

# $^{15}\text{N}/^{27}\text{Al}$ Double Resonance NMR Study of Monomethylamine Adsorbed on Zeolite HY

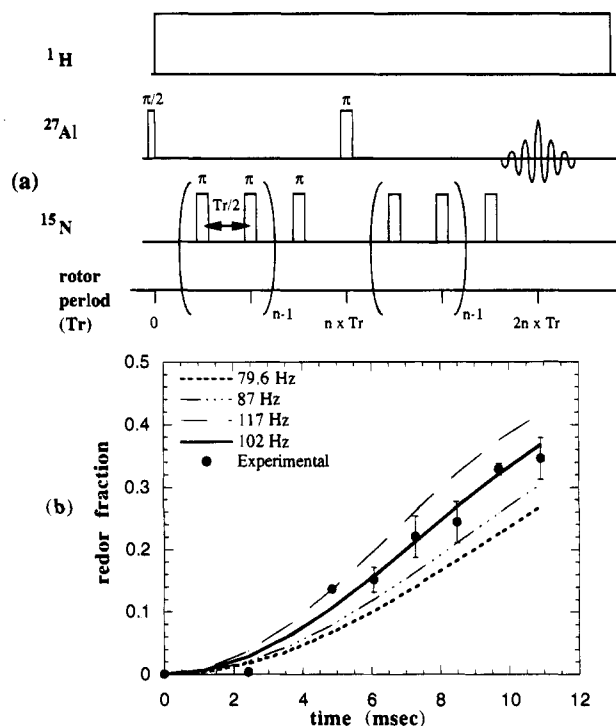
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The adsorption of basic molecules is one method often used to characterize the Brønsted and Lewis acidity of a surface. IR spectroscopy is used to characterize the complexes formed, and temperature-programmed desorption is used to determine the strength of binding.<sup>1</sup> In general, solid state NMR has been employed to study either the surface site or the adsorbed molecule, but not to correlate the site of adsorption with the adsorbed molecule.<sup>2</sup> A notable exception to this is found in the work of Slichter and co-workers.<sup>3</sup> They used SEDOR (spin echo double resonance) NMR to determine a  $^{195}\text{Pt}$ – $^{13}\text{C}$  distance, for CO adsorbed on a platinum surface.<sup>3</sup> Since SEDOR is a static NMR experiment, it cannot always be applied to systems with a variety of species and, consequently, many overlapping resonances. In this paper we demonstrate, for the first time, that the “high-resolution” double-resonance magic angle spinning (MAS) NMR experiments REDOR (rotational echo double resonance)<sup>4</sup> and TRAPDOR (transfer of populations in double resonance) NMR<sup>5</sup> can be applied to probe the proximity of bound molecules and surface sites. Both NMR methods probe the heteronuclear dipolar coupling and are based on similar principles. Refocusing (at the rotor echo) of one spin,  $I$ , which is dipolar coupled to another spin  $S$ , is prevented by applying either  $\pi$  pulses (REDOR) or continuous irradiation (TRAPDOR) to the  $S$  spins. We have chosen to study the adsorption of the basic molecule monomethylamine (MMA) on zeolite HY, since a relatively well-defined complex has been proposed.<sup>6</sup>

Ammonia and trimethylamine (TMA) adsorption on zeolite HY have been studied with  $^{15}\text{N}$  and  $^1\text{H}$  MAS NMR, and  $\text{NH}_4^+$  and  $(\text{CH}_3)_3\text{NH}^+$  were observed.<sup>7,8</sup> A  $^2\text{H}$  NMR study of MMA, dimethylamine, and TMA on zeolites HY and H-RHO showed that rigid complexes are formed at room temperature, in the time scale of the  $^2\text{H}$  experiment, for low loadings of these molecules. The  $\text{MMAH}^+$  cation ( $\text{CD}_3\text{NH}_3^+$ ) was proposed to bind with three hydrogen atoms to three oxygen atoms of the zeolite framework, so that the nitrogen atom sits directly above a T group.<sup>6</sup> Teunissen et al. have performed ab-initio quantum mechanical calculations of  $\text{NH}_3$  bound to protonated aluminosilicon clusters which showed that proton transfer from the zeolite cluster to  $\text{NH}_3$  is energetically favorable only if the  $\text{NH}_4^+$  formed binds to the oxygen atoms of the zeolitic cluster via two or three hydrogen bonds.<sup>9</sup> Al–N distances of 3.4 and 3.0 Å are obtained for these complexes, which are denoted 2H and



**Figure 1.** (a)  $^{27}\text{Al}/^{15}\text{N}$  REDOR pulse sequence. (b) Experimental and simulated REDOR NMR data for a spinning speed of  $1650(\pm 5)$  Hz. The loss of  $^{27}\text{Al}$  intensity at the spin echo (i.e., the REDOR fraction  $(1 - I/I_0)$ ) is shown as a function of the dephasing time. Intensities were determined from the height of the echo and by integration of the spectrum; error bars reflect the differences. Spectra were acquired with a triple-resonance CMX 360 spectrometer ( $^{15}\text{N}$   $\pi$  pulse = 12.2  $\mu\text{s}$ ). The  $^{27}\text{Al}$  pulse length was determined from aqueous  $\text{Al}_2(\text{SO}_4)_3$  and then adjusted for the zeolite, due to the greater nutation frequency of  $^{27}\text{Al}$  nuclei with large quadrupole coupling constants.

3H, respectively. In contrast, Ozin et al. have proposed from far-IR spectroscopy experiments that  $\text{TMAH}^+$  is primarily located in the site II positions of the supercage (i.e., in the hexagonal window of the sodalite cage) and possibly in site III.<sup>10</sup>

A resonance at  $-357$  ppm, relative to  $\text{CH}_3\text{NO}_2$ , is observed in the  $^{15}\text{N}$  MAS NMR spectrum of the  $^{15}\text{N}$  MMA-loaded HY sample,<sup>11</sup> which is shifted from the amine at  $-379$  ppm into the chemical shift range observed for protonated amines.<sup>12</sup>  $^{15}\text{N}$  and  $^{27}\text{Al}$  spin counting was performed by comparing the integrated intensity of the  $^{15}\text{N}$  and  $^{27}\text{Al}$  resonances of a known weight of sample with those from known amounts of  $^{15}\text{NH}_4\text{Cl}$  and aluminum acetylacetonate for  $^{15}\text{N}$  and  $^{27}\text{Al}$ , respectively.  $^{15}\text{N}$  spin counting showed that 22.5 molecules of MMA were adsorbed per unit cell (uc) of zeolite, while 50.2 molecules of aluminum/uc were visible in the  $^{27}\text{Al}$  spectra, i.e., 90% of the total aluminum in the sample.

Two sets of experiments were performed (Figures 1a and 2a). In the first,  $^{27}\text{Al}/^{15}\text{N}$  REDOR, the  $^{27}\text{Al}$  spins were monitored, and two  $\pi$  pulses were applied to the  $^{15}\text{N}$  channel per rotor period.<sup>13</sup> The intensity of the  $^{27}\text{Al}$  echo was measured with ( $I$ ) and without ( $I_0$ ) the  $^{15}\text{N}$  pulses, for a series of increasing numbers of rotor periods. In the second experiment,  $^{15}\text{N}/^{27}\text{Al}$

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(11) Samples were prepared by dehydrating  $\text{NH}_4\text{Y}$  (Linde catalyst LZ-62; Si/Al ratio = 2.4) at 100 °C for 8 h under vacuum and deammoniating at 300 °C overnight. Approximately 25 molecules of MMA/uc of zeolite were adsorbed, by exposing the zeolite to 99%  $^{15}\text{N}$  enriched MMA and monitoring the drop in pressure, over a known volume.

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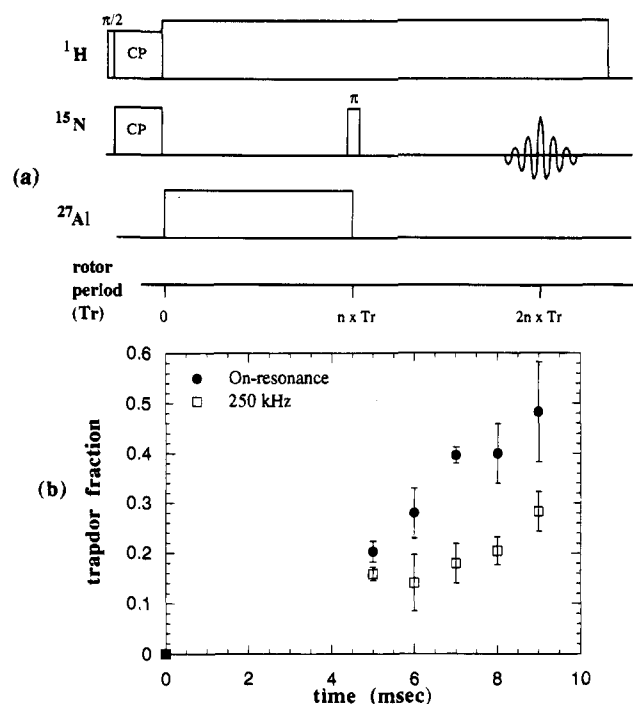
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**Figure 2.** (a)  $^{15}\text{N}/^{27}\text{Al}$  TRAPDOR pulse sequence. (b) The loss of  $^{15}\text{N}$  intensity ( $1 - I/I_0$ ) as a function of  $^{27}\text{Al}$  irradiation time, at a spinning speed of  $1000(\pm 5)$  Hz and  $-100^\circ\text{C}$ . Data for  $^{27}\text{Al}$  irradiation on-resonance and at an offset of 250 kHz are shown. ( $^{27}\text{Al}$  rf field strength = 44 kHz.)

TRAPDOR, the  $^{15}\text{N}$  spins were detected, while the quadrupolar nucleus  $^{27}\text{Al}$  was continuously irradiated for the evolution period of the  $^{15}\text{N}$  spin echo sequence. This experiment is based on the  $^{13}\text{C}/^{14}\text{N}$  and the  $^1\text{H}/^{27}\text{Al}$  TRAPDOR experiments that have been described in detail elsewhere.<sup>5</sup>

Figure 1b shows the loss of  $^{27}\text{Al}$  intensity in the  $^{27}\text{Al}/^{15}\text{N}$  REDOR NMR experiment performed at  $-140^\circ\text{C}$ . After 11 ms of dephasing, 35% of the signal intensity was lost. In contrast, no significant dephasing was observed at room temperature, while at  $-45^\circ\text{C}$ , a small loss in  $^{27}\text{Al}$  intensity was detected (e.g., 20% after 11 ms). The experimental  $^{15}\text{N}/^{27}\text{Al}$  TRAPDOR data, collected at  $-100^\circ\text{C}$ , are shown in Figure 2b. A large loss in the  $^{15}\text{N}$  signal is seen for on-resonance  $^{27}\text{Al}$  irradiation. Moving the irradiation frequency off-resonance by 250 kHz resulted in a much smaller TRAPDOR fraction, ( $1 - I/I_0$ ), and the effect was negligible for irradiation at an offset of 750 kHz. No loss of intensity was observed at room temperature.

Both double-resonance NMR methods demonstrate that there is a significant dipolar coupling present between the aluminum framework site and  $\text{MMAH}^+$ . The observed TRAPDOR fraction is larger than the observed REDOR fraction, for similar dephasing times. This is due to two reasons. Firstly, all the  $\text{MMAH}^+$  is bound to aluminum sites, but the converse is not true. Secondly, the TRAPDOR experiment detects coupling to all six  $^{27}\text{Al}$  Zeeman levels, while in the REDOR experiment, only the coupling between the  $^{27}\text{Al}$   $I = \pm 1/2$  Zeeman levels and the  $^{15}\text{N}$  spins is monitored; hence the effective dipolar coupling is larger for the TRAPDOR experiment. The observed TRAPDOR fraction will also depend on other factors, which include the spinning speed,  $^{27}\text{Al}$  quadrupole coupling constant, and  $^{27}\text{Al}$  rf amplitude.<sup>5</sup> The change in the TRAPDOR fraction as a function of the  $^{27}\text{Al}$  irradiation offset can be used to obtain an estimate of the  $^{27}\text{Al}$  quadrupole coupling constant of approximately 2.5 MHz, which is consistent with  $^1\text{H}/^{27}\text{Al}$  TRAPDOR experiments on this system, currently in progress.<sup>14</sup>

The experimental REDOR data can be compared with that calculated from the models proposed by Kustanovich et al. and

Tenunissen et al.<sup>6,9</sup> In these models, each  $\text{MMAH}^+$  is bound to one  $^{27}\text{Al}$  spin; hence, from the spin-counting data, only 45% of the observable  $^{27}\text{Al}$  spins are coupled to the  $^{15}\text{N}$  spins in  $\text{MMAH}^+$ . REDOR dephasing curves were calculated using equations given in ref 15, and the REDOR fractions were multiplied with a scaling factor of 0.45, to take the number of dipolar coupled spins into account. The best fit to the experimental data was obtained with a dipolar coupling constant  $D$  of 102 Hz (Figure 1b), which, assuming no motional averaging, corresponds to a distance of 3.14 Å. Variations in  $D$  of  $\pm 15$  Hz (shown for comparison in Figure 1b) result in changes of the internuclear distance of  $-0.14$  and  $+0.17$  Å. The calculated dephasing predicted for the 2H structure of Tenunissen et al.<sup>9</sup> ( $D = 79.6$  Hz) is also plotted in Figure 1b. This calculated dephasing is too small to account for the experimental results, and the distance measured experimentally is much closer to that predicted for the 3H structure. The difference between the measured distance of 3.14 Å and the computed value of 2.96 Å for the  $\text{NH}_4^+$  3H structure may be due to a variety of causes. Firstly, some  $\text{MMAH}^+$  may be present in the 2H structure: the data can be fitted by assuming that the 2H and 3H complexes are present in a ratio of 2:3 (2H:3H). Secondly, there may be residual motion of the complex, which could result in partial averaging of the dipolar coupling (and a longer apparent internuclear distance). Consistent with this is the decrease in  $D$  as the temperature is increased: the data obtained at  $-45^\circ\text{C}$  can be fitted to a value for  $D$  of 70 Hz, and  $D$  is negligible at room temperature. Thirdly, there may be small errors in the distances obtained from the ab-initio calculations, or small differences between the  $\text{NH}_4^+$  and  $\text{MMAH}^+$  complexes. Finally, we cannot presently exclude the possibility that the MMA is located in the site II position.<sup>10</sup> Experiments are in progress to test this model.

In conclusion, this study demonstrates that dipolar coupling between nuclei in an adsorbed molecule and  $^{27}\text{Al}$  spins on the surface sites can be detected with the REDOR and TRAPDOR experiments at low temperatures. A  $^{15}\text{N}-^{27}\text{Al}$  internuclear distance was obtained from the REDOR data, which is close to the distance predicted, assuming that the majority of the  $\text{MMAH}^+$  cations are bound with three hydrogen bonds to the zeolite framework. The  $^{27}\text{Al}-^{15}\text{N}$  dipolar coupling was observed to decrease with increasing temperature. Measurement of the temperature dependence of the dipolar coupling, in similar systems, should yield information concerning the mobility and dynamics of the bound molecules, leading to a fuller understanding of the mode of binding. Large losses of intensity were also observed in the TRAPDOR experiment, which qualitatively proves that a  $^{15}\text{N}-^{27}\text{Al}$  dipolar coupling exists, and that the two nuclei are in close proximity. This result has exciting implications, because the TRAPDOR experiment can be applied in some cases where the REDOR experiment is unsuitable: the  $^{15}\text{N}/^{27}\text{Al}$  TRAPDOR experiment can detect dipolar coupling to "invisible"  $^{27}\text{Al}$  spins and can be used to study molecules adsorbed on catalytic alumina surfaces, where it may be difficult to distinguish between the  $^{27}\text{Al}$  resonances from the surface and the bulk of the catalyst. Finally, the TRAPDOR experiment may prove to be a useful alternative to cross-polarization methods for selecting dipolar coupled nuclei on surfaces, when one or more of the nuclei are quadrupolar.

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