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NH₄⁺ in Zeolites: Coordination and Solvation Effects

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Proton transfer from a zeolitic cluster to NH₃ and subsequent coordination of the ammonium cation onto the zeolitic cluster are studied by using ab initio quantum chemical cluster calculations. Proton transfer from the zeolite cluster to NH₃ is favorable if, after proton transfer, the resulting NH₄⁺ cation is coordinated to the zeolitic cluster with two or three hydrogen bonds. These structures are referred to as 2H and 3H, respectively. Their adsorption energies, the energy needed for the process of proton transfer followed by the binding of the NH₄⁺ cation, are calculated to be -114 and -113 kJ/mol, respectively. The geometries were optimized at the SCF level and the adsorption energies were calculated at the second-order Møller–Plesset perturbation theory level (MP2), using the counterpoise correction (CPC) to avoid the basis set superposition error (BSSE). The basis set is the 6-311+G(d,p)/STO-3G one, which has previously been shown to give proper binding and proton transfer energies. The calculated heats of adsorption compare well with experimental heats of desorption. Proton transfer also occurs when another NH₃ molecule is coadsorbed. However, the process of coadsorption is energetically less favorable than the 2H and 3H structures: the adsorption energy per NH₃ molecule is only -30 kJ/mol. For the clusters the N–H stretching frequencies have been calculated at the SCF level in the harmonic approach. They have been compared with experimental spectra of the NH₄⁺ forms of some zeolites. The N–H stretching region of these spectra can be explained as a superposition of the spectra of the 2H and 3H structures. By comparison of the adsorption energy on a geometry optimized cluster and on a fixed geometry cluster, it was found that the choice of the geometry is important. On enlarging the fixed geometry cluster the adsorption energy remained constant.

Introduction

Proton transfer from acidic zeolites to NH₃ and the interaction of the NH₄⁺ cation with the zeolite lattice are widely studied subjects, both by experimentalists and theoreticians.^{1–34} In this paper we present a study in which these processes are studied by ab initio quantum chemical calculations on small zeolitic clusters. The calculated results will be compared with experimental heats of adsorption and infrared spectra.

In our earlier study¹ we found that proton transfer is not favorable if after protonation the NH₄⁺ ion is bonded to the zeolite with a single hydrogen bond. [The term hydrogen bond, through perhaps not appropriate for a fully ionic system, is used to characterize the geometrical arrangements studied.] However preliminary calculations indicated that multiple hydrogen bonding with the zeolite substrate might stabilize the NH₄⁺ to such an extent that proton transfer becomes favorable. The present paper reports a detailed analysis of the stabilization by double and triple hydrogen bonding to the zeolitic lattice and by coadsorption of a second NH₃ molecule. Vibrational analyses at the equilibrium geometries of the clusters will be represented as well.

In this study minimal size clusters will be used. Although it is not certain that these clusters represent the zeolite acidic site in the best way this choice is made because with these small clusters it is possible to use a basis set that adequately describes the proton-transfer process.

Survey of Experimental Data

NH₄⁺ adsorbed in zeolites has been studied by spectroscopic techniques such as IR and ¹⁵N NMR spectroscopies. Also the energy effects of the NH₃ adsorption have been measured by temperature-programmed desorption (TPD) and microcalori-

metry (MC). MC gives a direct measurement of the heat of adsorption. TPD gives the heat of activation for desorption, but this quantity is often interpreted as the heat of desorption.

In the infrared spectra of ammonium loaded zeolites the N–H stretching regions (2700–3400 cm⁻¹) are very similar (see refs 15 and 16 and the Results section of this paper). The same pattern can be found in all cases: broad intense bands around 2800, 3000, and 3200 cm⁻¹ and a less intense peak or shoulder around 3400 cm⁻¹. Only in less well resolved spectra these features are hard to find.¹⁵

¹⁵N MAS NMR measurements give detailed information about the siting and coordination of the NH₄⁺ tetrahedron around the acidic site. At relatively low temperatures the NH₄⁺ tetrahedron is localized at the AlO₄ tetrahedrons.³⁸ At these low temperatures (from 77 K to about 120 K) the NH₄⁺ is still rotating and tumbling around its own symmetry axes or jumping from one orientation to another. However, it remains located at a given AlO₄ tetrahedron, and there is very little translational motion away from it.^{13,33,38} At very low NH₄⁺ loading Earl et al.¹⁴ report two peaks. These are assigned to two different sites. At higher loadings more peaks appear in the spectrum. The authors suggest these peaks stem from hydrogen-bonded forms of NH₄⁺ and NH₃. The zeolite lattice appears to be a highly flexible structure: inelastic neutron scattering and infrared studies show that on deprotonation of the zeolite, i.e., on forming NH₄⁺, the zeolite lattice is distorted.^{7,8,13,39} The zeolite lattice has the ability to adjust its bond lengths and angles to the deprotonation.

The adsorption energy of NH₃ on a zeolite acidic site is not known with certainty. The values show a large range depending on the technique and the type of zeolite, but even the results of applying the same technique to the same system may differ significantly. If the adsorption energy is determined with MC,

there is some ambiguity in the choice of which part of the plot of the heat of adsorption against the amount adsorbed is due to adsorption at the zeolite acidic site. From various MC measurements an average adsorption energy of 146 ± 23 kJ/mol on different types of H and H/Na forms of zeolites is found.^{6,21,26,29,34} If the activation energy for desorption is interpreted as the heat of adsorption there is an ambiguity in the choice of the method to calculate the ΔE^{act} from the TPD spectrum. Different methods can give results that are quite different. From the TPD measurements activation energies for desorption in the range 112 ± 33 kJ/mol were found.^{9,11,12,24,25,27,28}

Methods

In this paper we will model the interaction between NH_4^+ and the zeolite wall using small molecular clusters. The zeolite wall is represented by an $\text{Al}(\text{OH})_n\text{H}_{4-n}^-$ fragment, because at low temperatures the NH_4^+ binds at the aluminum sites. The way the cluster is chosen depends on the coordination of the NH_4^+ . If the NH_4^+ is bonded to the zeolite wall with two hydrogen bonds, a $\text{Al}(\text{OH})_2\text{H}_2^-$ (Figure 1a) cluster will be used; this is the 2H structure. When NH_4^+ is bonded to the zeolite wall with three hydrogen bonds, the zeolite wall is modelled by an $\text{Al}(\text{OH})_3\text{H}^-$ (Figure 1b) cluster; this is the 3H structure. Some additional calculations on NH_4^+ bonded singly or doubly to the latter cluster have been performed as well. Finally, when dealing with the coadsorption of two NH_3 molecules on a single acidic site the $\text{H}_3\text{SiOHAlH}_3$ cluster was adopted (Figure 1c).

All the calculations are performed with the 6-311+G(d,p)/STO-3G basis set, used in our earlier paper.¹ This notation means that the hydrogens that saturate the dangling bonds are described with a STO-3G basis set,⁴⁰ the silicon and aluminum atoms with a 6-31G(d) basis set,⁴¹ the nitrogen with a 6-311G(d) basis set,⁴² the hydrogens which are attached to the nitrogen with a 31G(p) basis set,⁴³ and the oxygen atoms with a 6-311+G(d) basis set.^{42,44}

The cluster size is limited by the use of this basis set: in our earlier paper we have shown that a smaller basis set does not give reliable results. The equilibrium geometries were found by geometry optimization of the clusters at the SCF level, using gradient techniques. No counterpoise correction (CPC) was applied in this step. These optimizations were repeated with Al...N distances 0.1 Å shorter and longer than that found for the full geometry optimization. For each of these structures a calculation is performed in which electron correlation is included through second-order Møller-Plesset theory,³⁵ keeping the cores frozen. These data were used to obtain the final SCF and SCF/MP2 equilibrium Al-N distances and equilibrium interaction energies, both with and without CPC.

For each cluster, the adsorption energy of NH_4^+ is calculated by connecting a two-step process. The first one is the proton transfer at infinity. The second is the adsorption of NH_4^+ onto the anionic zeolite fragment. The proton-transfer energy at infinity is calculated, as the difference in proton affinity (PA) between the zeolitic anionic fragment and NH_3 :

$$\Delta E^{\text{PT}} = \text{PA}_Z - \text{PA}_{\text{NH}_3} \quad (1)$$

The required proton affinities are obtained as the difference in energy between the isolated and fully optimized NH_3 and OSiAlH_7^- molecules and the fully optimized and isolated NH_4^+ and OSiAlH_6^- ions, respectively.

In the second step the interaction energy between two fragments A and B is calculated from

$$\Delta E^{\text{int}} = E^{\text{AB}} - E^{\text{A}} - E^{\text{B}} \quad (2)$$

In (2) E^{AB} is the energy of the complex obtained by interpolating on the three Al...N distances considered, and E^{A} and E^{B} are the energies of the free optimized fragments (for example the optimized ions NH_4^+ and OSiAlH_6^-). However this interaction

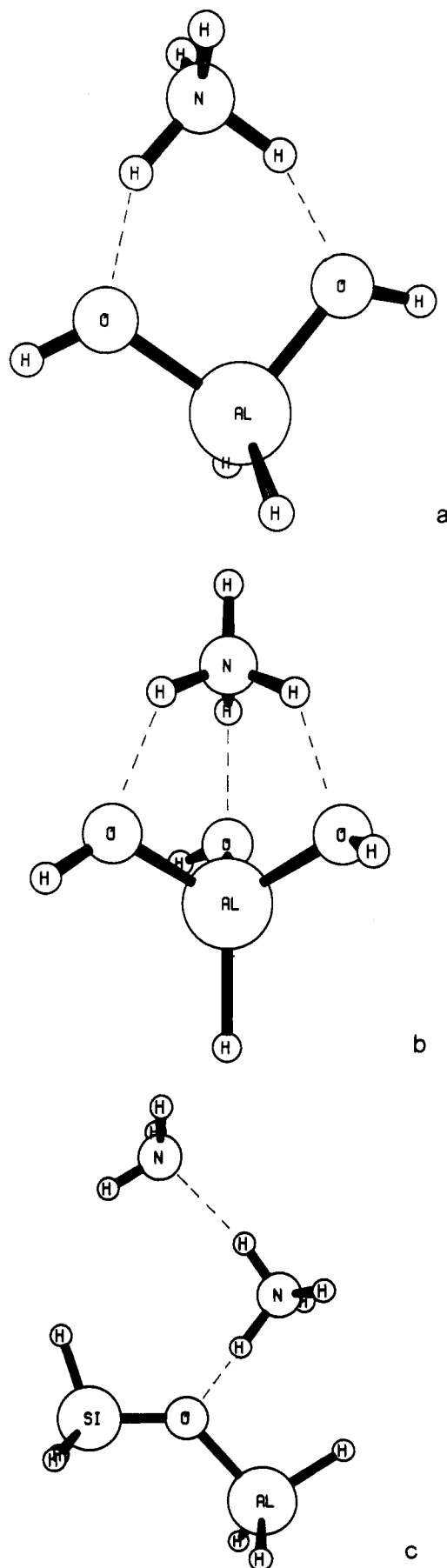


Figure 1. Geometries of the complex considered: (a) NH_4^+ doubly bonded to an $\text{Al}(\text{OH})_2\text{H}_2^-$ cluster (2H structure); (b) NH_4^+ triply bonded to an $\text{Al}(\text{OH})_3\text{H}^-$ cluster (3H structure); (c) $\text{NH}_3 \cdots \text{NH}_4^+$ coadsorbed on a $\text{SiH}_3\text{OHAlH}_3$ cluster.

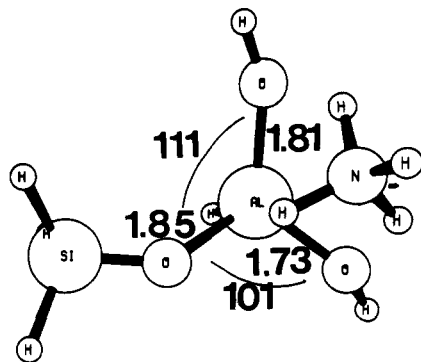


Figure 2. Al–O distances and O–Al–O angles of the rigid-geometry SiH₃OAl(OH)₂H[−] cluster triply bonded to NH₄⁺ used in discussing the importance of geometry optimization.

may be spoiled by the basis set superposition error (BSSE), and so the counterpoise correction (CPC) is applied.^{36,37} It is calculated from

$$E^{\text{BSSE}} = (E^{\text{A,comp}}(\chi_{\text{A}}) + E^{\text{B,comp}}(\chi_{\text{B}})) - (E^{\text{A,comp}}(\chi_{\text{A}} \oplus \chi_{\text{B}}) + E^{\text{B,comp}}(\chi_{\text{A}} \oplus \chi_{\text{B}})) \quad (3)$$

Here comp denotes that an energy is evaluated at the geometry of the molecules have in the complex, χ_{A} denotes the basis set of A, χ_{B} the basis set of B and $(\chi_{\text{A}} \oplus \chi_{\text{B}})$ the basis sets of A and B together. If this correction is added to the binding energy the calculation is labeled CPC.

Finally, the adsorption energy is the sum of the interaction energy and the proton-transfer energy:

$$\Delta E^{\text{ads}} = \Delta E^{\text{int}} + \Delta E^{\text{PT}} \quad (4)$$

Vibrational normal mode analyses were performed at the SCF level with analytical second derivatives, using the final, CPC-uncorrected, SCF equilibrium geometries. The N–H stretching frequencies were scaled with a factor of 0.92, which is the average of the ratio between the frequency of the experimental and the calculated N–H stretching frequencies of the NH₃ molecule.⁴⁵

The validity of the cluster choice and the importance of geometry optimization were tested by adopting the cluster in Figure 2. It has the same geometrical parameters as the rigid-geometry SiH₃OAlH₃[−] cluster discussed in ref 1 (partly taken from a force field calculation for a 1:1 Si/Al Na-faujasite,⁴⁶ but two hydrogens on aluminum were replaced by OH groups (using the faujasite geometry) to allow triple bonding by NH₄⁺). For the NH₄⁺ ion an experimental geometry was taken.⁴⁷ The binding energy for this cluster was calculated at the SCF level. In these calculations the internal geometry of the fragments was kept fixed, the only parameter optimized was the Al–N distance. These calculations were also performed with the OSiH₃ group being replaced by a OH group. Because this cluster has the same stoichiometry as the 3H structure the effect of the geometry optimization can be studied.

Results

Geometry-Optimized Clusters. The results of the optimizations of the Al(OH)₂H₂[−] and Al(OH)₃H[−] fragments are summarized in Figure 3. The protonated and deprotonated clusters show large deviations from a tetrahedral arrangement. Notably, the acidic forms of these clusters show a deformed water molecule forming a complex with an aluminum cluster with a somewhat flattened geometry. The cluster from which the reference proton affinity is taken, SiH₃OAlH₃[−], was also optimized with the same basis set. The deprotonation energies are given in Table I.

When the NH₄⁺ is adsorbed on the cluster, the internal geometry of the aluminum cluster and of the NH₄⁺ tetrahedron is distorted. For the 2H and 3H structures the resulting

deformations are summarized in Figure 4. The adsorption energies and equilibrium Al...N distances are given in Table II as calculated from the potential energy curves at four different levels of theory. The results confirm our earlier preliminary findings¹ that these proton-transferred structures are much favored over the singly-H-bonded structure studied in ref 1.

In our earlier paper,¹ we found that the proton was not transferred to the NH₃ to the zeolite if the NH₄⁺ was kept singly coordinated to the zeolitic cluster. However, if a second NH₃ is adsorbed to the cluster, the result of the geometry optimization is that the ionic state is stabilized to such an extent that NH₄⁺ is formed. For this coadsorbed structure the SCF/MP2/CPC calculations were performed at the SCF-optimized geometry only. Some of the geometrical parameters are given in Figure 5a.

In Table III the binding energies for the coadsorbed structure system are tabulated. The adsorption energy at the SCF-level is 59.8 kJ/mol per two adsorbed NH₃ molecules; i.e., only 30 kJ/mol per NH₃ molecule. Energetically this coadsorbed state is unfavorable compared to the 2H and 3H structures and also to the state where the proton is not transferred and a single NH₃ molecule is hydrogen bonded on a single site. From Table III it can be seen that the MP2 calculation overestimates both the adsorption and the binding energy. The SCF calculation gives almost the same value as the SCF/MP2/CPC calculation. In Table III also the interaction energies between all the individual pairs are tabulated, these are calculated in the absence of the third molecule. From the last column in Table III it can be seen that they are not additive. The three-body term, defined as the difference between the sum of the three binding energies between NH₃, NH₄⁺, and OSiAlH₇, is repulsive. The structure with the proton transferred may be a local minimum; this structure is given in Figure 5a. Also the structure in which the proton is not transferred and two NH₃ molecules are binding sequentially to the same OH group is also a minimum. In this case the O–N distance is 2.73 Å, the N–N distance 3.29 Å. The structure in which the proton is attached to the zeolite while hydrogen bonding to two NH₃ molecules is 15 kJ/mol lower at the SCF level. Since the anion is stabilized at the electron-correlated level, this difference will be smaller at the MP2 level. Thus in this structure there appears to be a very subtle balance between proton-transfer energies and differences in binding energies.

Calculated IR Spectra. In Figure 6 the N–H stretching region of the infrared spectrum of two NH₄⁺ containing zeolites is reported. In Figure 6a this region is shown for a NH₄–Y zeolite, whereas Figure 6b refers to the NH₄⁺ form of mordenite. These NH₄⁺ forms of zeolites were obtained by ion exchange of the sodium forms. The IR spectra were measured after evacuating the sample for 1 h at 500 °C followed by adsorption of NH₃. The features of these spectra have already been discussed.

For all the geometry-optimized clusters normal-mode analyses were carried out. From these analyses the N–H and O–H stretching frequencies were selected. This selection was simple because the N–H stretching frequencies were isolated from the other normal modes. In Table IV the results of these vibrational analysis is given.

Rigid-Geometry Calculations. To study the effect of both the cluster choice and the role of the geometry optimization, some rigid-geometry calculations were performed. The composition of the cluster was changed in order to study the effect of the cluster choice, and the effect of geometry optimization was studied by comparing the results of the rigid geometry calculations with the results for the 3H cluster, both having the same stoichiometry. We took the SiH₃OAl(OH)₂H, triply bonded to NH₄⁺ shown in Figure 2. The SiH₃OAl part was the same as used in our earlier paper on the subject.¹ The Al atom is located along one of the C₃ axes of the NH₄⁺ ion. Because the aluminum cluster did not have a 3-fold axis, the angle of rotation of the NH₄⁺ tetrahedron around the Al...N axis was optimized at the SCF level, using a

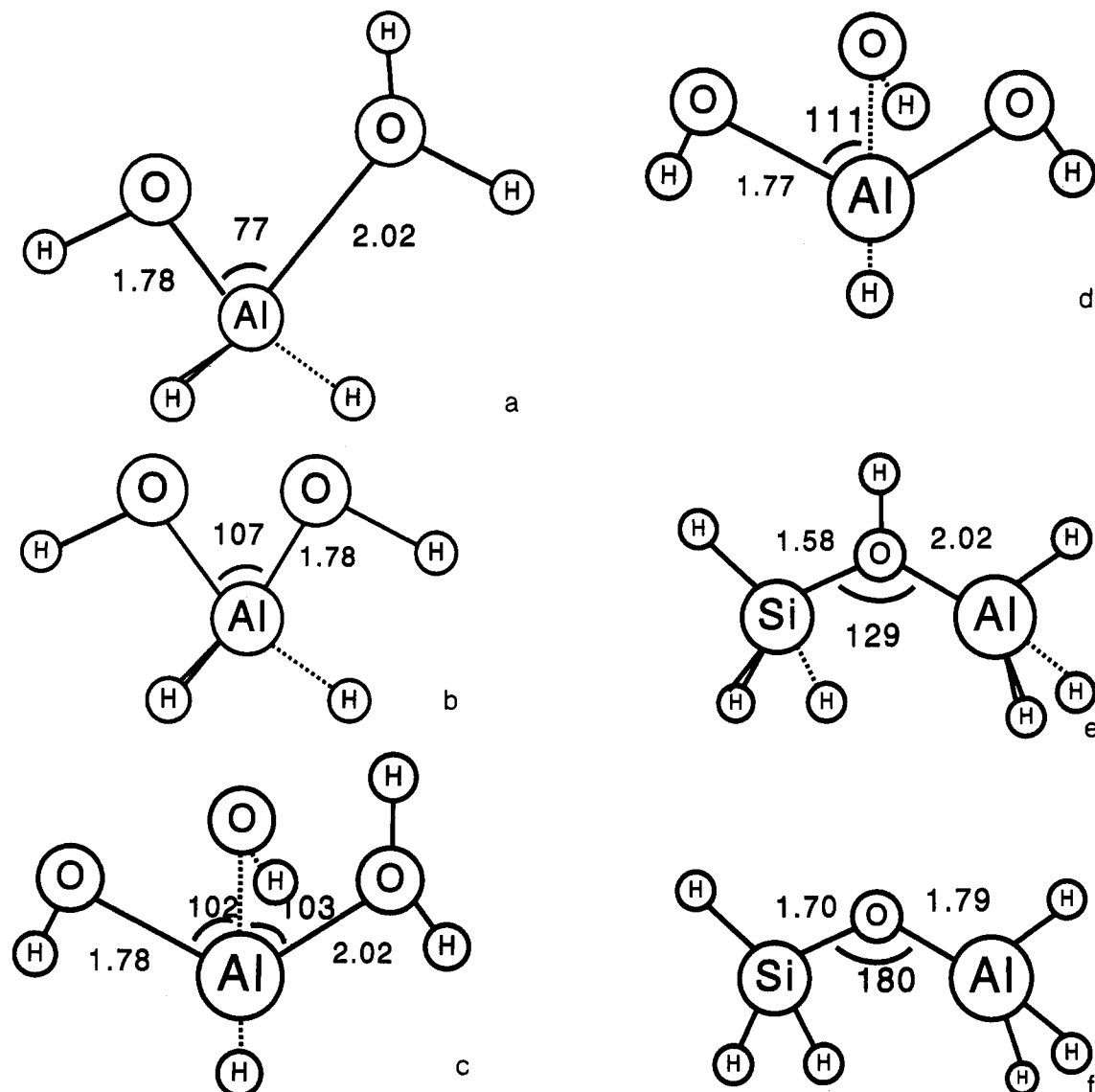


Figure 3. Optimized geometries of the clusters modelling the zeolite wall. Protonated forms (a, c, e) optimized in C_s symmetry. Anionic forms (b, d, f) optimized in C_{2v} , C_{3v} , and C_s , respectively.

TABLE I: Deprotonation Energies (kJ/mol) of the Clusters*

	$\text{Al}(\text{OH})_2\text{H}_2$	$\text{Al}(\text{OH})_3\text{H}_2$	$\text{H}_3\text{SiOHAlH}_3$	NH_4^+
SCF	1379	1364	1359	907
MP2	1377	1356	1358	905

* The deprotonation energies are defined as the difference in energy between the optimized ZH and Z^- forms of the clusters. They are given at the SCF and at the correlated level (deprotonation energy = $-PA$).

3-21G basis set. It was found that the minimum energy was reached if the Al-O...H-N dihedral angle had a mean value of 6° . Using a ΔE^{PT} in the rigid geometry at infinity of 444 kJ/mol the adsorption energy is -18.4 and -10.6 kJ/mol at the SCF and SCF/CP levels, respectively. The Al-N distances at these levels were 2.78 and 2.81 Å, respectively.

The calculations for this cluster were repeated with a reduced cluster size, replacing the OSiH_3 group by a OH group. The results do not differ much: the adsorption energies are -16.0 and -9.6 kJ/mol at the SCF and SCF/CPC levels, respectively. The Al-N distances are 2.77 and 2.79 Å, respectively. These results differ considerably from the results found for the corresponding geometry optimized cluster, the 3H structure.

Discussion

It is not surprising that if a second NH_3 is adsorbed on the acidic site the NH_4^+ is stabilized in the single-bonded form. From

our earlier paper it was seen that the ionic state is 52 kJ/mol higher in energy than the hydrogen bonded form.¹ The calculated binding energy between NH_3 and NH_4^+ is -99 kJ/mol,⁴⁸ whereas for the NH_3 dimer they are -19 , -14 , and -18 kJ/mol.⁵⁰⁻⁵² From the differences one could expect the charged form of the structure to become favorable over the true hydrogen-bonded one when another NH_3 is coadsorbed. The fact that the ionic state is stabilized by a single extra NH_3 is an indication of the strong acidity of this acidic site in the zeolite. It has been shown experimentally that gas-phase α -naphthol* ($pK_a \sim 0.5$) requires three additional NH_3 molecules to accomplish proton transfer to NH_3 .⁵³ This suggests that the acidic site of a zeolite is more acidic than strong mineral acids such as HI for which a pK_a of 0.77 has been reported.

The N...O length in the coadsorbed system is 2.55 Å. This is very close to the value for the $\text{NH}_4^+\cdots\text{OSiAlH}_7$ system.¹ The N...N distance however is longer than in the $\text{NH}_4^+-\text{NH}_3$ complex, which is 2.85 Å,⁵⁰ presumably because of repulsion between the anionic zeolite cluster and the NH_3 dipole.

The binding energy for the complex involving the NH_3 , NH_4^+ , and OSiAlH_6^- molecules is not equal to the sum of the binding energies for the separate pairs. The difference between this sum and the total binding energy, the three body term, is 29 kJ/mol at the CPC-corrected SCF level (of Table III). Electron correlation adds 2 kJ/mol to this three-body term. These numbers

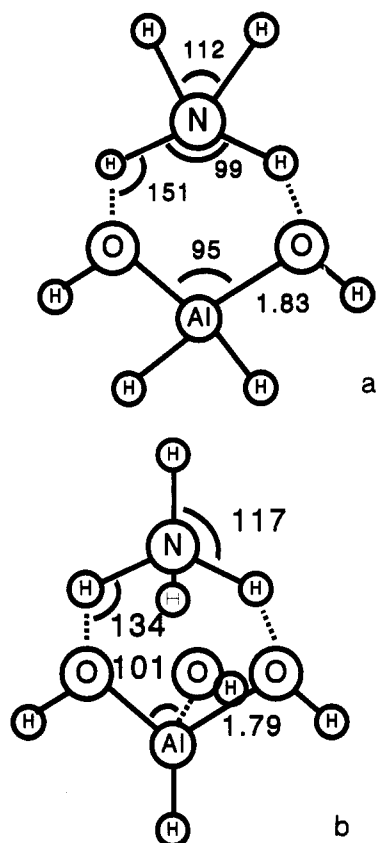


Figure 4. Deformation of the fragments induced by binding of NH₄⁺ to the Al cluster: (a) 2H structure; (b) 3H structure.

TABLE II: Characteristics of the Optimized 2H and 3H Structures at Different Levels of Theory^a

method	$R_{Al \cdots N}$		ΔE^{ads}	
	2H	3H	2H	3H
SCF	3.42	2.95	-110	-112
SCF/CPC	3.42	2.97	-98	-100
SCF/MP2	3.39	2.92	-141	-139
SCF/MP2/CPC	3.41	2.94	-114	-114

^a Distances in Å, adsorption energies in kJ/mol.

have an opposite sign and are somewhat larger than the values found for sequentially hydrogen bonding systems. For example, at the SCF level this term is -17 kJ/mol for the NH₃...HF...HF system.⁵⁴ For the water trimer this term was in the range of -3 to -5 kJ/mol, depending on the geometry. The contribution of the second order Møller-Plesset perturbation energy to this was almost negligible: 0.3 and 0.1 kJ/mol.⁵⁵ Since most of the SCF three-body energy is caused by polarization energy, it is to be expected that, in this system with two ions the three-body term is somewhat larger than in the other systems mentioned. The three-body term becomes repulsive because the polarization of the NH₃ under influence of the NH₄⁺ cation and the OSiAlH₆⁻ anion simultaneously is less than under the influence of these ions separately.

A single NH₄⁺ is stable only when it is forming two or three hydrogen bonds with the zeolite lattice, i.e., in the 2H/3H structures; if the NH₃⁺ is bonded to zeolitic cluster with a single hydrogen bond, the ionic form is not stable. As can be seen from formula 1, the stabilization of the ionic state relative to the singly bonded state can be caused by a change in proton affinity of the cluster or by a change in binding energy. Because for the proton affinity the value for the OSiAlH₆⁻ cluster is taken, the first possibility can be ruled out. Since the proton affinities are almost equal as can be seen from Table I, this choice for the proton affinity will not introduce erroneous artifacts. Thus the difference in stability between the single bond and the 2H and 3H structures

TABLE III: Analysis of the Binding Energies in the Coadsorbed Structure (Figure 5a)^a

method	total		pair energies			difference ΔE^{ABC}
	ΔE^{ads}	ABC	AB	AC	BC	
SCF	-59.8	-547.9	-495.1	13.6	-96.6	30.2
SCF/CPC	-40.6	-528.7	-480.5	15.9	-93.4	29.3
SCF/MP2	-92.8	-577.1	-512.9	11.0	-107.0	32.6
SCF/MP2/CPC	-59.8	-543.4	-488.5	14.6	-100.9	31.3

A = OSiAlH₆⁻ = Z⁻, B = NH₄⁺, C = NH₃

$\Delta E^{ads} = E^{ABC}(Z \cdots NH_4^+ \cdots NH_3) - E(Z) - 2E(NH_3)$

ABC = $\Delta E^{int} = E^{ABC}(Z \cdots NH_4^+ \cdots NH_3) - E(Z) - E(NH_4^+) - E(NH_3)$

AB = $\Delta E^{AB}(Z \cdots NH_4^+) = E(Z \cdots NH_4^+) - E(Z) - E(NH_4^+)$

AC = $\Delta E^{AC}(Z \cdots NH_3) = E(Z \cdots NH_3) - E(Z) - E(NH_3)$

BC = $\Delta E^{BC}(NH_4^+ \cdots NH_3) = E(NH_4^+ \cdots NH_3) - E(NH_4^+) - E(NH_3)$

$\Delta E^{ABC} = ABC - AB - AC - BC$

^a The total of the interaction energies and the interaction energies between the pairs of molecules. The interaction energies and CPC are calculated with the formulas (2) and (3). ΔE^{ads} is the ΔE^{ads} from formula (4) for the complete system of the three interacting particles. ΔE^{int} is the interaction energy for the three particles, as from formula (2) and (4). AB, AC, and BC denote the pair interactions (explanation given below the Table). ΔE^{ABC} is the three body-term.

TABLE IV: Frequencies of the Experimental and Calculated Infrared Spectra Given in cm⁻¹^a

MOR	FAU	BET	ERI	2H	3H	H	COAD
2780	2800	2970	2840	2623 (I)	3103 (I)	3142 (I)	3153 (I)
2930	3040		3068	2740 (I)	3141 (I)	3360	3363
3180	3270	3200	3260	3418	3478 (I)	3478	3401
3400	3360	3460	3384	3495		3483	3473
							3476
							3483

^a MOR denotes the NH₄⁺-mordenite, given in Figure 6a, FAU denotes the NH₄⁺-faujasite from Figure 6b. BET is the ammonium form of zeolite beta¹⁵ and ERI the ammonium form of erionite.¹⁶ The other spectra are the calculated ones. 2H and 3H are the notation of the doubly and triply bonded NH₄⁺ (Figures 1a and 1b, respectively). H is the structure in which the proton is attached to the zeolite, the peak given here thus is the OH-stretching. COAD is the structure as given in Figure 1c, N-H stretching of the proton pointed toward the zeolite is shifted to 2123 cm⁻¹, but is not included in the table because it is mixed with a Si-H stretching. (I) means that these peaks have a reasonable intensity, the other peaks have negligible intensity but are included for completeness.

is due to the enhanced interaction energy. The E^{int} is lowered by about -100 kJ/mol relative to the singly coordinated NH₄⁺. The high coordination of the cation to the anionic cluster seems to be the factor that makes the proton transfer favorable. An illustration for this is NH₄⁺ singly bonded to the Al(OH)₃H⁻ cluster. This structure was optimized keeping the proton attached to the nitrogen atom and one Al-O-N angle fixed to keep the cation singly coordinated. The O-N distance is 2.51 Å, the Al...N distance 3.73 Å, and the adsorption energy only -9.0 kJ/mol.

To test if the conclusion that both the 2H and the 3H structures are minima would be the same if the same cluster is used, we also performed a constraintless optimization in which the NH₄⁺ was doubly coordinated onto the Al(OH)₃H⁻ cluster used to describe the 3H structure. The result of the optimization was again a doubly coordinated structure. The binding energy was -109 kJ/mol at the SCF level, indicating the relative insensitivity to the cluster choice. The vibrational analysis on the 2H and 3H and the structure in which the NH₄⁺ was doubly coordinated onto the Al(OH)₃H cluster show that all these structures are minima when the coordination of the NH₄⁺ is concerned. Only the 3H structure showed one imaginary frequency. However, the vibrational amplitudes of this normal mode were completely located on the saturating hydrogens bonded to the oxygens.

Hydrogen bonds in ionic systems are in general relatively linear; for NH₃ bonded to NH₄⁺ a linear H bond was found, and for the H₃O⁺ bonded to water no larger deviation than 2.5° was found.⁴⁸ For the NH₄⁺...OH₂ system the N-H...O angle deviated less than

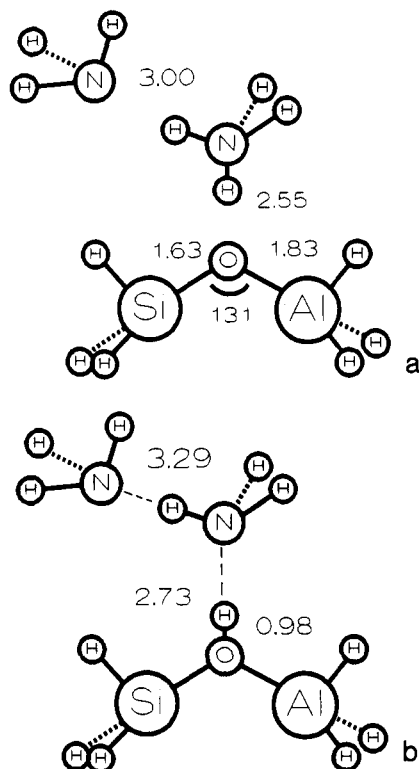


Figure 5. Coadsorbed structure (a) after proton transfer and (b) before proton transfer.

0.1° from linearity.⁴⁹ From the small difference in binding or adsorption energy between the 2H and 3H state, it can be seen that the binding energy is not proportional to the number of hydrogen bonds. Although the $N\cdots Al$ distance is much shorter in the 3H structure than in the 2H structure, the $O\cdots N$ distance in the hydrogen bonds are larger. This might be due to the somewhat more flattened geometry: In the 3H structure the $O-Al-O$ angle is 101° ; in the 2H structure it is 101° . Apparently in the case of an ion-ion interaction the exact alignment of the hydrogen bond does not seem to be very important, the factor determining the stability seems to be the short distance and the high coordination between the cation and the anion.

From the Si-O stretching frequency in the experimental spectrum³⁹ it is clear that the proton is transferred to the NH_3 . The interpretation of the experimental spectra from the calculated vibrational analyses is not completely straightforward. In this paper four geometry-optimized structures are discussed, features from all of them might appear in the experimental spectrum. The spectrum of the hydrogen bonded structure, i.e., the structure in which the proton is still attached to the zeolite is dominated by one single peak. The OH stretching frequency is shifted into the N-H stretching region. The spectrum of the coadsorbed structure is also dominated by a single peak at 3142 cm^{-1} (coming from the proton hydrogen bonding to the coadsorbed NH_3). These peaks are not likely to appear in an experimental spectrum since the 2H and 3H structures are energetically more favorable. At higher loadings peaks stemming from coadsorbed structures may appear.¹⁴

The two structures that are most likely to dominate the experimental spectrum are the 2H and 3H structures. From their almost equal adsorption energies it might be expected that the spectrum is a sum of the spectra of these two structures. However it should be remembered that the features of the infrared spectrum of the adsorbed NH_4^+ are influenced by the specific type of zeolite and that different sites may give different contributions to the spectrum. Still it is useful to compare the calculated and experimental frequencies. The spectrum of the 2H structure is dominated by two large peaks at 2623 and 2740

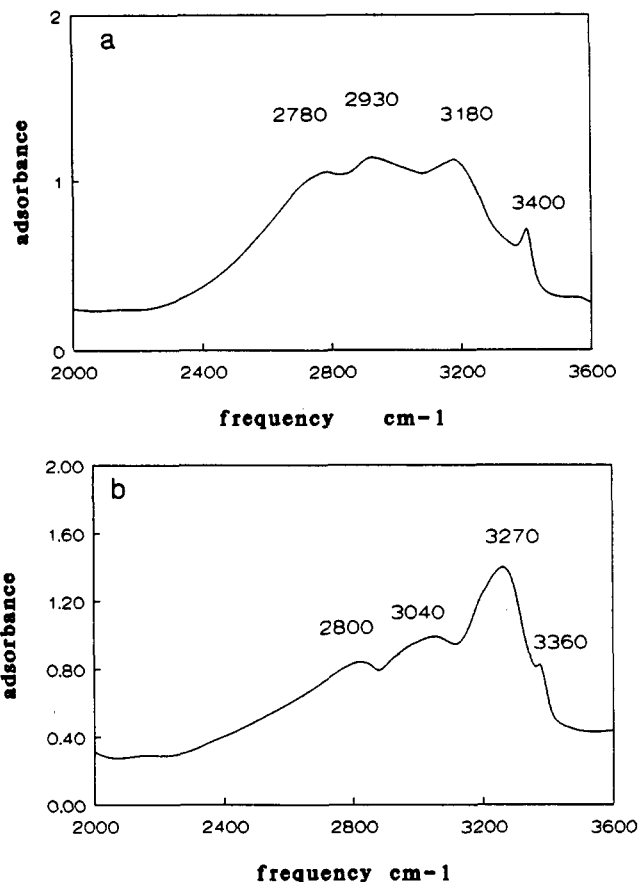


Figure 6. Experimental spectra: (a) experimental spectrum of NH_4^+ -Y; (b) experimental spectrum of NH_4^+ -mordenite. The intensities are normalized to 1.

cm^{-1} . They might correspond with the two bands that are present in the experimental spectrum at 2780 and 2930 (mordenite), 2800 and 3040 (faujasite), 2970 (beta) and 2840 and 3068 cm^{-1} for the erionite. However, the values are downshifted by about 250 cm^{-1} . The spectrum of the 3H structure has two large peaks relatively close together (3103 and 3141 cm^{-1}) which in an experimental spectrum will appear as one peak. It also has a less intense peak at 3478 cm^{-1} . The composite peak around 3120 cm^{-1} may correspond to the band in the experimental spectrum at 3180 (mordenite), 3270 (faujasite), 3200 (beta) and 3260 (erionite). The less intense peak at 3478 cm^{-1} may correspond to the less intense peak or shoulder appearing in the experimental spectra at 3400, 3360, 3460, and 3384 cm^{-1} for the zeolites mordenite, faujasite, beta, and erionite, respectively. If this interpretation is right, the numerical value of the first band is shifted by 100 cm^{-1} . The numerical value of the 3478-cm^{-1} peak seems to be right. In the cluster this frequency corresponds to the stretch of the proton pointing away from the zeolitic cluster. Since it is not hydrogen bonding, the harmonic approach might be sufficient.

As seen from this interpretation there is not a simple correspondence between the calculated harmonic frequencies and intensities and the experimental spectra. However, for some features a satisfactory explanation can be found, this explanation supports the suggestion that the 2H and 3H structures may both appear at the same time.

The calculated heats of adsorption for the fixed geometry and optimized geometry $Al(OH)_3H_2$ clusters differ about 100 kJ/mol , the latter more being favorable. From formula 4 it is seen that this difference may be caused by a difference in ΔE^{PT} or ΔE^{int} . There is only a small difference in ΔE^{PT} : 444 kJ/mol for the fixed geometry cluster and 452 kJ/mol for the optimized geometry cluster. Apparently the difference in adsorption energy is caused by the difference in interaction energy. The interaction energies for the fixed-geometry cluster are -460 and -453 at the

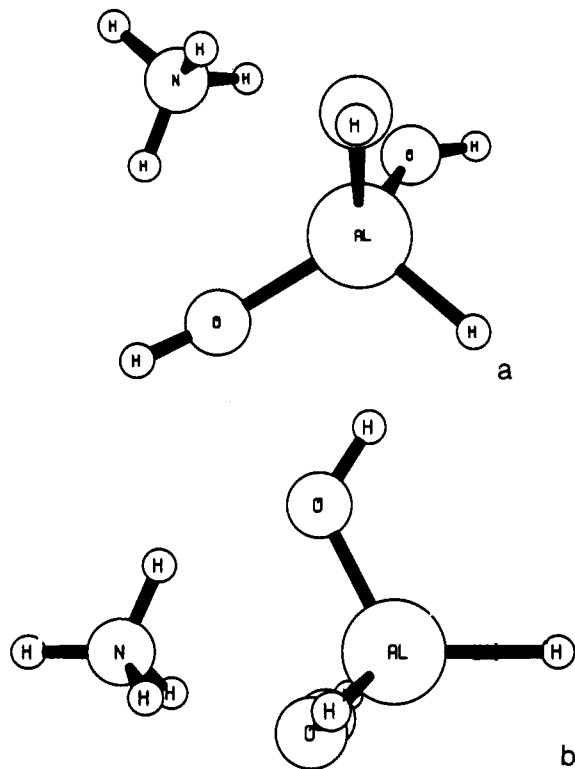


Figure 7. Difference in coordination between the fixed geometry and the optimized geometry structure. (a) The fixed geometry structure is relatively flat. Its dipole moment is small and the aluminum atom and the NH₄⁺ are exposed to each other. (b) The optimized geometry cluster enlarges its dipole moment by enlarging the H–Al–O angle. Because of this bending the hydrogen atoms of the NH₄⁺ and the oxygen atoms are close together and the aluminum is shielded.

SCF and SCF/CPC level, respectively. For the optimized-geometry cluster these numbers are –561 and –548 kJ/mol. The fixed-geometry cluster has an irregular shape. Therefore the protons cannot be coordinated to the oxygen atoms optimally. This relatively small loss in coordination causes a difference in interaction energy of –100 kJ/mol. This can be explained from the relation between the geometry and the dipole moment of the Al(OH)₃[–] cluster. In the fixed-geometry cluster the angles between the saturating hydrogen atom, the aluminum atom and the oxygen atom are 104°, 105°, and 108°. In the optimized geometry cluster this is 117°. Since the negative charge is more or less located on the oxygen atoms, there is a large difference in dipole moment (the origin is taken in the center of positive charge). In the fixed-geometry cluster the dipole moment is 0.6 D, in the optimized geometry cluster, in the complex equilibrium geometry this is 3.5 D. Although the dipole moment is not properly defined in a charged species, the difference in interaction energy can be understood. An important feature is also that in the optimized structure the OH groups are pointing their dipoles in the direction of the NH₄⁺ cation. The fixed-geometry cluster has a more flat geometry; because of this flat geometry a high coordination of the anionic oxygen to the NH₄⁺ cation implies the cation is also close to the aluminum atom which leads to repulsion. The deformation of the Al(OH)₃[–] cluster is relatively small. In the isolated state the H–Al–O angle is 108°, in the optimized 3H complex 117°, the deformation energy is 33 kJ/mol. In the complex, however, a large increase in the interaction energy results to compensate for this deformation energy. The differences in coordination between the fixed and optimized geometry are shown in Figure 7.

The adsorption energy calculated within the fixed geometry does not have a heat of adsorption that agrees with an experimental one. This is consistent with the proposed flexibility of the zeolite lattice. This flexibility is shown experimentally by infrared and

inelastic neutron-scattering spectra.^{7,8,12} Thus adsorption energies should be calculated by optimizing the geometries. As we see from our calculations, the extra binding energy compensates for the deformation energy. If the lattice should be less flexible than the clusters used, the adsorption energy is dependent on the geometry of the lattice. For example, if the AlO₄[–] tetrahedrons in the lattice would have the shape they have in the optimized 3H structure, the adsorption energy will increase by –33 kJ/mol because the deformation energy is absent. If, on the other hand, the lattice would have the shape of the isolated Al(OH)₃H[–] ion the adsorption energy will be a bit less than the –112 found for this cluster. In the fixed-geometry cluster the difference in adsorption energy between the Al(OH)₃H₂ cluster and the Al(OH)₂H₂OSiH₃ cluster is minimal. In this case the adsorption energy seems to be determined to a large extent by the atoms that are directly interacting with ammonium cation.

Conclusions

The proton transfer from a zeolite to NH₃ and the binding of NH₄⁺ is studied by quantum chemical cluster calculations. The geometries of the cluster were optimized at the SCF level. The adsorption energies are calculated at the SCF/MP2/CPC level i.e. electron correlation was included through second-order Møller–Plesset perturbation theory, and the counterpoise correction was applied to avoid the basis set superposition error. Four different structures have been studied. In one the proton was not transferred and NH₃ is forming a hydrogen bond with the zeolitic OH group. In two other structures the NH₄⁺ are forming two or three hydrogen bonds with the zeolitic cluster. Finally a structure was studied in which two NH₃ molecules are adsorbed on a single zeolitic OH group. The heats of adsorption calculated for these structures are –60, –110, –112, and –30 kJ/mol, respectively. Experimentally the heat of adsorption for different types of zeolites is in the range from –110 to –150 kJ/mol.

The two structures in which the NH₄⁺ is forming two or three hydrogen bonds with the zeolitic cluster are favorable because the ammonium cation has a high coordination with the cluster. If the geometry of these structures was not optimized a part of this high coordination is lost and the heat of adsorption is only –10 kJ/mol. If in the rigid-geometry cluster one of the dangling bond hydrogens is substituted by a SiH₃ group, the adsorption energy is not affected.

The vibrational frequencies of the clusters were calculated at the SCF level in the harmonic approach. They have been compared with experimental spectra of NH₄⁺ forms of zeolites. The features of the experimental spectrum can be explained from the calculated spectra.

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References and Notes

- Teunissen, E. H.; van Duijneveldt, F. B.; van Santen, R. A. *J. Phys. Chem.* **1992**, *96*, 366.
- Allavena, M.; Seiti, K.; Kassab, E.; Ferenczy, Gy.; Ángyán, J. G. *Chem. Phys. Lett.* **1990**, *168*, 461.
- Geerlings, P.; Tariel, N.; Botrel, A.; Lissillour, R.; Mortier, W. J. *J. Phys. Chem.* **1984**, *88*, 5752.
- Medin, A. S.; Borovkov, V. Y.; Kazansky, V. B.; Pelmeshnikov, A. G.; Zhidomirov, G. M. *Zeolites* **1990**, *10*, 668.
- Paukshtis, E. A.; Pankratev, Y. D.; Pelmeshnikov, A. G.; Burgina, E. B.; Turkov, V. M.; Yurchenko, E. N.; Zhidomirov, G. M. *Kinet. Katal.* **1986**, *27*, 1440.
- Auroux, A.; Vadrine, J. C. *Stud. Surf. Sci. Catal.* **1985**, *20*, 311.
- Corbin, D. R.; Abrams, L.; Jones, G. A.; Eddy, M. M.; Harrison, W. T. A.; Stucky, G. D.; Cox, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 4821.

- (8) McCusker, L. B. *Zeolites* **1984**, *4*, 51.
(9) Dima, E.; Rees, L. V. C. *Zeolites* **1990**, *10*, 8.
(10) Parker, L. M.; Bibby, D. M.; Meinhold, R. H. *Zeolites* **1985**, *5*, 384.
(11) Post, J. G.; van Hooff, J. H. C. *Zeolites* **1984**, *4*, 9.
(12) Schirmer, W.; Stach, H.; Fiedler, K.; Rudzinski, W.; Jagiello, J. *Zeolites* **1983**, *3*, 199.
(13) Udovic, T. J.; Cavanagh, R. R.; Ruch, J. J.; Wax, M. J.; Stucky, G. D.; Jones, G. A.; Corbin, D. R. *J. Phys. Chem.* **1987**, *91*, 5968.
(14) Earl, W. L.; Fritz, P. O.; Gibson, A. A. V.; Lunsford, J. H. *J. Phys. Chem.* **1987**, *91*, 2091.
(15) Hegde, S. G.; Kumar, R.; Bhat, R. N.; Ratnasamy, P. *Zeolites* **1989**, *9*, 231.
(16) Kogelbauer, A.; Lercher, J. A.; Steinberg, K.-H.; Roessner, F.; Soellner, A.; Dmitriev, R. V. *Zeolites* **1989**, *9*, 224.
(17) Ozin, G. A.; Baker, M. D.; Godber, J.; Gill, C. J. *J. Phys. Chem.* **1989**, *93*, 2899.
(18) Ozin, G. A.; Baker, M. D.; Helwig, K.; Godber, J. *J. Phys. Chem.* **1985**, *89*, 1846.
(19) Stock, T.; Dombrowski, D.; Fruwert, J.; Ratajczak, H. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2773.
(20) Stock, T.; Dombrowski, D.; Fruwert, J. *Z. Phys. Chem.* **1984**, *265*, 738.
(21) Tsutsumi, K.; Mitani, Y.; Takahashi, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1912.
(22) Itoh, H.; Hidalgo, C. V.; Hattori, T.; Niwa, M.; Murakumi, Y. *J. Catal.* **1984**, *85*, 521.
(23) Babu, G. P.; Hegde, S. H.; Kulkarni, S. B.; Ratnasamy, P. *J. Catal.* **1983**, *81*, 471.
(24) Topsøe, N.-Y.; Pedersen, K.; Derouane, E. G. *J. Catal.* **1981**, *70*, 41.
(25) Hidalgo, C. V.; Itoh, H.; Hattori, T.; Niwa, M.; Murakumi, Y. *J. Catal.* **1984**, *85*, 362.
(26) Vadrine, J. C.; Auroux, A.; Bolis, V.; Dejaifve, P.; Nacchace, C.; Wierzchowski, P.; Derouane, E. G.; Nagy, J. B.; Gilson, J.-P.; van Hooff, J. H. C.; van den Berg, J. P.; Wolthuizen, J. *J. Catal.* **1979**, *59*, 248.
(27) Karge, H. G.; Dondur, V. *J. Phys. Chem.* **1990**, *94*, 765.
(28) Karge, H. G.; Dondur, V.; Weitkamp, J. *J. Phys. Chem.* **1991**, *95*, 283.
(29) Shannon, R. D.; Staley, R. H.; Vega, A. J.; Fischer, R. X.; Baur, W. H.; Auroux, A. *J. Phys. Chem.* **1989**, *93*, 2019.
(30) Embaid, B. P.; Hunger, M.; Landrove, M. M.; Martin, R. Z. *Phys. Chem. (Munich)* **1990**, *166*, 109.
(31) Mestdagh, M. M.; Stone, W. E. E.; Fripiat, J. J. *J. Catal.* **1975**, *38*, 358.
(32) Michel, D.; Germanus, A.; Pfeiffer, H. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 237.
(33) Deininger, D.; Reimann, B. *Z. Phys. Chem.* **1972**, *251*, 5.
(34) Shi, Z. C.; Auroux, A.; Taarit, Y. B. *Can. J. Chem.* **1988**, *66*, 1013.
(35) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(36) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(37) van Lenthe, J. H.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *Adv. Chem. Phys.* **1987**, *69*, 521.
(38) Vega, A. J.; Leev, Z. *J. Phys. Chem.* **1987**, *91*, 365.
(39) van Santen, R. A.; de Man, A. J. M.; Jacobs, W. P. J. H.; Teunissen, E. H.; Kramer, G. J. *Catal. Lett.* **1991**, *9*, 273.
(40) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
(41) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
(42) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
(43) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
(44) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.
(45) Herzberg, G. *Molecular spectra and molecular structure, II: Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: New York, 1960.
(46) Kramer, G. J.; Farragher, N. P.; van Beest, B. W. H.; van Santen, R. A. *Phys. Rev. B* **1991**, *43*, 5068.
(47) Ibers, J. A.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *28*, 929.
(48) DelBene, J. E.; Frisch, M. J.; Pople, J. A. *J. Phys. Chem.* **1985**, *89*, 3669.
(49) Welti, M.; Ha, T.-K.; Pretsch, E. *J. Chem. Phys.* **1985**, *83*, 2959.
(50) DelBene, J. E. *J. Chem. Phys.* **1987**, *86*, 2110.
(51) Frisch, M. J.; Pople, J. A.; DelBene, J. E. *J. Phys. Chem.* **1985**, *89*, 3664.
(52) Latajka, Z.; Scheiner, S. *J. Chem. Phys.* **1986**, *84*, 341.
(53) Cheshnovsky, O.; Leutwyler, S. *J. Chem. Phys.* **1988**, *88*, 4127.
(54) Kurnig, I. J.; Szczyński, M. M.; Scheiner, S. *J. Phys. Chem.* **1986**, *90*, 4253.
(55) Chałasiński, G.; Szczyński, M. M.; Cieplak, P.; Scheiner, S. *J. Chem. Phys.* **1991**, *94*, 2873.