Supplementary Materials for

On the nature of decoherence in quantum circuits: Revealing the structural motif of the surface radicals in $\alpha$-Al$_2$O$_3$

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Supplementary Text

Energies of an unpaired electron spin coupled to a proton and an aluminum nuclei

As shown in Figure 1B, an unpaired electron spin \( S = \frac{1}{2} \) magnetically coupled to a proton \( I = \frac{1}{2} \) and an aluminum \( I = \frac{5}{2} \) nuclei has 24 states \( m_s, m_{1/2} H, m_{1/2} Al \) where \( m_s = \pm \frac{1}{2} \) are the spin quantum numbers of the electron, \( m_{1/2} H = \pm \frac{1}{2} \), of the proton and \( m_{1/2} Al = \left( \frac{5}{2}, \frac{3}{2}, \frac{1}{2} \right) \), of the aluminum nuclei. Their energies for a given applied magnetic-field, \( B_0 \), are:

\[
E \left( m_s, m_{1/2} H, m_{1/2} Al \right) = \left( g \beta_e m_s - \gamma_1 H m_{1/2} H - \gamma_2 Al m_{1/2} Al \right) B_0 + m_s m_{1/2} H A_{1/2} H + m_s m_{1/2} Al A_{1/2} Al + Q m_{1/2} Al^2
\]

The terms are: the electron Zeeman interaction defined by the \( g \)-value of the radical and the Bohr Magneton \( (\beta_e) \); the two nuclear Zeeman interactions given by the magnetogyric ratio, \( \gamma \), of the nuclei; the hyperfine couplings, \( A_i \), between the unpaired electron and the nuclear spins; and the nuclear quadrupolar interaction, \( Q \), of the \( 27 \)Al nuclei. A proton does not experience a quadrupolar interaction. \( g \), \( A \) and \( Q \) are fundamental quantities of the radical and its nuclear spins. Each is orientation dependent. In the text and following, \( A_{\text{eff}} \) and \( Q_{\text{eff}} \) refer to observed quantities which that on \( A \) and \( Q \) and the crystal orientation with respect to \( B_0 \). The quantity \( \nu_{N,NMR} = -\gamma B_0 \) is referred to the NMR(Zeeman) frequency.

Details regarding the 3-spin ELDOR-NMR spectra

The 3-spin resonances were difficult to detect due to their inherently low transition probabilities and not all resonances were fully resolved. Nonetheless, there was still sufficient information to establish connections between the nuclei. In the following, we describe in detail these resonances and the analysis of Figure 5.

For a proton coupled to an unpaired electron, the ELDOR-NMR frequencies of its two 2-spin \(^1\)H resonances satisfy the equations:

\[
\nu_{\text{ELDOR-NMR}} - \nu_{1H,NMR} = \pm \frac{1}{2} A_{1H,\text{eff}}
\]

and for an \(^{27}\)Al nuclei are:

\[
\nu_{\text{ELDOR-NMR}} - \nu_{27Al,NMR} = \pm \frac{1}{2} A_{27Al,\text{eff}} - Q_{\text{eff}} \left( m_{27Al} - \frac{1}{2} \right)
\]

where \( A_{1H,\text{eff}} \) and \( A_{27Al,\text{eff}} \) are respectively the observed proton and aluminum hyperfine couplings and \( Q_{\text{eff}} \), the observed \(^{27}\)Al nuclear quadrupolar coupling, for a given orientation of the crystal sample. \( \nu_{1H,NMR} \) and \( \nu_{27Al,NMR} \) are respectively the \(^1\)H and \(^{27}\)Al NMR (Zeeman) frequencies, 140 and 37 MHz for the magnetic fields in our measurements. Ignored in the above equations and those that follow is the contribution of the electron spin transition, which is fixed to 94.03 GHz in this study. The two corresponding 3-spin resonance frequencies for the \(^{27}\)Al and \(^1\)H nuclei coupled to the same unpaired electron are:

\[
\nu_{\text{ELDOR-NMR}} \pm (\nu_{1H,NMR} + \nu_{27Al,NMR}) = \pm \frac{1}{2} A_{1H,\text{eff}} \pm \frac{1}{2} A_{27Al,\text{eff}} - Q_{\text{eff}} \left( m_{27Al} - \frac{1}{2} \right)
\]

where \( (\nu_{1H,NMR} + \nu_{27Al,NMR}) \) is 177 MHz. For two protons, \( a \) and \( b \), coupled to the same unpaired electron, their two 3-spin frequencies are:

\[
\nu_{\text{ELDOR-NMR}} \pm 2\nu_{1H,NMR} = \pm \frac{1}{2} A_{1H,a,\text{eff}} \pm \frac{1}{2} A_{1H,b,\text{eff}}
\]

where \( 2\nu_{1H,NMR} \) is 288 MHz. A similar equation can be derived for the two \(^{27}\)Al nuclei case. Other 3-spin resonances appear about the difference NMR frequencies (i.e. about 0 for two proton and two \(^{27}\)Al cases and \( \pm (\nu_{1H,NMR} - \nu_{27Al,NMR}) \) for the one proton and one \(^{27}\)Al case where the two nuclear spins are excited in opposite direction).
The spectra corresponding to positive case of Equation S3 of the $^{27}$Al/$^{27}$Al, $^{27}$Al/$^{1}$H, $^{27}$Al/$^{3}$H and $^{1}$H/$^{1}$H transitions are shown as black traces in Figure 5A-C. The 3-spin $^{27}$Al/$^{1}$H transitions of Al$_{5}$, Al$_{12}$, H$_{16}$, H$_{25}$, and H$_{40}$, as given by the righthand side of equation S3, are found between -52 (Al$_{12}$ and H$_{40}$) and -21 MHz (Al$_{5}$ and H$_{16}$) and between +21 and +52 MHz or, in terms of VELDOR-NMR, span 125 to 156 MHz and 198 to 229 MHz. By comparison, the 2-spin $^{1}$H spectra extend from 88 to 192 MHz. This means the lower half of the 3-spin $^{27}$Al/$^{1}$H spectra overlaps with the 2-spin $^{1}$H spectra. Hence, the pink shaded regions of the 2-spin $^{1}$H spectrum in Figure 5B and C arise from 3-spin $^{27}$Al/$^{1}$H resonances. Although the intensity of these 3-spin $^{27}$Al/$^{1}$H resonances was appreciable in the $\theta_{CB} = -115$ spectra, they were much smaller in the -35º spectrum and not even detected at other orientations. This strong orientation dependence helped us to discriminate between the 2- and 3-spin resonances.

The manner in which the 2- and 3-spin spectra are plotted in Figure 3, 5 and S5 facilitates visual assignment of the 3-spin transitions. The frequency axes in these figures correspond to the left-hand side of Equations S1-4. The low frequency region, from 16 to 40 MHz, of the 3-spin $^{27}$Al/$^{1}$H (shaded gray in Figure 5) had corresponding intensity at the same frequencies in the 2-spin $^{1}$H spectra (shaded red). Equating Equations S1 and S3 shows the 3-spin transitions of H$_{16}$, H$_{25}$, and H$_{40}$ in this region must have involved Al$_{M}$, $^{27}$Al nuclei with small hyperfine couplings ($A^{27}_{Al,e} f - 0$). Likewise, the low frequency region of the 3-spin $^{1}$H/$^{1}$H spectra also matched the frequency span of the 2-spin $^{1}$H spectra demonstrating that H$_{16}$, H$_{25}$, and H$_{40}$ were associate with one or more H$_{M}$ (cf Equation S1 and S4).

Above 40 MHz, the 3-spin $^{27}$Al/$^{1}$H and $^{1}$H/$^{1}$H spectra (Figure 5) had no corresponding intensity in the 2-spin spectra (noting that the pink shaded regions in these spectra arose from 3-spin $^{27}$Al/$^{1}$H transitions). These regions were attributed to pairwise combinations of Al$_{12}$, H$_{16}$, H$_{25}$ and H$_{40}$ (shaded in blue). Due to insufficient resolution of the 3-spin spectra, it was not possible to determine how many of these combinations actually contributed. However, the high frequency edges of the -115º $^{27}$Al/$^{1}$H (~45 MHz) and -35º and -115º (~65 MHz) $^{1}$H/$^{1}$H spectra corresponded to the sum frequencies of Al$_{12}$ and H$_{40}$, and H$_{25}$ and H$_{40}$, respectively, and as such, were assigned to the 3-spin transitions involving these nuclei.

The 2-spin $^{27}$Al and 3-spin $^{27}$Al/$^{27}$Al ELDOR-NMR spectra are shown in Figure 5. They are plotted in the same manner described above. Their frequency axes are respectively $v_{ELDOR-NMR} - v_{27Al,NMR}$ and $v_{ELDOR-NMR} - 2 v_{27Al,NMR}$. Neither the 2-spin $^{27}$Al ELDOR-NMR nor the $^{27}$Al ENDOR spectra (Figure 6) had intensity corresponding to the blue shaded region in the 3-spin $^{27}$Al/$^{27}$Al spectra (Figure 5A) centered about 17 MHz. We assigned this intensity to the 3-spin transition involving Al$_{5}$ and Al$_{12}$. This resonance is flanked by the 2-spin double-quantum (DQ) resonances of Al$_{5}$ and Al$_{12}$. These are from the excitation of a single nuclear spin by two quanta ($\Delta m_s=2$, illustrate by the green arrows in Figure 1). The DQ resonances occur at twice the frequency of the 2-spin resonance. Protons are incapable of such transitions spin the have only two spin-states ($m_s = \pm \frac{1}{2}$). As described below, the 3-spin and DQ resonances could be reproduced in simulations of the $^{27}$Al ELDOR-NMR spectrum using the same hyperfine and nuclear quadrupolar coupling values for Al$_{5}$ and Al$_{12}$ that accounted for their ENDOR spectra (Figure 4 and S4B). This 3-spin Al$_{5}$ and Al$_{12}$ resonance along with those of Al$_{12}$ and H$_{40}$ and H$_{25}$ and H$_{40}$ demonstrated that all four nuclei were connected to a common radical center.

Information regarding H$_{16}$ was less definitive. The 2-spin $^{1}$H spectra were particularly narrow around $\theta_{CB} \approx -35º$. This is evident in Figure 5, as well as, from the $\theta_{CB} = -25º$ spectrum in Figure 3. Beyond 40 MHz, these spectra fell below the noise level. Close inspection of the 2-spin and 3-spin -35º $^{1}$H/$^{1}$H spectra showed that there was little or no overlap at ~41 MHz, the sum frequency of H$_{25}$ and H$_{16}$. On this basis, we assign the intensity in the 41 MHz region of the $\theta_{CB} = -35º$ $^{1}$H/$^{1}$H spectra to the 3-spin transition associated with H$_{25}$ and H$_{16}$ rather than H$_{40}$ and H$_{M}$. In both the $\theta_{CB} = -35º$ and -115º $^{1}$H/$^{1}$H spectrum, there was significant intensity at 55 MHz,
the sum frequency of H$_{16}$ and H$_{40}$. This suggested a 3-spin transition involving these two protons. However, the lack of resolution made these two latter assignments less than definitive, but did lend support to a connection between H$_{16}$ and H$_{25}$ and H$_{40}$.

Together, the 3-spin spectra provide evidence that Al$_5$, Al$_{12}$, H$_{16}$, H$_{25}$ and H$_{40}$ arose from a common $R_s$ center. It is also important to note that overlap between the 2-spin $^1$H and 3-spin $^1$H/$^1$H spectra demonstrated that H$_{16}$, H$_{25}$ and H$_{40}$ were associated with at least one H$_M$ nuclei — that is a proton in the environment of $R_s$. This demonstrated that $R_s$ was localized to a proton-rich environment.

The $^{27}$Al ENDOR spectra of $R_s$ and comparisons to $[\text{Al}_8\text{O}_{36}\text{H}_{35}]^+$ DFT model.

As described in the main text, there were two readily identifiable $R_s$ $^{27}$Al ENDOR resonances. In the $\theta_{CBO}=25^\circ$ spectra, they were centered at +5.1 and -11.7 MHz, the corresponding nuclei are referred to as Al$_5$ and Al$_{12}$ in the main text. Since the former was relatively isolated, its properties could be more completely examined. Fig. S4E shows how its frequency changed as a function of $\theta_{CBO}$. This anisotropy was due to the hyperfine and nuclear quadrupolar interactions. $^{27}$Al ENDOR frequencies to first order are

$$v_{^{27}\text{Al ENDOR}} = v_{^{27}\text{Al NMR}} \pm \frac{1}{2} A_{\text{eff}} - Q_{\text{eff}} \left( m_1 - \frac{1}{2} \right)$$  \hspace{1cm} (S5)

where

$$A_{\text{eff}} = A_{\text{iso}} + \left[ A_{zz} \cos^2 \alpha + (A_{yy} \cos^2 \beta + A_{yy} \sin^2 \beta) \sin^2 \alpha \right]$$

$$Q_{\text{eff}} = \frac{3e^2 qQ}{4I(2I-1)}[3\cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi]$$

for a $m_i \rightarrow m_{i-1}$ $^{27}$Al nuclear spin transitions. $A_{\text{eff}}$ is the effective hyperfine coupling and $A_{xx}$, $A_{yy}$ and $A_{zz}$ are the principal values of the corresponding hyperfine tensor and $Q_{\text{eff}}$ is the effective nuclear quadrupolar coupling defined by the nuclear quadrupolar coupling constant, $e^2 qQ$, and its asymmetry parameter, $\eta$. For both, the trigonometric terms define the orientation of $B_0$ with respect to their reference frames.

For a given EPR transition (black arrow, Figure 1), there are up to four associated ENDOR transitions. The +5.1 MHz resonance in the $\theta_{CBO}=25^\circ$ Davies $^{27}$Al ENDOR spectrum was isolated indicating that it arose from either a $m_i = -\frac{3}{2} \rightarrow -\frac{5}{2}$ or $m_i = \frac{5}{2} \rightarrow \frac{3}{2}$ transition (Figure 1, magenta arrows). Their corresponding frequencies are approximately

$$v_{^{27}\text{Al ENDOR}} = v_{^{27}\text{Al NMR}} \pm \frac{1}{2} A_{\text{eff}} + 2Q_{\text{eff}}$$  \hspace{1cm} (S6)

and

$$v_{^{27}\text{Al ENDOR}} = v_{^{27}\text{Al NMR}} \pm \frac{1}{2} A_{\text{eff}} - 2Q_{\text{eff}}.$$  \hspace{1cm} (S7)

As shown in Figure S4C and D, the -2.3 and +5.1 MHz resonances likely arose from the same EPR transition (similar to the red transitions in Figure 1). In this case, $|A_{\text{eff}}|=7.4$ MHz and $|Q_{\text{eff}}|=0.7$ MHz (for both $m_i = -\frac{3}{2} \rightarrow -\frac{5}{2}$ and $m_i = \frac{5}{2} \rightarrow \frac{3}{2}$ cases). We were not able to identify the companion to the -1.7 MHz resonance, but its frequency must have been within the range indicated in Figure S4A by the dotted green arrows, between 10.7 to 13.7 MHz. The corresponding ranges in $|A_{\text{eff}}|$ and $|Q_{\text{eff}}|$ were 22.4 to 25.4 MHz and 0.2 to 0.8 MHz, respectively.

These two $R_s$ $^{27}$Al hyperfine interactions were compared to those calculated for the structure 3 in Figure 5 to assess how descriptive the model was of the electronic structure of $R_s$. The nuclei experiencing the largest calculated hyperfine interaction with principal values of [-17.3, -19.9, -20.3] MHz (denoted as A$_1$) had a nuclear quadrupolar coupling value of $e^2 qQ=-5.9$ MHz with an asymmetry parameter of $\eta=0.7$. The second largest hyperfine interaction had principal values of [-7.5, -9.2, -9.6] MHz (denoted as A$_2$) and the corresponding nuclei had with $e^2 qQ=-10.5$ MHz and $\eta=0.9$. The ENDOR spectra were calculated using these DFT values and
compared to the experimental spectra. For this purpose, the Euler angles of the hyperfine and nuclear quadrupolar tensors were taken as adjustable parameters and scanned for the best fit. The $A_2$ values could reproduce the +5.1 and -2.3 MHz resonances. The $A_{eff}=7.4$ MHz determined from the ENDOR spectra was close in magnitude to the smallest $A_2$ principal value of -7.5 MHz. While the agreement made comparison between the calculated and measured ENDOR spectra favorable, the proximity of the values to a principal hyperfine direction was problematic. ELDOR-NMR resonances arise from the mixing of nuclear spin-states that do not occur along the principal directions of the hyperfine and nuclear quadrupolar interactions, this meant that the calculated ELDOR-NMR spectra based on the DFT calculated values did not have a resonance corresponding to 7.4 MHz with any appreciable intensity. The minimum change in the DFT values required to achieve a better consistency between the measured ENDOR and ELDOR-NMR spectra and those calculated based on the DFT derived spin parameters was to shift the $A_2$ principal hyperfine values by +1.2 MHz — that is by assuming the calculated isotropic hyperfine coupling were underestimated by this amount. The $A_1$ values could account for the -11.7 MHz resonance; however, they predicted that its corresponding positive frequency companion would have been outside the region indicated in Figure S4B. The minimum change to the DFT values in this case corresponded to a shift in the isotropic contribution by -3 MHz.

The hyperfine tensor values and Euler angles used to calculate the ENDOR spectrum shown in Figure S4A and the 3-spin and 2-spin double quantum ELDOR-NMR spectrum in Figure 5 were for $A_1$ [-20.3, -22.9, -23.3] with angles [0, $\pi/7$, 0] and $A_2$ [-6.3, -7.9, -8.4] MHz with angles [0, $\pi/4$, 0]. The DFT calculated nuclear quadrupolar interactions were used unchanged with Euler angles [0, $\pi/3$, 0] and [0, $\pi/4$, 0] for $A_1$ and $A_2$ respectively. It was possible to obtain the same level of agreement or better between the calculated and measured ENDOR and ELDOR-NMR spectra using other similar tensors values and angles. A complete study of the orientation dependence of the $^{27}$Al ENDOR spectra is need to make a quantitative comparison between the DFT model to the $R_1$ center and to refine the model. Nonetheless, there appeared to be a consistency between the computed values for the [Al$_9$O$_{30}$H$_{35}$]$^+$ DFT model and those measured for the $R_1$ which indicated that the electronic structure of this center was likely to resemble that of the DFT model (see below).

Simulations of the EPR and ELDOR-NMR spectra.

Simulations were based on numerical diagonalization of the specific spin-Hamiltonian. From the eigenvalues and eigenvectors, all possible transition energies ($|\varepsilon_i-\varepsilon_f|$) and electron and nuclear spin transitions probabilities ($|\langle \Psi_f | S_i | \Psi_i \rangle|^2$ and ($|\langle \Psi_f | I_i | \Psi_i \rangle|^2$) were calculated. In the case of the EPR spectrum, the spin-Hamiltonian was:

$$ H = B_0(g\beta S_z + g\beta N I_{1z} + g\beta N I_{2z} + g\beta N I_{127} + g\beta N I_{227} + S \cdot (A_1 H \cdot I_1 H + A_2 H \cdot I_2 H + A_{127} \cdot I_{127} + A_{227} \cdot I_{227})) $$

where $|A_1 H|=84$ MHz, $|A_2 H|=50$ MHz, $|A_{127}|=21.8$ MHz and $|A_{227}|=7.4$ MHz and $g=2.0065$. Transition energies and probabilities were calculated for each value of $B_0$. Probabilities of the transitions within the bandwidth of a 90 ns inversion pulse were summed at each field point to generate the spectrum.

Simulations of the $^{27}$Al ELDOR-NMR followed the procedure described by Cox et al. (64) using locally-written programs in Python and Fortran-95. In our case, we did not consider the cavity bandwidth. The spin-Hamiltonian in this case was:

$$ H = B_0(g\beta S_z + g\beta N I_{127} + g\beta N I_{227} + S \cdot (A_{127} \cdot I_{127} + A_{227} \cdot I_{227})) + \frac{e^2 Q_1}{4I(2I-1)} I_{127} \cdot Q_1 \cdot I_{127} + \frac{e^2 Q_2}{4I(2I-1)} I_{227} \cdot Q_2 \cdot I_{227} $$
Further description of DFT Calculations.

The predictive value of $^{27}$Al hyperfine and $g$-tensors of aluminum radicals from DFT calculations.

To gauge the predictive value of the DFT-computed spin-parameters, calculations were first carried out on paramagnetic aluminum complexes for which spin-parameters have been measured. These radicals did not necessarily carry any resemblance either structurally or electronically to those anticipated in $\alpha$-$\text{Al}_2\text{O}_3$. The spin-parameters for these complexes are summarized in Table S1. These include two different stable organoaluminium radicals that have been recently studied$^{(55)}$ as well as simple complexes isolated in inert gases$^{(56-58)}$. The $A_{iso}$ of Al(CO)$_2$, the Al:ethylene adduct, and AlH$^+$ complex were opposite of those of the organoaluminium radicals. Overall, the $^{27}$Al hyperfine and $g$-tensors from DFT calculation were in good agreement with the measured values. This demonstrated the DFT-derived values had satisfactory predictive value.

DFT calculations on the Al$_8$O$_{30}$H$_{36}$ nanoparticle models.

As described in the main text, the nanoparticle models were based on the $\alpha$-$\text{Al}_2\text{O}_3$ unit cell (Al$_8$O$_9$) and experimental studies of the water-$\alpha$-$\text{Al}_2\text{O}_3$ interface$^{(34)}$. Oxygens were added to the aluminum atoms so that each had a ligand sphere of 6 oxygens to form a Al$_8$O$_{30}$ core. Hydrogen atoms were added to all oxygens bridging two aluminum atoms. Another set of hydrogens were added in a quasi-random manner to the rest of the oxygens to form structures with overall neutral charges resulting in nanoparticles of the form Al$_8$O$_{30}$H$_{36}$. These structures were subsequently geometry optimized. To these optimized structures, a O$_2$ molecule was added and positioned within hydrogen bonding distance of the Al$_8$O$_{30}$ model, typically about 1.8 Å. These supermolecular complexes were re-geometry optimized with a total spin-multiplicity of 1. As described in the main text, in some cases optimization resulted in a protonated superoxide and oxidized nanoparticle radical pair. For these, the resulting oxidized nanoparticle radical was re-optimized by itself. The atomic coordinates of the optimized structures of the six molecules shown in Figure 6 are listed separately below. For the molecule shown in Figure 6 the five largest $^1$H hyperfine tensors (in MHz) were: [20, -29, -55], [18, -56, -87], [-4, 5, -13], [-2, -3, 5] and [-2, -4, 4] MHz. The three largest $^{27}$Al tensors were: [-17, -20, -20], [-7, -9, -10] and [0, 0, 1] MHz.
Fig. S1. The orientation of the magnetic fields and the Al₂O₃ crystal axes used in the 94 GHz measurements. $B_0$ is the applied magnetic field; $B_1$, the magnetic-field component of microwave excitation; and crystal $a$ and $c$ are indicated in red. $\theta_{cB_0}$ defines the angle of the crystal at which the data were taken.
Fig. S2. The pulse sequences used for the 94 GHz measurements of the radicals in α-Al₂O₃.

The Hahn echo sequence used to measure the EPR is shown at the top, Davies ENDOR in the middle and the ELDOR-NMR at the bottom. These are described in detail elsewhere (59) and the specific conditions are given in methods and materials. Briefly, the latter two techniques measure the spin-echo amplitude of the EPR transition at a fix B₀ as a function of the frequency of a pump pulse applied before the Hahn echo sequence. For ENDOR, the echo amplitude changes when the frequency of the pump matches the NMR transition (red transitions in Figure 1) of a nuclear spin connected to the EPR transition (black transition). For ELDOR-NMR, changes in the Hahn spin-echo amplitude occur when the pump frequency matches a transition that excites both the electron and one or more nuclear spins (blue, cyan and green transitions) that are connected to the EPR transition. The energy differences between these transitions and the EPR transition yield the frequency of the NMR transitions.
Fig. S3. The magnetic-field and $\theta_{cB_0}$ dependence of the 94 GHz $^1$H Mims ENDOR spectra of the H_M protons. 3.3550 T corresponds to $g_{eff}=2.0065$ in these spectra.
Fig. S4. The Davis-ENDOR spectra of Al₅ and Al₁₂. A. The 94 GHz $\theta_{CB_0}=25^\circ$ Davies $^{27}$Al ENDOR spectra of $\alpha$-Al₂O₃. The ENDOR spectrum was obtained at 3.3550 T ($g_{eff}=2.0065$). B. and C. The magnet-field dependence (relative to $g_{eff}=2.0065$) of the resonances indicated by the correspondingly colored arrows over the ENDOR spectrum in A. For the Al₅ resonance, its companion appeared to be the peak at -2.3 MHz shown in C. When shifted in frequency, the shapes and amplitudes of this resonance (blue traces in B) matched those of the 5.1 MHz $R_s$ resonances (red traces). At relative fields above 2.4 mT, the -2.3 MHz resonance becomes obscured by another resonance not associated with $R_s$ (shaded in gray). The dotted green arrows in A indicate the frequency region within which the companion peak to the -11.7 MHz Al₁₂ resonance must be present. E. the $\theta_{CB_0}$ dependence of the 5.1 MHz Al₅ resonance. The cyan trace in A is the calculated ENDOR spectrum based on the hyperfine and nuclear quadrupolar couplings obtained from ENDOR data and DFT calculations described in the text above. The asymmetric frequency offset relative to the $\nu_{^{27}Al\ NMR}$ of the -2.3 and 5.1 MHz resonance is due to the nuclear quadrupolar coupling of Al₅ ($Q_{eff}=0.7$ MHz in Equations S5-7) as confirmed by calculated ENDOR spectrum.
Fig. S5. Comparison the 94 GHz $\theta_{cB_0}=25^\circ$ 3-spin $^{27}$Al ELDOR-NMR spectrum of $R$, with a simulation based on DFT derived hyperfine and NQR coupling values. The 3-spin and 2-spin double quantum transitions (blue, upper abscissa) obtained at $g_{\text{eff}}=2.0065$ compared to the conventional 2-spin single-quantum ELDOR spectrum (solid back, lower abscissa) and inverted Davies ENDOR spectrum (black dotted, lower abscissa) are shown. There were no resonances in the ENDOR or 2-spin ELDOR-NMR spectrum corresponding to the 3-spin resonance. A simulation of the 3-spin (cyan) and 2-spin double quantum ELDOR-NMR spectrum using the same hyperfine and NQR coupling values derived from the DFT calculations and used to simulate the $^{27}$Al ENDOR spectrum of Al$_5$ and Al$_{12}$ in Figure S4B is shown. See text for details.
Fig. S6. Other Examples of O\textsubscript{2} molecule Al\textsubscript{8}O\textsubscript{30}H\textsubscript{36} nanoparticle interactions and possible “outer-sphere” reactions forming R\textsubscript{5}-like radicals. Structures A to D depict cases that are similar to those shown in Figure 6. Most O\textsubscript{2}:[Al\textsubscript{8}O\textsubscript{30}H\textsubscript{36}] pairs remained weakly interacting after geometry optimization. Structure B is one such case. However, geometry optimization of certain initial O\textsubscript{2}:[Al\textsubscript{8}O\textsubscript{30}H\textsubscript{36}] structures led to a HO\textsubscript{2}:[Al\textsubscript{8}O\textsubscript{30}H\textsubscript{35}]\textsuperscript{+} radical pair (structure A). However, the unpair electron spin densities and hyperfine couplings of the isolated [Al\textsubscript{8}O\textsubscript{30}H\textsubscript{35}]\textsuperscript{+} radical (structure C) were not the same as those of the radical 3 in Figure 6 due to differences in protonation. Structure D results from the transfer of an electron from [Al\textsubscript{8}O\textsubscript{30}H\textsubscript{36}] to O\textsubscript{2} followed by separation of resulting radical pair. The unpair electron spin density and hyperfine couplings of this cationic nanoparticle radical are shown superimposed. The large circles indicate atoms with Mulliken spin-densities > 10% and small circles > 1% with black corresponding to positive and red to negative spin densities. Black numbers indicate the calculated isotropic \textsuperscript{27}Al hyperfine couplings and the red the largest \textsuperscript{1}H hyperfine tensor element. The viewing plane is coincident with the crystal ab-plane.
Table S1. Calculated $^{27}$Al Hyperfine (Orca PBE0/6-31**) and G-tensors (Gaussian, B3LYP/6-31+G*) compared to measured values given in parentheses.

| Complex                         | $^{27}$Al Hyperfine | g       |
|--------------------------------|---------------------|---------|
|                                | Isotropic          | Dipolar |
| Organoaluminium complex 1      | -12.7 (15e)         | 5.3     | 2.0022 |
|                                | -1.1               | -1.1    | 2.0027 |
|                                | -4.1               | 4.1     | 2.0031 |
| Organoaluminium complex 2      | -22.2 (23e)         | 7.6     | 2.0023 |
|                                | -2.7               | 2.7     | 2.0027 |
|                                | -4.9               | 4.9     | 2.0031 |
| Al(CO)$_2$ in Ar               | +59.0 (+74.6)       | 68.4 (71.1) | 1.9989 (1.9990) |
|                                | -35.8 (-35.9)      | 2.0022 (2.0021) |
|                                | -32.7 (-35.1)      | 2.0056 (2.0043) |
| AlH$^+$ in Ne                  | +950 (+921)         | -43.6 (-44) | 1.9983 (2.001) |
|                                | -43.6 (-44)        | 1.9983 (2.001) |
|                                | 87.3 (88)          | 2.0023 (2.002) |
| Al Ethylene in Ar              | +46 (+50)          | -41.1 (-36.4) | 1.9956 (1.9965) |
|                                | -33.4 (-36.4)      | 2.0034 (2.0025) |
|                                | 74.5 (72.8)        | 2.0089 (2.0097) |

$^a$ ref (59), the listed EPR parameters are those recalculated from the published optimized structures using the density functional and basis-set used in the present study.

$^b$ ref (60)

$^c$ ref (61)

$^d$ ref (62)

$^e$ sign not determined

$^f$ modelled using an Ar matrix.
Data S1.
Optimized Geometries of Molecules in Figures 6 and S6 (xyz format).

| Charge=0, Spin Multiplicity=3 |
|------------------------------|
| O | -0.499829865445 | -4.492203142579 | -1.855324867910 |
| Al | -0.59849320139 | -2.803583851315 | -0.92388264523 |
| O | -1.731151815416 | -2.798194075720 | -2.385199391205 |
| O | -0.82195956254 | -3.084876494748 | 0.489579311094 |
| Al | 1.483333873957 | -1.712786395576 | 1.55476699904 |
| O | 1.62506122476 | -3.000897137161 | 3.371835670276 |
| O | -1.229911230625 | -1.198492624292 | -0.216210750850 |
| Al | -0.606851217146 | 0.177800454757 | 1.307149536570 |
| O | -0.825884122696 | 1.349878854409 | -0.135671598417 |
| Al | -1.945348164495 | 2.040754604069 | -1.622248415585 |
| O | -3.121219475959 | 2.427328789623 | -2.930739467248 |
| O | 0.680425604024 | -1.666547049392 | -1.891350196905 |
| Al | -0.059470408178 | -0.010113395316 | -1.23022948074 |
| O | -1.176176761123 | 0.462756278717 | -2.587619053338 |
| O | -1.342745895954 | -4.221538403590 | 0.021367484175 |
| O | 3.270854572030 | -1.976316764682 | 1.277876266768 |
| O | -0.14121788396 | -1.325682678432 | 2.435836184571 |
| O | 1.17507851571 | -0.281802908834 | 0.472836246035 |
| Al | 2.497877012348 | 0.900771677131 | -0.274571041407 |
| O | 3.194056422592 | -0.854735279902 | -1.21284816296 |
| O | 2.114943470752 | -0.232577870674 | 3.067133504180 |
| Al | -3.074031536099 | -0.782831124991 | 0.207963637336 |
| O | -3.539889939646 | -2.416793908284 | 0.972704199877 |
| O | -3.948688193008 | -1.769472439661 | -1.456476344774 |
| O | -2.375778289673 | 0.031418328490 | 1.750183536255 |
| O | -3.273059781822 | 0.767556838350 | -0.807685671572 |
| O | -5.049079667791 | -0.462808939903 | 0.938635376963 |
| O | 1.384117619594 | 1.077633208857 | -1.738644186785 |
| O | 3.919350468941 | 1.746867217171 | -1.52128056216 |
| O | 2.370581621824 | 2.262340636984 | 0.863610851337 |
| Al | -1.008988107507 | 2.943671791035 | 1.033275029086 |
| O | -2.535180395047 | 2.567262972322 | 2.03052200982 |
| O | 4.103823224165 | 0.472696541616 | 0.889658719733 |
| O | 0.006065193123 | 1.644248509118 | 2.225462921876 |
| O | 0.355011338092 | 3.954114509270 | 0.36853503415 |
| O | -0.828150152858 | 4.415791072997 | 2.552684186057 |
| O | -2.24978285717 | 3.492158817110 | -0.37274365408 |
| O | -0.363594261678 | 2.962698689097 | -2.21505946903 |
| O | 6.813553709727 | 0.236546639583 | -1.743979036207 |
| O | 7.137818045492 | -0.807840411764 | -1.216097529160 |
| H | 0.462206449583 | -1.746740570491 | -2.83496890506 |
| H | -2.674236309134 | 0.947208059494 | 1.988905303331 |
| H | 0.95423369031 | 1.877641225175 | 1.845653945118 |
| H | -1.893275804488 | -0.176802575700 | -2.882401510732 |
| H | 0.872549751745 | 1.936540908722 | -1.969327265992 |
| H | -0.935529955132 | -1.878741322022 | 2.340317221462 |
| H | 4.735650142494 | 1.219700928411 | -1.557964920056 |
| H | 3.396357104332 | -1.478029327054 | -0.471851733296 |
| H | 3.93702168180 | 1.188011126926 | 1.538917839307 |
| H | 1.792933853648 | -3.956457807456 | 3.409335759167 |
| H | 2.203101210055 | -0.582157075366 | 3.967772349718 |
| H | 3.693909414510 | -2.803393147945 | 1.539417794929 |
| H | -2.180764484068 | -4.561408241900 | -0.322768758050 |
Figure 6 Structure 2

Charge=0, Spin Multiplicity=3

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Figure 6 Structure 3

Charge=0, Spin Multiplicity=2
Figure S6A

Charge=0, SpinMultiplicity=3

| Atom | Coordinates | Atom | Coordinates |
|------|-------------|------|-------------|
| O    | 1.732583545374 | 2.592758299113 |
| Al   | -2.552424060704 | 1.32618037078 |
| O    | 0.510348252072 | 2.585428723283 |
| Al   | 0.70362560674 | 4.62573933961 |
| O    | -0.481976125079 | 2.872662237504 |
| Al   | -0.93053411904 | 0.14753975280 |
| O    | -0.75283765312 | -1.768754524223 |
| Al   | -0.337907992729 | 2.08101694210 |
| O    | 0.469852327373 | -2.01105458164 |
| Al   | -1.035225805829 | 1.19226554089 |
| O    | -2.323225505649 | 1.19226554089 |
| Al   | -3.822355842341 | 2.293495149415 |
| O    | -3.78073855294 | 3.016293681388 |
| Al   | -5.414587740934 | 4.071002770471 |
| O    | 2.147697247123 | 0.632832703008 |
| Al   | -0.319808799091 | 2.270730767863 |
| O    | 1.685617492066 | 0.211015459816 |
| Al   | -1.261922085578 | -1.59326719617 |
| O    | -2.983311931735 | 0.212258152636 |
| Al   | -4.491123119727 | -0.217022174740 |
| O    | -6.146472684844 | -0.429781940342 |
| Al   | -0.301899001581 | 1.036357165756 |
| O    | -2.098025070505 | 2.095236978148 |
| Al   | -3.280356257466 | -0.160598686818 |
| O    | -3.562904572843 | -1.309644590215 |
| Al   | -1.991363029438 | -2.316255055503 |
| O    | -5.528649515664 | 0.037028471741 |
| Al   | -4.841716580908 | 1.663071160105 |
| O    | -2.003290146513 | 0.581989978107 |
| Al   | -2.724263922450 | 0.02834088920 |
| O    | 4.499604782533 | -2.813212039400 |
| Al   | -5.280325304326 | -0.271663051578 |
| O    | -4.082942937625 | -2.278204190305 |
| Al   | -1.764779286071 | 3.109034848620 |
| O    | 0.766698319943 | 3.283509799449 |
| Al   | -3.930071957758 | 4.10653046454 |
| O    | -2.894577949174 | 4.565367495265 |
| Al   | 0.221421732329 | -3.82976155678 |
| O    | 1.317303039145 | 1.58901408751 |
| Al   | 2.496638269743 | -3.673228195017 |
| O    | 1.996839799399 | 4.680128646637 |
| H    | -0.045250594399 | 3.828927234738 |
| H    | -1.092959303156 | 2.277053830736 |
| H    | -2.09500913844 | -2.05831508684 |
| H    | -3.010688417418 | 1.035805355327 |
| H    | -1.920506030201 | 0.214739414666 |
| H    | -4.592883124134 | 1.785232196464 |
| H    | 0.023798958070 | 0.879018311821 |
| H    | -2.006341379196 | 4.720228245665 |
| H    | -4.610228100041 | 3.697524209602 |
| H    | 1.192371100887 | 4.15039240598 |
| H    | -0.979417602197 | 3.468167792945 |
| H    | -0.169018368284 | 5.136609876877 |
| H    | 1.769316000429 | -2.93650086441 |
| H    | 2.5056101213664 | 2.09701938061 |
| H    | 1.077871229980 | 0.48847987592 |
| H    | -6.49304986080 | -0.374172160501 |
| H    | -6.560770719612 | -1.282744800613 |
Figure S6B

Charge=0, Spin Multiplicity=3

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Charge=0, Spin Multiplicity=3

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76
O 3.4998128111 -1.9568394376 -2.092001732942
O 6.420672635815 -0.10211866552 0.151602316972
O 6.739554553355 -0.102211866552 0.151602316972
H -0.799768956481 -1.47735006850 3.135839535741
H 1.789664311874 0.49432936316 -2.391796648267
H -1.660931093740 1.795147605308 -2.362802988980
H 1.531291911907 -0.764391323431 2.4448528251736
H -1.107737796135 2.061534043991 2.683225082269
H -0.73559601702 -1.98394169452 2.327909091501
H -4.182031842991 -0.36552626231 1.260840226634
H -4.695571592050 2.364426890137 -0.483910954567
H -4.747941073451 -0.66068313474 1.913260314193
H -4.488431215607 -2.34064828286 0.623428880827
O 0.562130619636 -3.91645436828 0.911591884185
H -1.59227618025 -4.05243237099 2.891765398538
H 3.442904179295 -1.70581383808 3.023317933995
H 1.425704727344 -3.308683350110 2.697690256140
H -1.785922651344 -4.69397896264 1.518469362404
H 1.442156259891 4.714350075349 -0.034665419547
H 1.397143846211 3.065429609420 -2.76428624118
H 2.243801814747 -2.90023808000 1.137287103859
H 3.692662697761 1.500599703994 -0.84539835170
H 1.580831428569 2.51766328352 2.825019076797
H 3.63664500756 0.79141587178 0.431375806258
H -1.725428628007 3.77459672900 0.718126238560
H -2.460450249199 -3.39495953552 0.531833465814
H -0.479981376613 5.32169021186 2.143679126595
H -3.077517495444 2.466964145777 3.086871436867
H 1.288153536336 3.689284140808 1.191302547626
H 1.267176709123 -3.465762465485 2.808695152927
H -3.258607132633 -0.01793201148 2.496452734318
H -3.99741865727 0.69368795462 1.46116321460
H 2.665501174249 2.71191529178 0.037475138075
H -0.216670953829 -4.99982006254 0.104557765730
H 3.88428287777 2.02422138752 2.44618072208
H -4.065019670102 2.98751380156 2.507467506412
H 4.882147978203 1.14812683226 1.61507376758
H -2.907494133473 -3.61084239789 2.056655084889
H 3.00856739335 3.7168267751 2.44618072208

Figure S6C

Charge=0, Spin Multiplicity=2

73
Figure S6D

74
Charge=1, Spin Multiplicity=2
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| H | 0.2470210 | -3.936864 | -0.380702 |
| H | -3.570631 | 1.939450  | 0.626994  |
| H | 3.856387  | 1.640586  | 0.811935  |
| H | -5.091160 | 2.397232  | 2.432921  |
| H | 2.774287  | 3.732329  | 2.672590  |
| H | -3.915596 | 1.063004  | 1.093618  |
| H | 3.531323  | -2.027408 | -2.546865 |
| H | 0.012809  | 3.359369  | -2.792272 |
| H | -0.439072 | 3.987660  | 1.044191  |
| H | -3.149914 | -2.499962 | 1.153509  |
| H | 5.064684  | -0.930047 | -0.026593 |
| H | -2.598811 | -3.899630 | -2.387308 |
| H | -2.657364 | 4.132938  | -2.466094 |
| H | -1.824045 | -5.018012 | -1.605500 |
| H | 4.040941  | 2.799056  | 2.642740  |
| H | 2.965117  | -4.038288 | 0.165564  |
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