Dynamics of Water Molecules in VPI-5 and $AlPO_4$-5 Studied by ^2H NMR Spectroscopy

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Abstract: The dynamic properties of water and ammonia within the channels of VPI-5 and $AlPO_4$-5 were studied by ^2H NMR spectroscopy over a wide range of temperatures. The results were correlated with the corresponding ^{27}Al MAS NMR spectra. In both materials two distinct types of water molecules were detected, bound molecules and physisorbed molecules undergoing isotropic reorientation within the channels. The bound molecules were assigned to molecules coordinated to framework Al undergoing some local motion. In $AlPO_4$-5 the line shape changes were reproduced by using a dynamic model of a two-site exchange where one site corresponds to the bound water and the second to the free water molecules. The relative populations of the two sites were found to be temperature dependent. In VPI-5 the water exhibits a higher degree of order and the two-site jump between free and bound molecules is associated with an additional 3-fold-site jump, resulting in a 6-site system. In this case the relative populations are temperature independent within the temperature range of 0–60 °C. Three types of ND_3 molecules were distinguished in VPI-5 adsorbed with ammonia: physisorbed molecules, bound molecules undergoing a rotation about the N–Al axis, and rigid molecules. No exchange takes place between these three states within the NMR time scale.

Introduction

The new family of aluminophosphate molecular sieves (abbreviated as $AlPO_4$-*n*) has drawn considerable attention since some of their members form structures with relatively wide unidimensional channels.[1] $AlPO_4$-5 and VPI-5 are members of this family. VPI-5 has the widest channels known to date with openings of 12.1 Å circumscribed by 18 T (Al,P) atoms.[2,3] In $AlPO_4$-5 the channels are formed by rings of 12 T atoms and have openings of 7.3 Å.[4] While in all $AlPO_4$-*n* molecular sieves the amine used in the synthesis is found in the pores of the as-synthesized material,[1] in VPI-5 water molecules fill the pores after synthesis.[3] Recently, the structure of VPI-5 has been refined and it was found that, in contrast to the vast majority of hydrated zeolite structures, the water in VPI-5 is not disordered but reflects the symmetry of the sieve and it may play an important role as a structure-directing agent.[5] Seven different types of water molecules were found: two molecules are bound to framework Al, generating octahedral Al, and the other five water molecules are involved in the formation of a hydrogen-bonded chain between the different octahedral Al, creating a triple helix of water molecules along the channel's axis.[5] The temperature dependence of the ^{31}P MAS NMR spectra of VPI-5 was also explained in terms of the existence of a water structure within the pores.[6] Although framework Al in other $AlPO_4$-*n* structures, such as $AlPO_4$-5,[7-9] $AlPO_4$-11,[8] and SAPO-34,[10] are known to bind water molecules, this water ordering is so far unique to VPI-5.

The intriguing structure of the water molecules in VPI-5 should be manifested in unique dynamic properties as compared to other $AlPO_4$-*n*. In a previous study[11] we showed that in $AlPO_4$-5 two types of water molecules can be distinguished: bound molecules which we assigned as molecules coordinated to framework Al, and physisorbed molecules reorienting isotropically within the channels. We also found that the ability to coordinate to framework Al is not exclusive to water since ammonia showed similar behavior. In the present work we studied the motion of water and ammonia molecules within the channels of VPI-5 and $AlPO_4$-5 over a wide range of temperatures using ^2H NMR spectroscopy. ^2H NMR spectroscopy is a very useful method used to study the dynamic properties of adsorbates, and it has been successfully applied to investigate the motion of small organic molecules within the pores of zeolites.[12-16] Analysis of the ^2H NMR line shape provides information on the distribution of species, on the nature of the binding site, and on the motional characteristics of the sorbed molecules. The basic principles for analyzing ^2H powder line shapes of systems involved in a dynamic process are well established, therefore we will not repeat them here and refer to the cited literature.[17-19]

Table I. List of Samples Used

sample	treatment
1. $AlPO_4$-5 (AS)	as-synthesized $AlPO_4$-5
2. $AlPO_4$-5 (AS, D_2O)	as-synthesized $AlPO_4$-5 evacuated at room temperature rehydrated with D_2O
3. $AlPO_4$-5 (calc)	calcined, fully rehydrated $AlPO_4$-5
4. $AlPO_4$-5 (D_2O)	dehydrated calcined $AlPO_4$-5 rehydrated with D_2O
5. $AlPO_4$-5 (4.7% D_2O)	dehydrated calcined $AlPO_4$-5 partially rehydrated with 4.7 wt % D_2O
6. VPI-5	as-synthesized VPI-5
7. VPI-5 (D_2O)	dehydrated VPI-5 rehydrated with D_2O
8. VPI-5 (6.7% D_2O)	dehydrated VPI-5 partially rehydrated with 6.7 wt % D_2O
9. VPI-5 (ND_3)	dehydrated VPI-5 adsorbed with 23 wt % ND_3

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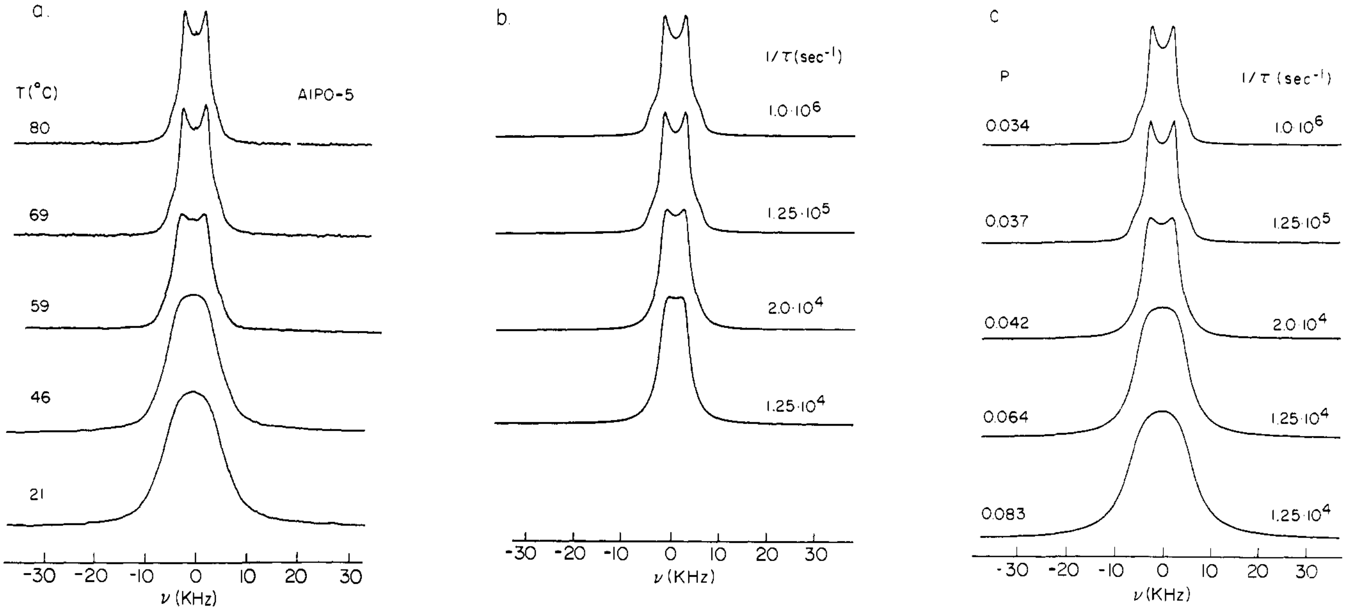


Figure 1. (a) ^{2}H NMR spectra of AlPO$_4$-5 (D$_2$O) as a function of temperature. (b) Calculated ^{2}H NMR spectra obtained for a model of two-site exchange with $(e^2qQ/h)_1$ = 210 kHz, $(e^2qQ/h)_2$ = 0.0 kHz, P = 0.034, $(T_2)_1$ = 4 ms, $(T_2)_2$ = 2 ms. (c) Same as (b) introducing temperature dependence in P.

Experimental Section

Synthesis. VPI-5 was synthesized as described previously.[20] AlPO$_4$-5 was synthesized according to methods reported in the literature[21] with triethylamine as a template. Calcination of AlPO$_4$-5 was performed at 550 °C under flowing dry air. The calcined material was left in open vials for a few days to adsorb water. Thus AlPO$_4$-5 samples referred to as calcined are fully hydrated. The sample purity was verified by X-ray powder diffraction and electron microscopy.

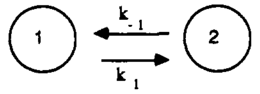
Sample Preparation. Dehydration of VPI-5 was done by evacuation at room temperature for 24 h. AlPO$_4$-5 was dehydrated either by room temperature evacuation (24 h) or by slow heating (30 °C/0.5 h) under vacuum to 400 °C where it was left at a residual pressure of 10^{-5} Torr for ~16 h. No differences were observed between samples prepared by these two procedures. Adsorption of D$_2$O and ND$_3$ was performed at room temperature in the gas phase on the vacuum line. The samples referred to as hydrated samples were prepared by letting the dehydrated sample equilibrate for 2–3 h with the vapors of liquid D$_2$O. The partially hydrated samples were prepared by adsorbing D$_2$O vapors at a given pressure and a constant volume. The adsorption of ND$_3$ was accomplished by exposing the sample to 600 Torr of ammonia for 2–3 h and reducing the pressure to 37 Torr prior to sealing the sample. All samples were sealed at 77 K. TGA measurements were performed on a Mettler TA3000 system at a heating rate of 10 °C/min. The various samples investigated are listed in Table I.

NMR Measurements. NMR experiments were performed on a Bruker CXP spectrometer operating at 121.44 MHz for ^{31}P, 78.17 MHz for ^{27}Al, and 46.07 MHz for ^{2}H. The MAS experiments were carried out on a Dotty probe, in Zirconia rotors with Kel-F caps at a spinning rate of 3–4 kHz. Care was taken to employ 15° pulses in the Al measurements to ensure quantitative comparison of signal intensities.[12] The chemical shifts given for ^{27}Al and ^{31}P are relative to a solution of Al(NO$_3$)$_3$ and to concentrated phosphoric acid, respectively. The ^{2}H spectra were recorded using the quadrupole echo sequence with $\pi/2$ pulses of 2.2 μs and the time interval between the pulses set to 20 μs. The temperature was controlled by a VT-100 variable-temperature unit with an estimated temperature accuracy of ±1 °C. For the MAS experiments we estimate the temperature error to be ±5 °C. ^{2}H NMR measurments were performed on sealed samples. Samples for the MAS NMR experiments were kept after preparation in a sealed tube and were transferred into tightly closed rotors in a dry nitrogen glovebox immediately before the measurements.

Results

AlPO$_4$-5. The ^{2}H spectra of AlPO$_4$-5 (D$_2$O), recorded at room temperature and below, reveal two signals, a rather broad singlet of ~11 kHz width superimposed on a powder pattern with edges at ~±75 kHz. As the temperature is reduced the relative intensity of the powder signal increases. We have previously attributed the powder signal to water molecules coordinated to framework Al and the singlet to physisorbed molecules undergoing rapid isotropic reorientation within the AlPO$_4$-5 channels.[11] When the temperature is raised above room temperature line shape changes take place as shown in Figure 1a. The singlet broadens, the powder signal disappears, and at 46 °C a new powder pattern characteristic of a reduced uniaxial quadrupole tensor starts to evolve. The spectrum obtained at 80 °C is a typical powder pattern of a spin I = 1 with an axially symmetric quadrupole tensor with ω_Q = 4.2 kHz, where ω_Q corresponds to the splitting between the perpendicular singularities in the spectrum.

These line shape changes can be explained assuming a two site exchange model



where $k_1 = (\tau P)^{-1}$, $k_{-1} = [\tau(1 - P)]^{-1}$, and P corresponds to the relative population of site 1. Site 1 represents a deuteron in a bound rigid water molecule for which e^2qQ/h = 210 kHz,[22] and site 2 corresponds to a free water molecule with e^2qQ/h = 0.0. The quadrupole splitting of the fast regime spectrum is given by

$$\omega_Q = (\tfrac{3}{4}e^2qQ/h)P$$

Figure 1b shows a series of simulations calculated by using the above model with P = 3.4%. Although the general evolution of the experimental and simulated spectra show similar features, the calculated spectra corresponding to the temperature range of 46–69 °C are too narrow. In these simulations P was considered to be temperature independent. This assumption does not agree with the low-temperature spectra which indicate that the relative populations are temperature dependent.[11] Indeed, a better fit was achieved when P was increased with decreasing rate (Figure 1c). The line shape evolution of such a model, with constant population, within the slow exchange rate region is shown in Figure 2. In

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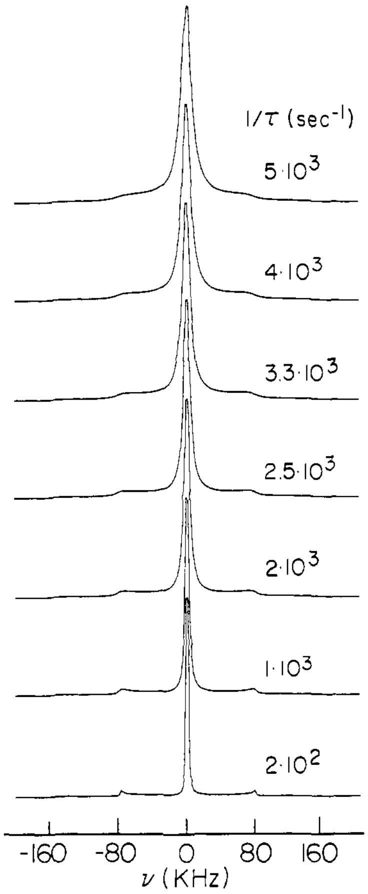


Figure 2. Calculated ^{2}H NMR spectra obtained for a model of two-site exchange as in Figure 1b with $P = 0.333$.

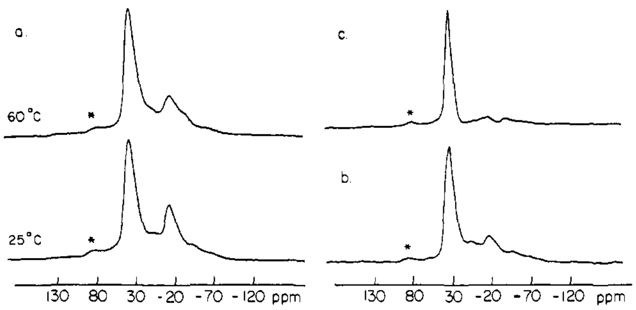


Figure 3. ^{27}Al MAS NMR spectra of (a) AlPO$_4$-5 (calc) recorded at 25 and 60 °C, (b) AlPO$_4$-5 (D$_2$O) recorded at 25 °C, and (c) AlPO$_4$-5 (4.7 wt % D$_2$O) recorded at 25 °C. The asterisks indicate spinning side bands.

this particular case P was taken as 33% to emphasize the contribution of the bound state.

It should be noted that the same line shape evolution can be obtained with a decreased e^2qQ/h and an increased P. This is possible if the bound molecules are not completely rigid as assumed but undergo a fast local hindered motion (at the temperature range of 20–80 °C) which leads to a reduced axial quadrupole tensor.

The temperature dependence of the ^{27}Al MAS NMR spectrum of AlPO$_4$-5 (calc) also indicates that P is temperature dependent as shown in Figure 3a. The spectra show two peaks, at 38 and −16 ppm corresponding to tetrahedral and octahedral Al, respectively.[7] Note the reduced relative intensity of the octahedral peak in the spectrum recorded at 60 °C. Reduction of the temperature to −20 °C introduced some broadening in both Al signals without significant changes in relative intensities. Unfortunately, due to experimental difficulties we could not reduce the temperature any further.

Figure 3 also shows the ^{27}Al MAS NMR spectra of AlPO$_4$-5 (D$_2$O) and AlPO$_4$-5 (4.7% D$_2$O) recorded at room temperature.

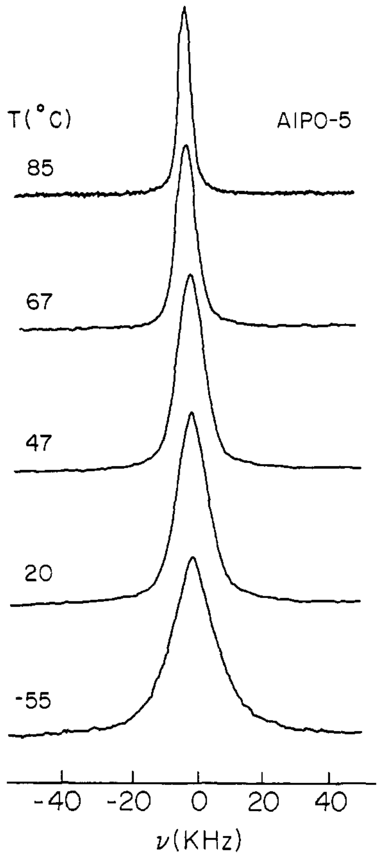


Figure 4. ^{2}H NMR spectra of AlPO$_4$-5 (4.7 wt % D$_2$O) as a function of temperature.

The peak of the octahedral Al in the spectrum of AlPO$_4$-5 (D$_2$O) is smaller than that of AlPO$_4$-5 (calc), indicating that in this particular case the total capacity of water (16%) has not been reached.[7] The octahedral peak in the spectrum of AlPO$_4$-5 (4.7% D$_2$O) is very small and hardly detectable as expected,[7,11] suggesting a reduction in the relative amount of the bound water molecules. This is also evident from the ^{2}H NMR spectra of this sample shown in Figure 4. The top trace, obtained at 85 °C, shows an axial powder pattern with ω_Q = 2.7 KHz which correspond to P = 2.1% as compared to 3.4% in AlPO$_4$-5 (D$_2$O). In this case a singlet is superimposed on the averaged powder pattern even at 85 °C. This singlet can be attributed to water molecules which were removed from the pores due to the relatively high temperature and are located either on the sample walls or on the external surface such that they do not participate in the exchange process.

The signal of the octahedral Al in AlPO$_4$-5 (AS), though small as compared to that in the calcined sample,[11] indicates that bound water molecules do exist. In this case, the template is located within the channels of the sieve and therefore is expected to reduce the amount of water present and to hinder the exchange between bound and free water molecules. Figure 5 shows the ^{2}H NMR spectra of AlPO$_4$-5 (AS, D$_2$O). The bottom spectrum, recorded at 19 °C, is in general similar to that observed for calcined AlPO$_4$-5 (D$_2$O) at the low-temperature range and consists of a singlet superimposed on a broad signal with edges at ±75 kHz. In the top spectrum, recorded at 85 °C, the broad powder features disappeared and were replaced by a powder component with singularities at ±7 kHz on which an intense singlet is superimposed. This singlet is attributed to water molecules which do not participate in the exchange due to the template blocking. (At this temperature the singlet can include also contributions from water molecules removed from the pores.) This also results in an increase of the relative amount of the bound water with respect to water participating in the exchange, yielding a relatively large ω_Q of 14 kHz. Note that there is a narrowing of the singlet probably due to faster reorientation of the physisorbed water molecules.

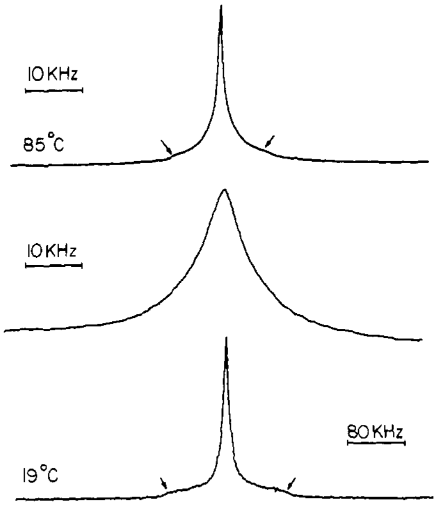
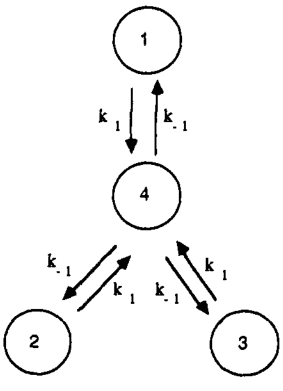


Figure 5. ^{2}H NMR spectra of AlPO$_4$-5 (AS, D$_2$O). The two bottom spectra were recorded at 19 °C and the upper one at 85 °C.

VPI-5. The water dynamic in VPI-5, below room temperature, is very similar to that observed in AlPO$_4$-5.[11] The ^{2}H NMR spectra of VPI-5 (D$_2$O) in the temperature range of −125 to −26 °C are shown in Figure 6. The spectrum recorded at −125 °C shows a slightly biaxial powder pattern with $\omega_Q \cong 140$ kHz, as expected from frozen D$_2$O,[22] and a relatively weak singlet superimposed on the powder. The general shape of the powder pattern differs from that expected for a completely rigid O–D bond thus suggesting that some slow motion already takes place at this low temperature. As the temperature is raised the relative intensity of the powder pattern decreases and the intensity of the singlet increases. The line width of the singlet does not significantly change in the range of −125 to −46 °C where it remains between 6 and 7 kHz. At −26 °C the powder features are no longer evident and further heating of the sample results in spectral changes that have gross features similar to those observed in AlPO$_4$-5, indicative of exchange between bound and free water molecules (Figure 7a). A close look, however, discloses significant differences manifested mainly in the evolution of the parallel singularities at ±6 kHz. The fast limit spectrum (80 °C), as in AlPO$_4$-5, shows a uniaxial powder pattern with $\omega_Q = 6.1$ KHz.

The line shape evolution in the range of 26 to 64 °C is very similar to that obtained from a three-site jump with a jump angle close to the tetrahedral angle or its supplementary angle.[23] Accordingly, we tried to fit the experimental spectra with a dynamic model which involves both exchange between bound and free states and a 3-fold jump. This can be described by the following 4-site system.



Sites 1, 2, and 3 correspond to the deuterons in three bound D$_2$O molecules with orientations related by a 3-fold symmetry axis. Site 4 represents free water molecules ($e^2qQ/h = 0$). In this model

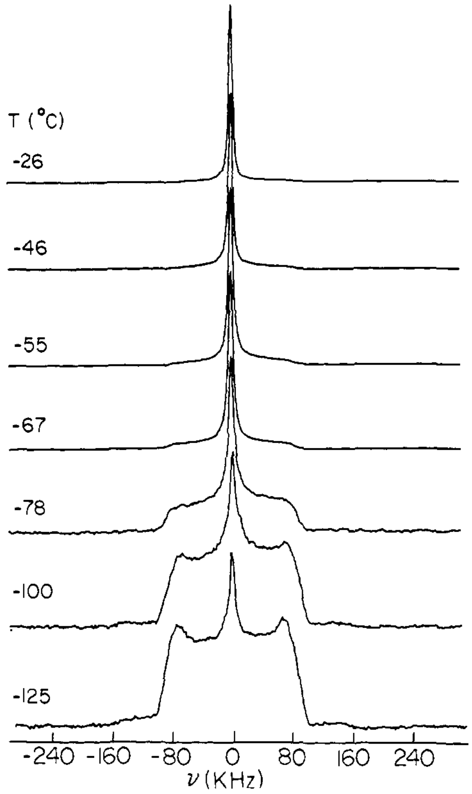


Figure 6. ^{2}H NMR spectra of VPI-5 (D$_2$O) recorded at the temperature range of −125 to −26 °C.

there is no direct exchange between the bound sites. The populations of sites 1, 2, and 3 are equal and given by

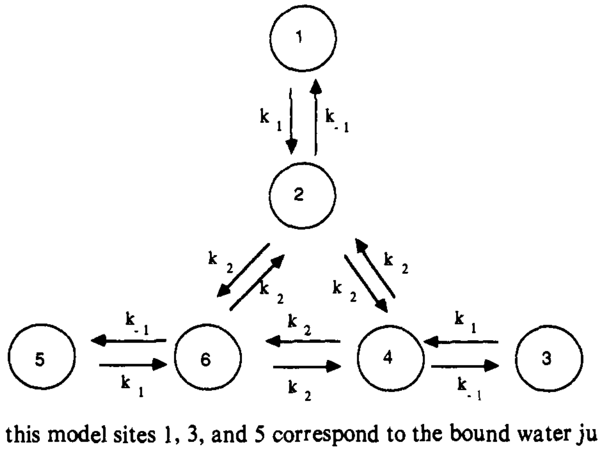
$$P = (1 - P_4)/3$$

where P_4 is the population of the free molecules and

$$k_{-1} = (\tau P_4)^{-1} \qquad k_1 = (\tau P)^{-1}$$

Figure 7b shows a series of simulations based on this model where $e^2qQ/h = 210$ kHz for sites 1, 2, and 3, $P = 0.052$, and the jump angle, θ, is 68°. This angle is the angle that the principal axis of the quadrupole tensor (approximately parallel to the O–D bond) makes with the C$_3$ axis relating sites 1, 2, and 3. In our calculations we neglected the small asymmetry parameter of the quadrupole tensor of the D$_2$O deuterons. This model provides a good fit for the spectra in the range 37–64 °C and at −29 °C. We could not, however, obtain a satisfactory fit for the spectra recorded at 2 and 26 °C.

A better fit can be achieved assuming a slightly different exchange mechanism which involves exchange between three pairs of sites:



In this model sites 1, 3, and 5 correspond to the bound water just

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(23) Poupko, R.; Luz, Z. Unpublished results.

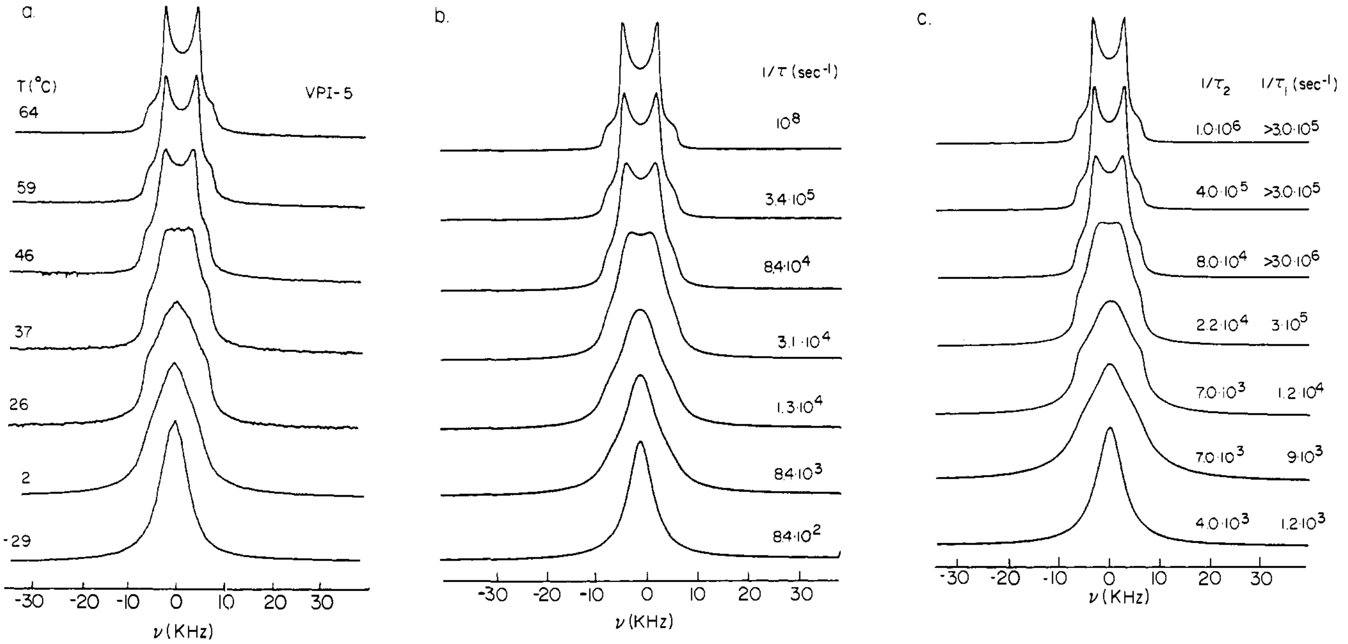

Figure 7. (a) ^{2}H NMR spectra of VPI-5 (D_2O) recorded between −29 and 64 °C. (b) Calculated ^{2}H NMR spectra for a four-site exchange model ($P = 0.052$, $T_{2\,\mathrm{bound}} = 4$ ms, $T_{2\,\mathrm{free}} = 2$ ms, and $\theta = 68°$). (c) Calculated ^{2}H NMR spectra for a six-site exchange model ($P = 0.04$, $T_{2\,\mathrm{bound}} = 4$ ms, $T_{2\,\mathrm{free}} = 2.8$ ms, and $\theta = 71°$).

as sites 1, 2, and 3 in the previous model, but site 4 has been split into three identical sites with equal populations. For all three pairs

$$P = P_1 = P_3 = P_5 \qquad P_2 = P_4 = P_6 = (1 - 3P)/3$$

and

$$k_{-1} = (\tau_1 P_2)^{-1} \qquad k_1 = (\tau_1 P_1)^{-1}$$

and

$$k_2 = (\tau_2)^{-1}$$

The main difference between this model and the previous one is that the probability of a free water molecule to jump to an adjacent bound state is different than that of returning to the bound state within the pair, i.e., $k_{-1} \neq k_2$. The simulations obtained from such a model are shown in Figure 7c where $\theta = 71°$ and $P = 0.04$. At the lower temperature range the line shape is mostly determined by the exchange rate within the pair ($1/\tau_1$) and is not sensitive to the 3-fold jump rate ($1/\tau_2$). Above 37 °C $1/\tau_1$ reaches the fast limit on the NMR time scale and the line shape changes are determined by $1/\tau_2$. At 26 °C, in the intermediate range, both rates affect the line shape. In these spectra, unlike in $AlPO_4$-5, the relative populations were taken as temperature independent. This, however, is not the case in the temperature range below −29 °C as indicated by the spectra shown in Figure 6. In this range probably the motion of the free molecule slows down and they gradually freeze and add to the powder signal. In this model, as in the case of $AlPO_4$-5/D_2O, we assumed that the bound molecules were completely rigid. Again the same line shape evolution within the higher temperature range, namely, 0–64 °C, could be obtained by assuming a fast local motion of the bound molecules leading to a reduced axial tensor and accordingly an increased P.

The ^{31}P and ^{27}Al MAS NMR spectra of the VPI-5 (D_2O) sample are shown in Figure 8. The ^{27}Al spectrum consists of one narrow signal at 41 ppm due to tetrahedral Al and a broad signal at −20 to −28 ppm corresponding to octahedral Al. The ^{31}P spectrum is composed of three peaks with equal intensities at −22.5, −27.3, and −33.1 ppm. These spectra are similar to those previously reported for VPI-5[3] and indicate that the dehydration procedure did not introduce any changes in VPI-5 such as transforming it to $AlPO_4$-8.[24]

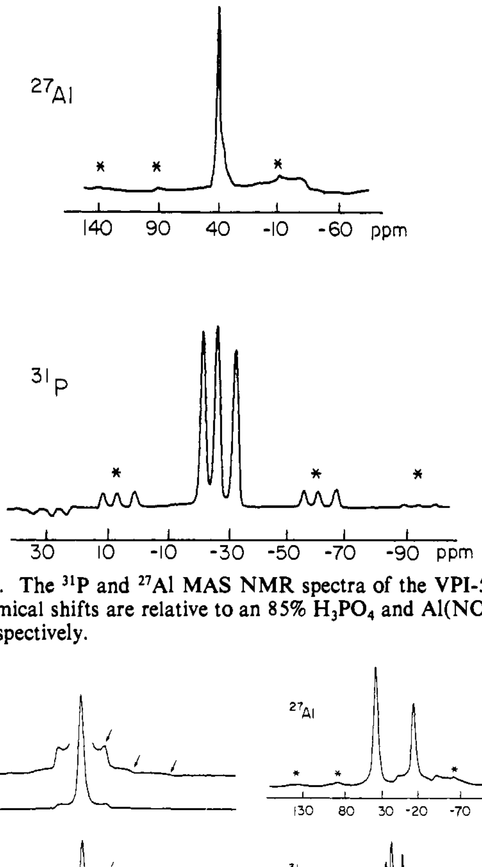

Figure 8. The ^{31}P and ^{27}Al MAS NMR spectra of the VPI-5 (D_2O). The chemical shifts are relative to an 85% H_3PO_4 and $Al(NO_3)_3$ solutions, respectively.

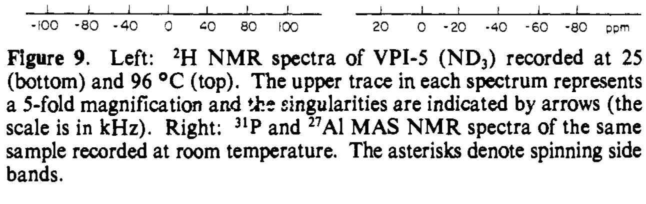

Figure 9. Left: ^{2}H NMR spectra of VPI-5 (ND_3) recorded at 25 (bottom) and 96 °C (top). The upper trace in each spectrum represents a 5-fold magnification and the singularities are indicated by arrows (the scale is in kHz). Right: ^{31}P and ^{27}Al MAS NMR spectra of the same sample recorded at room temperature. The asterisks denote spinning side bands.

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The ^2H NMR spectrum of VPI-5 (6.7 wt % D_2O) showed similar line shape evolution and the splitting of the averaged axial powder pattern was 6.7 kHz which is somewhat larger than that observed in VPI-5 (D_2O). This suggests that unlike with $AlPO_4$-5, reducing the amount of water does not decrease the relative amount of the bound water. The corresponding ^{27}Al spectrum is however significantly different; the octahedral Al line disappeared and the tetrahedral Al line is considerably broader and seems to consist of several unresolved lines. This is in agreement with the ^{27}Al spectrum of a partially hydrated VPI-5 sample obtained by using the double rotation technique (DOR)[25] which showed a number of resolved lines in the vicinity of the tetrahedral Al signal.

Ammonia, similar to water, binds to framework Al in VPI-5 and in $AlPO_4$-5.[11] Figure 9 shows the ^2H, ^{31}P, and ^{27}Al NMR spectra of a sample of VPI-5 after the adsorption of ND_3. The room temperature ^2H spectrum is composed of three signals, a broad singlet (width of 8.7 kHz), an axial powder pattern with $\omega_Q = 50$ kHz, where the parallel singularities can clearly be observed at ±50 kHz, and a powder pattern with singularities at ±90 kHz. We attribute the first two signals, which were observed in $AlPO_4$-5 as well,[11] to ND_3 molecules reorienting isotropically in the channels and to molecules coordinated to the Al, undergoing fast rotation about the Al–N axis leading to $\omega_Q = 50$ kHz. The deuterons quadrupole coupling constant can be obtained from the following relation

$$\omega_Q = \frac{3e^2qQ}{8h}(3\cos^2\theta - 1)$$

where θ is the angle between the N–D bond and the rotation axis. Assuming that the D–N–D angle is similar to the H–N–H angle, 107.2°, and that it is not affected by the coordination to the Al, simple trigonometric relations give $\theta = 68.3°$ and $e^2qQ/h = 226$ kHz. This value yields a rigid limit spectrum with perpendicular singularities at ±85 kHz. This value is very close to the edges we see for the third ND_3 signal, considering the experimental error in the determination of these singularities. Accordingly, we assign the latter to a bound rigid molecule. However, since the parallel singularities are not evident we cannot rule out the possible existence of some local hindered motion. Heating the sample up to 96° did not introduce significant changes in the spectra, besides a narrowing of the singlet to a width of 6.7 KHz, indicating that on the NMR time scale no exchange between the different motional states takes place.

The ^{31}P MAS NMR spectrum of VPI-5 (ND_3) consists of three lines of equal intensities at −24.9, −27.7, and −33.3 ppm (Figure 9). The adsorption of ammonia causes a shift of the low field line from −22.5 to −24.9 ppm as compared to the hydrated sample. This low field line is the most sensitive to the hydration state, it disappears upon dehydration,[3] and its intensity is temperature dependent.[6] Hence, it is not surprising that it is this line that is affected by the adsorption of ammonia. In $AlPO_4$-5 there were no detectable changes in the ^{31}P chemical shift due to adsorption of ammonia.[11]

The ^{27}Al MAS NMR spectrum of VPI-5 (ND_3) shows three signals, two narrow signals at 38 and −11 ppm and a broad weak signal at about −40 ppm (Figure 9). The later is probably part of a second-order quadrupole line shape which is somewhat obscured by spinning side bands. In order to obtain its chemical shift unambiguously a DOR spectrum is required.[25] We assign this signal to octahedral Al coordinated to two ammonia molecules. In hydrated VPI-5 the MAS NMR signal of the octahedral Al is also much broader than the tetrahedral due to a larger nuclear quadrupole interaction. We exclude the possibility that this line is due to Al coordinated to residual water since prolonged vacuum evacuation of VPI-5 causes the total removal of the octahedral signal, furthermore the signal appears at a different frequency than the octahedral signal in the hydrated sample. The peak at 38 ppm is of tetrahedral Al similar to that observed in hydrated VPI-5. The assignment of the −11-ppm line is ambiguous. It could be assigned to octahedral Al at a different T site, namely between 6- and 4-membered rings as opposed to the site between the two 4-membered rings which yields the −40-ppm signal or vice versa. Comparison with $AlPO_4$-5 favors the assignment of a narrow octahedral Al signal to a T atom between 4- and 6-membered rings. Another possibility is that it is due to pentacoordinated Al.[26] The spectrum of $AlPO_4$-5 adsorbed with ammonia also showed three signals, at 39, 0, and −16 ppm, but in this case all three signals were narrow. Furthermore no rigid ND_3 molecules were detectable in $AlPO_4$-5, only free molecules and those rotating about the Al–N axis.[11] In $AlPO_4$-5 the −16-ppm signal was assigned to octahedral Al and it was suggested that the 0-ppm signal corresponds to the pentacoordinated Al. TGA measurements of VPI-5 (ND_3) showed three peaks, at 50, 90, and 180 °C: the first and last peaks are narrow whereas the second is broad and intense. The total amount of adsorbed ND_3 was 23 wt %.

Discussion

The structures of $AlPO_4$-5 and VPI-5 are similar in the sense that they both consist of straight unidimensional channels and in both part of the framework Al coordinates water molecules. The channels, however, differ significantly in their openings, 7.3 and 12.1 Å, respectively. The ^2H NMR spectra of D_2O in both $AlPO_4$-5 and VPI-5 reflects the special dynamic properties of the water molecules within the channels, not observed in any of the closely related aluminosilicate zeolites. Although in both materials two distinct types of water molecules are evident, free and bound, TGA/DSC measurements indicate a two-stage water loss only in VPI-5.[3] In both materials the ^2H NMR line shape analysis showed that exchange between the two states takes place. Nonetheless, we found a fundamental difference in the mechanism of exchange in the two materials. While in $AlPO_4$-5 the only evident mechanism is the two-site exchange between the free and bound water, in VPI-5 it is accompanied by a three-site jump with a jump angle of 71°.

The exchange mechanism in VPI-5 has features which appear consistent with the water structure proposed by McCusker et al.[5] The bound molecules are those coordinated to the framework Al and the "free" molecules are the hydrogen-bonded molecules forming the triple-helix structure down the channel. Exchange within the pair corresponds to exchange between these two types of water molecules. The 3-fold-site jump between pairs is attributed to jumps between the three different chains forming the helix. However, there are several features in the model suggested by McCusker that are not consistent with typical water adsorption in molecular sieves. First, the absence of water in the six-ring void spaces is not consistent with principles of normal physical adsorption. Those should fill with water before the 18-ring-channel voids. Nonetheless, the unique structure of water in VPI-5 may provide a situation which overrides the normal energetically favored adsorption in the six-ring voids. Second, since all the water is located in the large channels, the density of water necessary for all the water molecules to be accommodated in the space is about 1.2 which is very large. Finally, water adsorption has been used for decades to measure the total void volume of microporous crystals,[27] and if one assumes that the total adsorption of water fills the total void space in aluminophosphate, then the void spaces calculated from the crystal structures are consistent with the total adsorption of water.[3]

Our NMR results and the mechanism presented to explain the line shape changes do not restrict the location of either the bound or the free water to a particular channel. The free water molecules may include water from all voids undergoing fast exchange. Accordingly, although our results are consistent with the McCusker model in terms of the symmetry of the water structure, it does not imply that indeed all the water molecules are located in the large channel. The exchange mechanism of the water in

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VPI-5 is also consistent with the distribution of the octahedral Al in the framework as proposed by Grobet et al.[28] which has a C_3 symmetry. The results given here prove that water has a structure in VPI-5 which is not observed in $AlPO_4$-5. This conclusion is in agreement with the speculations of van Braam Houchgeest et al.[6]

The quadrupole splitting, ω_Q, of the fast limit spectrum is given by

$$\omega_Q = |(^3/_8\, e^2qQ/h)(3P)\ (3\cos^2\theta - 1)|$$

Our simulations gave $P \approx 0.04$ which corresponds to a total of 12% bound molecules. This is significantly smaller than the 28% expected considering the total amount of water and the 33% of octahedral Al as shown by double rotation NMR spectroscopy.[25] Taking $P = 0.28/3$ and assuming that the bound molecules are completely rigid, i.e. $e^2qQ/h = 210$ kHz, for $\theta = 71°$ we obtain $\omega_Q = 15.3$ kHz. This value exceeds the experimental value, 6.1 kHz, by a factor of 2.5. The experimental value can be obtained if we set θ to 49°, but the line shape evolution is considerably different from the experimental observation. We found that the line shape changes are very sensitive to the jump angle and it had to remain close to 71°. There are two ways to explain this discrepancy: One is that the VPI-5 (D_2O) is not fully hydrated such that the relative amount of bound molecules is lower. We rule out this explanation since reducing the amount of adsorbed water increases ω_Q in the fast limit region rather than decreases it. The other possibility is that the bound molecules are not completely rigid but undergo some local motion which averages the quadrupole coupling constant such that it is reduced by a factor of about 2.5, i.e., $e^2qQ/h = 88$ rather than 210 kHz as taken in the simulations. In this case, this motion must be fast above room temperature (on the NMR time scale) as it does not affect the line shape, resulting in a final axial tensor. Since the NMR spectra do not provide us with a clue to the nature of this motion, we can only speculate that it may be a rotation or jumps about the Al–O axis or exchange between the two molecules coordinated to one Al. The latter seems less reasonable since we obtained similar line shape changes in a partially hydrated (6.7 wt%) sample that showed practically no octahedral Al and presumably some pentacoordinated Al.[25] The low-temperature spectra did not show any distinct line shape changes which could shed light upon the nature of this motion. Moreover, they are also affected by the freezing of the "free" water which complicates the dynamics significantly. The persistent edges at ±75 kHz may be indicative of π flips which at higher temperature may transform into a free rotation.

Although ammonia molecules bind to framework Al in VPI-5, no exchange between bound and free molecules was observed indicating a firmer binding of the ammonia as compared to water. This was confirmed by TGA measurements which showed that the highest desorption peaks of ammonia and water are at 180 and ~100 °C, respectively. We assign the ammonia molecules undergoing fast rotation about the Al–N axis to those bound to the Al, showing a signal at −11 ppm, and the more rigid ND_3 molecules to the octahedrally coordinated Al (signal at ca. −40 ppm), where steric hindrance prevents the rotation of the two ammonia molecules about the N–Al axis. As previously discussed, the assignment of the −11-ppm peaks remains ambiguous. A combination of DOR NMR spectroscopy, which can give precise relative intensities of the different Al signals, and quantitative determination of the relative amounts of the three types of ammonia molecules is required to unambiguously assign this signal.

In $AlPO_4$-5, the bound water molecules are also associated with octahedral Al. Reduction of the amount of adsorbed water decreased the relative population of the bound water as compared to the slight increase in VPI-5. This suggests that in VPI-5 the affinity of the water molecules to framework Al is larger.

The relative population of the bound water molecules in $AlPO_4$-5 (D_2O) at room temperature as obtained from the simulations is 8.3%. A coarse estimation of the relative amount of the octahedral Al, obtained by comparing the integrated areas of the center bands in the ^{27}Al spectrum, indicates that for this particular sample ~10% of the Al are octahedral. This method of determining relative amounts may not necessarily be correct since some signals are lost in the spinning side bands. In our previous study[11] we showed that the area of the tetrahedral peak in a dehydrated sample is equal within 10% to the total area of the octahedral and tetrahedral peaks in the same rehydrated sample. This indicates that the anisotropies of both signals are comparable and justifies the comparison of the center bands' intensities to obtain relative amounts of tetrahedral and octahedral Al. Taking into account that each octahedral Al binds two water molecules, the composition of the $AlPO_4$-5 (D_2O) sample is $Al_2O_3{\cdot}P_2O_5{\cdot}4.8D_2O$. This total amount of water exceeds by a factor of ~2 the maximum 16% water capacity of $AlPO_4$-5. Moreover, we know from the Al spectrum that our sample ($AlPO_4$-5 (D_2O)) is not saturated with water as the signal of octahedral Al is weak compared with that of fully hydrated calcined $AlPO_4$-5.[7,11] As in the simulations of the ^{2}H spectra of D_2O in VPI-5, we obtained the relative population of the bound water assuming a quadrupole coupling constant of a completely rigid water molecule. Reducing e^2qQ/h by a factor of 2–3, as in the case of VPI-5, will allow the increase of the P and will provide a better agreement with the composition of hydrated $AlPO_4$-5. As mentioned earlier such a reduction in the quadrupole coupling constant can be obtained by a local motion of the bound molecules. The motion mechanism however must lead to a completely averaged axial tensor in order to show the same line shape evolution. The similarity between the low-temperature spectra in both sieves suggests similar local motion.

The powder patterns in all ^{2}H spectra in the low-temperature range show edges at ±75 which can be a result of a two-site jump (180° flips) with an angle of 54°, yielding a biaxial powder pattern with $\eta \cong 1$.[11] Such a motion can take place about the Al–O axis. However, if such a motion were to previal in $AlPO_4$-5 at higher temperatures as well, the fast limit spectrum would be biaxial rather than uniaxial as observed.

The water dynamic in the as-synthesized $AlPO_4$-5 also fits the above picture of the water motion in the channels. At room temperature the relative amount of bound water seems rather large, about ~30%, yet the amount of octahedral Al is small.[11] This suggests that the relative amount of free water has been reduced due to the presence of the template. Furthermore, the template has a blocking effect, preventing some of the free molecules from exchanging with the bound molecules.

The dynamic properties of adsorbates are determined by steric factors imposed by the intracrystalline structure of the molecular sieve and/or by specific interactions with the framework binding sites. For instance, the dynamic state of aromatic molecules and small hydrocarbons in ZSM-5 is mostly determined by the size of the channels[29] whereas the motion of alkyl amines is determined by their binding to acid sites.[14,29] Water molecules do not show strong affinity to zeolite acid sites and are small enough to reorient isotropically within zeolite pores at high water loadings.[12] In $AlPO_4$-5 and VPI-5 the situation is entirely different since water molecules can bind to framework Al, thus their dynamic properties are determined by the binding sites and not by the steric factor imposed by the channel size. One may argue that the bound water corresponds to water molecules situated in the narrow six-ring channels where their motion is hindered and the exchange is with free water residing in the large channel. In this case one will have to assume that the three bound sites in VPI-5 are three different water orientations within the narrow channel. Such a picture is not favorable in $AlPO_4$-5 since the generation of a bound state of water or ammonia was associated with the appearance of octahedral Al, whereas the adsorption of methanol, which was found to reorient isotropically within the $AlPO_4$-5 channels,[11] did not yield octahedral Al.[11] Furthermore, if the bound water was to reside in the six-ring channel then there should have been no difference in the exchange mechanism in $AlPO_4$-5 and VPI-5.

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Conclusions

Two distinct types of water molecules were found in both $AlPO_4$-5 and VPI-5. The first corresponds to water molecules undergoing fast isotropic reorientation within the channels and the second to water molecules bound to framework Al. Exchange between the two types has been observed in both materials. In VPI-5, however, this exchange is accompanied by a 3-fold jump indicating a relatively high degree of water ordering within the channel. The order at which these two types of water form is different in both materials. In $AlPO_4$-5, reduction of the water content results in a decrease in the amount of bound water, whereas in VPI-5, the opposite takes place. The presence of the template in $AlPO_4$-5 hinders this exchange.

Sorbed ammonia molecules in VPI-5 are present in three distinct dynamic states, free physisorbed molecules, molecules bound to framework Al and undergoing a rotation about the N–Al axis, and rigid molecules bound to octahedral framework Al. Unlike in the case of water, no exchange between the three states was observed. Although the VPI-5 channel is larger than that of $AlPO_4$-5, the water exhibits a greater degree of order in VPI-5 which reflects the special role it may play in the structure stabilization.

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Hemoglobin R→T Structural Dynamics from Simultaneous Monitoring of Tyrosine and Tryptophan Time-Resolved UV Resonance Raman Signals

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Abstract: High quality ultraviolet resonance Raman (UVRR) spectra with 230-nm excitation are reported for deoxy- and CO-hemoglobin (Hb), and for the HbCO photoproduct, obtained with varying delay between photolysis and probe laser pulses. At 10- to 20-μs delays, the photoproduct–HbCO difference spectrum shows numerous Tyr and Trp difference signals that are indicative of having reached the T state, on the basis of their likeness to the static deoxyHb–HbCO difference spectrum. At earlier delays, the difference signals diminish in intensity and, at submicrosecond delays, are different in shape and frequency. Deconvolution analysis of the W3 band envelope and application of the correlation of W3 frequency with the dihedral angle, $\chi^{2,1}$, to the X-ray coordinates facilitated assignment of these components to the three inequivalent Trp residues, β37, α14, and β15. The Trp β37 assignment was confirmed via the UVRR spectrum of Hb Rothschild, in which Trp β37 is replaced by arginine. The unique environmental sensitivity of the W3 frequency makes this band a particularly rich source of information in the time-resolved UVRR difference spectra, as the different W3 components exhibit quite different temporal evolutions. Changes in these components were evaluated in terms of environmental effects with the aid of excitation profiles (EP's) for the Trp model, 3-methylindole in various solvents. Prompt (30 ns) spectral changes were shown, on the basis of the W3 assignments, to be associated with displacements of the A and E helices on the distal side of the heme pocket in the immediate photoproduct. The 1-μs transient is characterized by an upshifted W17 band, which suggest an intermediate protein structure in which the Trp β37 R-state H-bond is broken. The Tyr ν_{8a} and ν_{8b} (Y8a and Y8b) difference signals are shown to result from small upshifts, with a slight intensity loss in Y8a. These changes are detected in bands that result from six inequivalent but unresolvable Tyr residues. The crystal structures, however, indicate that the H-bonding environments of five of these residues differ insignificantly between the R and T states, and attention naturally focuses on the remaining Tyr α42 residue. This residue resides in the "switch" region of the $\alpha_1\beta_2$ interface, where it forms an H-bond with the carboxylate side chain of Asp β99 only in the T state. Elimination of this H-bond via mutations at Asp β99 is known to reduce cooperativity by destabilizing the T state. It has long been assumed that Tyr α42 is the proton donor to a deprotonated Asp β99 carboxylate in this H-bond. However, this should produce a *downshift* and intensification of Y8b on the basis of other proteins with donor Tyr–carboxylate H-bonds and of UVRR spectra of the Tyr model, *p*-cresol in solvents of varying donor and acceptor numbers. The observed Y8b *upshift* and loss of intensity in Y8a is instead consistent with Tyr α42 *accepting* a proton from a neutral Asp β99 in this critical H-bond. An acceptor H-bond is readily accommodated by the crystallographic coordinates, which show the Asp β99 side chain to be in a solvent-inaccessible hydrophobic environment. Whether this site can actually support protonation of carboxylate at neutral pH is discussed in the context of experimental and computational results.

Introduction

Hemoglobin is widely studied as a paradigm of allostery and of cooperative ligand binding to proteins.[1] The explanation offered 25 years ago by Monod, Wyman, and Changeaux,[2] that cooperativity results from a switch between low- and high-affinity states (T and R, respectively) upon partial ligation of the four heme sites, continues to provide a productive model of Hb function. Under various conditions, however, there are more than two states available to the Hb molecule.[3-5] The T and R states have been

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