Gallium Oxide and Dioxide: Investigation of the Ground and Low-Lying Electronic States via Anion Photoelectron Spectroscopy

Giovanni Meloni  
*University of San Francisco, gmeloni@usfca.edu*

S M. Sheehan

D M. Neumark

Follow this and additional works at: [http://repository.usfca.edu/chem_fac](http://repository.usfca.edu/chem_fac)

Part of the [Chemistry Commons](http://repository.usfca.edu/chem_fac)

Recommended Citation

Gallium oxide and dioxide: Investigation of the ground and low-lying electronic states via anion photoelectron spectroscopy

Giovanni Meloni, Sean M. Sheehan, and Daniel M. Neumark

Department of Chemistry, University of California, Berkeley, California 94720 and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

(Received 4 November 2004; accepted 30 November 2004; published online 9 February 2005)

The GaO and GaO\(_2\) molecules were investigated using negative ion photoelectron spectroscopy. All the photoelectron spectra showed vibrationally resolved progressions. With the aid of electronic structure calculations and Franck–Condon spectral simulations, different molecular parameters and energetics of GaO\(^+\)/GaO and GaO\(_2\)/GaO\(_2\) were determined, including the electron affinity of GaO, the vibrational frequency of GaO\(^-\), and the term energy, spin-orbit splitting, and vibrational frequency for the first excited \(\text{\textit{A}} \text{\textit{2}}\text{\textit{I}}\) \(\text{\textit{g}}\) state of GaO. The GaO\(_2\) photoelectron spectra comprised three bands assigned as transitions from the linear \(\text{\textit{X}} \text{\textit{1}}\text{\textit{Σ}}\) \(\text{\textit{g}}\) ground state of GaO\(_2\) to three linear neutral states: the \(\text{\textit{A}} \text{\textit{2}}\text{\textit{I}}\) \(\text{\textit{g}}\), \(\text{\textit{B}} \text{\textit{2}}\text{\textit{I}}\) \(\text{\textit{g}}\), and \(\text{\textit{C}} \text{\textit{2}}\text{\textit{Σ}}\) \(\text{\textit{g}}\) states. The symmetric stretch frequencies of the anion and three neutral states as well as the spin-orbit splitting of the neutral \(\text{\textit{2}}\text{\textit{I}}\) states were determined. Electronic structure calculations found the neutral lowest energy linear structure to be only 63 meV higher than the neutral bent geometry. © 2005 American Institute of Physics. [DOI: 10.1063/1.1850470]

I. INTRODUCTION

Increasing scientific and societal interest in nanotechnology has motivated investigations of new materials from which nanostructures can be built. Gallium oxide, Ga\(_2\)O\(_3\), is a candidate material for nanostructures because of its attractive bulk properties such as luminescence\(^1\) and conduction.\(^2\) Gallium oxide nanowires,\(^3\) nanosheets,\(^4\) and nanoribbons\(^5\) have been successfully synthesized. While much effort has been devoted to the characterization of these materials in the nanosize and bulk regimes, a systematic study of the electronic and molecular properties of smaller subunits has not been undertaken. In this paper, we explore the ground and low-lying electronic states of the GaO and GaO\(_2\) molecules using anion photoelectron (PE) spectroscopy, and compare the results with those of the better known AlO and AlO\(_2\) molecules.

Despite the fact that several experimental studies have been performed on the simplest gallium oxide molecule, GaO, relatively little is known about its electronic spectroscopy. The only bands analyzed so far lie in the 300–420 nm region and were identified as the \(\text{\textit{X}} \text{\textit{2}}\text{\textit{Σ}}\) \(\text{\textit{g}}\) \textit{S} bands. Several vibrational analyses of these bands have been carried out.\(^6\)\(^–\)\(^11\) The most recent of which\(^11\) give \(\omega_{\chi}(\text{\textit{X}} \text{\textit{2}}\text{\textit{Σ}}\) \(\text{\textit{g}}\)) and \(\omega_{\phi}(\text{\textit{B}} \text{\textit{2}}\text{\textit{Σ}}\) \(\text{\textit{g}}\)) values of 766.8 and 761.5 cm\(^{-1}\), respectively.

There have, however, been some difficulties in the rotational analysis due to overlapping bands and the presence of double heads attributed to the different isotopes. In particular, there are discrepancies regarding the \(r_{\chi}(\text{\textit{X}} \text{\textit{2}}\text{\textit{Σ}}\) \(\text{\textit{g}}\)) values which range from 1.725 (Refs. 12 and 13) to 2.08 Å.\(^14\) Electronic structure calculations by Kovba and Topol,\(^15\) Petsalakis \emph{et al.},\(^16\) and Gowtham, Costales, and Pandey\(^17\) report bond lengths of 1.688, 1.647, and 1.72 Å, respectively, closer to the lower experimental value of 1.725 Å. Gowtham \emph{et al.} found the bond length in GaO\(^-\) to be nearly the same as in GaO, and calculated the electron affinity of GaO to be 2.56 eV.

No information is available on the electronic spectrum of GaO\(_2\). The GaO\(_2\) molecule has been experimentally investigated only via IR spectroscopy of matrix isolated species.\(^18\)–\(^21\) Zehe \emph{et al.}\(^18\) analyzed the spectra obtained by the reaction of Ga atoms with O\(_2\) in cryogenic matrices of N\(_2\) and Ar and found that the simplest product is the bent superoxide GaO\(_2\). They assigned the vibrational frequency of 1089.5 cm\(^{-1}\) to the \(v_1\) \((a_1)\) mode corresponding to the O–O stretch, and frequencies of 380 and 285.5 cm\(^{-1}\) to the \(v_2\) \((a_1)\) and \(v_3\) \((b_2)\) modes corresponding to the symmetric and antisymmetric Ga–O stretch, respectively. Serebrennikov, Osin, and Mal'tsev\(^19\) reproduced the results of Zehe \emph{et al.}\(^18\) in a similar study of Ga atoms with O\(_2\) in an Ar matrix. Andrews and co-workers\(^20\),\(^21\) recorded the IR spectra of several gallium oxide species. They observed a band at 568.7 cm\(^{-1}\) and assigned it to the symmetric stretch of the \(\text{C}_2\text{\textit{g}}\) GaO\(_2\)\(^-\) anion based on \emph{ab initio} calculations and isotopic shifts. Moreover, they assigned a band at 912.7 cm\(^{-1}\) to the antisymmetric stretch mode of the linear centrosymmetric OGaO molecule. Andrews \emph{et al.}\(^21\) also performed \emph{ab initio} calculations on the GaO\(_2\) anion and determined it to have a linear and symmetric \(1\text{\textit{Σ}}\) \(\text{\textit{g}}\) ground state, whereas the anion \(\text{\textit{1}}\text{\textit{A}}\) \(\text{\textit{g}}\) bent structure is \(\approx 3.7\) eV higher in energy than the linear ground state at the second-order Møller–Plesset (MP2) level of theory.

Archibong and St-Amant\(^22\) and Bu, Chan, and Song\(^23\) performed computations up to the coupled cluster singles and doubles including a perturbational estimate of triples [CCSD(T)] level of theory and concluded that the neutral GaO\(_2\) lowest energy structure is bent with a \(\text{\textit{2}}\text{\textit{A}}\) \(\text{\textit{g}}\) ground state. Very recently, Gowtham, Costales, and Pandey\(^24\) investigated small gallium oxide clusters, Ga\(_m\)O\(_n\) \((m,n=1,2)\) at the Becke three-parameter exchange functional with the Lee, Yang, and Parr correlation functional (B3LYP) level of...
II. EXPERIMENT

The experiments were carried out on a tandem time-of-flight (TOF) negative ion PE spectrometer, incorporating a linear reflectron TOF mass spectrometer and a field-free TOF photoelectron analyzer. Details of this apparatus have been previously reported.24,25

GaO− and GaO2− were generated by focusing the second harmonic (532 nm, 10–15 mJ/pulse, 20 Hz) of a pulsed Nd:YAG laser (YAG—yttrium aluminum garnet) onto a rotating and translating GaN disk. The disk was produced by pressing a 99.9% pure GaN powder (Aldrich) in an isostatic press at 200 kpsi. Although some GaN2− anions were seen (for which PE spectra will be reported shortly), the mass spectrum was dominated by oxides, most likely from surface oxidation of the target. The plume created by laser ablation was crossed perpendicularly by a pulse of Ar gas from a piezoelectric valve and expanded through a 19 mm long clustering channel. It was then skimmed and entered the first differentially pumped region of the linear reflectron TOF, where the anions formed during the expansion were extracted at 90° from the molecular beam by a pulsed electric field and accelerated to 2.5 keV beam energy. The mass resolution m/Δm is ~2000. Each molecule has an isotopic distribution due to the natural isotopic abundance of Ga. In each case, the most intense mass peak was photodetached.

Mass-selected anions were photodetached with the third harmonic (355 nm, 3.493 eV), fourth (266 nm, 4.661 eV), or fifth harmonic (213 nm, 5.821 eV) of a pulsed fixed-frequency Nd:YAG laser. Typically, a pulse energy of 1–6 mJ was used. The electron kinetic energy (eKE) distribution was determined by TOF analysis in a 1 m field-free flight tube. The eKE scale was calibrated using the known PE spectra of O2− at 355 nm, Cl−, Br−, and I− at 266 nm, and Cl− and CN− at 213 nm. The energy resolution is 8–10 meV at 0.65 eV eKE and degrades as (eKE)3/2 at higher energy.

All the PE spectra presented in this study are plotted as a function of the electron binding energy (eBE), defined as

\[ eBE = hν - eKE = EA + E^{(0)} - E^{(-)} \]

where \( hν \) is the laser photodetachment energy (3.493, 4.661, and 5.821 eV), \( E^{(0)} \) is the internal energy of the neutral, and \( E^{(-)} \) the internal energy of the anion. The PE spectra were taken at two laser polarization angles, 0° and 90° with respect to the direction of electron detection. This angle was varied using a half-wave plate.

III. RESULTS

A. Photoelectron spectra

Figure 1 shows the PE spectra of GaO− taken at 355 and 266 nm, the 266 and 213 nm PE spectra of GaO2− are displayed in Fig. 2. No variation of relative peak heights with laser polarization angle θ was observed; setting θ=90° gave the highest electron signal. The 355 and 266 nm photoelectron spectra of GaO− comprise two distinct bands labeled as X and A. The 266 nm GaO− spectrum shows the same spectral features observed at 355 nm with a more extended progression of band A and lower resolution because of the higher eKE. The 266 nm GaO2− PE spectrum shows an intense band labeled X and several smaller features, while the 213 nm GaO2− spectrum comprises three bands marked as X, A, and B.
predicted to have a frequency of 810 cm\(^{-1}\). (Fig. 2) shows peaks with better-resolved doublets than band \(\text{X}1\). Since peak \(\text{X}\) is assigned to \(\text{X}1\), the extra band at \(\text{X}0\) of \(\approx 770\) cm\(^{-1}\) seems to be a partially resolved doublet with a splitting of \(\approx 160\) cm\(^{-1}\). The two small spectral features labeled as HB at \(\text{X}1\) and \(\text{X}2\), which GaO\(^-\) is produced by photodissociation of GaO\(_2\)\(^-\) at 213 nm followed by photodetachment. No evidence for photodissociation of GaO\(_2\) was seen at 213 or 355 nm.

Band \(\text{X}\) of the 266 nm spectrum, the first GaO\(_2\) feature, starts at \(\approx 4\) eV and comprises a resolved vibrational progression with a peak spacing of \(760\) cm\(^{-1}\). Moreover, the peaks reveal partially resolved doublets with a splitting of \(\approx 160\) cm\(^{-1}\). The two small spectral features labeled as HB at \(\text{X}0\) and \(\text{X}1\), yielding an approximate anion vibrational frequency of \(770\) cm\(^{-1}\). The 213 nm PE spectrum shows two additional bands, \(A\) and \(B\), beginning at \(4.84\) and \(5.46\) eV eBE, respectively. Band \(A\) has a resolved progression with a vibrational frequency of \(700\) cm\(^{-1}\), whereas band \(B\) consists only of two peaks, \(B_0\) and \(B_1\), with a separation of \(720\) cm\(^{-1}\). Band \(A\) also shows peaks with better-resolved doublets than band \(\text{X}\), with a splitting of \(220\) cm\(^{-1}\). The full assignment of these bands is discussed in Sec. IV B.

**B. Electronic structure calculations**

In order to interpret the measured photoelectron spectra, we performed DFT calculations with the B3LYP method. The correlation consistent polarized valence triple-\(\tilde{\zeta}\) (cc-pVTZ) basis set was used for both Ga (Ref. 26) and O.\(^{27}\) The computations were carried out with the GAUSSIAN98 program suite.\(^{28}\) We calculated the energetics (including zero-point vibrational energies, term energies, and adiabatic detachment energies), optimized geometries, and harmonic vibrational frequencies for the ground and various excited electronic states of GaO/GaO\(^-\) and GaO\(_2\)/GaO\(_2\)^\(-\).

Results are summarized in Table I. The electronic term energy \(T_0\) is reported for each anion and neutral state. For each neutral state the ADE is also given, defined as the energy difference between the \(\nu=0\) levels of the anion ground state and neutral electronic state in question.

The outer molecular orbital (MO) configuration for the GaO\(^-\) \(\Sigma^+\) ground state is found to be \(4\pi^1 10\sigma^2\) from our calculations. The highest occupied molecular orbital (HOMO) \(10\sigma^2\) is antibonding, with Ga 4s, Ga 4p, and O 2p character. The equilibrium bond length and harmonic vibrational frequency are found to be 1.715 Å and 821 cm\(^{-1}\). The \(a^3\Pi\) excited state, with an outer MO configuration of \(10\sigma^2 5\pi^1\), lies 22 930 cm\(^{-1}\) or 2.84 eV above the ground state. The neutral GaO ground state has been experimentally characterized but some uncertainties persist regarding its bond length. Our optimized computed value of 1.717 Å supports the earlier experimental determination of 1.725 Å (Refs. 12 and 13) but not the most recent result of 2.08 Å.\(^{14}\) The outer MO configurations of the GaO \(\Sigma^+\) and \(a^3\Pi\) states are \(4\pi^1 10\sigma^2\) and \(4\pi^1 10\sigma^2\), respectively. The computed bond distances of 1.888 Å for the \(a^3\Pi\) state is slightly
above the ground state has a bent structure and the states lie 8410 cm \(^{-1}\) lower than the previously calculated values of 1.804 Å (Ref. 16) and 1.836 Å.\(^{15}\) The calculated term value \(T_p(\Sigma^+_2)\) is 1860 cm \(^{-1}\) or 0.23 eV, close to the splitting between the apparent origins of bands \(X\) and \(A\) in the PE spectrum of GaO\(^{-}\). The harmonic vibrational frequencies of 827, 734, and 562 cm \(^{-1}\) for the anion ground state, the neutral ground state, and first excited electronic state, respectively, are in very good agreement with the values obtained from the PE spectra.

Our B3LYP/cc-pVTZ calculations of GaO\(^2\) yield a similar ordering of states as the work of Andrews et al.,\(^{21}\) with the \(1\Sigma_g^+\) centrosymmetric geometry as the ground state. The GaO\(^2\) \(2\Sigma_g^+\) outer MO configuration is \(12\pi^2 n^4 5\pi_2^2\). The \(5\pi_2^2\) HOMO has antibonding character, and it is composed primarily of linear combinations of Ga 3d and O 2p orbitals. The GaO\(^2\) V-shape structure with an apex angle of 48° lies 15 880 cm \(^{-1}\) or \(=2 eV\) above the \(X 1\Sigma_g^+\) state. On the other hand, the situation is inverted for neutral GaO\(^2\) for which the ground state has a bent structure (\(2\Sigma_u^+\)) and the first excited state (\(2\Pi_u\)) is linear. Our findings for the bent \(2\Sigma_u^+\) state of GaO\(^2\) are similar to previous theoretical calculations.\(^{17,22,23}\) According to our calculations the \(A 2\Pi_u\) state lies only 510 cm \(^{-1}\) or 63 meV above the ground state, and has an outer MO configuration of \(12\pi^2 n^4 5\pi_2^2\). Based on only these DFT energetics, we cannot rule out the possibility that the global minimum of GaO\(^2\) is indeed linear. We find \(r_{Ga-O}\) for the \(A 2\Pi_u\) state to be 1.695 Å, and the symmetric stretch of 757 cm \(^{-1}\) agrees very well with the experimental peak spacing of 760 cm \(^{-1}\) for band \(X\). The \(B 2\Pi_u\) and \(C 2\Sigma_u^+\) electronic states lie 8410 cm \(^{-1}\) (1.043 eV) and 11 250 cm \(^{-1}\) (1.395 eV) above the \(A 2\Pi_u\) state, close to the spacings between the origins of bands \(X\), \(A\), and \(C\).

### IV. DISCUSSION

Assignment of the electronic bands and vibrational progressions is facilitated by comparison with the molecular parameters and energetics provided by the electronic structure calculations described in the preceding section. In addition, the B3LYP/cc-pVTZ calculations supplied the force constants necessary for simulating the PE spectra within the Franck-Condon (FC) approximation. For GaO\(^{-}\), the electronic structure calculations indicate that bands \(X\) and \(A\) in the PE spectra should be assigned as transitions to the neutral \(X 2\Sigma^+\) and \(A 2\Pi\) states, respectively. The calculations suggest that in the GaO\(^2\) PE spectra, bands \(X\), \(A\), and \(B\) are from transitions from the linear anion to the three low-lying \(A 2\Pi_u\), \(B 2\Pi_u\), and \(C 2\Sigma_u^+\) linear neutral states. FC simulations of the GaO\(^2\) spectra were carried out within the parallel-mode approximation assuming harmonic oscillator potentials. Starting from the force constants and computed parameters obtained from the calculations for the initial state of the anion and the final state of the neutral, the normal coordinate changes, term energies, and vibrational frequencies were used as input for the simulations and successively optimized to reproduce the experimental PE spectra. Transition origins were taken from experiment, as well as the experimentally known parameters. The anion vibrational temperature was assumed to be 1000 K for both GaO\(^{-}\) and GaO\(^2\). The parameters used in the PE spectra simulations are listed in Table II, and the simulated spectra for GaO and GaO\(^2\) are shown in Fig. 3. Rotational broadening of the peaks is negligible because of the small rotational constants for GaO/GaO\(^{-}\) and GaO\(^2\)/GaO\(^2\).

#### A. GaO

One-electron photodetachment from the two highest lying molecular orbitals of GaO\(^{-}\) results in the neutral \(X 2\Sigma^+\) (4\(\pi^2\) 10\(\sigma^b\)) ground and \(A 2\Pi(4\pi^2 10\sigma^b)\) excited electronic states. In simulations of the PE spectra, the known neutral ground state bond distance\(^{12,13}\) and vibrational frequency\(^{11}\) were fixed at 1.725 Å and 767 cm \(^{-1}\), whereas the molecular parameters of the anion ground state, the neutral first excited state, and EA(GaO) were varied to achieve best fit.

The FC simulation of band \(X\) for the 355 nm PE spectrum yields the adiabatic EA(GaO) as 2.612±0.008 eV, 0.23 eV higher than our computed value of 2.38 eV, but very close to the value of 2.56 eV calculated by Gowtham, Costales, and Pandey.\(^{15}\) Band \(A\), assigned to the \(A 2\Pi\) → \(X 1\Sigma^+\) transition.
electronic transition, shows a resolved vibrational progression yielding a frequency of 580±30 cm$^{-1}$ for the $A^2P$ state. Each vibrational peak comprising band $A$ presents a partially resolved doublet that provides the determination of the spin-orbit splitting between the $2^3P_{3/2}$ and $2^3P_{1/2}$ states as 170±30 cm$^{-1}$. In addition, from the band $A$ vibronic origin, we derived the $A^2P$ term energy as 2850±90 cm$^{-1}$ or 0.353±0.011 eV.

The two smaller spectral features labeled as HB in the 355 nm spectrum are transitions from vibrationally excited levels of GaO$^-$.

The PE spectrum of GaO$^-$ is remarkably similar to the AlO$^-$ PE spectrum measured by Desai, Wu, and Wang. The AlO$^-$ spectrum also comprises two bands with the same state assignments as in the GaO$^-$ spectrum: a very short progression, assigned to the $X^2S^+\rightarrow X^1S^+$ transition, and a more extended band assigned to the $A^2P\rightarrow X^1S^+$ transition. Hence, the state orderings are the same, and changes in geometry upon photodetachment are similar. Remarkably, the electron affinities of GaO and AlO are almost identical: 2.612 and 2.60 eV, respectively. The vibrational frequencies for AlO$^-$ and the AlO ground state are higher by 95 cm$^{-1}$ and 212 cm$^{-1}$, respectively, than the GaO$^-$ and GaO frequencies. The term value for the $A^2P$ state in GaO, 0.353 eV, is about half the term value for the analogous state in AlO, 0.66 eV. The spin-orbit splitting of 128.7 cm$^{-1}$ for the AlO $A^2P$ state is not resolved in the PE spectra of Desai, Wu,

### Table II

| Molecule | Band | State | $\nu^{(\text{c})}$ | $\nu^{(\text{b})}$ | $|A_e|$ | $\Delta r_e$ | ADE | $T_e$ | $T$ |
|----------|------|-------|------------------|------------------|-------|-------------|-----|-------|-----|
| GaO      | $X$  | $^2\Sigma^+$ | 805 | 767 | 0.025 | 2.612±0.008 | ⋯ | 1000 |
|          | $A$  | $^3\Pi$    | 805 | 580 | 170 | 0.174 | 2.965±0.008 | 2.850 | 1000 |
| GaO$_2$  | $X$  | $^3\Pi_3$  | 770 | 760 | 160 | 0.028 | 4.008±0.008 | ⋯ | 1000 |
|          | $A$  | $^3\Pi_1$  | 770 | 710 | 210 | 0.069 | 4.839±0.010 | 6700 | 1000 |
|          | $B$  | $^3\Sigma^+$ | 770 | 720 | 0.018 | 5.464±0.008 | 11740 | 1000 |

The two smaller spectral features labeled as HB in the 355 nm spectrum are transitions from vibrationally excited levels of GaO$^-$. The spacing between the HB peaks and the vibronic origins of bands $X$ and $A$ provides the anion ground state frequency as 805±30 cm$^{-1}$. From the spectral simulations, we also obtain the absolute values of the bond distance change for the $X^2\Sigma^+\rightarrow X^1\Sigma^+$ and $A^2\Pi\rightarrow X^1\Sigma^+$ electronic transitions, as 0.025 and 0.174 Å. If we assume the signs of these optimized values of $\Delta r_{Ga-O}$ to be the same as the signs for the calculated $\Delta r_{Ga-O}$ values from Table I, we find equilibrium bond lengths of 1.70±0.01 and 1.87±0.01 Å for the $X^1\Sigma^+$ anion ground state and neutral $A^2\Pi$ state, respectively, in close agreement with the calculated bond lengths in Table I.

The PE spectrum of GaO$^-$ is remarkably similar to the AIO$^-$ PE spectrum measured by Desai, Wu, and Wang. The AIO$^-$ spectrum also comprises two bands with the same state assignments as in the GaO$^-$ spectrum: a very short progression, assigned to the $X^2\Sigma^+\rightarrow X^1\Sigma^+$ transition, and a more extended band assigned to the $A^2\Pi\rightarrow X^1\Sigma^+$ transition. Hence, the state orderings are the same, and changes in geometry upon photodetachment are similar. Remarkably, the electron affinities of GaO and AlO are almost identical: 2.612 and 2.60 eV, respectively. The vibrational frequencies for AlO$^-$ and the AlO ground state are higher by 95 cm$^{-1}$ and 212 cm$^{-1}$, respectively, than the GaO$^-$ and GaO frequencies. The term value for the $A^2\Pi$ state in GaO, 0.353 eV, is about half the term value for the analogous state in AlO, 0.66 eV. The spin-orbit splitting of 128.7 cm$^{-1}$ for the AlO $A^2\Pi$ state is not resolved in the PE spectra of Desai, Wu,

### Figure 3

Franck-Condon spectral simulations of GaO$^-$ and GaO$_2^-$ PE spectra (gray area) superimposed on the experimental spectra.
and Wang and is comparable to the resolved splitting of 170 cm\(^{-1}\) for GaO determined in this investigation.

### B. GaO\(_2\)

The computational results described in Sec. III B, together with other theoretical studies on the GaO\(_2\)/GaO\(_2\) molecules, indicate that the neutral and anion have different ground state geometries: the anion is linear and the neutral bent. At the B3LYP/cc-pVTZ level of theory, the outer MO configuration of the GaO\(_2\) ground state is 12\(\sigma^2_\text{u}, \pi^5_\text{u}\), and those of the neutral \(\mathbf{A^2\Pi_u, B^2\Pi_u,}\) and \(\mathbf{C^2\Sigma^+_u}\) states are 12\(\sigma^2_\text{u}, \pi^4_\text{u}, \pi^5_\text{v}\), 12\(\sigma^2_\text{u}, \pi^2_\text{u}, \pi^5_\text{v}\), and 12\(\sigma^2_\text{u}, \pi^4_\text{v}, \pi^5_\text{v}\), respectively. Since photodetachment is vertical, the transition between the linear anion and strongly bent (apex angle of 38°) \(\mathbf{A^2\Pi_u}\) state would be very weak, so we only observe transitions to the three neutral linear states. We thus cannot tell from the PE spectra whether the GaO\(_2\) ground state is bent or linear; assuming our calculated energy ordering of the neutral states is correct, we can only obtain ADEs for the three linear states and not the electron affinity of GaO\(_2\).

The best-fit FC simulations of the GaO\(_2\) PE spectra are shown in Fig. 3, and the optimized parameters used in these simulations are listed in Table II. All three bands show resolved vibrational structure. The FC analysis of band \(X\) indicates that ADE(\(B^2\Pi_u\)) is 4.008±0.008 eV. This band comprises a progression in the totally symmetric mode \(\sigma_v\), with a frequency of 760±30 cm\(^{-1}\), which is in perfect agreement of 0.07±0.01 Å. The B3LYP/cc-pVTZ u estimates that ADEs simulations are listed in Table II. All three bands show resolved splitting of 0.004 Å. In addition, each vibrational peak shows photodetachment, somewhat larger than the calculated change of 0.004 Å. In addition, each vibrational peak shows a partially resolved splitting that is assigned to the spin-orbit coupling of the \(\Omega=1/2\) and 3/2 components of the \(\mathbf{2^1\Sigma_u^+}\) state, yielding a spin-orbit splitting of 160±30 cm\(^{-1}\).

The vibrionic origin of band \(A\) provides the ADE(\(B^2\Pi_u\)) of 4.839±0.010 eV and yields an energy separation between the neutral \(\mathbf{2^1\Pi_u}\) and \(\mathbf{2^3\Pi_u}\) states of 6700±105 cm\(^{-1}\) or 0.831±0.013 eV. The computed \(\mathbf{2^1\Pi_u, 2^3\Pi_u}\) separation overestimates the experimental value by \(\approx 25\%\). Band \(A\) also presents a vibrational resolved progression, more extended than band \(X\), that is fit using the totally symmetric stretching mode \(\sigma_v\), of 710±30 cm\(^{-1}\). The calculated frequency is 53 cm\(^{-1}\) lower than the best-fit value. The \(\mathbf{Q^2}\) of 0.390 amu\(^{1/2}\) Å for this vibrational mode results in a \(|\Delta r_{\text{Ga-O}}|\) of 0.07±0.01 Å. The B3LYP/cc-pVTZ \(|\Delta r_{\text{Ga-O}}|\) for the \(\mathbf{2^1\Sigma_u^+}\) state is 0.65±0.03 Å. In both cases, three bands are observed and assigned to linear−linear electronic transitions. The calculated \(|\Delta r_{\text{Ga-O}}|\) values for the neutral GaO\(_2\) appears to be bent with an apex angle of 38°. The \(\mathbf{A^2\Pi_u}\) and GaO\(_2\) PE spectra both show a high ADE for the first band, 4.23 eV for AlO\(_2\) and 4.008 eV for GaO\(_2\). Also, the energy separation of the two excited electronic states relative to the first band is similar in the case of AlO\(_2\) and GaO\(_2\); \(T_{\text{e}}(\mathbf{A^2\Pi_u})\) and \(T_{\text{g}}(\mathbf{B^2\Sigma_u^+})\) for AlO\(_2\) are (0.65±0.03) and (0.85±0.03) eV, respectively.

### V. CONCLUSIONS

Vibrationally resolved anion photoelectron spectra of GaO\(^+\) and GaO\(_2\) are presented. These spectra show transitions to the ground and excited electronic states of the neutrals that were not previously observed. They are discussed in detail and analyzed with the aid of DFT calculations and FC simulations. In the GaO\(^+\) PE spectra, bands \(X\) and \(A\) are assigned to transitions from the anion ground state to the neutral ground and first excited state, yielding the first experimental determination of the anion symmetric stretching mode of 770±30 cm\(^{-1}\), in agreement with the calculated value of 775 cm\(^{-1}\).

Finally, we compare the findings for GaO\(_2\)/GaO\(_2\) with those for the isoelectronic AlO\(_2\)/AlO\(_2\) molecules. The AlO\(_2\) PE spectrum obtained by Desai et al.\, using 6.42 eV photon energy looks very similar to the 5.821 eV PE spectrum of GaO\(_2\). In both cases, three bands are observed and assigned to linear−linear electronic transitions. From theoretical calculations it is found that the neutral AlO\(_2\) has two almost isoelectronic isomers with the linear geometry being the global minimum. On the other hand, from our computations and other calculations\, the lowest energy structure of the neutral GaO\(_2\) appears to be bent with an apex angle of 38°. The \(\mathbf{A^2\Pi_u}\) and GaO\(_2\) PE spectra both show a high ADE for the first band, 4.23 eV for AlO\(_2\) and 4.008 eV for GaO\(_2\). Also, the energy separation of the two excited electronic states relative to the first band is similar in the case of AlO\(_2\) and GaO\(_2\); \(T_{\text{e}}(\mathbf{A^2\Pi_u})\) and \(T_{\text{g}}(\mathbf{B^2\Sigma_u^+})\) for AlO\(_2\) are (0.65±0.03) and (0.85±0.03) eV, respectively.
bent neutral with apex angle of 38°. Consequently, we were not able to resolve the issue of the neutral ground state geometry. Finally, we compared our experimental findings with those of the isoelectronic AlO−/AlO and AlO2−/AlO2 molecules.

**ACKNOWLEDGMENT**

The authors gratefully acknowledge the financial support by the National Science Foundation under Grant No. DMR-0139064.
