4)$$

For the hypothetical gas phase proton transfer reaction, ΔE_{PT} is obtained as

$$\Delta E_{PT}(\text{gas phase}) = \Delta E(1) + \Delta E(2)$$

where $\Delta E(1)$ is the energy of deprotonation of the surface OH group (related to the acidity) and $\Delta E(2)$ is the proton affinity of the adsorbate. The proton transfer energy of a heterogeneous reaction as considered here is the sum of the hypothetical gas phase energy and the change of the binding energy of the adsorbate on proton transfer, $\Delta E(3)+\Delta E(4)$:

$$\Delta E_{PT} = \Delta E_{PT}(\text{gas phase}) + \Delta E(3) + \Delta E(4)$$

where $\Delta E(3)$ is the negative adsorption energy of the neutral complex discussed above. Since it is known that the acidity of zeolite catalysts varies with their framework structure and composition, the ΔE_{PT} value can be slightly smaller or larger than the values calculated in this work. However, the variation will be small because there is some compensation between the energy of deprotonation (1) and the binding energy of the IP structure (4). If the surface OH becomes more acidic, i.e., $\Delta E(1)$ gets a less positive value, its conjugated acid becomes less basic and, hence, $\Delta E(3)$ gets a less negative value. Nevertheless, one could argue that for some catalysts the IP structure eventually becomes a minimum on the PES even for a loading of one molecule per Brønsted site. In this situation, the analysis of the NMR and IR spectra observed on adsorption on a particular zeolite becomes crucially important. The IR spectra observed for methanol on H-ZSM-5 and the ^{1}H NMR spectra observed for methanol on H-rho and H-ZSM-5 do not agree with the predictions from the present calculations for the IP structure.

If the loadings become higher, the IP structure becomes more likely because the proton affinity is larger for a methanol dimer or trimer than for a single molecule. IR spectroscopic evidence has been produced which seems to support this conclusion.[52]

Conclusions

We localized two stationary points on the PES of the adsorption complex of methanol with a series of zeolite models. Theoretical predictions were made for the ^{1}H NMR chemical shifts and the vibrational frequencies of two possible structure types of the adsorption complex, the neutral (NC) and the ion-pair (IP) structures which correspond to the stationary points. From the results we gather that the inclusion of electron correlation is essential for reliable predictions of the adsorption structures and, hence, of the vibrational frequencies and chemical shifts which are evaluated at these structures. Specifically, we reach the following conclusions:

(i) The IP structure of the methanol adsorption complex is not a minimum but a saddle point of first order (exceptionally second order for the shell-2 model complex) and, hence, represents a transition structure for the proton transfer between different O-sites of the lattice via an adsorbed methanol molecule. Even for a zeolite model comprising structural elements of the faujasite framework (Figure 2), an optimization which starts from an IP structure yielded the corresponding NC complex. We characterize the PES for the adsorption of methanol as a broad and shallow potential well which accommodates both the NC structure and the IP structure (Figure 3). The barrier for the proton transfer amounts to only a few kJ/mol. Comparing a recent experiment,[28] we predict a weaker interaction of methanol with the zeolite catalyst. The calculated adsorption energy is expected to increase when larger models can be treated and a larger portion of dispersion energy is obtained by extending the basis sets.

(ii) The hydroxyl proton signal observed in the ^{1}H MAS NMR spectra of adsorbed methanol can be explained by the chemical shift of one structure—the NC structure—while the predicted chemical shifts of the IP complexes are far off the observed hydroxyl signal. This renders the assumption of an equilibrium between both structures superfluous.

(iii) The calculated vibrational frequencies make it hardly conceivable that the observed bands of an IR spectrum are due to a surface methoxoniumion. The frequencies of the IP structure predicted on both the SCF and MP2 levels do not permit a consistent explanation of the observed spectrum. The interpretation in terms of an NC structure is only plausible if a spectroscopic model—the so-called A−B−C pattern—is adopted, which explains the observed bands as a result of Fermi

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resonance of the strongly perturbed zeolitic OH stretch with the OH bending overtones. We find that the required large red shift of the zeolitic OH stretch frequency and the blue shift of the in-plane and out-of-plane OH bending frequencies can be explained by H-bond formation with neutral methanol (NC structure) when electron correlation is taken into account. The assignment of the band observed at about 3500 cm^{-1} is not clear so far. Keeping in mind the broad and shallow potential well which connects both structures, we conclude that a nonconventional treatment of the dynamics may be necessary to understand the observed transitions between the eigenstates of the moving nuclei.

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