The $\text{Al}_3\text{O}_2$, $\text{Al}_3\text{O}_3$, $\text{Al}_4\text{O}_x$, $\text{Al}_5\text{O}_x$ ($x = 3–5$), $\text{Al}_6\text{O}_5$, and $\text{Al}_7\text{O}_5$ clusters are studied using negative ion photoelectron spectroscopy. At 266 nm (4.661 eV) laser photodetachment wavelength the spectra of $\text{Al}_3\text{O}_2$ and $\text{Al}_3\text{O}_3$ present vibrationally resolved features. They show three electronic transitions, due to two different isomers. From Franck–Condon simulations of the $\text{Al}_3\text{O}_2$ and $\text{Al}_3\text{O}_3$ photoelectron spectra, several vibrational frequencies together with the normal coordinate changes were derived. We obtained approximate electron affinities for $\text{Al}_3\text{O}_2$ and $\text{Al}_3\text{O}_3$ using the Gaussian 2 model, and calculated isomerization energies for both the anionic and neutral geometries and the experimental adiabatic detachment energies (ADE) of bands X and X. The larger aluminum oxide clusters present several structureless bands which likely also result from multiple isomers. The ADEs for the larger clusters increase with size within a cluster series, with the exception of $\text{Al}_5\text{O}_5$.

1. Introduction

Amorphous aluminium oxide based catalysts are among the most widely employed solid acid catalysts. They are used in the isomerization of olefins, paraffins, and alkyl aromatics, alkylation of aromatics with alcohols and olefins, and olefins oligomerization and catalytic cracking. They serve as supports or catalytic components for other reactions, such as combustion of methane, denitrogenation of nitrogen-containing heteroaromatic compounds, and dimerization of olefins. The importance of these catalysts has motivated a large number of experimental and theoretical studies to understand the interaction of aluminum with oxygen from a molecular point of view. Recently, the identification of the presence of corundum ($\text{Al}_2\text{O}_3$) in stellar grains has stimulated a new interest in aluminum oxide species and how these are formed from the reaction $\text{Al} + \text{O}_2$. These considerations have motivated a series of experiments in which the photoelectron (PE) spectra of size-selected $\text{Al}_3\text{O}_y$ anions have been measured in order to characterize the structural motifs and trends in the anion and neutral clusters, in particular their dependence on size and stoichiometry. In this paper, we present additional studies of this type, covering $\text{Al}_3\text{O}_x$ clusters with as many as seven aluminum atoms. This study represents the continuation of our investigations to understand the electronic and vibrational structure of group 13 element-containing clusters, such as $\text{B}_x\text{N}_y$, $\text{Al}_x\text{P}_y$, $\text{Ga}_x\text{P}_y$, $\text{Ga}_x\text{As}_y$, and $\text{In}_x\text{P}_y$.

Wang and coworkers reported the first PE spectra of aluminum oxide cluster anions, specifically $\text{Al}_3\text{O}_y$ ($x = 1–2$, $y = 1–5$) and $\text{Al}_4\text{O}_y$ ($y = 0–5$). These spectra yielded mainly unstructured bands corresponding to transitions between various anion and neutral electronic states, with partially-resolved vibrational structure seen only for $\text{Al}_3\text{O}_y$.

Varying the ion source conditions caused the relative intensities of the two lowest energy bands in the PE spectra of $\text{Al}_3\text{O}_2$ and $\text{Al}_3\text{O}_3$ to change considerably, suggesting that these bands originate from different anion isomers. A somewhat higher resolution PE spectrum of $\text{Al}_3\text{O}_2$ was measured by Akin and Jarrold, who also confirmed the presence of multiple isomers of $\text{Al}_3\text{O}_2$ in a hole-burning experiment.

Electronic structure calculations by Ghanty and Davidson find the V isomer to be the ground state for $\text{Al}_3\text{O}_2$ and $\text{Al}_3\text{O}_3$, while for $\text{Al}_4\text{O}_3$ the energy ordering is reversed in the anion and neutral; the book is the lowest energy structure for $\text{Al}_4\text{O}_5$ and the kite is the ground state for $\text{Al}_5\text{O}_5$. The most recent calculation by Martinez et al. a B3LYP/6-311+G(2d,p) DFT calculation with further optimization at the quadratic configuration interaction (QCISD) level, predicts the energy ordering of the isomers to be reversed.
in the anion and neutrals of both species. The kite is the global minimum for Al\(_2\)O\(_3\)\(^-\), while the V is the ground state for Al\(_2\)O\(_2\), and for Al\(_3\)O\(_3\) the orderings are the same as those found by Ghanty and Davidson.\(^{11}\) These energy reversals are attributed to less positive charge and hence less Coulombic repulsion between the Al atoms in the anions.

For both anions, the calculated energy differences between the two isomers are less than 1 kcal mol\(^{-1}\), with considerably larger splittings (~10 kcal mol\(^{-1}\)) for the neutral isomers. As a result, for each species, both anion isomers should be populated in the PE spectroscopy experiments, and the lowest energy bands in the PE spectra should correspond to transitions between the higher energy anion isomers to the ground state neutral structures (i.e. \(V\)–V for Al\(_2\)O\(_2\)\(^-\) and kite–kite for Al\(_3\)O\(_3\)\(^-\)). In the experimental spectra,\(^{13–16}\) the relative intensities and the vibrational structure of the lowest energy band for Al\(_2\)O\(_2\) are consistent with the proposed assignments, but a more definitive assignment of the Al\(_2\)O\(_2\)\(^-\) spectrum would be aided by the observation of resolved vibrational structure. In this paper, we report the first vibrationally resolved PE spectra of Al\(_2\)O\(_2\) at photodetachment energies of 3.493 and 4.661 eV, and somewhat better-resolved PE spectra of Al\(_3\)O\(_3\)\(^-\) than in ref. 16. Electronic structure calculations at the Gaussian 2 (G2) level are carried out in order to refine the energetics of the anion and neutral isomers. Franck–Condon simulations of the vibrational structure in the spectra yield information on the anion and neutral vibrational frequencies and the geometric changes that occur upon photodetachment. We also present the first PE spectra of the Al\(_2\)O\(_2\)\(^-\) and Al\(_3\)O\(_3\)\(^-\) cluster series and of the Al\(_4\)O\(_5\)\(^-\) and Al\(_5\)O\(_5\)\(^-\) clusters, using what we have learned from the smaller clusters to assign some of the features in these spectra.

2. Experiment

The negative ion photoelectron spectrometer used in this investigation has been described in detail previously;\(^{21–25}\) only a brief description will be given here. Al\(_2\)O\(_2\)\(^-\) anions were produced in a pulsed laser vaporization molecular beam source using argon as carrier gas. A rotating and translating disk of AlN ceramic (> 95% dense) or Al is ablated with the second harmonic (2.331 eV, 18 mJ/pulse) of a pulsed Nd:YAG laser. The laser pulses are focused onto the target with a 50 mm lens. The pre-pumped region. Negative ions formed during the expansion are extracted perpendicularly to their flow direction by a pulsed electric field and accelerated to a beam energy of 2.5 keV. The plasma is expanded through a 19 mm long clustering channel and entrained in a pulse of Ar carrier gas from a piezoelectric valve. The plasma is expanded through a 19 mm long clustering channel and then passes through a skimmer into a differentially pumped region. Negative ions formed during the expansion are extracted perpendicularly to their flow direction by a pulsed electric field and accelerated to a beam energy of 2.5 keV. The extracted ions enter a linear reflection time of flight (TOF) mass spectrometer, where they are separated in time and space according to their mass-to-charge ratios. The TOF mass spectrometer resolution is \(m/\Delta m \approx 2000\). For this particular experiment the instrument is operated at a repetition rate of 18 Hz.

Mass-selected anions are selectively photodetached with a fixed frequency Q-switched Nd:YAG probe laser. The third (355 nm, 3.493 eV) and fourth (266 nm, 4.661 eV) harmonics were used in this study. The laser is timed so as to photodetach ions of the desired mass. The photoelectron kinetic energy (eKE) is then analyzed by time-of-flight using a 1 m, field-free flight tube. The eKE scale is calibrated using the PE spectra of Cl\(^-\), Br\(^-\), and I\(^-\) at 266 nm and O\(_2\)\(^-\) at 355 nm. The energy resolution is 8–10 meV for an eKE of 0.65 eV and degrades as (eKE)\(^{3/2}\) at higher eKE. The PE spectra were taken at two laser polarization angles, 0° and 90° with respect to the direction of electron detection. The laser polarization can be rotated using a half-wave plate.

All photoelectron spectra presented here are plotted as a function of the electron binding energy (eBE) defined as

\[
eBE = hv - eKE = EA + E(0) - E(-)\]

where \(hv = 3.493\) and 4.661 eV is the photodetachment energy, \(EA\) is the electron affinity of the neutral cluster, and \(E(0)\) and \(E(-)\) are the internal (electronic + vibrational) energies of the neutral and anion, respectively.

3. Results

3.1 Photoelectron spectra

The 355 and 266 nm PE spectra of Al\(_2\)O\(_2\)\(^-\) and Al\(_3\)O\(_3\)\(^-\) are shown in Fig. 2 and 3, respectively. The 266 nm PE spectra of Al\(_2\)O\(_3\)\(^-\) and Al\(_3\)O\(_3\)\(^-\) (\(x = 3–5\)) are presented in Fig. 4 and those of Al\(_4\)O\(_5\)\(^-\) and Al\(_5\)O\(_5\)\(^-\) in Fig. 5. We report only the PE spectra taken at a laser polarization angle of 0° with respect to the flight tube axis; spectra at 90° are similar but lower in intensity. The photoelectron signal is plotted as a function of eBE. At 266 nm, three distinct spectral features are revealed by photodetachment of the Al\(_2\)O\(_2\)\(^-\) and Al\(_3\)O\(_3\)\(^-\) clusters and are labeled X', X, and A. The 266 nm PE spectra of the larger clusters exhibit several unresolved bands, labeled in alphabetical order.

The 355 nm PE spectrum of Al\(_2\)O\(_2\)\(^-\) shows a weak band, band X', followed by a much stronger band, band X. Band X', beginning around 1.5 eV, shows no obvious vibrational structure, but band X shows a partially resolved vibrational progression with a peak spacing of approximately 430 cm\(^{-1}\). The apparent origin of this band is at 2.17 eV. Band A, seen at 266 nm, shows a well-resolved vibrational progression with an apparent origin of 3.40 eV and a frequency of 410 cm\(^{-1}\). Although all three bands were seen previously, no vibrational structure was observed in either band X or A.

All three bands in the PE spectra of Al\(_3\)O\(_3\)\(^-\) show partially-resolved vibrational progressions. The apparent vibrational origin for band X' is at 2.06 eV, and the spectrum shows a

![Fig. 2 Photoelectron spectra of Al\(_2\)O\(_2\)\(^-\) at 355 nm (top) and 266 nm (bottom). The laser polarization angle was 0°.](image-url)
single vibrational progression with a frequency of approximately 770 cm\(^{-1}\). The vibrational structure of band X is more complex; multiple modes appear to be active with partially resolved features spaced by approximately 400 cm\(^{-1}\). Band A exhibits a 300 cm\(^{-1}\) progression with its origin at 3.60 eV. Vibrational structure in bands X\(^0\) and X was seen previously, but no structure in band A was observed in the earlier work. The X'/X intensity ratio is considerably larger in the Al\(_3\)O\(_3^-\) spectra than in the Al\(_3\)O\(_3\)\(^-\) spectra.

3.2. Electronic structure calculations

To aid in interpretation of the measured PE spectra, we carried out DFT electronic structure calculations on four structural isomers: the V and kite configurations for Al\(_3\)O\(_2\) and Al\(_3\)O\(_2\)\(^-\) species, and the kite and book structures for Al\(_3\)O\(_3\) and Al\(_3\)O\(_3\)\(^-\). We calculated the optimized geometry, energetics, and vibrational frequencies for the lowest electronic states of each of the anion and neutral isomers, and for the first excited states of the lowest electronic states of each of the anion and neutral isomers, and for the first excited states of the Al\(_3\)O\(_2\) kite and Al\(_3\)O\(_2\) book isomers.

The computations were performed using the GAUSSIAN98 program suite.\(^2\)\(^3\) The level of theory employed was the DFT
Results from the B3LYP and G2 calculations are summarized in Table 2. All calculated structures are planar and have $C_2\text{v}$ symmetry. The B3LYP geometries calculated for the lowest electronic states of each anion and neutral isomer are essentially identical to those calculated previously by Ghanty and Davidson and Martinez et al., and are not enumerated here. However, the geometries of the first excited states of the $\text{Al}_3\text{O}_2$ kite and $\text{Al}_3\text{O}_3$ book isomers were not reported previously and are shown in Fig. 1. Molecular orbital (MO) energy diagrams for the two lowest energy structures of $\text{Al}_3\text{O}_2$ and $\text{Al}_3\text{O}_3$ are similar to those reported by Ghanty and Davidson.

The electronic term energy $T_e$ is given for each anion and neutral state; $\Delta E^\text{norm}$ is the energy difference between the electronic and vibrational (assuming harmonic zero-point energy corrections) ground states of the two isomers for each anion and neutral species. For each neutral state, the ADE is listed; this is the energy difference between its vibrational ground state and that of the lowest energy anion isomer.

In the results shown in Table 2, similar to the previous DFT calculations by Ghanty and Davidson and Martinez et al., in particular, we find the energetic ordering of the $\text{Al}_3\text{O}_2$ isomers to be reversed in the anion and neutral, with kite and book isomers being the lowest energy structures for $\text{Al}_3\text{O}_2^-$ and $\text{Al}_3\text{O}_2$, respectively, just as in the earlier work. However, the energetic ordering of the $\text{Al}_3\text{O}_2$ isomers depends on the method and basis set used. At the B3LYP/cc-pVDZ level of theory, the anion and neutral have the same energetic ordering with the kite and book isomers being the lowest energy structures for $\text{Al}_3\text{O}_2^-$ and $\text{Al}_3\text{O}_2$, similar to those reported by Ghanty and Davidson. In the B3LYP/cc-pVTZ calculation, this difference is increased to 65 meV. With the smaller cc-pVDZ basis set, the ordering is inverted with the kite isomer slightly higher energy $\text{V}$ anion isomer which is expected to be less populated than the kite isomer of $\text{Al}_3\text{O}_2^-$.

In order to test our preferred assignment, simulations of bands X’ and A were performed within the Franck–Condor (FC) approximation. Using the B3LYP/cc-pVDZ force constants and optimized geometries for the initial state of the anion and the final state of the neutral, we determined the displacement in normal coordinates between the equilibrium structures of various states of $\text{Al}_3\text{O}_2$ and $\text{Al}_3\text{O}_2^-$, and we assigned band X to the $1\text{A}_1(\text{kite})$ transition, and band A to the $1\text{A}_1(\text{kite})$ transition. The lower intensity of band X’ relative to bands X and A reflects the fact that band X’ originates from the slightly higher energy V anion isomer which is expected to be less populated than the kite isomer of $\text{Al}_3\text{O}_2^-$. If, on the other hand, the V anion of $\text{Al}_3\text{O}_2^-$ is the ground state, then we would assign band X’ to the $\text{kite}$ transition originating from the excited anion isomer, and bands X and A to $\text{V}$ transitions (the comparable intensities of bands X and A indicate that they both originate from the lowest energy anion isomer). The experimental splitting between bands X and A (~1.2 eV) supports the first assignment, because it is close to the calculated splitting between the ground $1\text{B}_3$ and excited $1\text{A}_1$ states of the neutral kite isomer.

The electronic structure calculations described in the previous section leave some uncertainty regarding the ground state of $\text{Al}_3\text{O}_2^-$ and this uncertainty clearly affects the assignment of the experimental PE spectrum. If we assume that the energy orderings in the G2 calculations in Table 2 and ref. 19 are correct, we can assign band X’ of the $\text{Al}_3\text{O}_2^-$ PE spectrum to the $1\text{A}_1(\text{V}) \rightarrow 1\text{A}_1(\text{V})$ transition, band X to the $1\text{B}_3(\text{kite}) \rightarrow 1\text{A}_1(\text{kite})$ transition, and band A to the $1\text{A}_1(\text{kite}) \rightarrow 1\text{A}_1(\text{kite})$ transition. The lower intensity of band X’ relative to bands X and A reflects the fact that band X’ originates from the slightly higher energy V anion isomer which is expected to be less populated than the kite isomer of $\text{Al}_3\text{O}_2^-$. If, on the other hand, the V anion of $\text{Al}_3\text{O}_2^-$ is the ground state, then we would assign band X’ to the $\text{kite}$ transition originating from the excited anion isomer, and bands X and A to V transitions (the comparable intensities of bands X and A indicate that they both originate from the lowest energy anion isomer). The experimental splitting between bands X and A (~1.2 eV) supports the first assignment, because it is close to the calculated splitting between the ground $1\text{B}_3$ and excited $1\text{A}_1$ states of the neutral kite isomer.

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No vibrational structure is observed for band X in the experimental PE spectrum, nor is any seen in the FC simulation of this band, assuming it is the V → V transition using the calculated normal coordinate displacements and vibrational frequencies. The reason for the absence of structure is seen in Table 3. There are substantial displacements in all four totally symmetric modes. In particular, \( \Delta Q_4 \) is equal to 0.617 au/\(^2\) Å for the low frequency vibrational mode \( \nu_1^3 \) (36 cm\(^{-1}\)), corresponding to the symmetric wag of the two terminal Al atoms. These displacements result from the large change in the \( \angle \text{OAO} \) bond angle, from 99.8° for AlO\(_2\) to 121.7° for Al\(_2\)O\(_3\). As a result, there are overlapping extended progressions in a very low frequency mode, leading to an electronic band in the PE spectrum with no resolved vibrational structure.

At 355 nm, band X exhibits a partially resolved vibrational progression. From the Franck–Condon simulation (see Table 3) we could fit band X using three vibrational active frequencies, in cm\(^{-1}\): 329 ± 50 (\( \nu_3^4 \)), 430 ± 50 (\( \nu_4^4 \)), and 780 ± 50 (\( \nu_5^4 \)). The most active mode is the \( \nu_3^4 \) mode, which can be described as the stretching of the two Al atoms in the ring of the kite, Al(3)–Al(4) in Fig. 1. Activity in this mode results from a decrease in the Al(3)–Al(4) bond distance upon photodetachment, from 2.78 to 2.65 Å, according to the electronic structure calculations. The B3LYP computed vibrational frequencies agree well with those obtained in the simulation, and the normal coordinate displacements for the \( \nu_4 \) and \( \nu_3 \) modes used to simulate the spectrum are very close to those obtained from the electronic structure calculations. However, the value of \( \Delta Q_2 \) needed to fit the progression is larger by a factor of 1.8 than the value from the calculated geometries.

The better-resolved vibrational structure in band A can be fit with a FC simulation using frequencies, in cm\(^{-1}\), of 415 ± 30 (\( \nu_3^0 \)), 663 ± 50 (\( \nu_4^0 \)), and 768 ± 50 (\( \nu_5^0 \)), with \( \nu_3^0 \) as the main active mode. The computed vibrational frequencies and normal coordinates for both the anion and the neutral are close to those that fit the spectrum, with the exception of \( \Delta Q_2 \), which needed to be increased by a factor of 2.3 to fit the progression. A weak feature at 3.375 eV assigned as a hot band yields an anion vibrational frequency of \( \nu_3^1 = 350 \pm 80 \) cm\(^{-1}\).

Both simulations require that \( \Delta Q_2 \) be increased by about factor of two over the calculated values based on the geometries obtained from the electronic structure calculations. This discrepancy can be reduced by adjusting the geometry of either the anion or both neutral states. The extent of the required geometry change was examined by modifying the geometry of the \( ^1 \text{A}_1 \) electronic state of AlO\(_3\)\(^-\), keeping fixed the calculated geometries and force constants of the \( ^2 \text{B}_2 \) and \( ^2 \text{A}_1 \) states of AlO\(_2\). Using a Al(3)–Al(4) bond distance of 3.02 Å, 0.18 Å longer than the optimized calculated value for the \( ^1 \text{A}_1 \) electronic state of AlO\(_2\), we obtain normal mode displacements \( \Delta Q_2 \) of 0.514 au/\(^2\) Å for band X and 0.434 au/\(^2\) Å for band A, in better agreement with the best-fit \( \Delta Q_2 \) values in Table 3.

Overall, we find that all three bands in the AlO\(_2\)– PE spectra can be fit with relatively small adjustments to the calculated normal coordinate displacements, assuming the bands are assigned according to the energy ordering of the anion isomers yielded by the G2 calculations. Our analysis therefore confirms this assignment and energy ordering.

The electron affinity (EA) of AlO\(_2\) is defined as the energy difference between the \( v = 0 \) levels of the anion and neutral electronic ground states, which in this case are the \( ^1 \text{A}_1 \) kites for AlO\(_3\)\(^-\) and the \( ^2 \text{B}_2 \) V-structure for AlO\(_2\). No transitions between these two different isomers are observed in the PE spectrum. We can, however, determine the EA from the experimental ADE for band X and the calculated \( \Delta E_{\text{ion}} \) for the anion isomers, or from the experimental ADE for band X and the calculated \( \Delta E_{\text{ion}} \) for the neutral isomers, according to EA = ADE(X) – \( \Delta E_{\text{ion}} \) (anion) or EA = ADE(X) – \( \Delta E_{\text{ion}} \) (neutral). Using the values in Tables 2 and 3, these two determinations yield 1.65 and 1.58 eV, respectively, for the EA’s. We select as our best estimate the average of the two values, (1.62 ± 0.12) eV for EA(AlO\(_2\)). Here the overall error was estimated using the experimental resolution for bands X’ and X together with the uncertainty of the computed value of \( \Delta E_{\text{ion}} \).

### 4.2. Al\(_2\)O\(_3\)\(^-\)

Based on their own electronic structure calculations and those by Ghanty and Davidson,\(^{17}\) Akin and Jarrold\(^{15}\) assigned bands X and X in their PE spectrum of Al\(_2\)O\(_3\) to the \( ^2 \text{B}_2 \) (kite) – \( ^1 \text{A}_1 \) (kite) and \( ^2 \text{B}_2 \) (book) – \( ^1 \text{A}_1 \) (book) photodetachment transitions. Our electronic structure calculations are consistent with this assignment, and support the new assignment of band A in our spectrum to the \( ^2 \text{B}_2 \) (book) – \( ^1 \text{A}_1 \) (book) transition. The calculated G2 energetics in Table 2 indicate that the anion

<table>
<thead>
<tr>
<th>Species</th>
<th>Band</th>
<th>Structure</th>
<th>State</th>
<th>( \nu^1 )</th>
<th>( \nu^0 )</th>
<th>( \Delta Q )</th>
<th>ADE</th>
<th>T</th>
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<tbody>
<tr>
<td>Al(_2)O(_2)</td>
<td>X'</td>
<td>V-shape</td>
<td>( ^2 \text{A}_1 )</td>
<td>( \nu_1 = 41 ) (41)</td>
<td>36 (36)</td>
<td>0.617 (0.617)</td>
<td>1.50 ± 0.10</td>
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<tr>
<td></td>
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<td>( \nu_2 = 235 ) (235)</td>
<td>237 (237)</td>
<td>0.886 (0.886)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>( \nu_4 = 436 ) (436)</td>
<td>444 (444)</td>
<td>1.138 (1.138)</td>
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<td></td>
<td></td>
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<td></td>
<td>( \nu_5 = 954 ) (954)</td>
<td>962 (962)</td>
<td>0.045 (0.045)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>X</td>
<td>Kite-shape</td>
<td>( ^2 \text{B}_2 )</td>
<td>( \nu_1 = 266 ) (266)</td>
<td>329 (329)</td>
<td>0.047 (0.040)</td>
<td>2.186 ± 0.010</td>
<td>200</td>
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<td></td>
<td></td>
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<td></td>
<td>( \nu_2 = 352 ) (352)</td>
<td>430 (417)</td>
<td>0.455 (0.258)</td>
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<td></td>
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<td></td>
<td></td>
<td>( \nu_3 = 833 ) (833)</td>
<td>780 (780)</td>
<td>0.267 (0.238)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>A</td>
<td>Kite-shape</td>
<td>( ^2 \text{A}_1 )</td>
<td>( \nu_1 = 415 ) (391)</td>
<td>415 (391)</td>
<td>0.473 (0.203)</td>
<td>3.419 ± 0.008</td>
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<td></td>
<td>( \nu_2 = 671 ) (671)</td>
<td>663 (683)</td>
<td>0.077 (0.064)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \nu_3 = 833 ) (833)</td>
<td>768 (768)</td>
<td>0.134 (0.104)</td>
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</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>X'</td>
<td>Kite-shape</td>
<td>( ^2 \text{A}_1 )</td>
<td>( \nu_1 = 546 ) (546)</td>
<td>610 (573)</td>
<td>0.320 (0.223)</td>
<td>2.052 ± 0.010</td>
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<td>( \nu_2 = 578 ) (578)</td>
<td>808 (726)</td>
<td>0.490 (0.447)</td>
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<tr>
<td></td>
<td>X</td>
<td>Book-shape</td>
<td>( ^2 \text{B}_2 )</td>
<td>( \nu_1 = 210 ) (210)</td>
<td>275 (245)</td>
<td>0.385 (0.275)</td>
<td>2.805 ± 0.012</td>
<td>300</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td>( \nu_2 = 390 ) (412)</td>
<td>410 (427)</td>
<td>0.461 (0.329)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \nu_3 = 660 ) (664)</td>
<td>690 (623)</td>
<td>0.269 (0.095)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \nu_4 = 718 ) (718)</td>
<td>750 (699)</td>
<td>0.085 (0.055)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>Book-shape</td>
<td>( ^2 \text{A}_1 )</td>
<td>( \nu_1 = 210 ) (210)</td>
<td>283 (256)</td>
<td>0.565 (0.421)</td>
<td>3.610 ± 0.015</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \nu_2 = 390 ) (412)</td>
<td>460 (439)</td>
<td>0.255 (0.212)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \nu_3 = 660 ) (664)</td>
<td>630 (630)</td>
<td>0.265 (0.201)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

kite isomer is only 0.104 eV higher than book isomer of the anion. Hence, as in the Al$_{12}$O$_6$ PE spectrum, the lowest energy band does not originate from the anion ground state. However, the X'/X intensity ratio is clearly higher in the Al$_{12}$O$_6$ PE spectra than in the Al$_{12}$O$_7$ spectra, even though the ion source conditions were essentially the same when the PE spectra were taken for the two anions. This experimental observation is consistent with the G2 calculations, which show a smaller energy splitting between the two anionic isomers of Al$_{12}$O$_6$ than of Al$_{12}$O$_7$ ($\Delta E_{\text{iso}} = 0.145$ eV).

All three bands show resolved vibrational structure. The best-fit FC simulations are shown in Fig. 6, and the parameters used in these simulations are listed in Table 3. Band X' comprises progressions in the two totally symmetric $\nu_4^0$ and $\nu_8^0$ modes with frequencies of 610 and 808 cm$^{-1}$, respectively, with most of the activity in the $\nu_8^0$ mode. The $\nu_4$ and $\nu_8$ modes correspond to symmetric stretch and distortion vibrations, respectively, of the kite “head”. Activity in these mode results because the Al-O bond lengths in the “head” are longer and more asymmetric in the anion.$^{17,19}$ The ADE for this band is estimated using the experimental resolution for bands X and X', respectively. We select our best estimate for EA(Al$_{12}$O$_6$) the average of the two values yielding (2.12 ± 0.10) eV. Here the overall error was estimated using the experimental resolution for bands X' and X together with the uncertainty of the computed value of $\Delta E_{\text{iso}}$.

4.3. Larger aluminum oxide clusters

The photoelectron spectra of Al$_{12}$O$_x^-$, Al$_{12}$O$_y^- (x = 3–5), Al$_{12}$O$_x^-$ and Al$_{12}$O$_y^-$ measured at 266 nm represent the first experimental results on these clusters. These spectra do not exhibit resolved vibrational structure. Determination of the VDE's for each band is straightforward, as each corresponds to a band maximum. The ADE of the first band of every spectrum, marked as an arrow in Fig. 4 and 5, is determined from the measured electron binding energy spectrum by extrapolating the linear portion of the first leading edge in the PE spectrum to the energy axis.$^{25}$ The crossing between the axis and this line is our best estimate of the ADE. Using this method,
the error bars are 60–150 meV. The adiabatic electron detachment and vertical electron detachment energies are reported in Table 1.

The lowest ADEs increase as the number of Al or O atoms is increased, with the exception of the Al₃O₂⁻ PE spectrum, which has a lower ADE than the first band of either the Al₄O₄⁻ or Al₅O₅⁻ spectrum. Such a result suggests that neutral Al₃O₃ is particularly stable; further insight into why this might be the case would be greatly facilitated by electronic structure calculations in this size regime. No ab initio or density functional calculations have been performed on these species, except for the neutral Al₄O₃ cluster. The richness in different calculated low-lying energy isomers for the Al₃O₄ cluster is evidenced by five electronic transitions, A–E, observed in the PE spectrum (Fig. 4).

In light of the results for Al₂O₂ and Al₃O₃, contributions from multiple anion isomers are expected in the PE spectra of the larger clusters. The likeliest candidates for such effects are the Al₄O₄⁻ spectrum, where the weak band A could certainly arise from an anion excited structural isomer, and the Al₅O₅⁻ and Al₆O₆⁻ spectra, in which the overlapped bands A and B could originate from transitions from nearly degenerate anion isomers. The computations of Chang et al.26 find that neutral Al₅O₅ has nearly degenerate singlet di-bridged kite (D₂h) and triplet cubic isomers 1 (T₃), so these may be the pairs of isomers leading to bands A and B in the Al₅O₅⁻ PE spectrum. Finally, the appearance of bands A and B in the Al₅O₅⁻, Al₆O₆⁻, and Al₇O₇⁻ spectra are similar to bands X and X' in the Al₃O₂⁻ spectra, so these bands in the larger clusters may also arise from different anion isomers.

The Al₄O₄⁻ and Al₅O₅⁻ PE spectra show features at high electron binding energy. Smaller Al₄O₄⁻ or Al₅O₅⁻ (x < 5) clusters were not observed in the mass spectrum; this together with the high ADE’s suggests that Al₄O₄⁻ and Al₅O₅⁻ have high stability.

4. Conclusions

The vibrationally resolved photoelectron spectra of Al₂O₂⁻ and Al₃O₃⁻ together with PE spectra of larger aluminium oxide clusters have been presented. Three electronic bands in the PE spectra of Al₂O₂⁻ and Al₃O₃⁻ are discussed in detail and analyzed with the aid of electronic structure calculations and Franck–Condon simulations of vibrational structure. In the Al₂O₂⁻ PE spectrum, bands X and A are assigned to a transition originating from the lowest energy “kite” anion isomer, while band X’ originates from the slightly higher energy “V” anion isomer. While these assignments were proposed previously, they are confirmed by the intensities, energetics, and vibrational structure seen in our experimental spectra. Similarly, in the Al₃O₃⁻ PE spectra, bands X and A originate from the lowest energy “book” anion isomer, while band X’ originates from the slightly higher energy “kite” anion isomer.

Computations using the G2 method showed that for the Al₃O₃⁻ isomers is lower than ΔEₑₑₑ for Al₂O₂⁻, a result consistent with the relative intensities of band X’ and X in the Al₃O₃⁻ and Al₄O₄⁻ photoelectron spectra. Using G2 values of ΔEₑₑₑ for the anions and the neutrals, we could derive the EA(Al₂O₂) of (1.62 ± 0.12) eV and EA(Al₃O₃) of (2.12 ± 0.10) eV.

Although detailed assignments of PE spectra for the larger clusters were not attempted, the general appearance of these spectra also suggests contributions from multiple anion isomers. The results presented here imply that it is worthwhile to investigate the extent of the contribution from multiple isomers to the PE spectra of other semiconductor cluster anions.

Acknowledgements

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References