Supplementary Information

On the visibility of Al surface sites of γ-alumina: a combined computational and experimental point of view

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NMR experiments. Experiments were performed on a Bruker Avance III wide bore 850 (20.0 T) spectrometer operating at a ^{27}Al Larmor frequency of 221.5 MHz. The samples were packed in a 2.5 mm zirconia rotor inside an argon-filled glove box and then spun at 30 kHz using pure nitrogen gas. The single pulse experiments were acquired typically with a radio-frequency field ν_{rf} ($=\omega_{rf}/2\pi$) of 50 kHz and a pulse length of 0.5 µs (i.e. less than $\pi/6\omega_{rf}(I+1/2)$ to ensure quantitativity.[1] Large spectral widths were used to avoid folding of the spinning sideband's manifold followed by a manual baseline deconvolution, and 500 scans were accumulated. $\{^{1}H\}^{27}$Al Variable Amplitude Cross Polarizations experiments were performed at a spinning speed of 30 kHz using ^{27}Al and ^{1}H radio-frequency field strengths of 15 kHz (leading to an approx. 33kHz nutation frequency of the central transition) and 60 kHz respectively and a linear ramp on the ^{1}H channel (80% to 120% of the Hartmann-Hahn condition). A contact time of 1.5ms and a recycle delay of 1.3 s were used, 54000 (resp. 250000) scans being accumulated for the sample heat-treated at 300°C (resp. 500°C).

Simulations were performed using the Gaussian Isotropic Model[2,3] (Czjzek, d=5) implemented in the DMFit program[4] allowing to retrieve the relative populations, mean isotropic chemical shift (δ_{iso}), width of the Gaussian distribution of δ_{iso} (Δ_{CS}) and the mean quadrupolar coupling constant (C_Q). The simulation derived from the DFT calculations were performed using a model taking into account second-order quadrupolar broadening with an additional Gaussian distribution of isotropic chemical shift ($\Delta\delta_{iso}$ = 5 ppm) and quadrupolar coupling constant (ΔC_Q = 1 MHz). All lines were constraint to have the same area. Isotropic chemical shielding σ_{iso} were converted to isotropic chemical shift δ_{iso} using previously published correlations.[5]

Calculations. Geometry optimization was performed in periodic boundary using the Perdew-Wang (PW91) functional,[6] as implemented in the VASP code.[7,8] The Projected Augmented Wave (PAW)[9] method was adopted for the description of atomic cores. A tight convergence of the plane-wave expansion was obtained with a cut-off of 400 eV, in accordance with the selected PAW atomic radii. Structural optimization was stopped when forces on individual atoms were below 0.01 eV/Å. On surface slabs the Brillouin zone integration was performed with a 3 x 3 x 1 k-point grid generated by the Monkhorst-Pack algorithm,[7] while a 5 x 5 x 5 k-point grid was used for the bulk of γ-Al_2O_3. For the optimization of the bulk the "Accurate" setting of VASP was chosen and the cut-off energy and convergence criterium on the forces were increased to 520 eV and 0.001 eV/Å respectively. We use a γ-Al_2O_3 bulk model generated by the simulated dehydration of

boehmite (γ-AlOOH).[10] This model adopts the $P2_1/m$ space group. Our reoptimized cell parameters are a = 5.577 Å, b = 8.399 Å, c = 8.069, α = 90.528°, V = 377.95 Å^3 and thus very close to the originally published values. The unit cell contains 16 Al and 32 O atoms of which 12 Al (75%) are in octahedral and 4 (25%) are in tetrahedral coordination.

NMR parameters were calculated with the CASTEP code on structures optimized with VASP. The PBE functional[11,12] and on-the-fly generated ultrasoft pseudopotentials were used. For the cut-off energy a value of 489 eV was used, corresponding to the "Fine" setting. NMR parameters are known to be very structure-sensitive, therefore we checked the accuracy of the calculated parameters on a bulk γ-Al_2O_3 unit cell expanded or compressed by 2 vol%, the typical accuracy of DFT-GGA calculations. Compared to the optimized cell, the maximal deviations of δ, C_q and η_q were 2.1 ppm, 0.6 Mhz and 0.04, respectively, and thus negligible. The NMR calculation were carried out with the PBE functional and ultrasoft on-the-fly generated pseudopotentials on structures optimized with PW91 and PAW potentials. To check if this would introduce any error, we also optimized the bulk in CASTEP (5x5x5 Monkhorst-Pack grid, 489 eV, finite basis correction, fixed number of plane waves), yielding a very similar structure (a = 5.568 Å, b = 8.380 Å, c = 8.042, α = 90.473°, V = 375.26 Å^3) and NMR parameters almost identical to those found with the VASP-optimized bulk. Experimentally $Al(NO_3)_3$ in nitric acid was used as reference but from a computational point of view the description of this system is not trivial. Therefore α-Al_2O_3 (corundum) was used as reference. The structure was optimized in VASP using a 9x9x9 Monkhorst Pack Γ-centered grid. The calculated unit cell volume was 255.3 Å^3 which is in excellent agreement with the experimental value (253.5 Å^3).[13] NMR was calculated in CASTEP using the same k-point grid, yielding an absolute magnetic shielding value for Al, $\sigma_{(}\alpha$ - Al_2O_3), of 531.38 ppm. The experimental isotropic chemical shift of α-Al_2O_3 with respect to $Al(NO_3)_3$ is 10.7 ppm, therefore all chemical shifts are referenced as follows:

$$\delta = \sigma_{(}\alpha - Al_2O_3) - \sigma_{iso} + 10.7 \text{ ppm}$$

σ_{iso} being the calculated absolute magnetic shieldings of the nucleus in question. The Electric Field Gradient (EFG) tensor is described by the quadrupolar coupling constant, $C_Q = eQV_{zz}/h$ and the assymetry parameter $\eta_q = (V_{xx} - V_{yy})/V_{zz}$. Note, that while C_Q can have positive or negative values this information is only accessible by calculation. Experiments only provide the absolute value. The calculated C_Q value for the octahedral Al in α-Al_2O_3 is 2.43 MHz, which is in excellent agreement with the experimental value of 2.38 MHz.[14] For the quadrupole moment of ^{27}Al, we used the default value of 0.1466 barn set in CASTEP and recommended by Pyykkö.[15]

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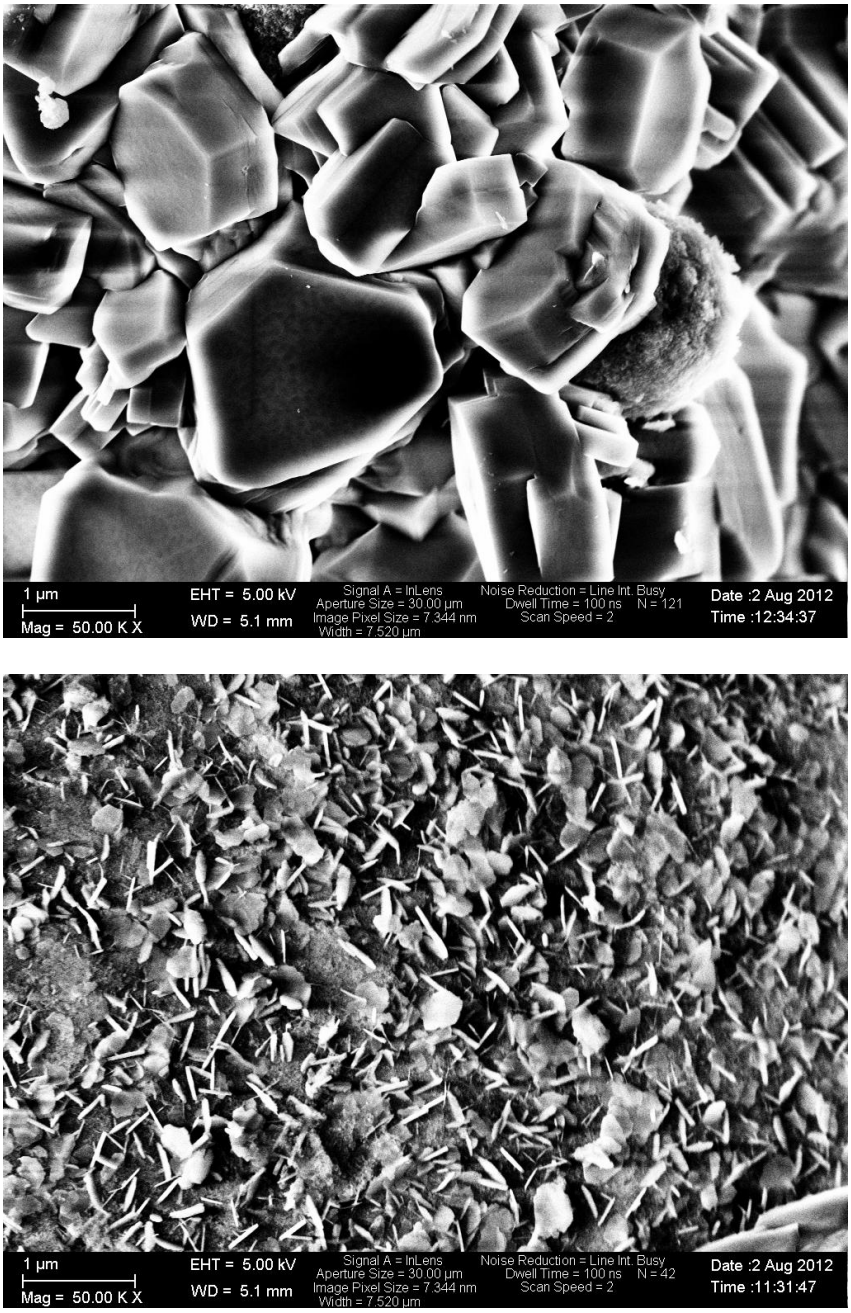

Figure S1. SEM micrographs of the γ-Al_2O_3 used in this study. The length scale in the bottom left corner corresponds in both pictures to 1 μm.

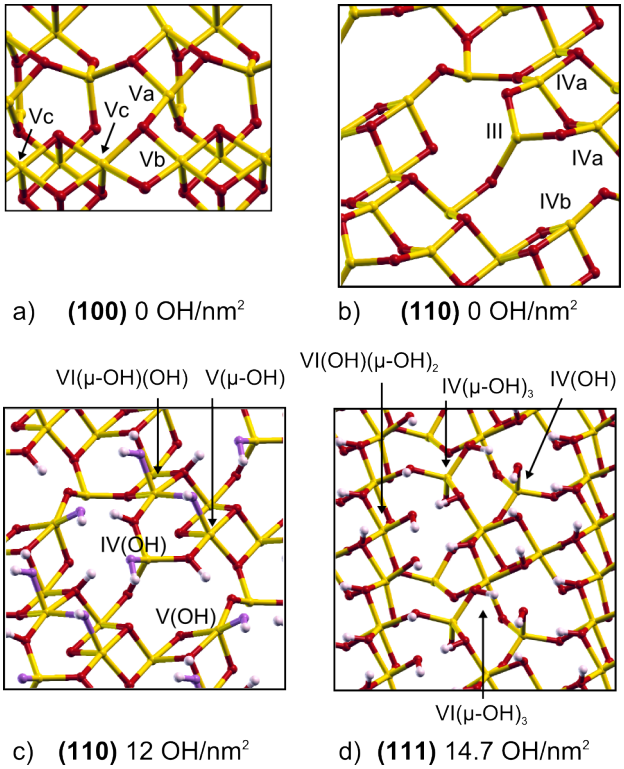

Figure S2. Tilted view of the structures given in figure 1: a) fully dehydrated (100), b) fully dehydrated (110), c) hydrated (110), and d) hydrated (111) terminations of γ-Al_2O_3 showing different types of surface Al atoms. $X(\mu\text{-OH})_w(OH)_y$ represents an Al atom with a total coordination number of X, including w bridging μ-OH and y terminal OH-groups. Only the top two layers are shown. Al: yellow, O: red, H: white balls.

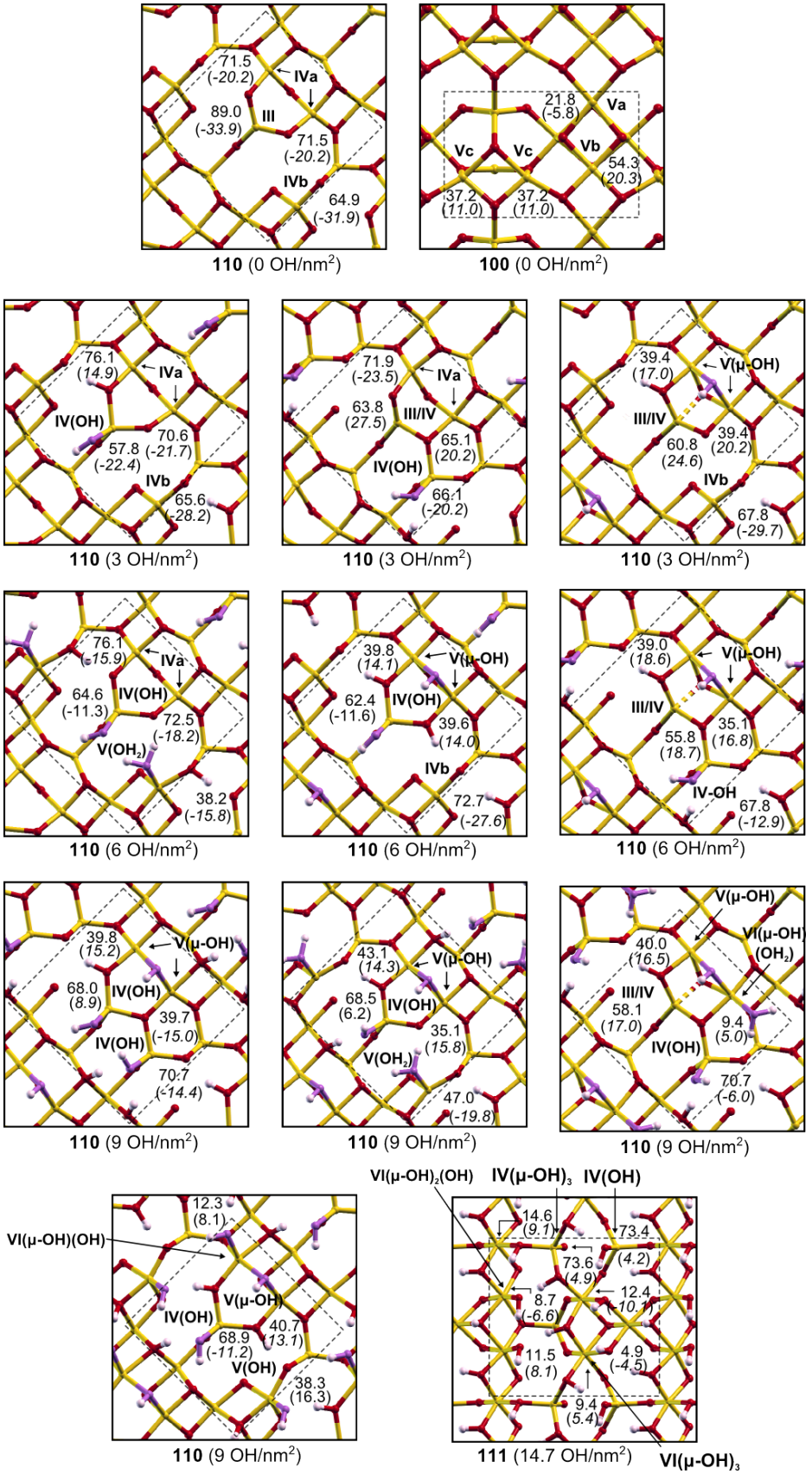

Figure S3. NMR parameters (δ_{iso}, C_Q in brackets) for the (partially) hydrated (110) and (111) terminations of γ-Al_2O. Only the top two layers are shown. A dashed line indicates the unit cell. Al: yellow, O: red, H: white balls.

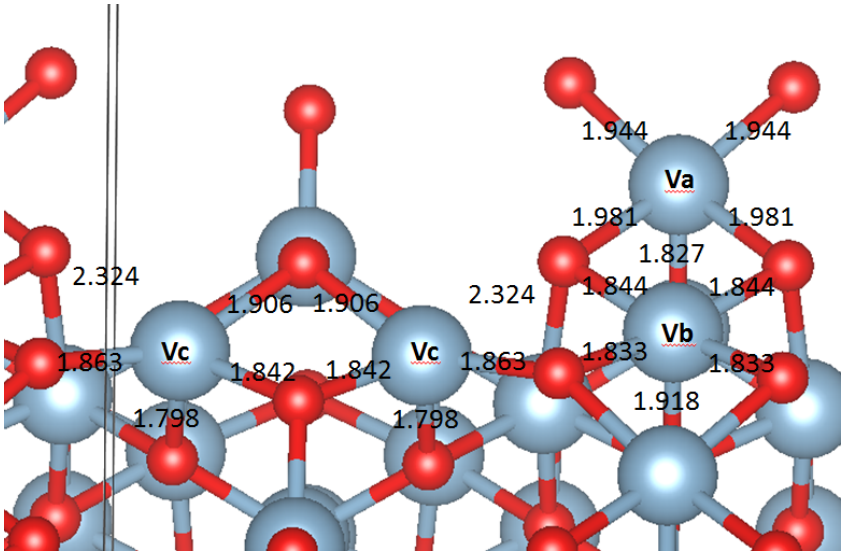

Figure S4. Tilted top view of the (100) termination of γ-Al_2O_3. Al: grey, O: red. Distances are indicated in Å.

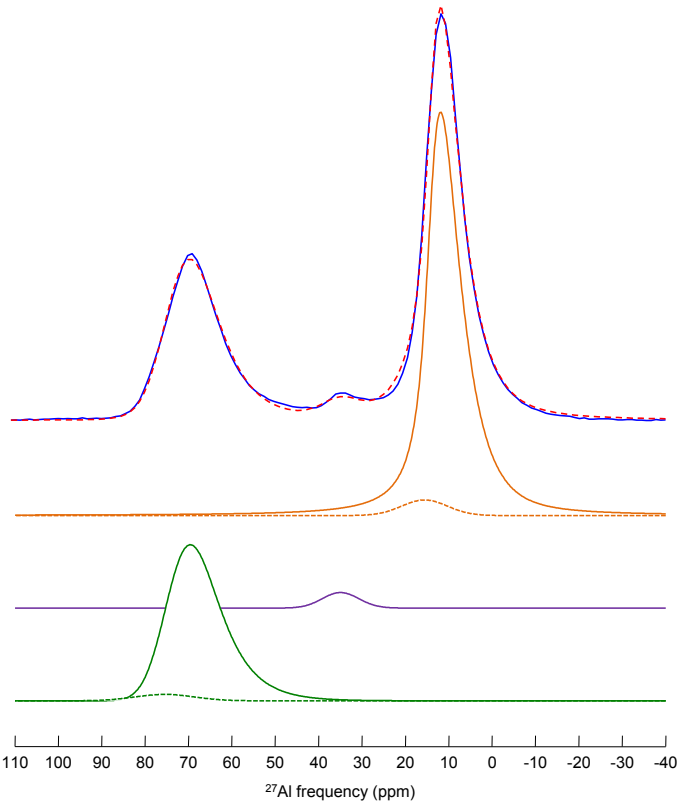

Figure S5. "Direct" quantitative one-pulse experiment on γ-Al_2O3. heat treated at 300°C along with its simulation (red dashed line) and individual components (orange, purple and green) using the GIM model.

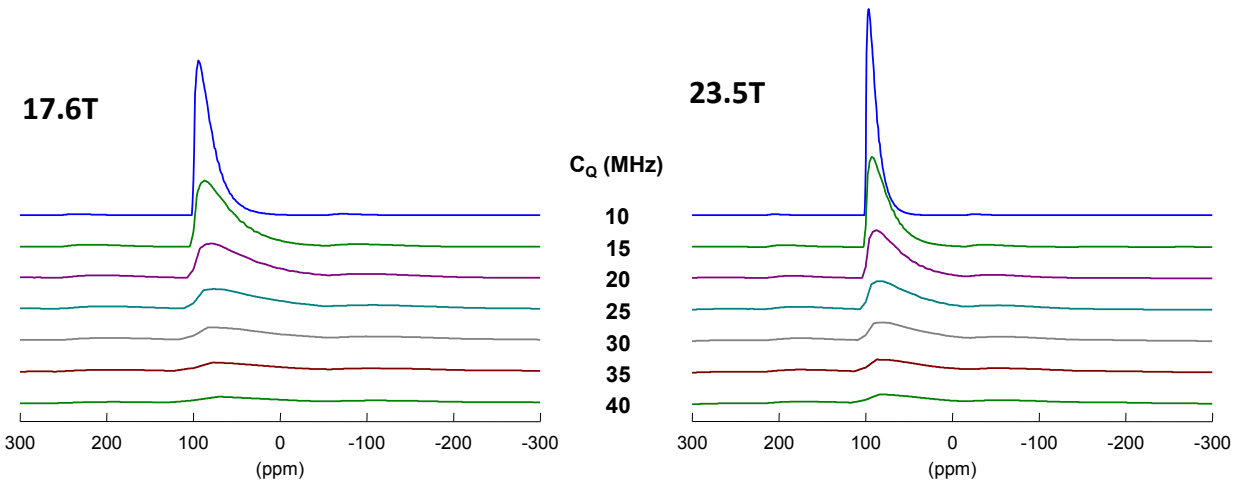

Figure S6. Simulations, using the GIM model, of ^{27}Al NMR lines shapes as a function of increasing C_Q and for two different magnetic fields. The areas have been normalized and a spinning speed of 30 kHz has been assumed.