

The $[(\text{Al}_2\text{O}_3)_2]^-$ Anion Cluster: Electron Localization–Delocalization Isomerism

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Three-dimensional bulk alumina and its two-dimensional thin films show great structural diversity, posing considerable challenges to their experimental structural characterization and computational modeling.^[1,2] Recently, structural diversity has also been demonstrated for zero-dimensional gas phase aluminum oxide clusters.^[3,4] Mass-selected clusters not only make systematic studies of the structural and electronic properties as a function of size possible, but lately have also emerged as powerful molecular models of complex surfaces and solid catalysts.^[5–8] In particular, the $[(\text{Al}_2\text{O}_3)_{3–5}]^+$ clusters were the first example of polynuclear main-group metal oxide cluster that are able to thermally activate CH_4 .^[7] Over the past decades gas-phase aluminum oxide clusters have been extensively studied both experimentally^[3,4,7–10] and computationally,^[3,4,7,11–14] but definitive structural assignments were made for only a handful of them: the planar $[\text{Al}_3\text{O}_3]^-$ and $[\text{Al}_5\text{O}_4]^-$ cluster anions,^[9c,f] and the $[(\text{Al}_2\text{O}_3)_{1–4}(\text{AlO})]^+$ cluster cations.^[4] For stoichiometric clusters only the atomic structures of $[(\text{Al}_2\text{O}_3)_4]^{+/0}$ have been unambiguously resolved.^[3]

Herein we report on the structures of the $[(\text{Al}_2\text{O}_3)_2]^{-/0}$ clusters combining photoelectron spectroscopy (PES) and quantum-chemical calculations employing a genetic algorithm^[3] as a global optimization technique. The $[(\text{Al}_2\text{O}_3)_2]^-$ cluster anion shows energetically close lying but structurally distinct cage and sheet-like isomers which differ by delocalization/localization of the extra electron. The experimental results are crucial for benchmarking the different computational methods applied with respect to a proper description of electron localization and the relative energies for the isomers which is of considerable value for future computational studies of aluminum oxide and related systems.

Figure 1 shows the PES spectra of $[(\text{Al}_2\text{O}_3)_2]^-$ at 355 nm (3.496 eV) and 193 nm (6.424 eV) photon energies. The 355 nm spectrum reveals two bands (labeled as X and X'; Figure 1a).

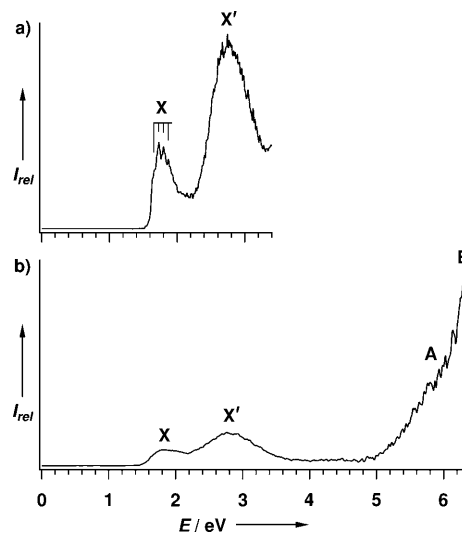


Figure 1. Photoelectron spectra of $[(\text{Al}_2\text{O}_3)_2]^-$ at a) 355 nm (3.496 eV) and b) 193 nm (6.424 eV). The vertical bars in (a) represent resolved vibrational structures.

Band X exhibits a vibrational progression with an average spacing of 570 cm^{-1} (Table 1). The 0–0 transition at 1.65 eV defines the ground-state adiabatic detachment energy (ADE),

Table 1. Experimental and theoretical adiabatic (ADE) and vertical (VDE) detachment energies in eV and vibrational frequency in cm^{-1} .

	ADE Exp. ^[a]	Calc. ^[b]	VDE Exp.	Calc. ^[b]	Vib. freq. Exp. ^[c]	Calc. ^[d]
X	1.65 ± 0.02	1.50 (T_d)	1.72 ± 0.02	1.66 (T_d)	570 ± 50	532, 619
X'	2.30 ± 0.05	2.05 (C_s)	2.80 ± 0.05	2.83 (C_s)		
A	~ 5.1		~ 5.9			

[a] The ADEs of X and X' bands correspond to the electron affinities for the T_d and C_s isomers of $(\text{Al}_2\text{O}_3)_2$. [b] Best theoretical estimates (see Table S2 in Supporting Information). [c] Observed vibrational spacing corresponding to the ground state of the T_d $(\text{Al}_2\text{O}_3)_2$ neutral. [d] There are two totally symmetric modes due to the breathing motions of Al or O with calculated frequencies of 532 and 619 cm^{-1} , respectively (MP2 result, see Table S3 in Supporting Information).

which is also the electron affinity of the neutral $(\text{Al}_2\text{O}_3)_2$ species. The ground-state vertical detachment energy (VDE) is measured to be 1.72 eV from the 1–0 transition. Band X' appears to be broader and more intense relative to band X. No vibrational structures can be resolved for band X'. Its VDE is measured from the peak maximum as 2.80 eV, whereas an ADE of 2.30 eV is evaluated from the band onset. As revealed in the

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193 nm spectrum (Figure 1 b), the next PES bands are located at rather high binding energies: A (VDE: ~ 5.9 eV) and B (VDE: ~ 6.3 eV). The neutral $(\text{Al}_2\text{O}_3)_2$ is a stoichiometric cluster, thus in $[(\text{Al}_2\text{O}_3)_2]^-$ anion the extra electron should occupy an Al based molecular orbital, well-separated from the occupied O 2p derived orbitals with a sizable energy gap. The observed PES pattern therefore seems to be inconsistent with this expectation, hinting that bands X and X' may originate from coexisting isomers in the $[(\text{Al}_2\text{O}_3)_2]^-$ cluster beam, as borne out from our theoretical calculations.

Global optimizations using density functional theory (DFT) with the B3LYP functional^[15,16] for the neutral $(\text{Al}_2\text{O}_3)_2$ cluster yield the known^[12] cage-like T_d symmetric structure (cf. Figure 2 c), whereas for the $[(\text{Al}_2\text{O}_3)_2]^-$ anion in addition to this cage-like T_d structure (Figure 2 c) a sheet-like C_{2h} symmetric structure (Figure 2 b) is found, which is 31.2 kJ mol^{-1} less stable (Table S2, Supporting Information). Alternative optimized anion structures are over 60 kJ mol^{-1} higher in energy. When second order Møller-Plesset perturbation theory (MP2) is applied, the C_{2h} anion structure proves unstable. Lowering its symmetry to C_s (Figure 2 a) it becomes $\sim 8 \text{ kJ mol}^{-1}$ more stable than the T_d structure. Conversely, the C_s structure proves unstable at the B3LYP level. Since the C_s and C_{2h} structures differ by electron

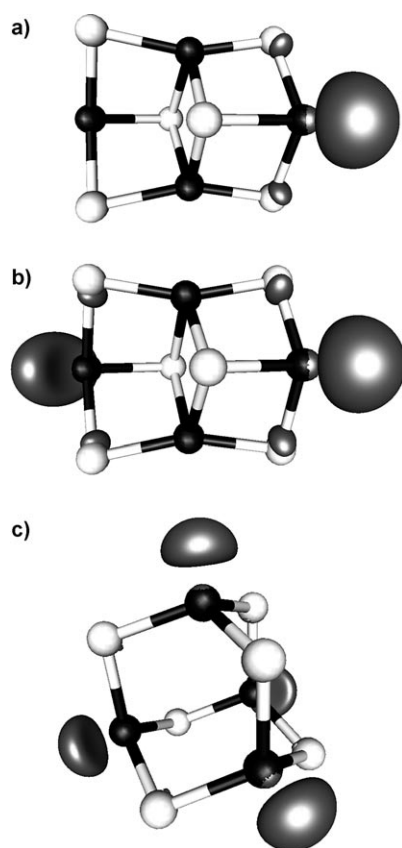


Figure 2. Optimized structures of $[(\text{Al}_2\text{O}_3)_2]^{0-}$ clusters along with isosurface plots of spin density for $[(\text{Al}_2\text{O}_3)_2]^-$ cluster anions. a) The C_s symmetric structure (unpaired electron of cluster anion localized on one Al atom). b) The C_{2h} symmetric structure (unpaired electron of cluster anion delocalized over two Al atoms). c) The T_d symmetric structure (unpaired electron of cluster anion delocalized over all four Al atoms). Al: black, O: gray, spin density: dark gray.

localization (Figure 2), we conclude that in this case the B3LYP functional fails to properly describe the localization phenomenon, which has been attributed to overestimation of the self-interaction part by the exchange functionals.^[17] The BHLYP functional^[15,18] with a larger contribution of Fock exchange gives a stable C_s isomer (at this level the C_{2h} structure is a transition state connecting two C_s isomers), but the relative stability of the T_d and C_s structures is too small or even reversed, depending on the basis set used (Table S2, Supporting Information). A similar dependence of electron localization properties on the amount of Fock exchange was observed for vanadium oxide cluster anions,^[19] but in that case B3LYP performed well. In the present case, MP2 and CCSD(T) calculations, with the majority of the basis sets used, consistently predict that the C_s structure is more stable than the T_d structure by $5.5\text{--}16.7 \text{ kJ mol}^{-1}$. Our best estimate [CCSD(T) with basis set extrapolation]^[20] predicts the C_s structure 6.8 kJ mol^{-1} more stable than the T_d structure, consistent with the experimental observation that the X' band (C_s isomer) is more intense than the X band (T_d isomer). The corresponding best estimates for VDEs and ADEs for the T_d and C_s cluster anion structures (Table 1) are in excellent agreement with the experimental measurements, lending considerable credence to both isomeric structures predicted by our structural searches.

Additional structural evidence comes from the resolved vibrational structure of the X band (Figure 1 a). Since only totally symmetric modes are allowed in photodetachment transitions, this observation suggests that both anion $[(\text{Al}_2\text{O}_3)_2]^-$ and neutral $(\text{Al}_2\text{O}_3)_2$ states that are responsible for band X should have high symmetry. Indeed, a vibrational frequency analysis at the MP2 level reveals two totally symmetric modes for the T_d isomer: 532 and 619 cm^{-1} (Table S3, Supporting Information), due to the breathing movements of the Al and O atoms, respectively. Both modes are allowed, but their frequencies are too close to be resolved under our experimental conditions. In fact, the plain average of the two frequencies is in excellent accord with the experimental value ($570 \pm 50 \text{ cm}^{-1}$).

We further performed CC2 calculations for the lowest triplet excited state of the neutrals at the anion geometries. The calculated excitation energies are 3.75 and 2.59 eV for the T_d and C_s isomers, respectively. If we add these excitation energies to the corresponding best estimates of VDEs of each isomer, we obtain nearly identical values for both C_s and T_d isomers: 5.42 and 5.41 eV . Time dependent BHLYP calculations for both isomers also yield similar excited state VDE values: 5.66 (C_s) and 5.82 eV (T_d). We thus conclude that the experimentally observed band A may contain contributions from both isomers. The observed band B (Figure 1) should be due to higher (triplet and singlet) excited states involving O 2p-derived orbitals, but are not pursued computationally considering the anticipated high density of states.

The overall agreement between experiment and theory leads to unambiguous structural assignments of the X and X' bands to the T_d and C_s isomers for $[(\text{Al}_2\text{O}_3)_2]^-$ in which the extra electron is delocalized and localized, respectively. These results are significant for several reasons. First, both the T_d and C_s isomers are structurally unique with very different coordination

environments which bear no resemblance to Al_2O_3 bulk crystals or thin films.^[1,2] Second, the energy gaps for $[(\text{Al}_2\text{O}_3)_2]^-$, ~ 3.5 and ~ 2.8 eV for the T_d and C_s isomers (estimated from the ADE difference for bands X–A and bands X'–A), respectively, are substantially smaller than those in the bulk (8.7 eV for $\alpha\text{-Al}_2\text{O}_3$)^[21] and model thin films (~ 6.7 eV).^[22] Interestingly, band gap energies as low as ~ 3.2 and ~ 2.6 eV are observed for Al_2O_3 films due to surface defects.^[23] The current $[(\text{Al}_2\text{O}_3)_2]^{-0}$ clusters may potentially serve as useful molecular models for such surface defect sites. Third, the distinct spin density distributions in the T_d versus C_s isomers are remarkable. In the T_d cage isomer the spin density is delocalized over all four Al atoms (Figure 2c), whereas in the C_s sheet-like isomer it is primarily localized on a single Al atom (Figure 2a). The delocalization or localization of the extra electron also leads to an interesting spectroscopic consequence: A large reorganization energy for the C_s isomer (0.50 eV as evaluated from the difference of experimental ADE and VDE) on electron detachment versus a very small reorganization energy for the T_d isomer (0.07 eV). A localized electron significantly alters the local bonding environment around a metal center and hence induces large anion-to-neutral geometric changes upon photodetachment; and vice versa.^[19,24] The X and X' band shapes of $[(\text{Al}_2\text{O}_3)_2]^-$ thus provide indirect spectroscopic evidence for the electron delocalization in the T_d isomer and electron localization in the C_s isomer. Lastly, the current spectroscopic data also allow an assessment of various computational methods (Table S2, Supporting Information) with respect to the proper description of electron localization phenomena in the sheet-like $[(\text{Al}_2\text{O}_3)_2]^-$ isomer which appears to be challenging for quantum chemistry, in particular for widely used density functionals.

Experimental Section

The magnetic-bottle PES apparatus has been described in detail elsewhere.^[25] $[\text{Al}_m\text{O}_n]^-$ clusters were produced by laser vaporization of a pure Al disk target in the presence of a helium carrier gas seeded with 0.5% O_2 . The cluster anions were extracted from the cluster beam and analyzed using a time-of-flight mass spectrometer. The $[(\text{Al}_2\text{O}_3)_2]^-$ clusters of interest were mass selected and decelerated before being intercepted by a laser beam for photodetachment. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The photoelectron time-of-flight spectra were calibrated using the known spectra of Au^- and Rh^- and converted to the electron binding energy spectra by subtracting the kinetic energy (E_k) spectra from the photon energy. The resolution of the PES apparatus was $\Delta E_k/E_k \sim 2.5\%$, that is, ~ 25 meV for 1 eV electrons.

DFT calculations^[20] were performed using the TURBOMOLE program package.^[26] Global optimizations of the cluster structures at the DFT level used our own implementation of the genetic algorithm.^[3] The MP2 and CC2 calculations were performed with the RICC2 module of TURBOMOLE using the resolution of identity method.^[27] For CCSD(T) the MOLPRO program was used.^[28] In all CCSD(T) calculations the value of T_1 diagnostics was below 0.02.

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