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The Location of the Protons in Dehydrated Y-Faujasite

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The broadline proton magnetic resonance spectrum of the H^+ form of Y-faujasite has been examined in detail. The second moment of the proton magnetic resonance curve is consistent with a model of an isolated Al–H pair with an internuclear distance of 2.38 ± 0.03 Å. These results, coupled with published infrared and X-ray studies indicate that the protons are located on the type 1 and 3 oxygen atoms, with a O–H bond distance of 1.00 to 1.03 Å.

INTRODUCTION

Protons in crystalline zeolites are apparently responsible for much of the catalytic activity of the materials for hydrocarbon reactions (*1–5*). The chemistry of these protons, especially in Y-faujasite, have been investigated by a number of techniques in an attempt to correlate structure with catalytic activity.

Infrared spectroscopic studies of the protons in Y-faujasite (*1*, *5–11*), especially when coupled with gas adsorption experiments (*12–16*) have been useful in describing their location. A single crystal X-ray structure determination gives other details about the locations of protons in dehydrated Y-faujasite (*17*).

Ward was able to reconcile the apparently inconsistent results of these studies, arriving at the assignment of the 3540 cm^{-1} band to protons on the O_3 and the 3640 cm^{-1} band to protons on the O_1 oxygen atom (*18*). Aside from the probable locations, little else is known about the local environment of the proton. Knowledge about the bond angles and internuclear distances would probably be fundamental in any attempt to correlate structure with activity.

Most methods conventionally used for studying solids are not sensitive or definite enough to locate protons in low concentrations. Fortunately, the proton has nuclear spin, which makes it possible to study its magnetic properties by NMR. For this reason, it was decided to use the broadline nuclear magnetic resonance technique to measure the magnetic field surrounding the proton in the zeolite structure. It was felt that the results of such measurements would provide information on the location of the proton with respect to other atoms with nuclear spin.

The Broadline Nuclear Magnetic Resonance Technique

Magnetic nuclei in a strong magnetic field display a resonance absorption at some radio frequency. The frequency depends upon the strength of the magnetic field and the magnetogyric ratio of the nucleus. The strength of the magnetic field experienced by a particular nucleus is given by

$$H = H_0 + H_{\text{local}},$$

where H_{local} is the magnetic field resulting from the direct interaction of the magnetic moments of neighboring nuclei. In a rigid lattice, the orientation of magnetic moments is fixed with respect to the direction of

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the applied magnetic field, H_0. As a result, the strength of the local fields as experienced by an individual nucleus differs significantly from the applied field (*19*). Thus, the width of the NMR line is increased. This effect is more than 100 times larger than the phenomenon responsible for the "chemical shift" of a nucleus. The strength of the local magnetic field, H_{local}, decreases as the distance separating the magnetic nuclei increases. Thus, it is possible to relate the width of the resonance curve to interatomic distances (*19*). The theory of broadline NMR has been reviewed by several authors (*19–23*). For rigid polycrystalline solids, the second moment M_2 (i.e., the root-mean-square width) of the resonance curve depends upon the sum of the inverse sixth power of the internuclear distances between nuclei having nuclear spin.

In Y-faujasite, H^1, Al^{27}, and Na^{23} are the only atoms present in sufficient abundance to affect the magnetic environment of the protons. The equation

$$M_2 = 358 \sum_{\mathrm{H} \neq \mathrm{H}'} \frac{1}{r^6} + 126 \sum_{\mathrm{Al-H}} \frac{1}{r^6} + 125 \sum_{\mathrm{Na-H}} \frac{1}{r^6}, \qquad (1)$$

can be derived to relate the second moment, M_2, to the sum of the internuclear distances separating the magnetic nuclei (*20*). Because of the r^{-6} dependence, broadline NMR is an extremely sensitive technique for measuring internuclear distances. It is not necessary to compensate for the vibrational motion of the atoms in order to obtain internuclear distances to 3% accuracy (*22*).

If any of the atoms are moving, however, the interpretation of the shape of the resonance curve is not as simple. The more rapid the translational motion, the narrower the resonance curve becomes, until a limit imposed by the sweep modulation frequency is reached. The variation of the width of the resonance curves with temperature enables one to tell if the curve is narrowed due to translational motion (*19*).

EXPERIMENTAL

The properties of the zeolite samples are presented in Table 1. Sample (1) was prepared by calcining Linde SK40 (powder, lot 1280-133) for 2 hr at 550°C. After cooling over fresh P_2O_5, it was inserted into the NMR tube under an atmosphere of dry nitrogen. The proton magnetic resonance spectrum was not significantly different from the background signal obtained when the sample was removed from the probe. Sodium ion was removed from the synthetic Y-faujasite (Linde SK40) by ion exchange with NH_4NO_3 solution. The conditions and number of the exchange treatments were varied in order to produce a significant variation in the sodium content. After the final exchange, the catalyst was washed thoroughly with water, calcined at 550°C (2 hr), then bottled in order to minimize water absorption. X-ray diffraction scans indicated that all the samples were highly crystalline at this point. Catalysts with various amounts of hydrogen and deuterium contents were prepared by slurrying a 20 g portion of the calcined catalyst with 50 ml of $H_2O + D_2O$ of the desired isotopic composition (Table 1). After filtering to remove the excess water, the cake was dried at 130°C for 2 hr in an oven with a nitrogen or helium blanket. The crushed cake was calcined (3 hr, 550°C) in a quartz tube with an upward flow of helium or mole sieve-dried nitrogen. The powder was held in the tube with a quartz wool plug. The material was removed from the calcination tube while hot and was allowed to cool in a nitrogen or helium-filled vacuum dessicator. X-ray diffraction scans of Samples 6b and d, 7a and c, indicate that the crystallinity had not been destroyed. A significant amorphous background was observed in the X-ray diffraction scan of Sample 8a.

X-ray fluorescence analysis indicated that the concentrations of heavy metal ions which might interfere with the magnetic measurements are less than 150 ppm. Since the calcination temperatures were only 550°C, the samples were prepared under

TABLE 1
PROPERTIES OF BROADLINE NMR SAMPLES OF Y-FAUJASITE

				Atom %			
Sample	wt % Na	Percent exchange	Sample temp (°C)	H	D	M_2	Crystallinity
1	8.7	0	25	100	N[a]	No signal	100%
2	2.3	74	25	100	N	0.743	100%
3	0.24	97	25	100	N	0.731	
			−45			0.739	
			−113			0.719	
4			RT[b]			0.67	
5						0.83	
6a	2.3	73	RT	100	N	0.68	
6b	2.3	73	RT	80	20	0.70	100%
6c	2.3	73	RT	50	50	0.66	
6d	2.3	73	RT	30	70	0.73	100%
6e	2.3	73	RT	10	90	0.68	
7a	0.81	91	RT	100	N	0.71	100%
7b	0.81	91	RT	80	20	0.71	
7c	0.81	91	RT	50	50	0.71	100%
7d	0.81	91	RT	30	70	0.71	
7e	0.81	91	RT	10	90	0.69	
8a	0.22	97	RT	80	20	0.69	Partially amorphous
8b	0.22	97	RT	50	50	0.69	
8c	0.22	97	RT	10	90	0.69	
					Average	0.71 ± 0.04	

[a] N, assumed natural isotopic abundance of D_2O.
[b] RT denotes Room Temperature.

conditions which would not be expected to produce the "ultra stable Y-faujasite" reported by McDaniel (*24*).

Proton Spectra

The proton magnetic resonance curves were obtained at 40 mhz by substituting a Varian Model 4310 crystal tuned oscillator for the variable frequency oscillator of the Varian Model V-4200A NMR spectrometer, and sweeping the magnetic field. At resonance, the magnetic field strength was 9390 gauss. Distortion effects arising out of saturation and audio field modulations were held to a minimum. The derived second moments were corrected for the residual spurious broadening due to audio field modulation. In all cases, the amplitude of the signal was adjusted to almost 10 in. peak-to-peak by means of the amplifier gain selector. The shape of the derivative traces of the individual proton spectra of the SK40 samples was the same for all samples. No evidence of RF saturation was noted even for the most dilute proton samples.

RESULTS

The width (second moment) of the proton magnetic resonance curve is remarkably constant over a wide range of temperatures as well as sodium and proton content (Table 1). The average width, $M_2 = 0.71 \pm 0.04$ (± standard deviation) is consistent with the observation that the general shape of all the curves was the same except when some absorbed water was present. When water was inadvertently present, the absorption trace either exhibited a small narrow component superposed upon the broad band, or when extremely wet, a very strong, narrow signal. The water was removed by recalcination at 550°C. The second moment of the nuclear magnetic resonance curve can be related to structural parameters only if it can be shown that the line width is not decreased by translational motion and if the nuclei responsible for the broadening of the line can be identified. The measured second moments are essentially constant over the temperature range +25° to —113°C. (See Table 1.) Thus, there is no apparent change in the motion or environment of the proton within this temperature range. Furthermore, it is doubtful that any change in the line width due to a change in motion would occur below —113°C, since Kvlividze has observed that absorbed water is no longer moving in Na–X-faujasite at —113°C (*25*). The remaining question to be answered is which nuclei are responsible for the dipolar broadening of the NMR curve. The data in Table 1 show that the value of M_2 is independent within ±0.04 gauss^2 of the sodium content, indicating that the distance separating a proton and a Na^{23} ion is greater than 3.5 Å (Fig. 1). The only nuclei remaining that possess a magnetic moment and, therefore, could be responsible for dipolar broadening are H^1 and Al^{27}. Attempts to observe the Al^{27} resonance were unsuccessful, probably because of quadrupole coupling with the asymmetric field gradient of oxygen atoms (see below). In order to determine the relative importance of Al–H and H–H dipolar broadening, various amounts of deuterium were substituted for hydrogen (Table 1). Since deuterium possesses a much smaller magnetic moment, the contribution of H^1–H^1 dipolar broadening to the second moment should be decreased as deuterium is substituted for H^1. An appropriate term must

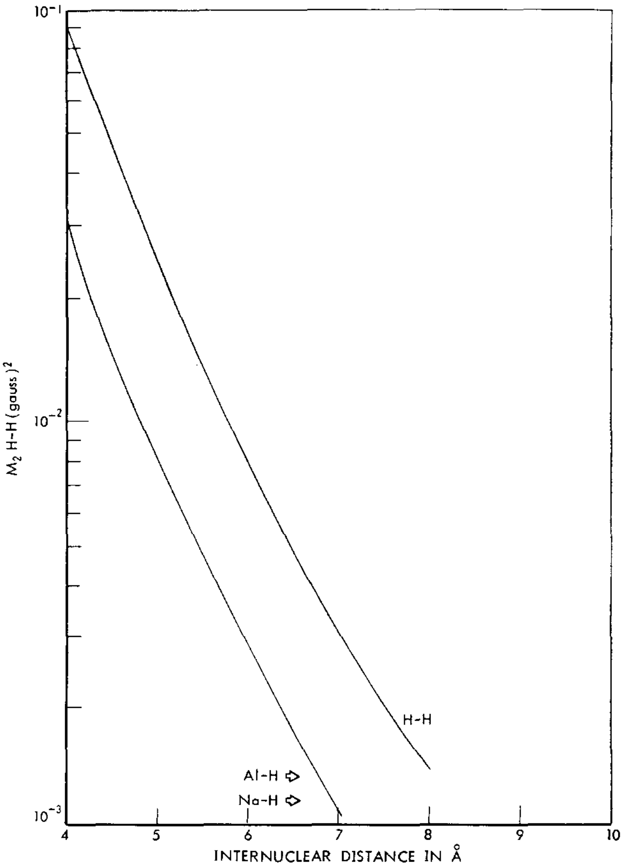


FIG. 1. Second moment vs the internuclear distance between a proton and other magnetic nuclei.

be added to Eq. (1) to account for the H^1-H^2 dipolar interaction (Eq. 2).

$$M_2 = 358 \sum_{H \neq H^1}^{\infty} \frac{1}{r^6} + 126 \sum_{Al-H}^{\infty} \frac{1}{r^6} + 126 \sum_{Na-H}^{\infty} \frac{1}{r^6} + 20.5 \sum_{D-H}^{\infty} \frac{1}{r^6}. \quad (2)$$

This equation predicts that the line width (second moment) should decrease as the deuterium content increases if the proton–proton dipolar interaction is significant. For instance, the contribution of a proton 4 Å away should be reduced from 0.088 to 0.005 gauss^2 when it is replaced by a deuterium nucleus. Such a decrease should be observable, even at the relatively low signal-to-noise ratios of the highly deuterated samples. The results (Table 1) of the isotopic dilution of the proton show that any decrease in the second moment of the resonance curve is less than the uncertainty in the measurement (±0.04 gauss^2), but that the signal intensity decreases as the dilution increases (Fig. 2), reflecting the lower H^1 content. These results indicate that the proton is 4.5 Å or more from its nearest neighbor. Such a distribution is possible if significant numbers of the protons are in the super cages of Y-faujasite. Thus, since the NMR curve is not broadened by either neighboring H^1 or Na^{23} ions, the dipolar broadening can only come from a neighboring Al^{27} nucleus. In Y-faujasite, because of its very open structure and low concentration of magnetic nuclei, the contribution of non-nearest neighbor nuclei to the NMR line width is small. Assuming that the distribution of nuclei with magnetic moments is uniform throughout the unit cell, it can be shown that the effect of nuclei greater than M distance away can be calculated from

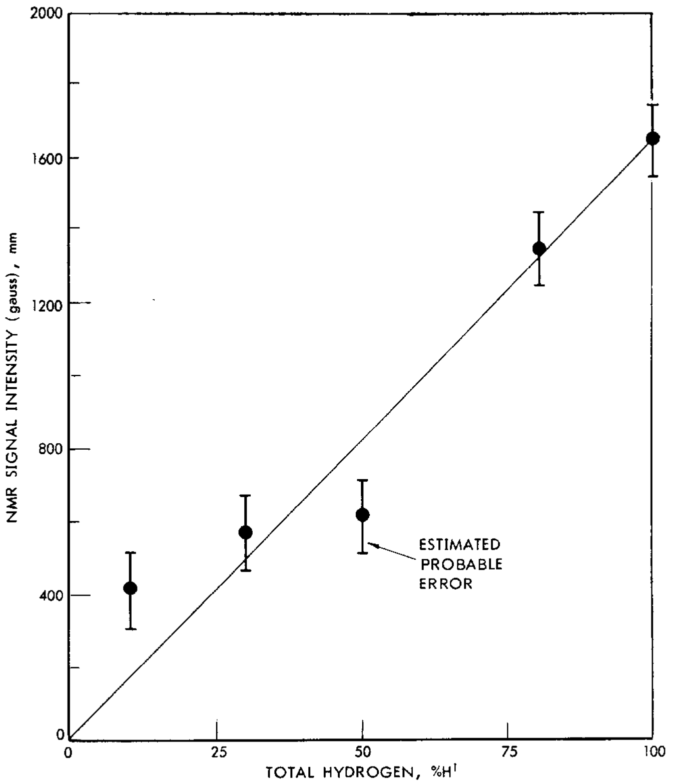


FIG. 2. Signal intensity vs the proton content of Y-faujasite (2.3% Na calcined at 550°C).

$$\sum_{r_{jk}>m} \frac{1}{r^6} = \frac{4\pi n_k{}^1}{3M^3V}, \tag{3}$$

where n_k refers to the number of atoms, and V is the unit cell volume in Å³ (*22*). Some values for the contribution of non-nearest neighbor nuclei are presented in Table 2 for a unit cell of $H_{41}NA_{15}Al_{56}Si_{136}O_{384}$, and a cell constant of 24.5 Å (corresponding to Samples 6a–e).

TABLE 2

CALCULATED CONTRIBUTION OF NON-NEAREST NEIGHBOR NUCLEI TO THE SECOND MOMENT OF THE PROTON MAGNETIC RESONANCE LINE OF Y-FAUJASITE

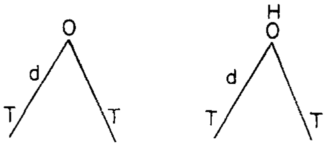
M_A	N_a	Al	H	Total (gauss)^2
4.5	0.0059	0.022	.046	0.0739
5.0	0.0043	0.016	.033	0.0533
5.5	0.0032	0.012	.025	0.0400
6.0	0.0024	0.0093	.019	0.0310
6.5	0.0019	0.0073	.015	0.0240

Examination of a molecular model for Y-faujasite indicates that a reasonable value for M is 6 Å. Subtraction of 0.031 gauss² from the observed second moment of 0.71 ± 0.04 gauss² gives a value of 0.68 ± 0.04 gauss² which must be due to the dipolar broadening of an isolated Al–H pair. The corresponding internuclear distance is 2.38 ± 0.03 Å.

DISCUSSION

Recent studies by infrared (*1*, *7*) and X-ray diffraction on the H⁺ form of faujasite (*8*, *9*) present evidence that there are two proton locations. The 3650 cm⁻¹ absorption has been assigned to protons in the zeolite super cage and the 3550 cm⁻¹ to protons in the hexagonal prism (*7*). A recently reported single crystal X-ray structure determination of the H form of natural faujasite indicates that the protons reside on the type 1 and 3 oxygen atoms (*17*).

Since the protons have negligible electron density and therefore no X-ray scattering ability, the assignment of the proton location was made indirectly from a consideration of the bond lengths between oxygen and the tetrahedral silicon and aluminum cations, (T). Olson notes that for faujasite in the H form, the O_1–T distance is larger-than-average in contrast to that usually observed for dehydrated faujasite containing various cations (Table 3) (*17*). Intuitively, one would expect that an oxygen atom coordinated to an exchangeable cation would have its T–O bond order reduced somewhat, resulting in an increase in T–O bond length. This is precisely what is observed in all cases except silver faujasite, where the unusual preference of Ag(I) for linear "*sp*" coordination (*16*) may impose an unusual structure on the system (Table 3). Thus, in decationized faujasite, it is probable that there are both



units where d′ > d.

It is important to remember that NMR experiments examine the average micro environment of the protons, while X-ray diffraction yields an average macro-structure of the entire lattice. In order to form a model consistent with the X-ray and NMR results and still have a reasonable, (0.95–1.03 Å), O–H distance (*17*), it is necessary for the Al–O bond distance to be 1.72 Å or greater. It is probable that the Al–O–Si bonds in faujasite are asymmetric about the oxygen; that is, the Si–O bond distance is shorter than the Al–O distance, since this is the order found in other minerals (*28*) and the unit cell constant expands as the aluminum content of faujasite increases (*29*). It seems reasonable to expect the average Al–O bond to be at least 0.02 Å longer than a corresponding Si–O bond in faujasite. This mechanism may be instrumental in explaining the relatively large uncertainties associated with all the oxygen positions in the reported structures. If Olson's reasoning on the location of the protons on types 1 and 3 oxygen atoms is correct (*17*), then the T–O_3 and T–O_1 bond lengths he obtained in his X-ray crystal structure are actually

TABLE 3

Summary of Reported Values for the Structure of Dehydrated Faujasites

Cation	Ca(II)		Ca(I)		Ni(II)		Sr(II)		H$^{\oplus}$		Na(I)		K(I)		Ag(I)	
No. Al/unit cell	102[a]		57		48[a]		84[a]		59		57		57		57	
% Exchange	100[a]		100		100(?)[a]		100[a]		100		100(?)[b]		100(?)[b]		100(?)[b]	
Sample condition	crx.[c]		crx.		crx.		crx.		crx.		pwdr.[d]		pwdr.		pwdr.	
Reference	*(17,30)*		*(32)*		*(17, 30 31)*		*(17, 20)*		*(17)*		*(33)*		*(33)*		*(33)*	
Occupancy factor																
O_1									27							
O_3									32							
SI[e]	0.47		0.89		0.66		0.70				0.48		0.75		1.00	
SI′[e]	0.54		0.08		0.16		0.22				0.61		0.44		.33	
SII[e]	0.54		0.35		0.20		0.13				0.95		0.94		.89	
SII′[e]	0.35				0.59		0.61									
	D(Å)	%[f]		%[f]	*D*(Å)	%[f]		%[f]	*D*(Å)	%[f]	*D*(Å)	%[f]	*D*(Å)	%[f]	*D*(Å)	%[f]
O_1–Si(Al)	1.653	0	1.633	0	1.633	0	1.655	0	1.653	28	1.63		1.60		1.62	
O_2	1.673	82	1.651	35	1.641	26	1.682	74	1.634	0	1.63	95	1.68	94	1.65	89
O_3	1.678	100	1.671	97	1.695	76	1.680	92	1.663	33	1.70	1.09	1.71	1.19	1.61	1.33
O_4	1.650	0	1.620	0	1.613	0	1.654	0	1.623	0	1.58		1.66		1.61	
Mean	1.664		1.644		1.646		1.668		1.644		1.635		1.662		1.62	

[a] Calculated from data given in reference.

[b] Assumed, reference is incomplete.

[c] Single crystal sample, crx.

[d] Powder sample, pwdr.

[e] SI is in the center of the hexagonal prism; SI′ is adjacent to SI, and in the sodalite cage, SII′ is in the sodalite cage adjacent to the supercage six-ring and SII is in the supercage adjacent to SII′. The occupancy factor is the percent of such positions occupied.

[f] Percent of the oxygen atoms coordinated to ion exchangeable cation.

population averages of two different groups, i.e., T–O_3–T and protonated, $\text{T—}\overset{\text{H}}{\overset{|}{\text{O}}}_3\text{—T}$. Estimating the unprotonated T–O_3–T bond to be equal in length to the T–O_2 bond as found in hydrated natural faujasite (*34*), the $\text{T—}\overset{\text{H}}{\overset{|}{\text{O}}}_3$ bond length can be calculated from

$$(\text{T—}\overset{\text{H}}{\overset{|}{\text{O}}}_3) = \frac{\overline{(\text{T—O}_3)} - (\text{T—O}_2)}{P} + (\text{T—O}_3)$$

and

$$(\text{T—O}_2) \cong (\text{T—O}_3),$$

where $\overline{\text{T–O}_n}$ is the bond length in Å. $\overline{\text{T–O}_3}$ is the population average bond length reported by Olson, and P is the fraction of protonated oxygen atoms. Thus, the $\text{T—}\overset{\text{H}}{\overset{|}{\text{O}}}_3$ bond length 1.72 Å is 0.09 Å longer than the T–O_3 bond. Similar considerations for type 1 oxygen atoms yields 1.71–1.72 Å as the probable $\text{T—}\overset{\text{H}}{\overset{|}{\text{O}}}_1$ distance. On the assumption that the Al–O bond is 0.02 Å longer than Si–O, then the Al–O_3 distance could be 1.74 Å and the Al–O_1 1.73 Å. The O–H distances calculated on the basis of Al–O_3 being 1.72 to 1.74 Å are 1.03 and 1.00 Å, respectively, values well within the expected range for O–H bonds. On this basis, the Al–O–H bond angle is found to be about 116°. Thus the results of the NMR experiments, coupled with the X-ray and infrared studies, are consistent with the model of protons located on specific oxygen atoms, probably types 1 and 3 in Y-faujasite. Furthermore, if the above analysis of the Al–O_3 and $\text{Al—}\overset{\text{H}}{\overset{|}{\text{O}}}_3$ bond distances is correct, then it is not necessary to propose an unusual distance for the O–H bond. Figure 3 is an illustration of the proposed model for the H form of Y-faujasite.

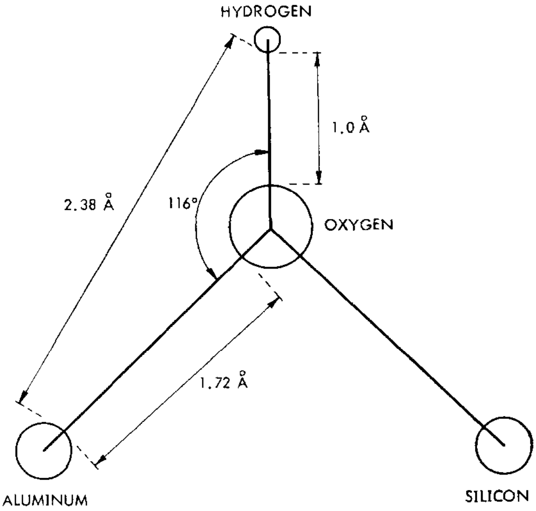


FIG. 3. Local environment of the hydrogen atom in the hydrogen form of Y-faujasite.

Placing two protons on type 3 oxygen atoms in adjacent rings of the hexagonal prism is not precluded by the results of the deuterium exchange experiments, since the two protons should be separated by at least 4.5 Å. In addition, the O_3 oxygen positions are protonated only when the sodium level is very low, otherwise the sodium ion itself undoubtedly is coordinated to the O_3 oxygens (*7*). Even at sodium levels of < 1%, such a separation would require subtraction of only 0.02 gauss^2 (0.5 × 0.04 gauss^2) from the observed second moment, since only about 50% of the protons in the sample are on the type 3 oxygen atoms. Consideration of a molecular model of faujasite shows that the protons on type 1 oxygen atoms are much more remote from magnetic nuclei other than its neighboring Al atom.

The experimental uncertainty of the NMR second moment as well as the uncertainty in the estimation of the $\text{Al—}\overset{\text{H}}{\overset{|}{\text{O}}}_3$ bond length precludes formation of a more definitive picture of the local environment of the proton at this time. It is interesting that the Al—O—H bond angle (Fig. 3) calculated above is 116°, close to the

120°C required for the "sp^2" coordination. If this is true, then part of the acidity of zeolites may be due to the decreased "p" character of hybridization of the oxygen atoms. It is known that the C–H bond becomes more acidic as the "p" character of the carbon atom decreases.

The X-ray evidence for the H-form of natural faujasite indicated that the protonated oxygen atom is a significantly greater distance away from the aluminum atom than the other three oxygens. This should produce an asymmetric electric field around the Al^{27} atom. Since Al^{27} has a large quadrupole moment, there should be a large coupling, thereby broadening the NMR signal to such an extent that it is lost in the instrumental noise. However, when H_2O is present, the proton is probably hydrated, possibly as $H_9O_4^+$, as is found in liquid water, and removed from the localized position of the zeolite oxygen. Thus, the oxygen would return to a bond length nearly equal to the other three oxygen atoms, creating a symmetric electric field around the Al^{27} atom. This would destroy the quadrupole broadening and thereby allow the resonance to be seen.

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