A study of the structure and bonding of small aluminum oxide clusters by photoelectron spectroscopy: $Al_xO_y^-$ (x=1–2, y=1–5)

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The structure and bonding of aluminum oxide clusters, Al_xO_y (x=1–2, y=1–5), are studied with anion photoelectron spectroscopy (PES) and are compared with preliminary *ab initio* calculations. The spectra were obtained at four detachment photon energies: 2.33, 3.49, 4.66, and 6.42 eV. The 6.42 eV spectrum for AlO^- reveals the $X\ ^2\Sigma^+$ ground state and two excited states of AlO. The 6.42 eV spectrum for AlO_2^- also shows three states for AlO_2: $X\ ^2\Pi_g$ ground state and the $A\ ^2\Pi_u$ and $B\ ^2\Sigma_g^+$ excited states. The spectra for $Al_2O_y^-$ clusters show vibrationally resolved ground states which come from Al *sp*-type orbitals and also high binding energy excited states, which are mainly of oxygen $2p$ character. Al_2O_2, which has a D_{2h} rhombus structure, has an electron affinity (EA) of 1.88 eV and its singlet–triplet excitation energy is measured to be 0.49 eV. Much higher EAs are measured for the larger Al_2O_y clusters. The PES spectra of $Al_2O_3^-$, $Al_2O_4^-$, and $Al_2O_5^-$ show very similar electronic and vibrational structure. Furthermore, the ground state vibrational frequencies of these three molecules are also similar. These observations lead us to suggest that these molecules all have a rhombuslike structure, similar to Al_2O_2, with the oxygen atoms sequentially attaching to the terminal aluminum atoms. The spectra are consistent with an ionic bonding view of these clusters and the vibrational frequencies are in good agreement with the theoretical results. Significant information about the structure and bonding of these small aluminum oxide clusters is obtained and discussed. [S0021-9606(97)02904-8]

I. INTRODUCTION

Aluminum oxide not only forms the basis of an important class of ceramic materials, but is also important in many minerals. There has been a great deal of interest in the study of various oxide surfaces to understand the role that defect sites play in their properties.[1] Small clusters of these oxide materials provide useful models to understand the physics and chemistry of the surfaces. The smaller sizes of the clusters make it possible to obtain detailed electronic, geometric, and bonding information, that can also be used to benchmark theoretical calculations.

The reaction of metal atoms with oxygen is also of major importance because of the use of oxides as catalysts and substrate materials.[1] Most commercial catalysts consist of microscopic metal particles supported on oxide surfaces such as Al_2O_3. Clusters of these materials have, consequently, been studied both theoretically and experimentally to better understand the structure and bonding between aluminum and oxygen. The experimental technique that has been used to study the neutral clusters has been mainly low-temperature matrix isolation,[2–18] while other methods have been used to study the positive cluster ions.[19–23] However, the previous matrix isolation experiments have often led to conflicting and contradictory assignments due to the lack of direct information about the identity of the molecular species present for the $Al+O_2$ system.

The goal of this paper is to present a systematic study of small aluminum oxide clusters containing one and two aluminum atoms (AlO_y^-, y=1,2; $Al_2O_y^-$, y=2–5) using size-selected anion photoelectron spectroscopy (PES). PES is a powerful method to study atoms, molecules, and clusters, providing both vibrational and electronic information.[24–36] We focus on aluminum oxide clusters with a fixed number of metal atoms and varying oxygen compositions. These species represent an increasing degree of oxidation of the metal atoms and clusters and provide systematic structural and bonding information. Furthermore, theoretical *ab initio* calculations have been performed to obtain detailed structural and bonding information. We show that the PES technique

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provides a clear advantage over the matrix isolation technique because it allows the unambiguous identification and assignment of cluster identities.

The simplest aluminum oxide molecule, AlO, has been extensively studied in low-temperature matrices,[5,10–13,18] in the gas phase,[37–47] as well as by theory.[48–50] There has also been a theoretical study of the AlO^- anion.[51] We have previously reported the PES spectra of AlO^-, at lower photon energies (3.49 eV and 4.66 eV), that only allowed the ground ($X\ ^2\Sigma^+$), and the first excited states ($A\ ^2\Pi$) of the neutral molecule to be observed.[52] AlO_2 has also been studied using the matrix isolation technique,[9–11,13,14,16,18] and has been the subject of several theoretical investigations.[53,54] There has been only one gas-phase study of this molecule by us.[52] *Ab initio* calculations have suggested that there are two, almost isoenergetic, isomers for AlO_2: a symmetric linear OAlO molecule, and a cyclic species.[54] The linear arrangement is known to be the global minimum. A theoretical study of the AlO_2^- anion suggested that it too has a $D_{\infty h}$ linear structure.[55] We have concluded previously that both AlO_2 and AlO_2^- are linear, based on our PES study.[52]

For the Al_2O_y clusters, both Al_2O and Al_2O_2 were observed by mass spectrometry in the vapor above Al_2O_3.[56] More recent studies have also used mass spectrometry to characterize aluminum oxide clusters.[57] Various matrix isolation experiments, on species formed by the reaction of aluminum with oxygen molecules, have been performed, and species of Al_2O_y have been proposed to be responsible for certain spectral lines.[6,7,10,11,13,18] In some cases, the data have led to difficulty and errors in the assignment of infrared frequencies to the correct clusters.[6,7,10,11,13,18] Numerous theoretical investigations of Al_2O_y clusters have been performed and they have suggested that both Al_2O and Al_2O_3 have symmetric linear arrangements with $D_{\infty h}$ symmetry.[58] The Al_2O_2 molecule is believed to be a rhombus structure with a D_{2h} symmetry[58–63] and Al_2O_4 is proposed to be a complex of two twisted AlO_2 molecules with a C_{2v} symmetry.[58,64] No previous calculations have been performed for Al_2O_5.

In this paper, we report the first photodetachment PES experiments on AlO_y^- ($y=1,2$) at a photon energy of 6.42 eV, and $Al_2O_y^-$ ($y=2-5$) at several photon energies. The spectra of AlO^- and AlO_2^- both show previously unobserved excited states at high binding energies (BEs), in addition to the ground electronic states of the neutral molecules. The spectra of $Al_2O_2^-$ show two sharp and vibrationally resolved bands at relatively low BEs and a broad feature at higher BE. The spectra of the higher $Al_2O_y^-$ clusters all show a broad and vibrationally resolved ground state feature at relatively high BE. The broad nature of the ground electronic states of Al_2O_3, Al_2O_4, and Al_2O_5 suggests a geometry change from the anion to the neutral. The spectra of $Al_2O_3^-$, $Al_2O_4^-$, and $Al_2O_5^-$ are very similar. Furthermore, a significant increase in the electron affinity (EA) is observed when progressing from Al_2O_2 to Al_2O_3, and from AlO to AlO_2.

The paper is organized as follows. In the next section, the experimental apparatus and procedure are briefly described, followed by a brief description of the theoretical method in Sec. III. The PES spectra and major observations are presented in Sec. IV. The results and the structure and bonding of these clusters are discussed in Sec. V, based on the experimental observations and on comparisons with theoretical calculations. Finally, a summary is provided in Sec. VI.

II. EXPERIMENT

The details of the experimental apparatus have been published elsewhere and will only be given briefly.[34] The apparatus is composed of a laser vaporization source, a modified Wiley–McLaren time-of-flight (TOF) mass spectrometer[65] and an improved magnetic-bottle TOF electron analyzer.[24,66] A pulsed laser beam (532 nm 10–20 mJ, 10 Hz) is focused down to a 1 mm diameter spot onto a pure aluminum target, producing a plasma containing aluminum atoms in both charged and neutral states. A helium carrier gas, seeded with 0.5% O_2 and delivered by two pulsed molecular beam valves, is mixed with the plasma. The reactions between the plasma and the oxygen produce a distribution of clusters of the form, $Al_xO_y^-$. The helium carrier gas and the clusters undergo a supersonic expansion and form a cold molecular beam which is collimated by a skimmer. The negative clusters are extracted at 90° to the molecular beam axis and are subjected to a TOF mass analysis. The desired cluster is then mass selected and subsequently decelerated before undergoing photodetachment by a pulsed laser beam. The harmonics of a Q-switched Nd:YAG laser [532 (2.33 eV), 355 (3.49 eV), and 266 (4.66 eV) nm] and the output of an ArF excimer laser (193 nm, 6.42 eV) are used for photodetachment. Typically, a pulse energy of 0.5–5 mJ is used. Higher pulse energies are used at 532 and 355 nm while lower pulse energies are used at 266 and 193 nm to reduce low energy electron noise coming from surfaces due to scattered photons.

The spectra are taken at 10 Hz for the 532 and 355 nm detachment wavelengths. For the higher photon energies, spectra are taken at 20 Hz with the vaporization laser off at every alternating shot for background subtraction. However, significant noise is still present for the 193 nm spectra at lower BEs due to the high noise levels present at this photon energy. The electron kinetic energy distributions are calibrated with the known spectrum of Cu^- and smoothed with a 5 meV or 10 meV window function. The presented electron binding energy spectra are obtained by subtracting the kinetic energy spectrum from the photon energy. The energy resolution of our apparatus is better than 30 meV at 1 eV electron energy. Due to the dependence of resolution on electron energies for TOF type electron analyzers, various photon energies are used in the current experiments. The lower photon energies yield better resolved spectra, while the high photon energies allow more excited states of the neutral clusters to be observed.

A continuous composition of oxide clusters can usually be produced by tuning source conditions and O_2 concentrations. However, the PES spectra that are presented here, for the $Al_2O_y^-$ series, start with $Al_2O_2^-$ because Al_2O^- was not observed in our mass spectra, despite numerous attempts to

TABLE I. Selected, scaled symmetric vibrational frequencies of Al_2O_y clusters at the HF/6-31$G(d)$ and MP2/6-31$G(d)$ levels.

Species	Symmetry	HF[a]	MP2[b]	Expt
Al_2O_3	C_{2v} (Rhombus)	888 cm^{-1}	804 cm^{-1}	850 (80) cm^{-1}
	$D_{\infty h}$	904 cm^{-1}	868 cm^{-1}	
	C_{2v} (Planar)	1097 cm^{-1}	1073 cm^{-1}	
Al_2O_4	D_{2h}	932 cm^{-1}	---------	930 (60) cm^{-1}
	C_{2v} (1)	968 cm^{-1}	914 cm^{-1}	
	C_{2v} (2)	1019 cm^{-1}	964 cm^{-1}	
Al_2O_5	C_{2v}	1023 cm^{-1}	964 cm^{-1}	900 (60) cm^{-1}

[a]HF frequencies have been scaled by 0.89 (Ref. 69).
[b]MP2 frequencies have been scaled by 0.94 (Ref. 69).

produce it at various source conditions. It is expected that Al_2O and Al_2O^- might be too reactive to be present with any appreciable concentrations under our source conditions.

III. COMPUTATIONAL METHODS

Using the Gaussian 94 systems of programs,[67] preliminary calculations on low-lying neutral singlets of Al_2O_3, Al_2O_4, and Al_2O_5 have been performed. Geometric structures, energies, and harmonic frequencies have been obtained at the Hartree–Fock (HF) and second-order perturbation (MP2) levels of theory, using the 6-31$G(d)$ basis set. The MP2 calculations employed the frozen core convention. The results are presented in Table I, while a more detailed analysis will be published elsewhere.[68] HF frequencies have been scaled by 0.89 and MP2 frequencies by 0.94.[69]

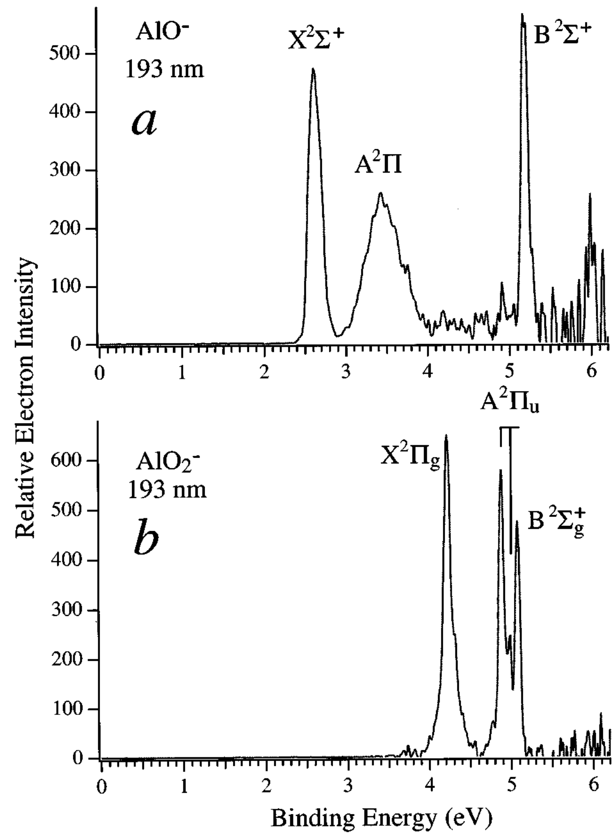

FIG. 1. (a) Photoelectron spectrum of AlO^- at 6.42 eV (193 nm) photon energy and (b) Photoelectron spectrum of AlO_2^- at 6.42 eV.

IV. RESULTS

Figure 1 shows the PES spectra of AlO^- and AlO_2^- at a photon energy of 6.42 eV. For AlO^- a sharp peak is observed at 2.60 eV ($X\ ^2\Sigma^+$) and a broad feature ($A\ ^2\Pi$) at higher binding energy is also observed. The spectrum also shows a sharp peak ($B\ ^2\Sigma^+$) at 5.19 eV. Significant noise is present at the high BE side and the feature near 6 eV is really due to imperfect background subtraction. The spectrum of AlO_2^- shows a sharp peak ($X\ ^2\Pi g$) at 4.23 eV and two additional features at 4.88 eV ($A\ ^2\Pi_u$) and 5.08 eV ($B\ ^2\Sigma_g^+$). The feature at 4.88 eV also appears to contain vibrational structure.

Figure 2 displays the spectra of $Al_2O_2^-$ taken at photon energies of 2.33 eV and 3.49 eV. In Fig. 2(a), a sharp peak ($X\ ^1A_g$) is observed followed by peaks at higher binding energies, which are members of a vibrational progression. The spectrum at 3.49 eV shows a second band ($A\ ^3B_{3u}$) at higher binding energy, which is nearly identical to the $X\ ^1A_g$ band, with a slightly higher relative intensity.

Figure 3 shows the spectra of $Al_2O_y^-$ (y=2–5) clusters at both 4.66 and 6.42 eV photon energies. The noise problem at high photon energies, mentioned above, can be clearly seen for the 6.42 eV spectra, on the high BE side. The spectrum for the $Al_2O_2^-$ molecule at the higher photon energies reproduces the two features ($X\ ^1A_g$ and $A\ ^3B_{3u}$) observed at the lower photon energies. Additionally, a third broad feature ($B\ ^3B_{3g}$) at high BE (5.1 eV) is also revealed at the 6.42 eV photon energy. For $Al_2O_3^-$, the 4.66 eV spectrum shows a weak, broad band (X) at lower BE and a sharp peak (A) at a BE of 4.32 eV. At 6.42 eV photon energy, the intensity of the low BE broad feature is considerably enhanced and the vibrational progression is much better defined. This feature represents the ground electronic state of the neutral Al_2O_3 and is characterized by a strong wavelength dependent photodetachment cross section. A third feature (B) may also be present at higher BE, but the severe noise problem makes its identification rather difficult. The spectra for $Al_2O_4^-$ and $Al_2O_5^-$ also exhibit a vibrationally resolved ground state (X) and an excited state at high BE (5.1 eV). The similarity among the spectra of $Al_2O_3^-$, $Al_2O_4^-$, and $Al_2O_5^-$ suggests that they may have very similar electronic and geometric structures, most likely based on the rhombus configuration, as will be discussed in the next section.

The obtained energies and spectroscopic constants are summarized in Table II.

V. DISCUSSION

The aluminum atom has a $3s^23p^1$ valence configuration while the oxygen atom has a valence configuration of $2s^22p^4$. The three valence electrons mean that aluminum has an optimum oxidation state of +3, which is well known and found in all Al compounds including Al_2O_3. When forming bonds with the oxygen atom, the aluminum atom tends to donate its valence electrons to the oxygen atom to form a σ

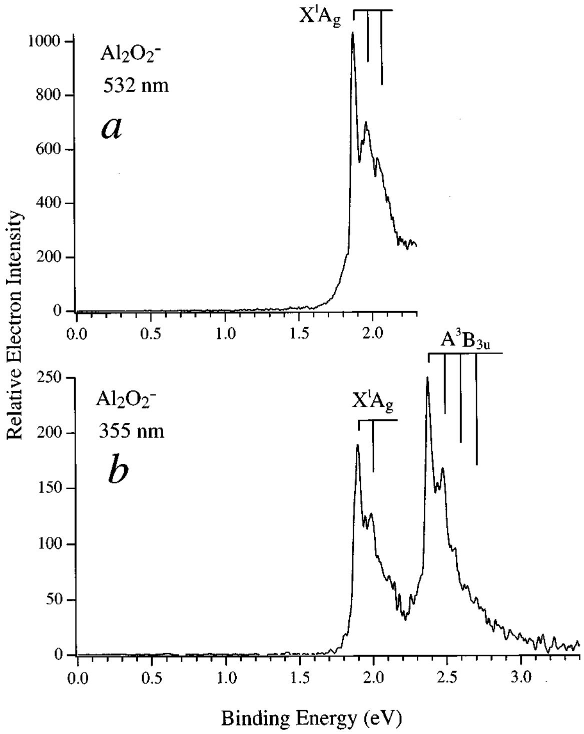

FIG. 2. (a) Photoelectron spectrum of $Al_2O_2^-$ at 2.33 eV (532 nm) photon energy. (b) Photoelectron spectrum of $Al_2O_2^-$ at 3.49 eV (355 nm) photon energy. Vibrational structure is indicated by vertical lines.

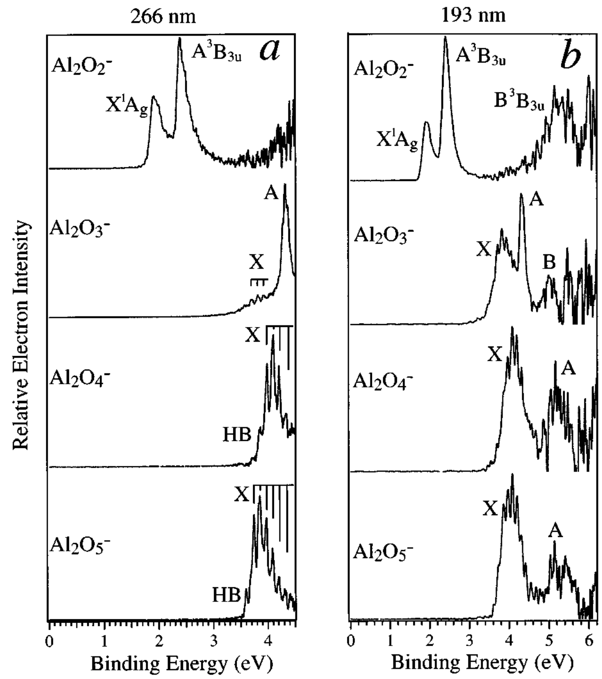

FIG. 3. (a) Photoelectron spectra of $Al_2O_y^-$ (y=2–5) clusters at 4.66 eV (266 nm). (b) Photoelectron spectra of $Al_2O_y^-$ (y=2–5) clusters at 6.42 eV (193 nm). Peaks labeled ''HB'' refer to hot bands.

bond and two π bonds and the Al–O chemical bonding is dominated by ionic character. In the case of the diatomic AlO, which has a valence electronic configuration of $2\sigma^2 1\pi^4 3\sigma^1$, a single electron occupies a σ-type molecular orbital which is mainly of Al 3s character.[50] Since the O atom is of valence II (-2), this electron may be viewed as an excess electron. In AlO_2, however, there is an electron deficiency since four electrons are required to saturate the valence of the two O atoms. Thus, AlO_2^- is expected to be very stable and the AlO_2 molecule is expected to have a high EA. For the Al_2O_y clusters, a similar bonding character may be

TABLE II. Observed spectroscopic values for Al_xO_y clusters.

Species	Electronic states	BE (eV)[a]	EA (eV)	Term value (eV)[c]	Vib. freq. (cm^{-1})[d]
AlO	$X\ ^2\Sigma^+$	2.60(2)	2.60[b](2)	0	
	$A\ ^2\Pi$	3.26(2)		0.66(2)	
	$B\ ^2\Sigma^+$	5.19(4)		2.59(3)	
AlO_2	$X\ ^2\Pi_g$	4.23(2)	4.23[b](2)	0	
	$A\ ^2\Pi_u$	4.88(4)		0.65(3)	810(60)
	$B\ ^2\Sigma^+$	5.08(4)		0.85(3)	
Al_2O_2	$X\ ^1A_g$	1.88(3)	1.88(3)	0	660(80)
	$A\ ^3B_{3u}$	2.37(3)		0.49(2)	730(80)
	$B\ ^2B_{2g}$	5.1(1)		3.22(8)	
Al_2O_3	X	3.71(3)	3.71(3)	0	850(80)
	A	4.32(4)		0.61(2)	
	B	4.9(1)		1.19(8)	
$Al_2O_4^-$		0			1090(60)
Al_2O_4	X	3.98(3)	3.98(3)	0	930(60)
	A	5.1(1)		1.12(8)	
$Al_2O_5^-$		0			1170(60)
Al_2O_5	X	3.75(3)	3.75(3)	0	90(60)
	A	5.1(1)		1.35(8)	

[a]Adiabatic binding energy.
[b]Value obtained from previous study at lower photon energy (Ref. 52).
[c]The uncertainty for this value is less because it is a difference of the two BE values.
[d]Vibrational frequency for the totally symmetric mode.

expected. For Al_2O_2, there is an excess of valence electrons, and therefore, a low EA and low-lying exited states are expected. In Al_2O_3, which is of the same stoichiometry as in the bulk oxide, the valences of both the Al and O atoms are saturated. This is expected to result in a closed shell molecule with a significant gap between its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). This gap is directly accessible from the anion PES spectrum. The higher Al_2O_y clusters have excess O atoms and are electron deficient. They are expected to have high EAs. The experimental observations from the PES spectra are consistent with this general view. In the following, each cluster is discussed in detail.

A. AlO^-

The photoelectron spectrum of AlO^- at 6.42 eV detachment energy is shown in Fig. 1(a). The X and A bands have been observed before at lower photon energies, which yielded much better resolved spectra.[52] We will emphasize the new feature observed at high BE ($B\ ^2\Sigma^+$). As mentioned above, the valence configuration for AlO can be written as $2\sigma^2 1\pi^4 3\sigma^1$. In the anion, the extra electron enters the 3σ orbital, giving a closed-shell ground state with a configuration of $2\sigma^2 1\pi^4 3\sigma^2 (X\ ^1\Sigma^+)$. The first feature, at 2.60 eV, corresponds to the removal of an electron from the 3σ orbital, yielding the $X\ ^2\Sigma^+$ ground state of the neutral AlO. The second feature, at 3.26 eV, corresponds to the removal of a 1π electron to give the $A\ ^2\Pi$ excited state of AlO.

The third feature at 5.19 eV then must be due to the removal of a 2σ electron to give the $B\ ^2\Sigma^+$ excited state of AlO. The excitation energy of this state relative to the ground state is 2.59 eV, which is in excellent agreement with the available literature value[38] for this excited state. Therefore, the spectrum shown in Fig. 1(a) reveals the full valence MOs of the AlO molecule. However, it is surprising that little vibrational excitation is observed for the $B\ ^2\Sigma^+$ state, suggesting that the 2σ orbital is rather nonbonding. This is contrary to the expectation of simple MO arguments, that the 2σ orbital should be a strongly bonding MO representing the Al–O σ bond.

B. AlO_2^-

Matrix isolation experiments suggested the existence of two isomers for this molecule; one is a symmetric linear molecule and the other is a complex of an aluminum atom with an oxygen molecule.[13] Calculations have found that the two isomers are almost isoenergetic with the linear molecule being the global minimum.[54] Our previous work with the vibrationally resolved ground state (X), at a photon energy of 4.66 eV, has established that the AlO_2^- anion produced in our laser vaporization source was the symmetric linear one without any indication of a second isomer.[52] The very high EA of AlO_2^- compared to AlO was already revealed. Figure 1(b) shows two more new features, which should be due to the excited states of the linear OAlO molecule.

The valence electronic configuration of AlO_2 can be written as $4\sigma_g{}^2 1\pi_u{}^4 2\pi_g{}^3$ and that of the anion as $4\sigma_g{}^2 1\pi_u{}^4 2\pi_g{}^4$.[70] Therefore, the first feature, at 4.23 eV, is attributed to the removal of a $2\pi_g$ electron resulting in the $^2\Pi_g$ ground state of AlO_2. The peak at 4.88 eV is attributed to the removal of a $1\pi_u$ electron to give the $A\ ^2\Pi_u$ excited state of AlO_2. It has an excitation energy of 0.65 eV relative to the ground state. A vibrational frequency of 810 (60) cm^{-1} is obtained for the $A\ ^2\Pi_u$ state. The third peak ($B\ ^2\Sigma_g^+$) at 5.08 eV is due to the removal of a $4\sigma_g$ electron. This state has an excitation energy of 0.85 eV relative to the ground state. Both the $A\ ^2\Pi_u$ and $B\ ^2\Sigma_g^+$ excited states of AlO_2 have never been experimentally observed before.

C. $Al_2O_2^-$

Figures 2, 3(a), and 3(b) show photoelectron spectra for $Al_2O_2^-$ at 532 and 355, 266, and 193 nm, respectively. All the high photon energy spectra are consistent with those obtained at lower photon energies. The spectrum at 532 nm shows a sharp peak at 1.88 eV followed by a vibrational progression with a frequency of 660 (80) cm^{-1}. The spectrum at 355 nm reveals a second band at 2.37 eV, which also contains a vibrational progression. The second band has a similar Franck–Condon envelope as the first band, with a similar vibrational frequency [730 (80) cm^{-1}]. The spectrum at 266 nm does not show any new features, while a new feature is observed at 193 nm and at a much higher BE of about 5.1 eV. The first peak corresponds to the ground state of the neutral molecule, whose EA is measured to be 1.88 eV. The second peak is due to the first excited state of Al_2O_2 with an excitation energy of 0.49 eV relative to the ground state. The third band, well separated from the first two bands and only observed at 193 nm, belongs to the second excited state of the molecule.

Several matrix isolation experiments have been performed on Al_2O_2.[6,7,10,11,13,18] However, there have been noticeable disagreements in the assignment of the observed infrared bands to the most energetically favored structure, which is a cyclic D_{2h} molecule, as determined by several theoretical calculations.[58–63] Figure 4(a) shows a schematic of this structure. Although there have been some experimental studies that have either discounted the existence of the D_{2h} isomer in the matrix[18] or have proposed alternative structures for Al_2O_2,[10] several theoretical calculations have shown quite convincingly that the D_{2h} structure corresponds to the global minimum on the total potential energy surface.[58–63]

Semiempirical and *ab initio* calculations performed on Al_2O_2 suggested that there were two stable isomers, one was a square cyclic structure (D_{2h}) with an AlO optimized bond length of 1.7 Å and the other was a linear configuration which was less stable than the cyclic structure by 0.65 eV.[59] Later calculations using SCF and MP2 methods determined that there are two minima, one almost square and the other a rhombus, both with a D_{2h} symmetry and a ^1A_g ground state.[58,60,61,63] More recent calculations have shown that the singlet D_{2h} (rhombus) structure is the global minimum and that the previous spectroscopic identification of two rhombic isomers of Al_2O_2 should be attributed to the ^1A_g ground state

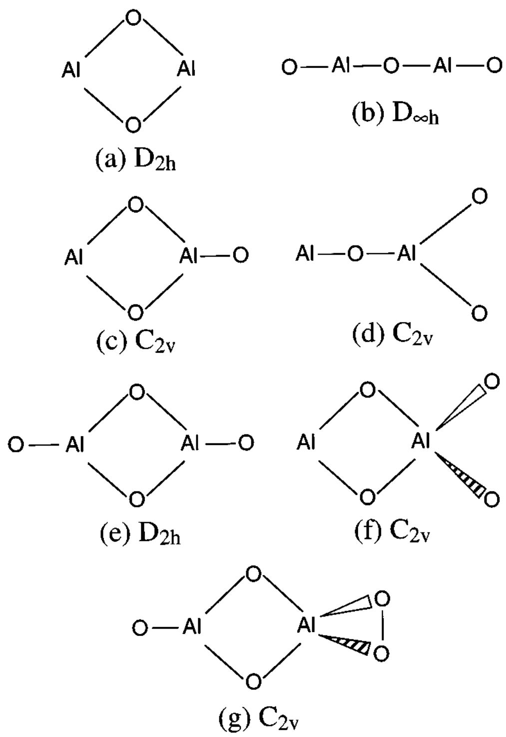

FIG. 4. Possible structures of the Al_2O_y clusters, based on experimental observations and preliminary calculations at the Hartree–Fock and MP2 levels. The rhombus-type structures are suggested to be the ones observed in the current experiments.

and a ^3B_u excited state of the same D_{2h} Al_2O_2 molecule.[62] With this structure, it is expected that each aluminum atom in Al_2O_2 would have an unpaired electron, giving rise to a biradical configuration. However, calculations have suggested that the two electrons pair up into a σ-type orbital with a closed-shell ground state configuration that can be written as, $1a_g^2 1b_{2u}^2 2a_g^2 1b_{3u}^2 1b_{1g}^2 1b_{1u}^2 2b_{2u}^2 1b_{3g}^2 3a_g^2 (^1A_g)$, where the HOMO $(3a_g)$ is a σ-type orbital.[58] The $Al_2O_2^-$ anion, then, has an electron configuration of...$1b_{3g}^2 3a_g^2 2b_{3u}^1$, where the $2b_{3u}$ orbital is the LUMO of the neutral molecule.

Therefore, the first peak in the PES spectra [Figs. 2(a), 2(b), 3(a), and 3(b)] corresponds to the removal of the $2b_{3u}$ electron to give the $X\ ^1A_g$ ground state of Al_2O_2. The second peak corresponds to the removal of an electron from the $3a_g$ orbital to leave the Al_2O_2 molecule in the $A\ ^3B_{3u}$ excited state with a configuration of...$1b_{3g}{}^2 3a_g{}^1 2b_{3u}{}^1$. The obtained singlet–triplet excitation energy of 0.49 eV is in good agreement with the value obtained by a previous calculation[62] for the D_{2h} Al_2O_2. There are two totally symmetric A_g vibrational modes for the D_{2h} Al_2O_2, one with a lower frequency (553 cm^{-1}) and another with a higher frequency (861 cm^{-1}).[58] The obtained vibrational frequencies for the ground state of Al_2O_2 [660 (80) cm^{-1}] and the first excited state [730 (80) cm^{-1}] are not in agreement with either of the totally symmetric A_g vibrational modes. From the PES spectra of $Al_2O_2^-$, there is evidence that both modes are active. Therefore, we believe that the apparent vibrational frequencies [660 (80) cm^{-1} and 730 (80) cm^{-1}] are an average of the combination of the two A_g vibrational modes, which cannot be resolved in the current experiment. The slightly lower apparent frequency, for the ground state [660 (80) cm^{-1}], compared to that of the first excited state, is a result of the prominence of the low frequency mode in the ground state. In the first excited state, the higher frequency mode dominates, resulting in a slightly higher apparent frequency. The third band at approximately 5.1 eV, which is the $^3B_{3u}$ excited state, is a result of the removal of an electron from the $1b_{3g}$ orbital, which is probably of oxygen $2p$ character.

The second band in the spectrum was attributed to the removal of a spin-down $3a_g$ electron, giving rise to the triplet $^3B_{3u}$ excited state. A singlet $^1B_{3u}$ excited state is also expected by removing a spin-up $3a_g$ electron. This state is expected to be similar to the triplet state with similar vibrational features. However, it is not clearly observed in our spectrum. This could be due to two factors: (1) The excited singlet state is at very high binding energy and is, therefore, beyond the energy range of the experiment; or (2) This state is very close to the excited triplet state in energy such that they overlap and cannot be resolved in the current experiment. From the higher intensity of the $A\ ^3B_{3u}$ band, we suggest that the latter is the case. More accurate calculations will be required to confirm this conclusion. No previous calculations have been done on such an excited singlet state for a D_{2h} Al_2O_2.

Interestingly, a recent photodetachment study of cyclooctatetraene showed the existence of an excited triplet state ($^3A_{2u}$), due to the formation of a diradical, and a ground singlet state ($^1A_{1g}$), where the electrons are paired up in the HOMO.[71] The appearance of the ground state as a singlet was suggested to be in apparent violation of Hund's rule, which predicts that degenerate, nonbonding molecular orbitals with two electrons should have a triplet ground state. The electronic structure of Al_2O_2 seems to be similar to this more complicated organic molecule.

D. Al_2O_3

Figures 3(a) and 3(b) show the PES spectra of $Al_2O_3^-$ at 266 nm and 193 nm, respectively. At 266 nm, a broad band is observed at lower BE and a sharper peak is observed at 4.32 eV. The broad band corresponds to the ground state of Al_2O_3 and is observed much more clearly in the 193 nm spectrum. This implies that the wavelength dependence on the photodetachment cross section of the ground state is quite significant (see below). The first band (X) yields an electron affinity of 3.71 eV and a vibrational frequency of 850 (80) cm^{-1} for Al_2O_3. The second peak (A), at 4.32 eV, belongs to the first excited state of the molecule, with an excitation energy of 0.61 eV relative to the ground state. A third peak, at a high BE of approximately 4.9 eV, may be present but background noise prevents us from definitively identifying it.

Matrix isolation experiments[13,18] have attempted to identify Al_2O_3 by comparing the observed IR and Raman bands with the values obtained by calculations.[58,72] These matrix experiments suggested that an unsymmetrical, C_1, isomer and the symmetric linear OAlOAlO, $D_{\infty h}$, molecule were observed.[13] Although the previous calculations indicated a planar C_{2v} structure to be very close in energy to the linear structure, they found that the lowest energy structure on the singlet potential surface is the linear, $D_{\infty h}$ species.[58,72] However, our calculations have also found the C_{2v} (rhombus) structure to be a true minimum. These are shown schematically in Fig. 4.

In Fig. 3(b) the broad vibrational progression in the ground state of Al_2O_3 implies that there is a significant change in the geometry between the anion and the neutral. Also, this progression is very similar to that of $Al_2O_4^-$ and $Al_2O_5^-$ (see below). It is expected that, for the C_{2v} [rhombus, Fig. 4(c)] structure, the extra electron in the anion would be located on the terminal aluminum atom that is attached to three oxygen atoms. Therefore, the broad vibrational progression in the ground state is consistent with the removal of an electron from a bonding orbital, presumably Al sp in character. The enhancement in the intensity of the ground state of Al_2O_3, at 6.42 eV photon energy, indicates that it results from the removal of an Al π-type electron. This reasoning is based on the observation that for high angular momentum initial states, photoemission cross sections generally increase as the photon energy increases.[73] Such cross section dependence on photon energies has been observed in photodetachment experiments of the $4s$ and $3d$ electrons of Cu^- anion[74] and transition metal clusters.[75] The sharp peak at higher BE (4.32 eV) is consistent with the removal of an electron from a nonbonding orbital. This state is probably a result of the removal of an electron from the aluminum atom that is bonded to only two oxygen atoms. The nature of the first excited state in Al_2O_3 is probably similar to that of the ground and excited states of Al_2O_2, both of which are also results of the removal of nonbonding electrons on Al atoms bonded to two O atoms. The third peak at about 4.9 eV belongs to the second excited state of Al_2O_3 and is presumably from a bonding orbital of oxygen $2p$ character.

Our calculations, at both the HF and MP2 levels, found a true minimum for the rhombus (C_{2v}) species depicted in Fig. 4(c). We obtain a scaled, totally symmetric vibrational frequency of 888 cm^{-1} at the HF level of theory, and a scaled frequency of 804 cm^{-1} at the MP2 level, in excellent agreement with the experimentally observed value. Furthermore, the similarity among the PES spectra of $Al_2O_3^-$, $Al_2O_4^-$ (see below) and $Al_2O_5^-$ (see below) and the vibrational frequencies of the ground states lends support to the assignment of a rhombus [C_{2v}, Fig. 4(c)] structure to the species observed in our experiment.

Other isomers with higher energies were also considered in our calculations at the HF and MP2 levels. A minimum was found for another planar C_{2v} species (Fig. 4d), which can be described as an Al-O-Al unit with two oxygen atoms added to one aluminum. Also, the linear molecule (Fig. 4b) was found to be a true minimum at both the HF and MP2 levels. It is expected that the electron affinities of the linear and C_{2v} molecules would be significantly different and calculations to determine this value may help provide another piece of information to differentiate among these isomers.

E. $Al_2O_4^-$

Figures 3(a) and 3(b) show the PES spectra of $Al_2O_4^-$ at 266 and 193 nm, respectively. Both the 266 and 193 nm spectra show a broad, vibrationally resolved band at lower BE. Two well resolved hot band features are observed in the 266 nm spectrum yielding a vibrational frequency of 1090 (60) cm^{-1} for the anion (Table II). The spectrum at 193 nm reveals an additional band at higher BE which is broad and not well defined. The first band corresponds to the ground state (X) of the neutral molecule with an EA of 3.98 eV. The second band corresponds to the first excited state (A) of the neutral molecule and occurs at about 5.1 eV.

The presence of Al_2O_4 was suggested in previous matrix isolation experiments.[13] Previous calculations indicated that the molecule is a complex of two AlO_2 molecules which are twisted with respect to each other to give a C_{2v} symmetry.[64] However, our preliminary calculations for this molecule indicate that the symmetric D_{2h} Al_2O_4 is also a true minimum. This structure is shown schematically in Fig. 4(e), along with the C_{2v} structure [Fig. 4(f)].

The ground state of the neutral molecule is characterized by a vibrational progression with a frequency of 930 (60) cm^{-1} and an electron affinity of 3.98 eV. Upon formation of the anion, it is expected that, for the D_{2h} molecule, the extra electron will be localized on an aluminum atom because the Al atoms are expected to possess significant positive charges as a result of strong electron transfer between aluminum and oxygen. Therefore, we suspect that the ground state vibrational progression is a result of removing an electron from a bonding orbital localized on the aluminum atoms.

The second peak at approximately 5.1 eV corresponds to the first excited state of Al_2O_4. This state is probably due to the removal of a more tightly bound O $2p$ electron from the bridging oxygen atoms. Although previous calculations have suggested the C_{2v} ''twisted pair'' structure, it seems to make more chemical sense for the two nonbridging oxygen atoms to bind to each of the aluminum atoms to form the D_{2h} species. In the C_{2v} ''twisted pair'' structure, one set of bonds between the bridging oxygens and the tetrahedrally bonded aluminum atom are very long and are, therefore, expected to be relatively weak.

In our preliminary calculations, a true minimum was obtained at both the HF and the MP2 levels for the symmetric D_{2h} species. The highest A_g vibrational frequency calculated for this molecule is 932 cm^{-1} at the (scaled) HF level, which is in excellent agreement with the experimentally obtained value. However, at the MP2 level, the Al–O bonds are considerably lengthened. Based on the agreement of the vibrational frequency (HF) and the similarity of the electronic and vibrational structure among Al_2O_3, Al_2O_4, and Al_2O_5 (see below), we suggest the D_{2h} species [Fig. 4(e)] as a candidate for Al_2O_4. It is expected that Al_2O_4 would be made by taking a C_{2v} [Fig. 4(c)] Al_2O_3 molecule and adding an oxygen atom to the aluminum atom that is attached only to the two bridging oxygen atoms. This would create the symmetric D_{2h} Al_2O_4 molecule. A similar structure was proposed for the $Al_2O_4^+$ cation, in an experiment to study the stabilities and reactivities of aluminum oxide clusters.[23]

Other isomers that were considered in our calculations include the C_{2v} ''twisted pair'' minimum [Fig. 4(f)], with scaled frequencies of 968 and 914 cm^{-1} at the HF and MP2 levels, respectively. Another C_{2v} minimum, but with longer Al–O bonds and at a higher energy, was found with scaled frequencies of 1019 and 964 cm^{-1} at the HF and MP2 levels, respectively. It is important to note that assignment of the D_{2h} form to the experimentally observed species is tentative, since the calculated energy ordering of the D_{2h} and ''twisted pair'' C_{2v} structures changes with the inclusion of electron correlation. Calculations at higher levels of theory, and also of electron affinities, will provide more definitive identification of the observed isomer.

F. $Al_2O_5^-$

There have been no previous theoretical or experimental studies of Al_2O_5. Figures 3(a) and 3(b) show the PES spectra of $Al_2O_5^-$ at 266 and 193 nm, respectively. The spectra display a broad, vibrationally resolved band at lower BE and a broad, unresolved band at higher BE, at 193 nm. A well resolved hot band is observed at 266 nm yielding a vibrational frequency of 1170 (60) cm^{-1} for the anion. The first band corresponds to the ground state of Al_2O_5 with an EA of 3.75 eV and with a vibrational frequency of 900 (60) cm^{-1}. The relative intensities of the vibrational progression appear to be different at the two detachment wavelengths: the vibrational features at ~4 eV and above are enhanced in the 193 nm spectrum. This is likely due to imperfect background subtractions or autodetachment transitions at 193 nm. The high BE feature, at approximately 5.1 eV, corresponds to the first excited state of Al_2O_5. The ground state is a result of the removal of an electron from the LUMO, which is likely to be of Al sp character and is expected to be bonding in nature. The similarity among the ground and the excited states in Al_2O_5, Al_2O_4, and Al_2O_3 suggests that the three molecules have similar structures and the corresponding ground and excited states have similar origins. As is seen in our previous studies,[35,36] when the total valency of the oxygen atoms exceeds that of the metal atoms in the M_xO_y oxide clusters, the molecule becomes electron deficient and begins to form O–O bonds. In other words, an O_2 unit tends to replace an oxygen atom in these types of clusters. It is expected that Al_2O_5 would be made by replacing a terminal O atom in a D_{2h} Al_2O_4 with an O_2 unit [as seen in Fig. 4(g)]. The decrease in the EA between Al_2O_4 and Al_2O_5 is similar to our previous observations involving Cu_2O_y clusters.[36] In our calculations, the only minimum found thus far for Al_2O_5 is a twisted C_{2v} structure with one aluminum tetrahedrally bonded and the other aluminum atom bound to three oxygens. This structure is exactly the same as that proposed above, and is based on the similarity among the spectra of $Al_2O_3^-$, $Al_2O_4^-$, and $Al_2O_5^-$. The totally symmetric scaled vibrational frequencies calculated are 1023 and 964 cm^{-1}, at the HF and MP2 levels, respectively. The correct prediction of the Al_2O_5 structure and the similarity among the PES spectra of $Al_2O_3^-$, $Al_2O_4^-$, and $Al_2O_5^-$ lends strong credence to the rhombus-type structures proposed for these clusters.

VI. CONCLUSIONS

The photoelectron spectra of small aluminum oxide clusters involving one and two aluminum atoms are reported at several photon energies. The spectra for AlO^- and AlO_2^- at 193 nm showed additional excited states which were not previously observed at lower photon energies. We obtained vibrationally resolved spectra for the ground states for all the $Al_2O_y^-$ species ($y=2$–5). Additionally, high BE features are observed at 193 nm due to the removal of electrons from oxygen $2p$-type orbitals. The electron affinities and vibrational frequencies of these clusters are obtained and are compared with existing theoretical calculations and those that are in progress for this work. Probable structures are proposed for all the clusters consistent with the experimental observations and the various theoretical studies, which have shown these Al_xO_y species to be predominantly ionic with significant configuration mixing and strong correlation effects. Structural and bonding information are obtained from the current experiments, which can be compared with more accurate calculations. The Al_2O_2 rhombus is a major structural feature in bulk aluminum oxide materials, formed between two AlO_4 units sharing two O atoms. We show evidence that this bulk structural feature exists in the Al_2O_x series of clusters.

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