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Integrated NMR and Ab Initio Study of Acetonitrile in Zeolites: A Reactive Complex Model of Zeolite Acidity

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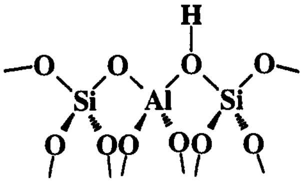
Abstract: Experimental and theoretical methods have provided a detailed view of the mechanism of proton transfer from a zeolite to a weak base. The NMR behavior of acetonitrile in acidic zeolites differs significantly from that in superacid solution and implies a different structure for the protonated species. ^{13}C and ^{1}H chemical shifts are strongly and reversibly temperature dependent for acetonitrile in zeolite HZSM-5—in the high-temperature range used for most catalytic applications of zeolites. The experimental results were first used to propose a qualitative model in which progressive proton transfer occurs with increasing temperature, resulting in a partial charge on the nitrile carbon. Ab initio Hartree–Fock–Roothaan calculations using finite clusters to model the acid site were carried out to refine this model and test alternate hypotheses. The minimum energy conformation for the acetonitrile–zeolite cluster in a large channel is a hydrogen-bonded complex. The effects of increased temperature and reduced channel size were simulated by introducing constraints prior to the geometry optimization in a manner so as to sample higher energy conformations and close contact with the channel wall. Those calculations yielded a family of structures describing proton transfer from the zeolite to the weak base within the complex. Hydrogen-bonded acetonitrile bends at higher energies; for bend angles near 165°, the energies for zeolite protonation and N protonation cross. The accuracy of the calculated structures was tested by using ab initio methods to calculate the ^{1}H and ^{13}C chemical shifts of the clusters and related models. Only bent structures accounted for the ^{13}C shifts, and calculated ^{1}H shifts for the cluster models were in complete agreement with experiment. The (reversible) reaction between the Bronsted acid site and the weak base acetonitrile should be viewed as a cooperative or concerted process, rather than simple proton transfer from a superacid to a base. Changes in the structure of the base drive proton transfer as the complex moves along the reaction coordinate. The temperature-dependent NMR behavior of acetonitrile in various zeolites is sensitive to differences in acid strength and zeolite framework. Relative energies derived from Hartree–Fock–Roothaan calculations were used to construct potential wells for quasi-one-dimensional models of zeolites with different pore diameters. These models rationalize the different temperature dependence in the medium and large pore zeolites and suggest that confinement of the weak base near the acid site is an important aspect of reactivity in acidic zeolites. The integration of experiment and calculation demonstrated here is a more rigorous alternative to the use of qualitative chemical shift arguments to deduce structure, and it permits closure between theory and experiment.

Introduction

The interaction of weakly basic reactants with the Bronsted sites of zeolites[1-3] and other solid acids is central to an understanding of heterogeneous catalysis. As established by a number of experimental and theoretical studies, the local structure of the Bronsted site of zeolites looks much like the cluster shown below. The acidic proton is covalently bound to one of the oxygens on the lattice aluminum for which it provides charge compensation.



One of the means by which a description of the acidity of solids is emerging is the use of theoretical methods to calculate properties such as the proton affinity for clusters like the one above with the dangling bonds terminated by hydrogen.[4,5] As pointed out by Kramer and van Santen, however, this approach neglects the possibility that the properties of the specific conjugate base influence the acidic behavior of the cluster.[6] Furthermore, there is some indication based on experimental[7,8] and theoretical studies that the framework oxygens of the zeolite may also participate in the stabilization of species that are formally carbenium[9,10] or carbonium[11] ions.

Experimental approaches for the characterization of solid acidity have included nuclear magnetic resonance (NMR)[12-17]

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or infrared spectroscopy (IR)[18-21] studies of various probe molecules on acidic sites. In some cases these probes have been strong bases that should not be expected to model well the interaction of the acid site with the weak bases (such as hydrocarbons) that are the reactants in many catalytic processes. Furthermore, most spectroscopic studies of probe molecules on zeolites have been carried out at room temperature in spite of the fact that most catalytic applications of zeolites require elevated temperatures. Thus, many studies have failed to distinguish between measuring acid strength per se and chemical reactivity. Another fundamental problem with most spectroscopic studies of adsorbates on surfaces has been the need to invoke qualitative arguments to develop models to account for spectroscopic observables such as chemical shift changes and the difficulty of testing such models.

Experimental and theoretical methods for studying zeolite acid sites have begun to mature in recent years, and the convergence of these approaches is a realistic goal. We report extensive NMR experiments and ab initio calculations probing the structure of the adsorption complex formed between acetonitrile and the zeolite Bronsted site. Acetonitrile was selected for a number of reasons. It is a weak base that can discriminate between different degrees of strong acidity. Its size and structure are evocative of typical reactants in zeolite-catalyzed reactions, but unlike olefins,[7,22] ketones,[23] or alcohols,[24,25] it does not decompose or oligomerize, even at 623 K. Thus one can observe structural changes in the reactive complex formed between acetonitrile and the acid site without loss in steady-state concentration due to product formation. This complex does indeed react, if water is present, to form acetamide. The acetonitrile–zeolite system provides a variety of spectroscopic observables, and using suitable cluster models for the acid site, this system is tractable by a variety of ab initio molecular orbital methods. Temperature dependence was introduced into the structural calculations by introducing constraints that allowed exploration of higher energy coordinates in configuration space.

The essence of the approach used here was as follows. Qualitative models for the interaction of acetonitrile with the acid site were developed from NMR and, to a lesser extent, infrared experiments. These models were tested, and the promising ones were refined by using restricted Hartree–Fock–Roothaan calculations of the structures and energies of acetonitrile–zeolite clusters subject to various constraints. The resulting models were then compared with experiment by using other ab initio methods to calculate spectroscopic observables (chemical shifts) for each theoretical structure. This procedure resulted in a self-consistent view of an acid–base reaction in zeolites that is significant in both its detail and its differences from conventional acidity in either the solution or gas phase. We conclude that proton transfer from the zeolite to acetonitrile is a temperature-dependent cooperative process. Adsorbed acetonitrile becomes bent at higher temperatures; the bent structure is more basic, and it is possibly stabilized by interaction with the zeolite framework. This explains the appreciable temperature dependence of the ^{13}C and ^{1}H chemical shifts of the acetonitrile–HZSM-5 system. Ab initio chemical shift calculations show that the proposed proton-transfer process fully accounts for the temperature dependence of the ^{1}H shift. The large experimental downfield shift of the nitrile carbon could only be reproduced for calculations of bent structures.

Acetonitrile reveals substantial differences between acidity in zeolites and acidity in solution. Experiments with larger pore zeolites and consideration of the disassociation of the acetonitrile–acid cluster suggest that confinement of the weak base near the acid site by the zeolite channel is a previously unsuspected characteristic of reactivity in acidic zeolites. The ^{13}C NMR behavior of acetonitrile in zeolites has nothing in common with that in superacid solution, reflecting differences in the strength and mechanism of acidity and the structures of the protonated species in the two media.

This study strongly suggests that the details of the interaction of specific weak bases with the acid site must be considered in treatments of catalysis by zeolites. Theoretical methods for calculating structures have matured to a level such that they can be used to develop models for adsorption complexes in zeolites. The recent availability of procedures for accurate ab initio calculations of chemical shifts[26,27] makes it possible to obtain closure between theory and experiment and to test the accuracy of proposed models with less dependence upon qualitative arguments.

Experimental Section

Materials. Zeolite HZSM-5 was obtained from various sources. For consistency, all of the experiments reported here were obtained on a sample with Si/Al = 19 from UOP Corp. Conventional samples of zeolite HY were obtained from UOP (Si/Al = 2.5) and PQ Corp. (Si/Al = 2.55 and 19). A sample of steamed HY (Si/Al = 5) which has increased reactivity was obtained from Prof. Jack Lunsford.[28]

Anhydrous acetonitrile was obtained from Aldrich. Acetonitrile-d_3, acetonitrile-*1,2*-$^{13}C_2$, acetonitrile-*1*-^{13}C, and acetonitrile-^{15}N were obtained from Cambridge Isotopes.

NMR Spectroscopy. Zeolite samples were converted to the proton form (if necessary) and activated using procedures described elsewhere.[7] Adsorptions were performed using CAVERN methods.[29,30] Acetonitrile was studied using a wide range of loadings; most of the experiments reported here had loadings of 0.4–2.0 equiv (acetonitrile/acid site). NMR experiments were performed with magic angle spinning (MAS) using a Chemagnetics CMC-200 (^{13}C), CMX-300 (^{1}H), and CMX-360 (^{13}C and ^{15}N). Typically, several dozen scans were acquired for each ^{1}H spectrum, several hundred scans for each ^{13}C spectrum, and several thousand scans for each ^{15}N spectrum. All of the spectra reported in this contribution were obtained using quantitative Bloch decay conditions. ^{13}C T_1 values were measured by the inversion–recovery method, and ^{13}C T_2 values were measured using spin echoes with the τ period fixed as one or several times the rotor period. Active spin speed control was used for the latter experiments.

Acetonitrile was also studied in magic acid (Aldrich), on a Varian XL-200. The magic acid used was 25% SbF_5 in FSO_3H, giving a Hammet acidity of ca. −16.

Infrared Spectroscopy. Acetonitrile and acetonitrile-d_3 were studied on zeolite HZSM-5 using a Nicolet Model 510P FT-IR equipped with a Spectra Tech catalytic reaction chamber and a diffuse reflectance

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Table 1. Isotropic ^{13}C Chemical Shifts of Acetonitrile in Various Media (ppm)

	$-^{13}C{\equiv}N$	$-^{13}CH_3$
$CDCl_3$	117	1.8
magic acid[41]	108	-3.2
magic acid (this work)	108.5	0.1
HZSM-5 at 296 K	119	0.4
HZSM-5 at 433 K	138	1.3
HZSM-5 at 523 K	167	1.8

accessory. A flow system based on several MKS mass flow controllers was used to activate the catalyst in situ under flowing nitrogen and then to introduce or remove the adsorbate as the temperature was stepped up or down.

Structural Calculations. The atomic positions of Si, Al, and nonbridging oxygens were fixed at their experimentally observed positions in the zeolite HZSM-5 crystal structure.[31] Terminal hydrogen atoms were fixed using the normal O–H distance of 0.96 Å and the tetrahedral angle. The positions of the two bridging oxygens were optimized along with the carbons and nitrogen of acetonitrile and the acidic proton.

Basis sets with ab initio effective core potentials were employed in these calculations.[32,33] Geometry optimizations at the restricted Hartree–Fock–Roothaan[34,35] level were implemented using the GAMESS software package.[36] For the fixed OH groups, an ECP valence-only basis set in minimal contraction was used for oxygen atoms and an STO-3G basis set was used for hydrogen atoms. Double-ζ basis sets were used for all other atoms.[32,33]

These calculations were carried out on the Cray YMP-M98-4Gw-8 at the Supercomputer Center of Cray Research, Inc.

Chemical Shift Calculations. These were carried out using the TURBOMOLE[37] and TurboNMR[38] programs.[39] TurboNMR uses the gauge-independent atomic orbital/coupled-perturbed Hartree–Fock method to calculate nuclear shielding tensors.[26,27,40] All results are reported as chemical shifts in ppm from tetramethylsilane (calculated values). TURBOMOLE and TurboNMR employ the direct self-consistent field methodology for efficient use of computer resources. Calculations were carried out on workstations including a SGI Power Series 320 and a SGI Indigo 2/Extreme.

Results

NMR Studies of Acetonitrile in Solution. The protonation of acetonitrile in superacid solution was originally studied in the 1960s using INDOR to measure ^{13}C shifts,[41] the results of that investigation were repeated and confirmed by the present authors using direct ^{13}C observation. Some of the more pertinent experimental ^{13}C chemical shifts are summarized in Table 1.

Acetonitrile (**1**) is a relatively weak base, and superacids such as FSO_3H/SbF_5 (magic acid) are required to drive the protonation equilibrium to completion. It was previously recognized that distinct valence isomers could be written for protonated acetonitrile;[41] structure **2** places the charge on nitrogen and preserves sp hybridization, but structure **3** proposes a charge on carbon and sp^2 hybridization. Qualitative chemical shift arguments would suggest a modest upfield shift in the nitrile ^{13}C resonance upon formation of **2** but a large downfield shift upon formation of **3**. As shown in the previous work[41] and confirmed here, protonation of acetonitrile in magic acid solution results in a 10-ppm upfield shift. We agree with Olah and co-workers that structure **2** accounts for protonated acetonitrile in solution.

$H_3C{-}C{\equiv}N$

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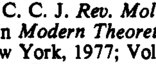
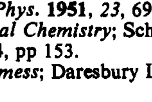


$H_3C{-}C{\equiv}\overset{+}{N}{-}H$

2



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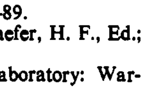

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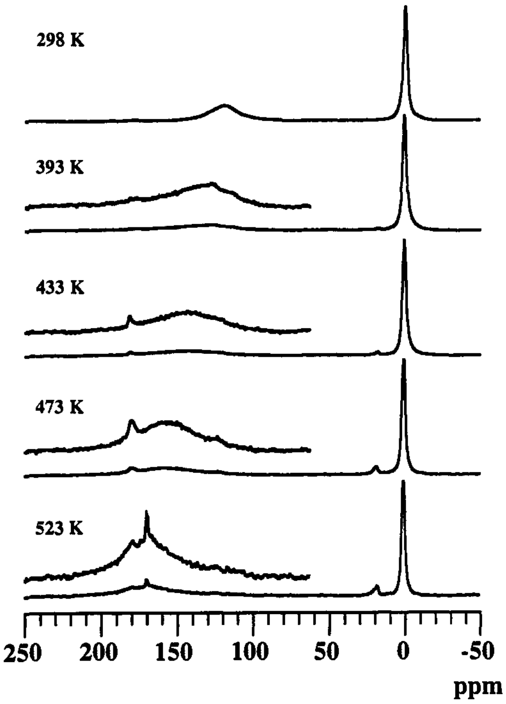

Figure 1. Variable-temperature ^{13}C MAS NMR spectra of acetonitrile (1.4 equiv) on zeolite HZSM-5. The essential observation is a reversible downfield shift of the nitrile carbon resonance with increasing temperature. Irreversible formation of a small amount of acetamide can also be seen in this figure.

NMR Studies of Acetonitrile in Zeolite HZSM-5. The NMR properties of acetonitrile in acidic zeolites have little in common with their properties in superacid solutions. Figure 1 reports a representative variable-temperature ^{13}C MAS NMR study of acetonitrile-*1,2-*^{13}C (1.4 equiv) in zeolite HZSM-5. The shifts and line widths observed for this system scaled in the expected manner with acetonitrile loading; with 1 equiv or less of acetonitrile, the lines were too broad for easy observation at higher temperatures, and with 2 or 3 equiv, smaller shifts and narrower lines were observed. The chemical shift of the nitrile ^{13}C in HZSM-5 at 298 K was essentially identical to its value in $CDCl_3$ (Table 1), although it was obviously broadened at that temperature (Figure 1). Increasing the temperature resulted in progressively larger downfield shifts and greater line widths for the nitrile ^{13}C and smaller effects in the same directions for the methyl ^{13}C. The chemical shift observed for the nitrile ^{13}C at 523 K, 170 ppm (or higher if normalized by the loading), is clearly inconsistent with the superacid solution structure **2**.

With dry samples, the effects of cycling the temperature between 298 and 523 K were completely reversible and no reactions were observed. When water was also present on the zeolite, acetonitrile was hydrolyzed at temperatures of ca. 473 K and higher to form acetamide **4**. This reaction was confirmed by adsorbing various amounts of water as well as by extracting **4** from the zeolite and identifying it by GC–MS.

The source of line broadening in spectra like Figure 1 and the dynamics of acetonitrile in HZSH-5 were studied by standard methods. No spinning sidebands were observed in ^{13}C or ^{15}N

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Table 2. ^{13}C Spin-Lattice (T_1) and ^{13}C Spin-Spin (T_2) Relaxation Times for Acetonitrile on Zeolite HZSM-5 (All Times in ms)

		4.7 T		8.4 T	
		$-^{13}C{\equiv}N$	$-^{13}CH_3$	$-^{13}C{\equiv}N$	$-^{13}CH_3$
296 K	T_1	63.3	118.2	58.5	93.8
	T_2	0.8	2.0	0.4	1.8
353 K	T_1	32.5	92.6	41.6	75.8
	T_2	0.6	1.6	0.4	1.4
433 K	T_1	20.5	79.1	*a*	69.9
	T_2	0.4	1.8	*a*	1.0

[a] Resonance too broad at this temperature to calculate relaxation parameters.

MAS spectra of acetonitrile, even at very low spinning speeds. Thus, large-amplitude motions are present for acetonitrile on HZSM-5 at $T > 298$ K on a time scale of 10^{-3} s or less, and these average out the orientation dependence of the ^{13}C chemical shift. ^{13}C T_1 and T_2 values were measured at several temperatures at 4.7 T and 8.4 T; these data are presented in Table 2. No simple model seems to explain these data quantitatively, but the gross effects of temperature and field suggest a combination of CSA and dipole–dipole relaxation mechanisms on the long correlation time side of the T_1 minimum, i.e., $\tau_c > 1/\omega_0$.[42] The possibility that the line broadening resulted from proton exchange on the time scale of decoupling[43] was excluded by measuring the line width on deuterated zeolite samples. Our view of the dynamics of acetonitrile on HZSM-5 at loadings slightly above 1 equiv is that exchange between free molecules and molecules adsorbed on the acid site occurs with a rate of $>10^3$ s^{-1}, even at 298 K, and that the molecule undergoes large-amplitude motions with a correlation time 10^{-8} s $< \tau_c < 10^{-3}$ s over the temperature range studied.

Figure 2 reports a variable-temperature ^{15}N MAS study of acetonitrile-^{15}N on HZSM-5. Severe line broadening was apparent for this nucleus when the temperature was raised slightly above ambient, even with high sample loadings. We did not investigate the mechanism of line broadening for ^{15}N. We speculate that the same relaxation mechanisms that broaden the nitrile ^{13}C are even more effective for ^{15}N in this case. We were unable to measure the temperature dependence of the ^{15}N shift with any confidence, and this nucleus is excluded from further discussion.

^1H MAS NMR has been used extensively to characterize the acid site in zeolites[44–46] and also to probe its interactions with adsorbates.[47–49] Prior to adsorption, the Bronsted proton site had a chemical shift of 4.3 ppm (Figure 3), but this was shifted to 11.5 ppm by adsorption of acetonitrile (0.9 equiv) at 298 K. Heating resulted in an initial further increase in the chemical shift to 11.7 ppm, but this shift reversed direction at 400 K and moved back to 9.2 ppm at 523 K.

NMR Studies of Acetonitrile in HY Zeolites. Significant differences in the ^{13}C MAS NMR behavior of acetonitrile were observed in other types of zeolites. Figure 4 shows plots of nitrile ^{13}C shifts vs temperature for different preparations of zeolite HY and HZSM-5 for comparison. The chemical shift in HZSM-5 increased continuously with temperature over the entire range studied. Steamed samples of zeolite HY prepared in the manner of this one are believed to be more acidic than standard samples as a result of the reduced framework aluminum content[50] as well as the electron-withdrawing effect of the extraframework aluminum species.[28,51–54] Figure 5 shows that the behavior of

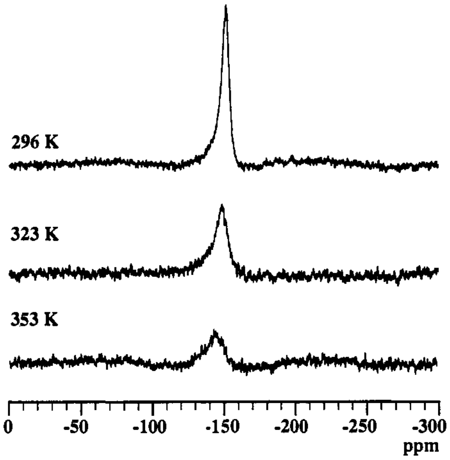

Figure 2. Variable-temperature ^{15}N MAS NMR spectra of acetonitrile (2.0 equiv) on zeolite HZSM-5. This nucleus also broadened at higher temperature, so much so that a determination of the temperature dependence of the chemical shift was precluded.

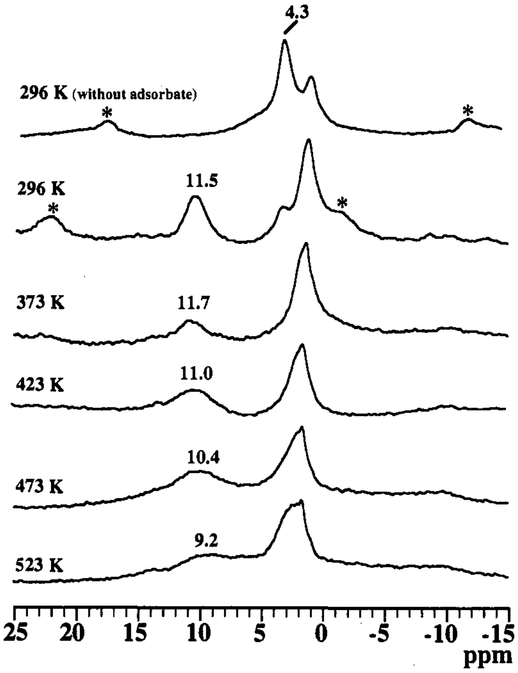

Figure 3. Variable-temperature ^1H MAS NMR spectra of acetonitrile-d_3 (0.9 equiv) on zeolite HZSM-5. Adsorption at room temperature shifted the Bronsted proton resonance from 4.3 to 11.5 ppm, and the temperature dependence of this shift is indicated. The signal intensity in the vicinity of 2.5 ppm increased when acetonitrile-d_3 was adsorbed, indicating proton–deuterium exchange with the zeolite after several hours. * denotes small spinning sidebands seen at lower temperatures with or without adsorbate.

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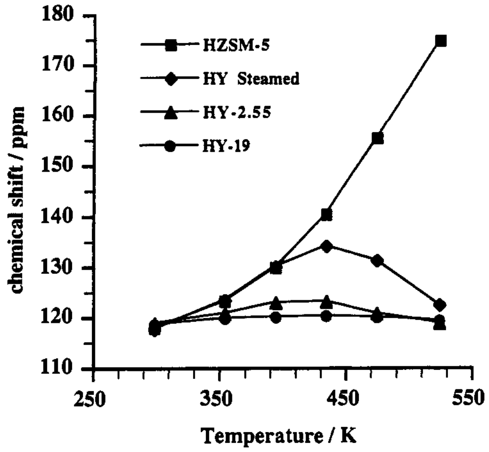

Figure 4. Summary of the temperature-dependent ^{13}C isotropic chemical shifts for the nitrile carbon of acetonitrile on various zeolites (see text). Loadings were in the range of 0.3–0.9 equiv.

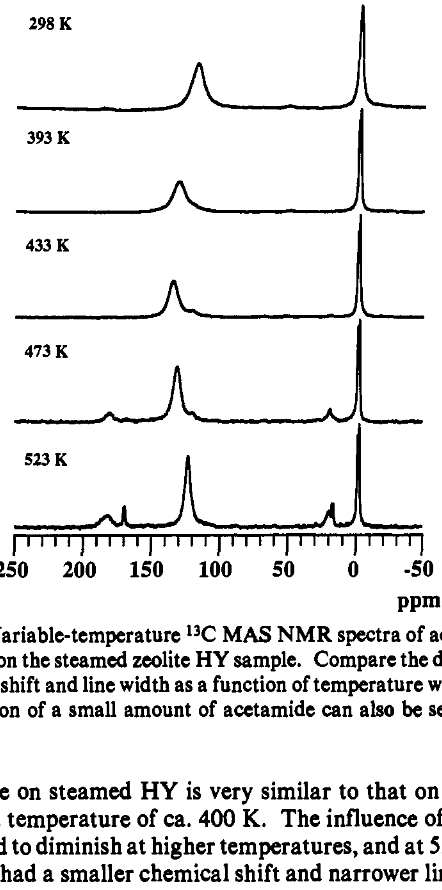

Figure 5. Variable-temperature ^{13}C MAS NMR spectra of acetonitrile (0.4 equiv) on the steamed zeolite HY sample. Compare the differences in chemical shift and line width as a function of temperature with Figure 1. Formation of a small amount of acetamide can also be seen in this figure.

acetonitrile on steamed HY is very similar to that on HZSM-5—up to a temperature of ca. 400 K. The influence of the acid site seemed to diminish at higher temperatures, and at 523 K, the resonance had a smaller chemical shift and narrower line width. Several samples of Si/Al ratio around 2.5 were studied, and all showed a very slight downfield shift with temperature followed by a reversal to the ambient chemical shift. The HY sample with a Si/Al ratio of 19 showed no effect with temperature (see Figure 4). This agrees with previous reports that very high Si/Al ratio zeolites are not strongly acidic.[50]

Infrared Experiments. Acetonitrile and acetonitrile-d_3 were studied on zeolite HZSM-5. The deuterated compound is preferred, as the location of the C—D stretch avoids a Fermi resonance between C—H stretch and an overtone of the C≡N stretch.[55] Figure 6 shows variable-temperature spectra of acetonitrile-d_3 on zeolite HZSM-5 acquired in diffuse reflectance mode. The region below 1600 cm^{-1} was dominated by framework absorptions, and the bending modes in the far-infrared could not be observed on the instrument used. Studies similar to this one also showed that slow H–D exchange between the adsorbate and zeolite commenced upon prolonged heating as evidenced by the gradual replacement of the O—H stretches for the free Bronsted site (3610 cm^{-1}) and external silanol (3740 cm^{-1}) and bands due to complexed acid sites with their analogous O—D stretching bands. Other infrared studies (not shown) confirmed formation of acetamide when water was introduced at high temperature.

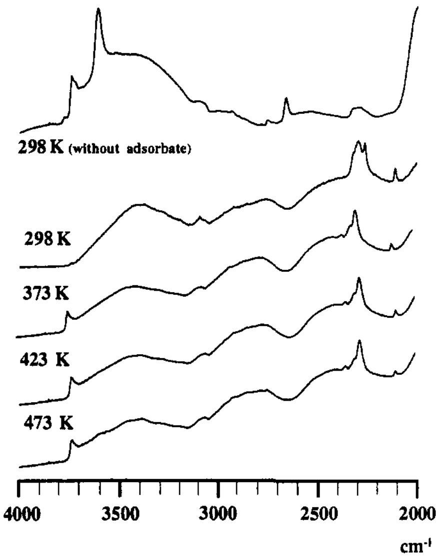

Figure 6. Variable-temperature FT-IR diffuse reflectance spectra of acetonitrile-d_3 flowing over a bed of zeolite HZSM-5.

Previous studies have used infrared spectroscopy to study acetonitrile on diverse catalysts at room temperature.[20,21,56] Most recently, van Santen and co-workers have used ab initio methods to assign some of the bands in the spectrum of acetonitrile-d_3 in various zeolites; the reader is referred to that paper for the full details of the assignment.[57] Briefly, the broad signals at 2900 and 2500 cm^{-1} at 298 K were shown to be characteristic of hydrogen bonding linking the nitrogen to the Bronsted proton and that in turn to the lattice oxygen. Figure 6 shows that the hydrogen-bonded complex persists at higher temperatures as well.

Ab Initio Structural Calculations. All calculations were performed for structures intended to model zeolite HZSM-5. Previous calculations of aluminum ordering in this zeolite[58,59] have shown that the most probable site for aluminum substitution is T6, which is located in a ten-ring, though the energy difference for Al substitution in other sites is small (3–5 kcal/mol). Figure 7 shows a depiction of acetonitrile hydrogen bonded to an acid site associated with T6. This view shows the molecule lying in the plane of the ten-ring directly above T6 and T5, although other orientations are also possible.

A number of preliminary calculations using different cluster models and various basis sets were performed in order to identify a model that could be handled with reasonable computation times. The excised cluster that we settled on for the ab initio calculations included the T5, T6, and T2 sites and the connecting oxygens (the tetrahedral sites are labeled in Figure 8;[31] thus, we treated three tetrahedral sites rather than the two-site models that are more commonly used. For simplicity, all of the calculations reported here were performed with the three heavy atoms of acetonitrile and the two bridging oxygens of the zeolite cluster constrained to the same plane.

The basis sets and methods used are expected to give reasonably accurate energy-minimized structures, a reliable sense of the

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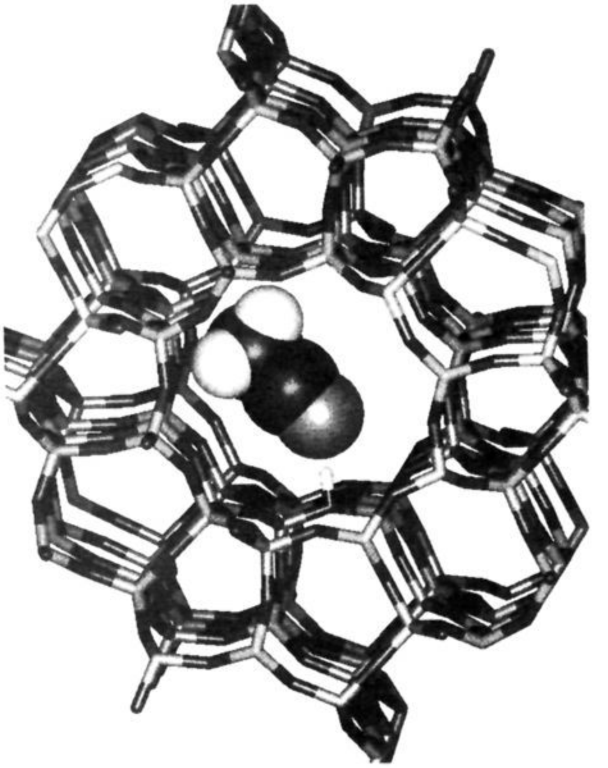

Figure 7. Depiction of an acetonitrile molecule hydrogen bonded to an acid site on T6 (Al) in zeolite HZSM-5. The view is down a straight channel; zig-zag channels run perpendicular. The van der Waals radii are shown for the adsorbate but (for clarity) not for the zeolite.

relative energies of various structures, but less accuracy for the absolute energies. Each of the structures shown in Figures 8, 9, and 10 required ca. 20 h of processor time on a Cray YMP.

Figure 8 models the formation of the adsorption complex when acetonitrile is adsorbed in zeolite HZSM-5 at low temperature. Taking the cluster and free acetonitrile at infinite distance (A) as zero, energy is released when the adsorbate and cluster form their minimum energy conformation B. This structure shows that acetonitrile forms a hydrogen bond to the Bronsted site with the lone pair on the nitrogen and the proton resides on the zeolite. This structure is similar to what one would predict on the basis of the rules developed for the structures of gas-phase hydrogen-bonded dimers.[60] The pair of nonbonding electrons on nitrogen preferentially interact with the acidic protons of HF,[61,62] HCl, and HC≡N[63] over the π-cloud electrons of the C≡N. Several calculations were attempted in which the proton was forced onto an undisturbed acetonitrile molecule to form the ion **2**; in every case, the proton was transferred back to the zeolite when the structure was allowed to relax. As suggested in Figures 7 and 8, structure B is too large for many possible locations in zeolite HZSM-5, which has channels on ca. 5.5 Å in diameter. Structure C was generated by constraining the distance between the nitrile carbon and the lattice oxygen bridging T5 and T6 to 2.85 Å. This change reduces the analogy to the gas-phase structure, but the energy difference between structures B and C is moderate. One implication of this and other calculations is that the potential well for the hydrogen-bonded complex is not steep in some directions, and this provides one mechanism for the large-amplitude motions inferred from the NMR studies.

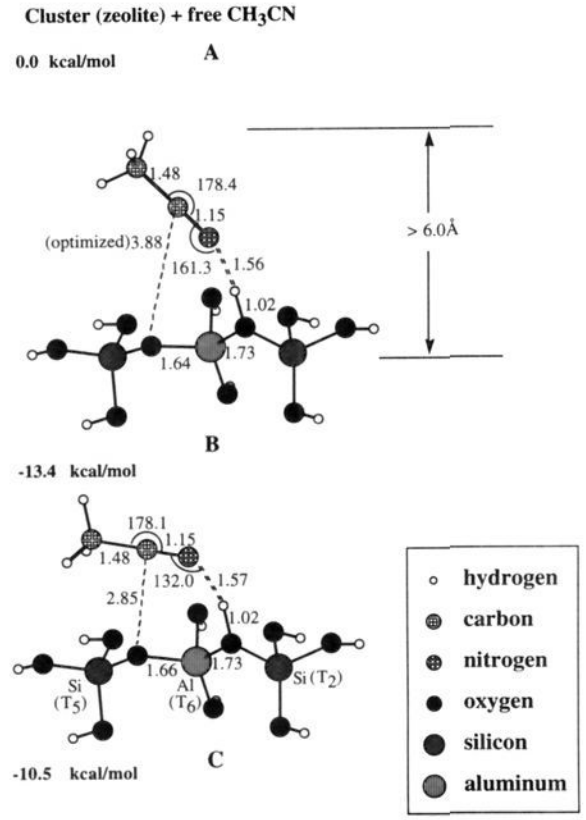

Figure 8. Hartree–Fock–Roothaan minimized structures for the finite clusters used to model acetonitrile on acidic zeolites and their associated energies (shown below each structure). Structure B is the lowest in energy, while structures such as C could be sterically favored in smaller channels.

These ab initio calculations seek to determine structures with the lowest energies subject to defined constraints and do not explicitly include temperature or vibrational motion. A method for treating higher temperatures is to explore the potential surface with suitable constraints to identify conformations that are thermally accessible either as equilibrium structures or as instantaneous displacements from equilibrium in vibrational motions. Figures 9 and 10 present sets of structures that were generated by two of the more interesting constraints that were explored.

Figure 9 shows the effects of shortening the constraint between the nitrile carbon and the T5–T6 bridging oxygen from 2.85 Å in structure C to 1.55 Å in structure H. In the Discussion we will argue that at higher temperatures the acetonitrile molecule collides with the zeolite acid site with greater force and, thus, spends more time sampling the higher energy conformations nearer to the wall. Figure 9 suggests that three concerted structural changes occur as the O–C distance is shortened to simulate higher temperatures: acetonitrile becomes bent; as this bending progresses, the N–H hydrogen bond becomes shorter, and as the angle reaches ca. 165°, the proton is transferred to the nitrogen; and these processes are accompanied by a shift in the coordinate bonding of aluminum from T2 to T5. Even though the acetonitrile is bent well away from 180° in many of the structures in Figure 9, the carbon–nitrogen bond distance remains consistent with sp hybridization until structures G or H.

We also considered bent structures in which the proton was constrained to be on nitrogen. For moderately bent structures, i.e. E, the energy difference between O protonation and N protonation was small; Figure 10 shows an example of this. Indeed, structure I was discovered before structure E as a result of a local minimum when the calculation was started with the proton on oxygen.

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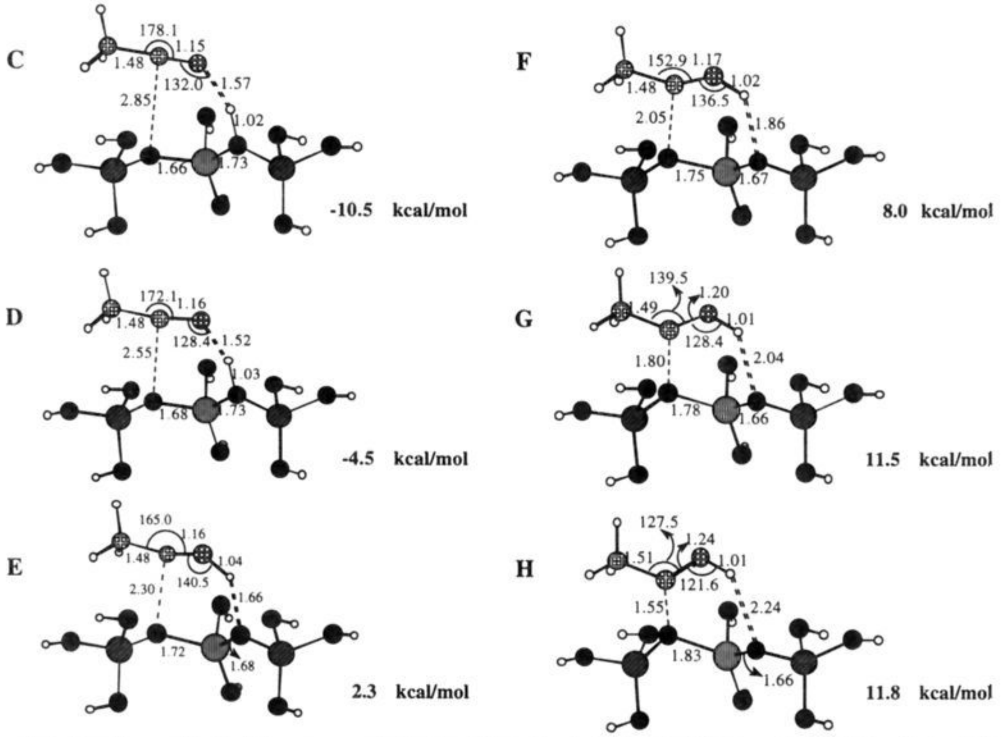

Figure 9. Hartree–Fock–Roothaan minimized structures exploring the effects of reducing the O–C distance to model the effects of higher temperature. As an artifact of this approach, the O–C distance must be shortened excessively to achieve the changes in structures shown. More accurate treatments would be expected to show comparable bend angles with slightly long O–C constraints. The trends in energies are expected to be accurate, but the values themselves (shown to the right of the structures) are exaggerated by the method used.

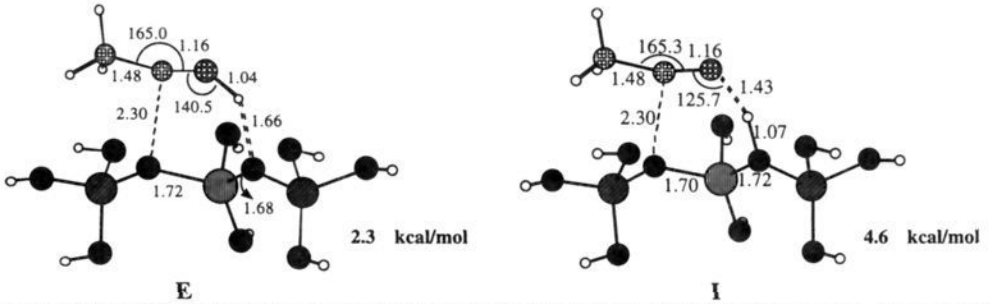

Figure 10. Illustration of the double potential well for the acidic proton that forms for moderate bending angles. These structures, which have comparable energies, were calculated using identical constraints but by starting the energy minimizations with the proton on N for structure E and on O for structure I.

In tracing out an approximate reaction path in this manner, i.e., by fixing one coordinate and relaxing all other coordinates as that fixed coordinate is moved over the reaction surface, one must be aware that the fixed coordinate will either underestimate or overestimate its true reaction path value depending on the slope of the reaction surface at that point. In other words, as the acetonitrile comes in closer to the zeolite surface because we are forcing an ever shorter C(nitrile carbon)–O(zeolite) distance, the C–O interaction will be overestimated (this C–O distance will be underestimated.) Thus, for most of the bent acetonitrile geometries, our structures should overestimate the effect that the zeolite's oxygen has on acetonitrile's chemical shifts and overestimate the energy required to reach the given geometry.

Table 3. Calculated ^{13}C Isotropic Chemical Shifts[a] for Acetonitrile Using Various Basis Sets

	STO-3G	DZ	DZP	6-31G**	expt[b]
$-^{13}C{\equiv}N$	107	127	117	116	117
$-^{13}CH_3$	16.2	−0.2	−0.3	1.3	1.8

[a] All values in ppm relative to calculated values for TMS. [b] In $CDCl_3$ solution.

Ab Initio Chemical Shift Calculations. The use of molecular orbital methods of varying levels of approximation to rationalize experimental chemical shift observations has a long history,[64] but only recently has the ab initio gauge-independent atomic orbital (GIAO) method of Ditchfield[40] developed for determining chemical shifts by Pulay and co-workers[26,27] allowed the accuracy of calculation to approach that of experiment, even for simple molecules. Recently, Grant and co-workers have demonstrated that these methods provide very accurate ^{13}C tensor data for crystalline aromatic hydrocarbons.[65–67]

Our starting point was to examine the effect of basis set on these calculations. Other workers[26,40] have previously shown that fairly high level basis sets are required for accurate calculations, and we also saw this. Table 3 reports values for the isotropic ^{13}C chemical shifts of free acetonitrile calculated with various basis

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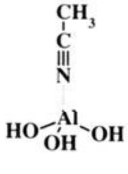
sets. It was necessary to go to the DZP or 6-31G** level in order to obtain accurate numbers for simple molecules like acetonitrile and tetramethylsilane. This reflects the failure of small basis sets to accurately represent the effective magnetic field felt by each nucleus due to the electron distribution around it. In order to be assured of accurate results, all-electron (no ECP) calculations using the 6-31G** basis set are reported here. Since these calculations were performed on computer workstations, a 28-atom zeolite–acetonitrile cluster can require ca. 21 h to obtain a single-point energy SCF in addition to ca. 12 h for the subsequent NMR chemical shift calculation on all nuclei. These timings are based on using a SGI Indigo 2/Extreme.

The NMR chemical shift calculations were used to test various models for the structure of acetonitrile in acidic media and thus provide closure between theory and experiment. These calculations determined the entire shielding tensors for each nucleus, but only isotropic shifts are reported, as the dynamics of the adsorbate precluded measurement of the anisotropy. ^{15}N calculations are not reported here, as we were unable to measure that nucleus experimentally at high temperature.

One hypothesis considered was that the chemical shift of the solution structure of protonated acetonitrile was strongly influenced by solvation in the superacid medium and that structure **2** could have very different ^{13}C shifts in different media. We tested this hypothesis by calculating shifts for an isolated **2** cation and obtained values almost identical to those measured in magic acid. This is not really surprising since an important property of superacids is that they are weakly coordinating. A second rejected hypothesis was that Lewis acid sites were somehow forming in the zeolite at high temperature and these were in some way responsible for the large downfield nitrile ^{13}C shift, in spite of some evidence to the contrary. Chemical shift calculations were performed for the two Lewis structures considered in ref 57 for zeolites prepared with Lewis sites, e.g. **5** and **6**. The calculated nitrile ^{13}C shifts were 112 and 110 ppm, respectively; these upfield shifts are in the expected direction for acetonitrile on Lewis acids. We thus conclude that Lewis sites do not account for the downfield shifts observed in the present investigation.



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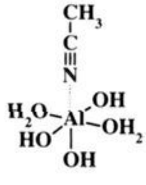

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The only models that provided large downfield shifts for the nitrile ^{13}C required the acetonitrile molecule to be bent. A number of calculations were performed for various bent structures excised from structures B–I, variations on those excised structures, and several of the full clusters in Figure 9. The latter were near the upper limit of complexity for the workstation used to perform the chemical shift calculations. Figure 11 introduces some of the structures on which chemical shift calculations were performed for the specific example of structures derived from cluster **F**. Analogous structures were derived using the appropriate bond distances and angles in Figure 9. Figure 11 also suggests the nomenclature scheme used for tabulating the calculated isotropic shifts in Table 4. Structure F′ is a free bent acetonitrile molecule excised from cluster F. F′H$_t$ and F′H$_c$ are bent protonated acetonitrile molecules in *trans* and *cis* conformations, respectively. F′H$_t$ has its structure taken directly form cluster F, and a 180° rotation of the N–H bond about the C–N bond generates F′H$_c$ from F′H$_t$. Structural calculations using models analogous to those in Figure 9 showed that *trans* geometries were preferred to possible *cis* arrangements. Chemical shift calculations are presented for the *cis* structures to reinforce the conclusion that the large downfield shift of the nitrile ^{13}C is a general consequence of the bending of the molecule and is not an artifact of a specific model. It should be recognized that structure F′H$_t$ is essentially the cation **3**. In a few cases, the zeolite lattice was approximated with two water molecules, and this structure would be named F′(H_2O)$_2$ for the structure derived from cluster F.

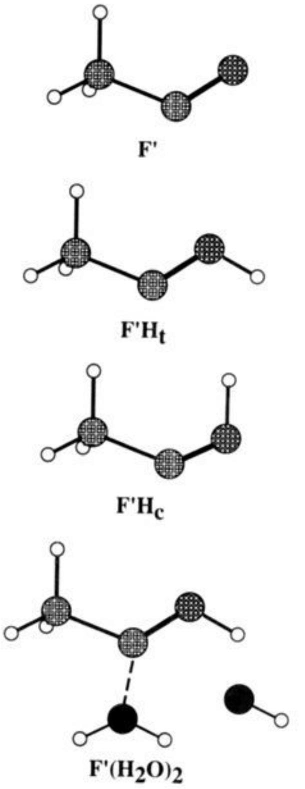


Figure 11. Depiction of the models derived from Figures 9 and 10 for tha ab initio chemical shift calculations reported in Table 4. The specific example of structures derived from cluster F is shown.

Table 4 shows that all of the bent structure types considered generate large downfield shifts for the nitrile carbon and this shift increases with the angle of bend. For the ^{13}C shifts, we have the greatest confidence in the calculations for the bent protonated species in the *trans* conformation (i.e., X′H$_t$ because these structures most closely model the proton transfer and bending processes without overemphasizing the interaction with oxygen expected as an artifact of the methods used for the constrained geometry optimizations. The trends observed in the series C′H$_t$ to H′H$_t$ (Table 4) reproduce the trend of the ^{13}C shifts as the temperature was increased.

In order to model the ^{1}H chemical shift, it is necessary to explicitly include hydrogen bonding to oxygen, and this requires either the full clusters or possibly the analogs constructed with water molecules. The ^{1}H shift should not be overly influenced by the degree of interaction between the nitrile carbon and the zeolite lattice. As Table 4 shows, the ^{1}H shifts calculated for the full clusters B, D, E, F, and H reproduce the temperature dependence of the Bronsted proton shift in every respect.

Discussion

Time Scales. Before comparing the results of different forms of spectroscopy and calculations, it is essential to consider the trajectory of the acetonitrile–HZSM-5 system through the space of populated conformations and the extent to which the various methods average over this trajectory.

The geometry-optimized calculations yielding structures A–I provide instantaneous views of possible conformations and a sense of the relative values for their associated energies. Consideration

Table 4. Calculated ^{13}C and ^{1}H Isotropic Chemical Shifts[a] for the Structures Defined in Figures 9 and 11

	$-^{13}C{\equiv}N$	$-^{13}CH_3$	acid ^{1}H
A	119	5.4	*b*
B′	115	4.5	*b*
$B'H_t$	118	6.1	21.7
$B'H_c$	118	6.1	21.6
B	115	5.3	13.4
C′	117	4.2	*b*
$C'H_t$	151	7.5	21.5
$C'H_c$	152	7.6	21.6
D′	117	4.3	*b*
$D'H_t$	156	7.9	20.7
$D'H_c$	160	8.5	21.1
D	130	11	15.9
$D'(H_2O)_2$	125	8.6	12.1
E′	118	4.3	*b*
$E'H_t$	143	8.0	9.6
$E'H_c$	151	9.5	11.1
E	115	5.3	13.4
F′	125	6.0	*b*
$F'H_t$	154	13	8.5
$F'H_c$	172	16	11.7
F	128	18	13.6
$F(H_2O)_2$	122	15	14.8
G′	140	8.4	*b*
$G'H_t$	180	21	8.2
$G'H_c$	222	27	14.0
H′	159	8.7	*b*
$H'H_t$	215	33	8.1
$H'H_c$	302	42	17.2
H	143	23	12.8
$H(H_2O)_2$	135	19	13.6
I′	119	4.7	*b*
$I'H_t$	161	9.1	19.2
$I'H_c$	170	10.0	20.0

[a] All values in ppm relative to calculated values for TMS. [b] Not applicable.

of vibrational motion and/or other dynamics requires calculations of structures and energies defining a much larger part of the potential surface.

The NMR experiments clearly show that this system is dynamic at the temperatures and loadings studied. Exchange occurs between free and bound acetonitrile and is fast on the NMR chemical shift time scale (10^{-3}–10^{-4} s, depending on nucleus and field strength). Large-amplitude isotropic reorientation is facile for uncomplexed acetonitrile, and large-amplitude restricted motions are implied for complexed acetonitrile by the low energy differences between some of the calculated structures, e.g. B and C. Since the dynamics are fast on the time scales of the NMR observables, i.e., ^{13}C and ^{1}H chemical shift, and ^{13}C T_1 and T_2, a weighted average picture of the system is given at any temperature.

The time scale of the infrared experiments is intermediate. A resolved infrared band should result from any mode that persists for at least a small number of vibrations, although this can be complicated by coupling between different modes. The time scale of several vibrations (ca. 10^{-12} s) is shorter than the time scales derived from the NMR measurements, so the infrared spectrum should be a superposition of subspectra from discrete species. Indeed, we have reproduced the observation of resolved $C{\equiv}N$ stretches for free acetonitrile and acetonitrile in various weak adsorption states as distinct species on the infrared time scale (see Figure 6, ca. 2300 cm^{-1}). In the case of strongly adsorbed acetonitrile, a number of mechanisms exist for homogeneous and inhomogeneous broadening of the bands as well as changes in transition probabilities. It is challenging to interpret the details of these spectra, especially with the interference from zeolite framework absorptions. Furthermore, we were unable to observe the bending modes in the far infrared.

Acetonitrile in Zeolite HZSM-5. The NMR properties of acetonitrile in HZSM-5 are clearly dissimilar from superacid solutions for which structure **2** was established. The ^{13}C isotropic shifts of **2** cannot be rationalized as being dependent on solvation. Structure **2** is rejected as a description of acetonitrile in zeolite HZSM-5. The only way in which we were able to reproduce the experimentally observed ^{13}C chemical shifts was with bent structures similar to **3**. The ab initio structural calculations in Figure 9 provide a plausible mechanism by which this bending occurs, and bending was required for transfer of the proton from the zeolite to the adsorbate. This model accounts in detail for the temperature dependence of the ^{1}H chemical shift.

The bent structures for acetonitrile are not unreasonable. The liquid-phase Raman spectrum of acetonitrile reveals that the degenerate bending modes are at very low energy, 380 cm^{-1} (ca. 1 kcal·mol^{-1}).[43] Reduction in symmetry by formation of B lifts the degeneracy of these modes, and the in-plane mode is expected to be further reduced in energy by hydrogen bonding.

The chemical shift calculations for the full clusters quantitatively reproduce the observed ^{1}H shifts as a function of temperature, but the calculated ^{13}C shifts are more accurate for excised structures such as the *trans* protonated species, $X'H_t$. As stated previously, an expected artifact of the method of introducing constraints into the Hartree–Fock–Roothaan calculations is that bending of the molecule and other structural changes lag behind the reduction in the O–C restraining distance. A more complete treatment of the dynamics would be expected to give bent structures with longer O–C distances. Furthermore, we constrained the acetonitrile to lie in the plain of the bridging oxygens, and this may over emphasize the O–C interaction. Thus, the fact that the $X'H_t$ structures model the chemical shift behavior of ^{13}C better than the full clusters is not surprising. Chemical shift calculations on the $X'(H_2O)_2$ structures as well as the enol tautomer of acetamide also attenuated the downfield shift of the nitrile ^{13}C and created an excessive shift for the methyl ^{13}C. In summary, we consider the chemical shift calculations to support the structures in Figure 9 in every respect except that either the O–C distance should be slightly longer or acetonitrile should lie outside the plane of the bridging oxygens.

Acetonitrile in HY Zeolites. Figures 4 and 5 show that the NMR behavior of acetonitrile is significantly different in different zeolites. This is a useful discovery; a number of NMR probe molecules have been proposed for examining solid acidity, but the ability to distinguish between zeolites of different acid strength or different framework has been demonstrated in only a few cases. The standard HY samples are expected to be weaker acids as a result of the well-established effect of framework aluminum content. The mechanism of strong acidity in mildly dealuminated HY has been described elsewhere.[28] Comparison of the ^{13}C NMR spectra in Figure 1 and 5 suggests that the interaction of the probe molecule acetonitrile with the acid sites of steamed HY is very similar to that in zeolite HZSM-5, at lower temperatures, but at higher temperatures the effect reverses.

Figure 12 shows a depiction of acetonitrile in zeolite HY analogous to that in Figure 7 for zeolite HZSM-5. A rigorous calculation of differences in the adsorption properties of the two zeolites could require a treatment of the unit cells, and this is beyond our present capabilities. Figure 13 suggests a very approximate model intended only to rationalize the differences in the temperature-dependent ^{13}C shift of acetonitrile. HZSM-5 has an intersecting channel structure with diameters of ca. 5.5 Å (see Figure 7). The faujasite structure of HY has pores ca. 7.4 Å in diameter and supercages ca. 12 Å in diameter (see Figure 12). Figure 13 describes two hypothetical quasi-one-dimensional zeolite structures. Each has two walls consisting of identical Bronsted acid clusters of the type used for the calculations in Figures 8–10. Acetonitrile can lie anywhere between these acid sites on opposing walls, but it is not allowed to diffuse away from this line. The two structures in Figure 13 differ only in the distance between the walls, 5.7 Å in one case and 11.4 Å in the other. The

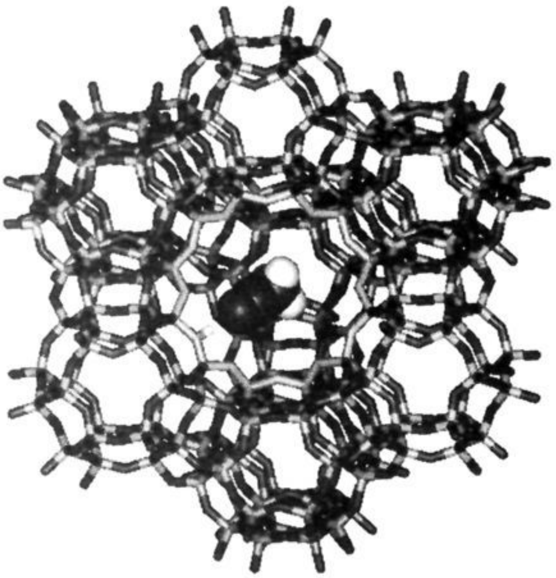


Figure 12. Depiction of an acetonitrile molecule hydrogen bonded to an acid site in the supercage of zeolite HY. Compare with Figure 7.

interactions between acetonitrile and the acid sites are modeled using the structures and energies in Figures 8 and 9. Figure 13 also shows the potential wells derived from the two models. For the smaller one-dimensional zeolite (intended to model HZSM-5), the acetonitrile molecule is forced to interact with an acid site in all of its possible conformations. At higher temperatures, acetonitrile samples the higher energy conformations of these model structures (i.e., C–H).

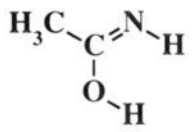
The larger structure gives rise to more complex behavior. The minimum in the potential well is very slightly deeper because structure B is accessible in the larger zeolite. Conformations C and D are sampled at moderate temperatures, but desorption from the acid site to form a "free" acetonitrile in the center of the channel is energetically favored over formation of structures E–H. This model qualitatively generates a temperature dependence for the NMR behavior in qualitative agreement with Figure 5, but much more detailed three-dimensional models and more accurate calculations of energies would be required for the explicit calculation of other observables.

Conclusions Regarding Zeolite Acidity. The acid strength of protonated acetonitrile ($H_o = -10.3$) has been estimated to be slightly below that of 100% sulfuric acid ($H_o = -12$) on the basis of solution measurements. Superacids, like magic acid ($H_o = -16$ in this experiment), are required to drive the protonation equilibrium to completion. The acid strength of a zeolite, like the acid strength of anything, is an operationally defined quantity, and different workers prefer different formalisms or figures of merit for quantifying acid strength. One recent proposal relates the degree of protonation of the weak base mesityl oxide as measured by ^{13}C chemical shifts to equivalent shifts in solution acids of varying strength.[68,69] Using this figure of merit, the acid strength of HZSM-5 has been estimated to be analogous to that of 70% sulfuric acid,[23] which has an acid strength of only $H_o = -6.4$. The observation that acetonitrile is not protonated to form **2** to a measurable extent is in agreement with the mesityl oxide study and would support a reclassification of zeolites as strong acids rather than superacids as they are commonly classified. Proton transfer to acetonitrile occurs at high temperature. Given the reactions catalyzed by zeolites, it may be reasonable to claim that they are superacidic at high temperatures, but in this study, proton transfer occurred at high temperatures within a complex whose structure is very different from that in superacid solution.

The most significant conclusion of this work is that the detailed properties of the reactive complex including the structural changes driving proton transfer are essential to an understanding of acid catalysis by zeolites. This implies that a half-reaction view of zeolite acidity, in which the properties of the specific weak base are ignored, may not be sufficient for an understanding of reaction chemistry. Indeed, it should be recognized that intrinsic acid strength and chemical reactivity are distinct properties and chemical reaction rates are strongly dependent on the properties of the transition state.

This study reveals some of the limitations of invoking analogies between zeolite acidity and either solution or gas-phase acidity. Acetonitrile in HZSM-5 did not form the same protonated structure that it forms in superacid solutions, but the interaction of the adsorbate with the zeolite framework is weakly analogous to solvation of the conjugate acid, an important consideration in solution equilibria. Structure B is analogous to the gas-phase hydrogen-bonded dimers formed between acids like HCl and many weak bases with unshared pairs of electrons. Yet, confinement of the adsorbate in the zeolite channels leads to deviations from the gas-phase analogy: structure B is too large for many orientations in medium-pore zeolites; confinement in the zeolite channel leads to a very high effective concentration of acid sites relative to most gas-phase studies; and the possible interaction of the base with zeolite lattice oxygens is not easy to treat with simple gas-phase models. Analogies between zeolites and solution or gas-phase results should be invoked when they provide organizing principles, but their limitations should be understood.

Reaction Chemistry—Acetamide Formation. A virtue of acetonitrile for this study was its unreactivity. Probes like propene, acetone, or acetylene interact with zeolite acid sites in interesting ways, but their oligomerization chemistry provides added complexity to their spectroscopic study, especially at higher temperatures. The one reaction of acetonitrile observed in this investigation was hydrolysis at high temperature to make acetamide. The standard mechanism for this reaction in acidic solution involves the formation of the enol of acetamide (**7**), which then tautomerizes to the amide form. Structure H in Figure 9 bears a close analogy to **7**. Several spectroscopic studies[7,8] and some theoretical work[9] have described the formation of species covalently bound to zeolite oxygens which are very readily hydrolyzed to the corresponding alcohols. The vinyl species formed from acetylene in HZSM-5 hydrolyzed to form acetaldehyde through the corresponding enol.[70] A reasonable explanation for the formation of acetamide in this study is that formation of bent structures such as H lowers the barrier for hydrolysis of acetonitrile.



$H_3C{-}C(OH){=}N{-}H$

7

Synergism between Theory and Experiment. This study and several other recent investigations[10,11] have demonstrated that the combination of experimental and theoretical approaches is both possible and productive for zeolite chemistry. The cluster models used in the present investigation are actually easier to treat with ab initio molecular orbital calculations than many organometallic compounds for which these approaches are already resolving structural controversies.[71–73]

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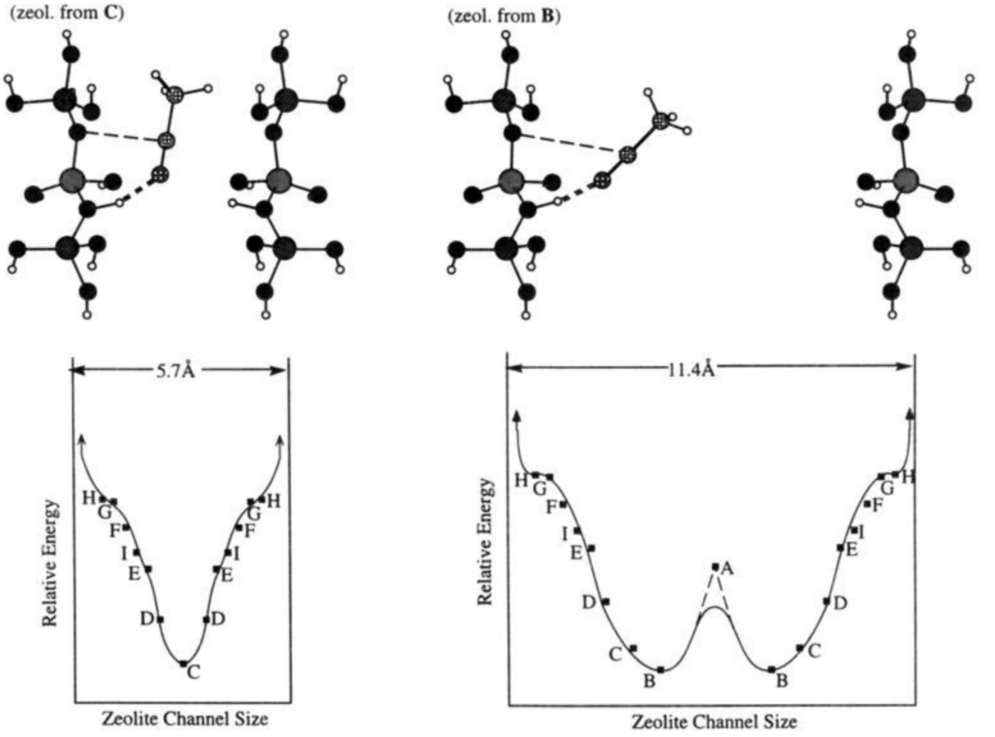

Figure 13. Quasi-one-dimensional models of acetonitrile in two hypothetical zeolites with medium (5.7 Å) and large (11.4 Å) channels. The potential wells shown were based on the relative energies for structures A–H. For the large-pore model, acetonitrile can dissociate from the acid site at higher energies (temperatures) and experience additional degrees of freedom. In the medium-pore model, higher energies require greater structural change because the adsorbate cannot get far from an acid site on one wall without encountering the opposing wall.

The maturation of ab initio chemical shift calculations has important consequences for the practice of NMR spectroscopy in surface chemistry, at least for systems in which the chemical and magnetic properties are accurately modeled by tractable clusters. The chemical shifts of all nuclei except protons are dominated by large diamagnetic and paramagnetic contributions of opposing sign, and the chemical shift is one of the least intuitive of physical properties commonly used to determine molecular structure. Although many formalisms have been developed for rationalizing differences in chemical shifts between structurally related compounds on the basis of concepts such as electronegativity, neighboring group anisotropy contributions, and so on, the application of the chemical shift interpretation to organic species bound to surfaces requires much skill and is naturally not always conclusive. The ability to propose a structure for an adsorbed species on the basis of NMR evidence, refine that structure using theoretical methods, and then finally test the model by calculating chemical shift tensors could change the way in which NMR is applied to problems in surface science and catalysis.

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