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

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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 $A\,^2\Pi_\Omega$ state of GaO. The GaO_2^- photoelectron spectra comprised three bands assigned as transitions from the linear $X\,^1\Sigma_g^+$ ground state of GaO_2^- to three linear neutral states: the $A\,^2\Pi_g$, $B\,^2\Pi_u$, and $C\,^2\Sigma_u^+$ states. The symmetric stretch frequencies of the anion and three neutral states as well as the spin-orbit splitting of the neutral $^2\Pi$ 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_2O_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 $B\,^2\Sigma^+$-$X\,^2\Sigma^+$ transition.[6–8] Several vibrational analyses of these bands have been carried out,[6–11] the most recent of which[11] give $\omega_e(X\,^2\Sigma^+)$ and $\omega_e(B\,^2\Sigma^+)$ 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 $r_e(X\,^2\Sigma^+)$ values which range from 1.725 (Refs. 12 and 13) to 2.08 Å.[14] Electronic structure calculations by Kovba and Topol,[15] Petsalakis 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 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 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 $Ga^+O_2^-$. They assigned the vibrational frequency of 1089.5 cm^{-1} to the ν_1 (a_1) mode corresponding to the O–O stretch, and frequencies of 380 and 285.5 cm^{-1} to the ν_2 (a_1) and ν_3 (b_2) modes corresponding to the symmetric and antisymmetric Ga–O stretch, respectively. Serebrennikov, Osin, and Maltsev[19] reproduced the results of Zehe 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 C_{2v} $Ga(O_2)^-$ anion based on *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 et al.[21] also performed *ab initio* calculations on the GaO_2^- anion and determined it to have a linear and symmetric $^1\Sigma_g^+$ ground state, whereas the anion $^1A_1$ 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 $^2A_2$ ground state. Very recently, Gowtham, Costales, and Pandey[17] investigated small gallium oxide clusters, Ga_mO_n ($m,n=1,2$) at the Becke three-parameter exchange functional with the Lee, Yang, and Parr correlation functional (B3LYP) level of

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theory. They found the lowest energy isomer of the neutral GaO_2 to have a C_{2v} symmetry, the neutral linear isomer to lie 0.12 eV above the bent structure, and the lowest energy isomer of the anion to be linear and centrosymmetric.

In this investigation, we report the first photodetachment PE experiments on GaO^- and GaO_2^- using photon energies of 5.821 (213 nm), 4.661 (266 nm), and 3.493 eV (355 nm). We observed the lowest excited electronic state of GaO and transitions to three linear electronic states from linear GaO_2^-. The PE spectra of GaO and GaO_2 show vibrationally resolved features. Electronic structure calculations and Franck–Condon spectral simulations were performed yielding neutral and anion vibrational frequencies as well as geometric changes that occur upon photodetachment. We also obtained the electron affinity (EA) of GaO and adiabatic detachment energies (ADE) for three linear electronic states of GaO_2.

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 GaO_2^- 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 $Ga_xN_y^-$ 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 $m/\Delta m$ 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 (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 O_2^- 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
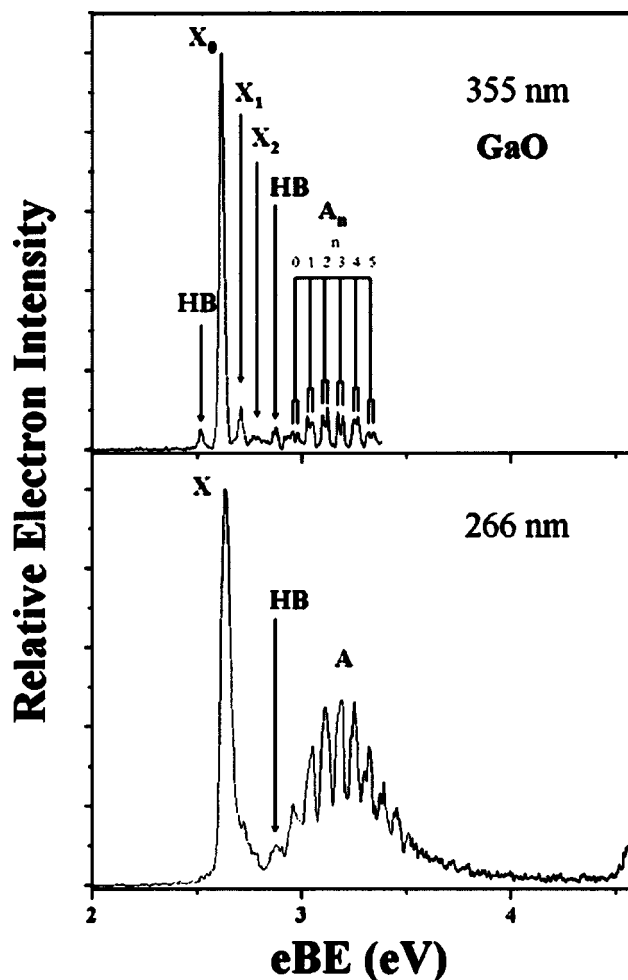

FIG. 1. Photoelectron spectra of GaO^- at 355 nm (top) and 266 nm (bottom) photodetachment wavelengths taken with $\theta=90°$.

$$eBE = h\nu - eKE = EA + E^{(0)} - E^{(-)}, \qquad (1)$$

where $h\nu$ 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 GaO_2^- are displayed in Fig. 2. No variation of relative peak heights with laser polarization angle θ was observed; setting $\theta=90°$ 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 GaO_2^- PE spectrum shows an intense band labeled X and several smaller features, while the 213 nm GaO_2^- spectrum comprises three bands marked as X, A, and B.
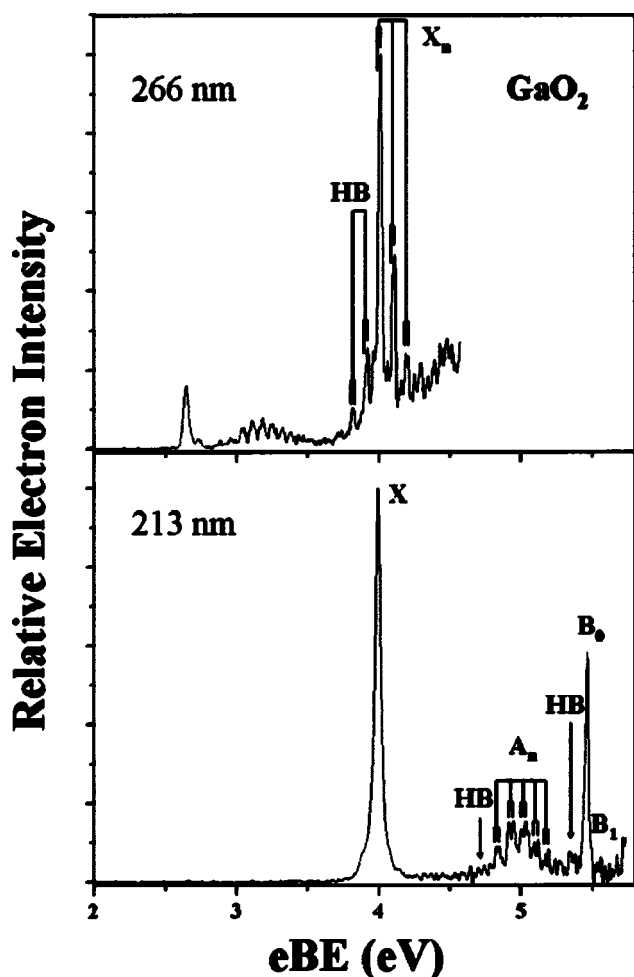
FIG. 2. Photoelectron spectra of GaO_2^- at 266 nm (top) and 213 nm (bottom) photodetachment wavelengths taken with $\theta=90°$.

In the 355 nm PE spectrum of GaO^-, the main band X, beginning at 2.61 eV (X_0), shows a resolved vibrational progression with a peak spacing ($X_0–X_1$) of ≈ 770 cm^{-1}, very close to the literature value[11] of 767 cm^{-1} for the fundamental vibrational frequency of the $X\,^2\Sigma^+$ state. The short progression shows that the geometry change is small upon photodetachment. Band A comprises a more extended vibrationally resolved progression starting at 2.97 eV (A_0) with a peak spacing of ≈ 600 cm^{-1}. Moreover, each peak of band A seems to be a partially resolved doublet with a splitting of 160 cm^{-1}. According to our density functional (DFT) calculations (see following section), the first excited electronic state of GaO is the $A\,^2\Pi$ state, while the GaO^- anion is predicted to have a $X\,^1\Sigma^+$ electronic ground state with a $a\,^3\Pi$ state lying at ≈ 2.9 eV above the ground state. Consequently, we assign peak X_0 and A_0 to the vibrational origins of the $X\,^2\Sigma^+ \leftarrow X\,^1\Sigma^+$ and $A\,^2\Pi \leftarrow X\,^1\Sigma^+$ electronic transitions. Since peak X_0 occurs at eBE=2.95 eV, this is the approximate adiabatic EA of GaO. Two smaller peaks are present in the 355 nm PE spectrum, labeled as HB, at 2.51 and 2.87 eV eBE, each lying 810 cm^{-1} from X_0 and A_0. They are assigned to anion vibrational hot bands, yielding an anion vibrational frequency of 810 cm^{-1}.

In Fig. 2, the first two bands at lowest eBE in the 266 nm spectrum of GaO_2^- appear at the same eBE as bands

X and A in the GaO^- spectra and are not present in the 213 nm GaO_2^- PE spectrum. Indeed, when the 266 nm GaO^- spectrum is superimposed to the 266 nm GaO_2^- spectrum, the bands perfectly match. The appearance of GaO^- signal in the GaO_2^- PE spectrum suggests the presence of a dissociative state of GaO_2^- at ≈ 4.6 eV. Then, it is straightforward to assign the GaO^- bands to a two photon process, according to which GaO^- is produced by photodissociation of GaO_2^- at 266 nm followed by photodetachment. No evidence for photodissociation of GaO_2^- was seen at 213 or 355 nm.

Band X of the 266 nm spectrum, the first GaO_2 feature, starts at ≈ 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 ≈ 160 cm^{-1}. The two small spectral features labeled as HB at eBE=3.82 and 3.91 eV are assigned as hot band transitions, 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 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-ζ (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_e is reported for each anion and neutral state. For each neutral state the ADE is also given, defined as the energy difference between the $v=0$ levels of the anion ground state and neutral electronic state in question.

The outer molecular orbital (MO) configuration for the GaO^- $X\Sigma^+$ ground state is found to be $4\pi^4\,10\sigma^2$ 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 $10\sigma^1\,5\pi^1$, 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 $X\,^2\Sigma^+$ and $A\,^2\Pi$ states are $4\pi^4\,10\sigma^1$ and $4\pi^3\,10\sigma^2$, respectively. The computed bond distance of 1.888 Å for the $A\,^2\Pi$ state is slightly

TABLE I. B3LYP/cc-pVTZ computed optimized molecular parameters (r_{Ga-O} and r_{O-O} in angstrom, α in degrees, and ν in cm^{-1}), zero-energy vibrational energies (ZPE in eV), term energies (T_e in cm^{-1}), and adiabatic detachment energies (ADE in eV).

Molecule	State	r_{Ga-O}	r_{O-O}	α	ν_1[a]	ν_2	ν_3	ZPE	T_e	ADE
GaO$^-$	$^1\Sigma^+$	1.715			827			0.051	$\cdots$	
	$^3\Pi$	1.786			591			0.037	22 930	
GaO	$^2\Sigma^+$	1.717			734			0.045	$\cdots$	2.38
	$^2\Pi$	1.888			562			0.035	1 860	2.61
GaO$_2^-$	$^1\Sigma_g^+$	1.691		180	206	775	930	0.132	$\cdots$	
	$^1A_1$	1.901	1.550	48	435	506	824	0.110	15 880	
GaO$_2$	$^2A_2$	2.080	1.340	38	286	389	1173	0.115	$\cdots$	
	$^2\Pi_g$	1.695		180	185	757	661	0.111	510	3.56
	$^2\Pi_u$	1.725		180	158	657	1133	0.130	8920	4.61
	$^2\Sigma_u^+$	1.701		180	167	724	819	0.116	11 760	4.99
	$^2A_1$	1.814	1.624	53	576	555	792	0.119	13 960	

[a]For linear molecules ν_1 is the bending π, ν_2 the symmetric stretching σ_g, and ν_3 the antisymmetric stretching σ_u mode; for nonlinear molecules ν_1 is the antisymmetric stretching b_2, ν_2 the symmetric stretching a_1, and ν_3 a_1 the bending mode.

longer than the previously calculated values of 1.804 Å (Ref. 16) and 1.836 Å.[15] The calculated term value $T_e(A\,^2\Pi)$ 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$_2^-$ Σ_g^+1 outer MO configuration is $12\sigma_u^24\pi_u^45\pi_g^4$. The $5\pi_g^4$ 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 ($^2A_2$) and the first excited state ($^2\Pi_g$) is linear. Our findings for the bent $^2A_2$ state of GaO$_2$ are similar to previous theoretical calculations.[17,22,23] According to our calculations the $A\,^2\Pi_g$ state lies only 510 cm^{-1} or 63 meV above the ground state, and has an outer MO configuration of $12\sigma_u^24\pi_u^45\pi_g^3$. Based only on 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 $A\,^2\Pi_g$ 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 $A\,^2\Pi_g$ 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 con-

stants 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 $A\,^2\Pi_g$, $B\,^2\Pi_u$ 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 $X\,^2\Sigma^+$ ($4\pi^4\,10\sigma^1$) ground and $A\,^2\Pi$ ($4\pi^3\,10\sigma^2$) 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.[17] Band A, assigned to the $A\,^2\Pi \leftarrow X\,^1\Sigma^+$

TABLE II. Optimized parameters used in the FC simulation of the PE spectra. The vibrational modes ν and the spin-orbit constants A_e are in cm^{-1}, the equilibrium bond distance change Δr_e in angstrom, the ADE in eV, the term energies T_e in cm^{-1}, and the anion vibrational temperature T in K.

Molecule	Band	State	$\nu^{(-)}$	$\nu^{(0)}$	$|A_e|$	Δr_e	ADE	T_e	T
GaO	X	$^2\Sigma^+$	805	767		0.025	2.612 ± 0.008	$\cdots$	1000
	A	$^2\Pi$	805	580	170	0.174	2.965 ± 0.008	2 850	1000
GaO$_2$	X	$^2\Pi_g$	770	760	160	0.028	4.008 ± 0.008	$\cdots$	1000
	A	$^2\Pi_u$	770	710	210	0.069	4.839 ± 0.010	6700	1000
	B	$^2\Sigma_u^+$	770	720		0.018	5.464 ± 0.008	11 740	1000

electronic transition, shows a resolved vibrational progression yielding a frequency of 580 ± 30 cm^{-1} for the $A\,^2\Pi$ state. Each vibrational peak comprising band A presents a partially resolved doublet that provides the determination of the spin-orbit splitting between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states as 170 ± 30 cm^{-1}. In addition, from the band A vibronic origin, we derived the $A\,^2\Pi$ 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 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 $X\,^2\Sigma^+ \leftarrow X\,^1\Sigma^+$ and $A\,^2\Pi \leftarrow X\,^1\Sigma^+$ electronic transitions, as 0.025 and 0.174 Å. If we assume the signs of these optimized values of Δr_{Ga-O} to be the same as the signs for the calculated Δr_{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 AlO$^-$ PE spectrum measured by Desai, Wu, and Wang.[29] The AlO$^-$ spectrum also comprises two bands with the same state assignments as in the GaO$^-$ spectrum: a very short progression, assigned to the $X\,^2\Sigma^+ \leftarrow X\,^1\Sigma^+$ transition, and a more extended band assigned to the $A\,^2\Pi \leftarrow X\,^1\Sigma^+$ 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[30] 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[30] is not resolved in the PE spectra of Desai, Wu,
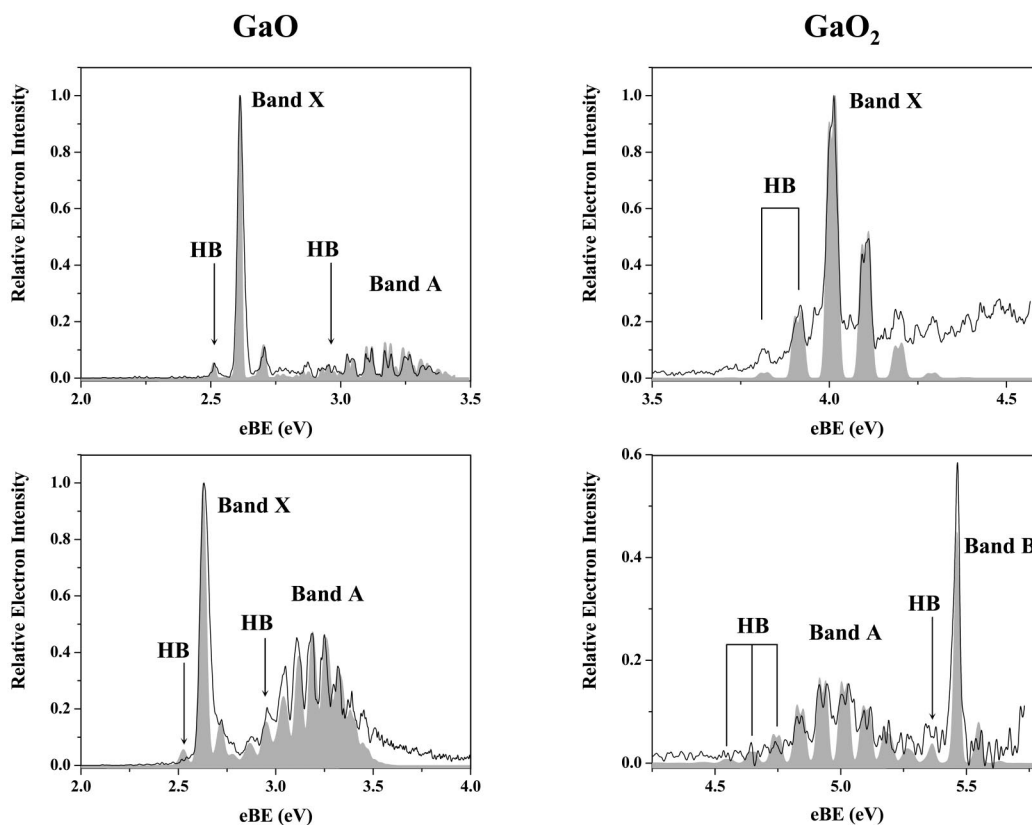
GaO   **GaO$_2$**

FIG. 3. Franck–Condon spectral simulations of GaO$^-$ and GaO$_2^-$ PE spectra (gray area) superimposed on the experimental spectra.

and Wang[29] 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[21–23] 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 $12\sigma_u^2 4\pi_u^4 5\pi_g^4$, and those of the neutral $A\ ^2\Pi_g$, $B\ ^2\Pi_u$, and $C\ ^2\Sigma_u^+$ states are $12\sigma_u^2 4\pi_u^4 5\pi_g^3$, $12\sigma_u^2 4\pi_u^3 5\pi_g^4$, and $12\sigma_u^1 4\pi_u^4 5\pi_g^4$, respectively. Since photodetachment is vertical, the transition between the linear anion and strongly bent (apex angle of 38°) $^2A_2$ 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 $ADE(A\ ^2\Pi_g)$ is 4.008 ± 0.008 eV. This band comprises a progression in the totally symmetric mode σ_g with a frequency of $760\pm30\ cm^{-1}$, which is in perfect agreement with the computed B3LYP/cc-pVTZ value. The normal mode displacement of $0.160\ amu^{1/2}$ Å for this mode needed to fit the spectrum corresponds to $|\Delta r_{Ga-O}|=0.03\pm0.01$ Å upon 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 $^2\Pi_g$ state, yielding a spin-orbit splitting of $160\pm30\ cm^{-1}$.

The vibronic 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 $^2\Pi_g$ and $^2\Pi_u$ states of $6700\pm105\ cm^{-1}$ or 0.831 ± 0.013 eV. The computed $^2\Pi_g$-$^2\Pi_u$ separation overestimates the experimental value by $\approx25\%$. Band A also presents a vibrational resolved progression, more extended than band X, that is fit using the totally symmetric stretching mode σ_g of $710\pm30\ cm^{-1}$. The calculated frequency is $53\ cm^{-1}$ lower than the best-fit value. The ΔQ of $0.390\ amu^{1/2}$ Å for this vibrational mode results in a $|\Delta r_{Ga-O}|$ of 0.07 ± 0.01 Å. The B3LYP/cc-pVTZ $|\Delta r_{Ga-O}|$ value for the $A\ ^2\Pi_g \leftarrow X\ ^1\Sigma_g^+$ transition is 0.034 Å. As for band X, each vibrational peak of band A is split by $210\pm30\ cm^{-1}$, because of the spin-orbit coupling in the $^2\Pi_u$ state.

From the FC simulation of band B, we derive the $ADE(C\ ^2\Sigma_u^+)$ of 5.464 ± 0.008 eV, yielding an energy separation between the neutral $A\ ^2\Pi_g$ and $C\ ^2\Sigma_u^+$ states of $11740\pm90\ cm^{-1}$ or 1.456 ± 0.011 eV. The calculated $^2\Pi_g$-$^2\Sigma_u^+$ separation underestimates the experimental finding by only 4%. The small vibrational excitation for band B denotes a small geometry change upon removing the $12\sigma_u$ electron. From the FC simulation, we derive the totally symmetric stretching mode of $720\pm30\ cm^{-1}$ with an associated $|\Delta r_{Ga-O}|$

of 0.02 ± 0.01 Å for the $^2\Sigma_u^+$ state. The computed frequency is in excellent agreement with the best-fit result, whereas the calculated Δr_{Ga-O} is 0.01 Å. No doublet splitting was observed for band B, consistent with our assignment of the $^2\Sigma_u^+$ state.

All the three bands show smaller spectral features labeled as HB that are assigned to transitions from vibrationally excited levels of GaO_2^-. The spacing between the HB peaks and the vibronic origins of bands X, A, and B provides the first experimental determination of the anion symmetric stretching mode of $770\pm30\ cm^{-1}$, 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.*[31] 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$\leftarrow$linear electronic transitions. From theoretical calculations[32] it is found that the neutral AlO_2 has two almost isoenergetic isomers with the linear geometry being the global minimum. On the other hand, from our computations and other calculations[21–23] the lowest energy structure of the neutral GaO_2 appears to be bent with an apex angle of 38°. The AlO_2^- 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; $T_e(A\ ^2\Pi_u)$ and $T_e(B\ ^2\Sigma_u^+)$ 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 EA(GaO) and $T_e(A\ ^2\Pi)$. The vibrational frequencies for the anion ground state and the neutral first excited state were also obtained. Moreover, the resolved splitting of band A allowed the determination of the spin-orbit coupling of the $A\ ^2\Pi$ state. The GaO_2^- PE spectrum shows three bands X, A, and B that also present resolved vibrational structure. These bands are assigned to linear$\leftarrow$linear electronic transitions. From the electronic structure calculations, we ascertained that the neutral GaO_2 has two almost isoenergetic isomers, with the bent structure being the global minimum at only 63 meV below the linear structure. From the FC analysis, we obtained the values of the symmetric stretching modes of the anion ground state, and three neutral linear excited electronic states, together with the bond distance changes for these transitions. Energy separations of the $B\ ^2\Pi_u$ and $C\ ^2\Sigma_u^+$ relative to the first excited state $A\ ^2\Pi_g$ were derived from the experimental ADE values. We did not observe the bent$\leftarrow$linear electronic transition because of the very different geometries of the linear anion and

bent neutral with and 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 AlO_2^-/AlO_2 molecules.

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