existence of an "H-bonded" association between adsorbed 
O2 and N2 and the -OH groups of a silica surface; (iii), the 
recent suggestion that a comparable HBB competitive 
complexation process controls the potency of fluorocarbon 
anesthetics; and (iv), the observed effects of H-bonds 
donors on the glass transition temperature of linear alcohols. 
Further work is underway and a longer report will be 
issued shortly.
s), a home-built 180-MHz spectrometer ($\nu_{Al} = 46.9$ MHz; 90° pulse duration, 8 ms; repetition time, 0.5 s), and a home-built 60-MHz spectrometer ($\nu_{Al} = 15.6$ MHz; 90° pulse duration, 8 ms; repetition time, 0.5 s). The repetition times give full relaxation because $T_1$ values are of the order of 10 ms. For all three spectrometers the same spinner was used, a cylindrical Delrin spinner supported by two air bearings. A spinning frequency of $\sim 3$ kHz proved to be sufficient.

Magic Angle Spinning NMR of a Quadrupolar Nucleus

Aluminum nuclear spins in an aluminosilicate are subjected to three anisotropic interactions: dipolar interactions with neighboring nuclei like $^1$H and $^{29}$Si, interaction of the nuclear quadrupole moment with electric field gradients, and the anisotropic chemical shift interaction. Of these three interactions the quadrupole interaction will prove to be the most important for our experiments. A discussion of the effect of magic angle spinning on the NMR spectra of quadrupolar nuclei can be found at several places in the literature. Here we want to mention only the outcome of these theories.

For half-integer nuclear spins like $^{27}$Al, the anisotropic quadrupole interaction causes a severe line broadening in solid-state NMR spectra, except for the $m = 1/2 \leftrightarrow m = -1/2$ transition if the quadrupole interaction is small compared to the Zeeman interaction of the nuclear spin. It is easy to show that for this $1/2 \leftrightarrow -1/2$ transition the quadrupole interaction contributes only in second- and higher-order perturbation theory. In practice, therefore, only this transition is observed in solid samples, showing a characteristic powder pattern depending on the value of the asymmetry parameter $\eta$. Magic angle spinning reduces but does not eliminate the width of this powder pattern. A formula for the frequency of the $1/2 \leftrightarrow -1/2$ transition under fast magic angle spinning conditions has been derived by Kundla et al. and can be rewritten as

$$v_{1/2,-1/2} = v_2 - \frac{1}{16} \frac{\nu_{Q}^2}{v_2} \left\{ (I+1) - \frac{3}{4} \right\} \{ A(\alpha) \cos^4 \beta + B(\alpha) \cos^2 \beta + C(\alpha) \}$$

where

$$v_2 = -\gamma B_0 (1 - \sigma) / 2\pi$$

$$\nu_{Q} = 3e^2 qQ / [2(2I - 1)\hbar]$$

$$A(\alpha) = \frac{1}{2} - \frac{1}{2} \eta \cos 2\alpha + (7/18)\eta^2 \cos^2 2\alpha$$

$$B(\alpha) = -3 + 3\eta^2 + \frac{5}{3} \eta \cos 2\alpha - 7/9 \eta^2 \cos^2 2\alpha$$

$$C(\alpha) = \frac{1}{2} - \frac{1}{2} \eta \cos 2\alpha + (7/18)\eta^2 \cos^2 2\alpha$$

and $\alpha$ and $\beta$ are the polar angles of the spinning axis with respect to the principal axes of the quadrupole tensor.

Singular points and discontinuities in the powder pattern are found when $\partial v_{1/2,-1/2} / \partial \alpha = \partial v_{1/2,-1/2} / \partial \beta = 0$. Figure 1 shows the pattern for $\eta = 0$, $\eta = 0.75$, and $\eta = 1$. Equation 1 shows in addition that the width of powder pattern decreases with magnetic field. Therefore, when in an experimental situation it is found that the line width of a line decreases with field, then this points to the existence of quadrupole broadening. This is in contrast to a broadening due to a distribution of chemical shifts, a common source of line broadening in magic angle spinning NMR, which increases with field.

Results and Discussion

Figure 2 shows $^{27}$Al spectra of H-ZSM-5 at three different magnetic fields at 78.2, 46.9, and 15.6 MHz with 3-kHz magic angle spinning. All spectra are obtained at room temperature. The hydrated spectra are the result of 10 000 (at 78.2 MHz), 130 000 (at 46.9 MHz), and 350 000 (at 15.6 MHz) $f$ID's. The spectra of the dehydrated material needed 250 000 (at 78.2 MHz) and 180 000 (at 46.9 MHz) $f$ID's. At 15.6 MHz no signal was obtained of the dehydrated material after 750 000 $f$ID's.
chemical shift anisotropy is eliminated by magic angle spinning, the initial decrease of the line width has to be due to the fact that the line width is caused by a distribution of \(^{27}\text{Al}\) chemical shifts. Only at the lowest fields, where the chemical shift distribution in frequency units is small, does the quadrupole broadening become important. At frequencies below 15 MHz the line width is expected to increase again.

For the dehydrated samples, however, the situation is very different. Figure 2 shows that the line width increases from 1100 Hz at 78.2 MHz to 1700 Hz at 46.9 MHz to undetectably broad at 15.6 MHz. Dehydration clearly makes the \(^{27}\text{Al}\) line broader, by a factor 2 at 78.2 MHz, by a factor 4 at 46.9 MHz, and by a much larger factor at 15.6 MHz. The field dependence of the line width shows that quadrupole interaction is the dominant factor determining the line width in the dehydrated samples. Clearly, dehydration causes a strong increase of the quadrupole interaction.

By comparing the experimental line shapes to the theoretical shapes of Figure 1, one can conclude that the resulting electric field gradient at aluminum is highly asymmetric (no separate quadrupole pairs are observed). At this point we should mention that proton decoupling during acquisition of the \(^{1}H\) free induction decay does not affect the \(^{27}\text{Al}\) NMR line width, not in the hydrated case nor in the dehydrated situation. Dipolar interaction between protons and \(^{27}\text{Al}\) apparently is so weak that it can be eliminated by magic angle spinning alone.

Figure 3 displays \(^{27}\text{Al}\) spectra of Na–ZSM-5 as a function of water content at 78.2 MHz. All spectra represent 25 000 fID's and are obtained with 3-kHz magic angle spinning.

![Figure 3](image)

Figure 3. \(^{27}\text{Al}\) spectra of Na–ZSM-5 as a function of water content at 78.2 MHz. All spectra represent 25 000 fID's and are obtained with 3-kHz magic angle spinning.

When the sample is dried at 250 °C, the tetrahedral \(^{27}\text{Al}\) line at 53 ppm collapses; hydration for a variable length of time makes this line slowly appear again. In the dehydrated sample, evidently, the quadrupole interaction becomes so strong that the tetrahedral \(^{27}\text{Al}\) line of the genuine ZSM-5 aluminum becomes too broad to be detectable, even at 78.2 MHz. Apparently, the increase of quadrupole interaction on dehydration is much stronger for Na–ZSM-5 than for H–ZSM-5. Dehydration of the Na–ZSM-5 sample has no effect on the broad lines at 5 and 65 ppm; the narrow line at -1 ppm disappears and does not come back at hydration.

The same experiments were carried out on faujasite H–Y and amorphous SiO\(_2\)/Al\(_2\)O\(_3\). For faujasite H–Y the situation is just the reverse of that for ZSM-5: the \(^{27}\text{Al}\) line width of the hydrated sample increases on going to the lower frequency (750 Hz at 78.2 MHz, 1350 Hz at 46.9 MHz). Apparently, even in the hydrated form there is already a considerable broadening due to quadrupole interaction, showing the existence of distorted tetrahedra. This distortion may be inherent to the structure which is different from H–ZSM-5, and possibly due to the presence of aluminum in higher coordination spheres (faujasite H–Y has a Si–Al ratio of 2.81). On dehydration the faujasite H–Y \(^{27}\text{Al}\) line width at 78.2 MHz increases to 1800 Hz, showing a considerable extra distortion around aluminum.

Figure 4 shows the \(^{27}\text{Al}\) spectrum of amorphous SiO\(_2\)/Al\(_2\)O\(_3\) at 78.2 MHz for hydrated and dehydrated material. Only the peak at -52 ppm from tetrahedrally surrounded aluminum broadens on dehydration, indicating that strong chemisorption of water takes place only at the tetrahedral sites, not at octahedrally coordinated aluminum.

As a conclusion of this work we can then state that in both Na–ZSM-5 and H–ZSM-5 dehydration causes a lowering of local symmetry around aluminum as evidenced by the increase in quadrupole interaction of aluminum. This increase is cation dependent. Similar effects are observed in faujasite H–Y and amorphous SiO\(_2\)/Al\(_2\)O\(_3\). On the crucial question of what precisely causes this lowering of local symmetry, we can at this moment only speculate. As mentioned in the Introduction it is believed that in

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hydrated material the cation forms a cluster with water molecules. On dehydroxylation the cation presumably comes nearer to aluminum. This causes a change in the distribution of charges around aluminum and possibly a distortion of the aluminum-oxygen tetrahedra. Both effects, the change in charge distribution and distortion of the tetrahedra, can give rise to an increase in electric field gradient at the aluminum nucleus. However, from the observation that the increase in quadrupole interaction on dehydration is stronger for Na-ZSM-5 than for H-ZSM-5, we tend to believe that the distortion of the tetrahedra is more important for the increased electric field gradient than the redistribution of charges, although of course the latter effect may induce the local distortions.

In the case of dehydrated H-ZSM-5 it is often indicated that the H+ ion exists in a Al–OH+ band. For a perfect tetrahedron with an Al–O distance of 1.59 Å and an O–H distance of 1 Å, the dipolar interaction between Al and H would give rise to a broadening of the Al NMR line of 2300 Hz. Such a broadening, however, is not observed, suggesting either that the Al–H+ distance is much larger or that the H+ ion is mobile.

Finally, we want to comment on the statement made earlier in this paragraph that in hydrated H–ZSM-5 the 27Al line width is caused by a distribution of 27Al chemical shifts. Preliminary 27Al spin–lattice relaxation (T1) experiments clearly reveal several species with distinct T1 values and distinct chemical shift. Further investigations are needed to establish the origin of these different 27Al sites which together form the line shapes discussed in this paper.

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Exponential Fluorescence Decay from Single Rovibrational Levels of S₁ Acetaldehyde

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Single rotational level S₁ emission has been observed for jet-cooled acetaldehyde and α-monodeuterated acetaldehyde. All the levels studied (up to Ecm = 1760 cm⁻¹) yielded single exponential decays, the vibronic origin being the longest-lived levels (CH₃CHO, 220 ns; CH₃CDO, 1.52 μs). The data are correlated with previous room temperature studies.

Introduction

Acetaldehyde is a molecule of atmospheric significance¹ as well as a possible model for the photosensitization and kinetic behavior of larger aldehydes.² Because it is a seven-atom molecule with 15 vibrational degrees of freedom and small rotational constants (A″ = 1.8870, B″ = 0.3387, C″ = 0.3033 cm⁻¹),³ the room temperature electronic spectrum is too congested to obtain detailed rovibrational information. In spite of this congestion, the weak nature of the S₁ → S₀ transition, and the less than unity quantum yield for fluorescence, several attempts have been made to study its S₁ dynamics by absorption and emission spectroscopic measurements.²,⁴⁻⁵

A recently reported experiment by Speiser et al. is the closest to a single vibrational level collision-free study.⁶ In this experiment an uncorrected frequency doubled dye laser (fwhm > 1 cm⁻¹) was used to excite low-pressure (≥ 25 mtorr) acetaldehyde vapor at 320 nm. This wavelength was arbitrarily chosen to lie below the predissociative threshold (≥ 31 250 cm⁻¹).⁷ These authors reported the first observation of biexponential decay for S₁ acetaldehyde (at 25 mtorr: τ_fast ~ 29 ns, τ_slow 94 ns) and estimated the fluorescence quantum yield as 7.5 × 10⁻⁴, whereas a prior study² in our laboratory found the longest lifetime at 10 torr to be 3.7 ns at 325 nm. The biexponential decay observed by Speiser et al. was found to be pressure dependent: the slow component was preferentially quenched up to 400 mtorr (self-quenching rate coefficient: 6.7 × 10⁷ Torr⁻¹ s⁻¹) at which pressure the decay appeared single exponential. Above 400 mtorr the decay continued to be self-quenched at the same rate. The authors attributed this overall behavior to the process of rapid reversible intersystem crossing followed by internal conversion. This is a model which has been introduced and used to explain the same behavior in α-dicarbonyls by Kommandeur and co-workers.⁸

As part of our overall studies into the dynamics of small molecules in electronically excited states, we have observed the laser-induced fluorescence decay from single rovibrational levels of S₁ acetaldehyde and α-monodeuterated acetaldehyde. The assignment of these levels was known from our acetaldehyde (CH₃CHO, CH₃CDO, CH₃CHO, 1.52 μs). The data are correlated with previous room temperature studies.

1. See, for example, B. J. Fievelson and J. N. Pitta, Jr., Science, 192, 111 (1976).