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Vibrationally resolved anion photoelectron spectra of the low-lying electronic states of GaP_2^-, Ga_2P^-, and $Ga_2P_3^-$

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Abstract. Anion photoelectron spectra of GaP_2^-, Ga_2P^-, and $Ga_2P_3^-$ have been taken at photodetachment wavelengths of 266 nm (4.657 eV), 355 nm (3.493 eV), 416 nm (2.977 eV), and 498 nm (2.491 eV). Using this variety of wavelengths has allowed us to vibrationally resolve the low-lying electronic states of these species. We report electron affinities, term values, and vibrational frequencies of the corresponding neutral and anion states where possible. Results are in qualitative agreement with current *ab initio* studies.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters – 33.60.Cv Ultraviolet and vacuum ultraviolet photoelectron spectra

1 Introduction

Anion photoelectron spectroscopy combines size-selectivity with reasonable spectral resolution, making it an indispensable method for investigating the spectroscopy of semiconductor clusters. In an effort to understand how the electronic and vibrational structure of semiconductor clusters changes as a function of size, we have recently completed a study of the electronic structure of Ga_xP_y clusters having 18 atoms or fewer [1]. Here, we carry these studies further by obtaining higher resolution, vibrationally resolved anion photoelectron spectra of GaP_2^-, Ga_2P^-, and $Ga_2P_3^-$ clusters.

The vibrational spectroscopy of III-V semiconductor clusters has been limited to a few studies. Li *et al.* [2] used Fourier-transform infrared spectroscopy to record the vibrational spectra of the diatomic and triatomic isotopomers of GaP, GaAs, and GaSb in an inert gas matrix. Arnold *et al.* [3] characterized the spectroscopy of the In_2P^-/In_2P and InP_2^-/InP_2 systems using zero electron kinetic energy (ZEKE) spectroscopy. Lemire *et al.* [4] have studied diatomic GaAs via resonant two-photon ionization spectroscopy. Their studies afforded spectroscopic constants for the $^3\Sigma^-$ ground state and the $3^3\Pi$ spin-orbit states.

Andreoni [5] and Balasubramanian [6–9] have carried out theoretical investigations of Ga_xP_y clusters. Andreoni used the Car-Parrinello molecular dynamics method to study the structures, stability, and melting of small stoichiometric GaAs, GaP, and AlAs clusters. Balasubramanian and Feng [6–9] have performed *ab initio* calculations on a series of Ga_xP_y clusters with five or fewer atoms. They calculated ground and excited state geometries and energies at the complete active space self-consistent field (CASSCF) and multi-reference singles-doubles configuration interaction (MRSDCI) levels of theory with a basis set composed of relativistic effective core potentials and valence Gaussian basis sets.

Here we present vibrationally resolved photoelectron spectra of the low-lying electronic states of selected Ga_xP_y clusters. Our term values are compared with Balasubramanian's *ab initio* results. Identification of the vibrational structure is made by comparison with our previous study on the In_2P^-/In_2P and InP_2^-/InP_2 systems.

2 Experimental

The anion photoelectron spectrometer used in this study has been described in detail previously [10, 11]. Cluster anions are generated in a laser ablation/pulsed molecular beam source. A rotating and translating single crystal disc of GaP (Crystallode Inc.) is ablated with the second harmonic (532 nm) of a pulsed Nd:YAG laser. The laser pulses are typically 5.0–7.5 mJ/pulse before focussing onto the target with a 1 m lens. The resulting plasma is entrained in a supersonic beam of argon, which then passes through a skimmer into a differentially pumped region. Negative ions in the beam are extracted perpendicular to their flow direction by a pulsed electric field and injected into a linear reflectron time-of-flight (TOF) mass spectrometer [12, 13], affording a mass resolution $m/\Delta m$ of 2000. The ions of interest are selectively photodetached with photons having wavelengths of 266 nm (4.657 eV), 355 nm (3.493 eV), 416 nm (2.977 eV), and 498 nm (2.491 eV). The photon wavelengths, 266 and 355 nm, were obtained by frequency quadrupling and tripling the fundamental of

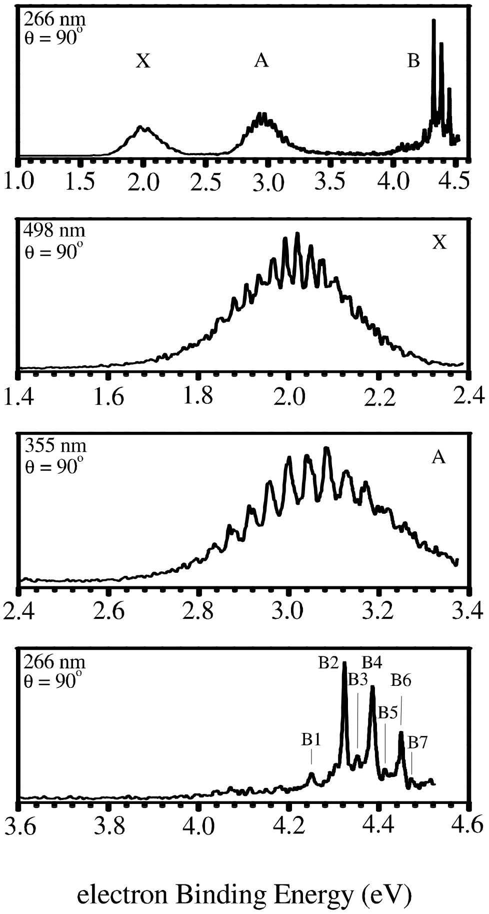

Fig. 1. Photoelectron spectra of GaP_2^- taken at the photodetachment wavelengths of 266, 355, and 498 nm. Laser polarization angle is $\theta = 90°$ with respect to the direction of electron collection.

a pulsed Nd:YAG laser. To generate light at 416 and 498 nm the third harmonic was passed through a Raman cell filled with hydrogen at high pressure (325 psig). The electron kinetic energy (eKE) distribution is determined by TOF analysis in a 1 m field-free flight tube. The energy resolution is 8–10 meV at 0.65 eV eKE and degrades as $(\text{eKE})^{3/2}$ at higher eKE; this is about a factor of three better than in our previous study of Ga_xP_y clusters, in which a shorter (30 cm) flight tube was used. The laser polarization angle can be rotated by means of a half-wave plate. Due to the natural isotope abundance of gallium (Ga^{69}:Ga^{71}, 100.0 : 66.4) each cluster stoichiometry has a mass distribution. In each case the most intense mass was photodetached.

3 Results

Photoelectron spectra have been taken of GaP_2^-, Ga_2P^-, and $Ga_2P_3^-$. While several other $Ga_xP_y^-$ clusters were investigated, these were the only clusters showing vibrational resolution apart from GaP^- which will be treated in a future publication. The spectra are shown in Figs. 1–3, respectively. The photoelectron spectra are reported in electron binding energy, eBE, which is defined as $\text{eBE} = h\nu - \text{eKE}$. The polarization angle, θ, is the angle between the electric vector of the photon and the axis along which the electrons are detected. Peaks having different polarization dependences generally result from transitions to different neutral electronic states, hence this is a useful means of distinguishing contributions from overlapping electronic bands. Our spectral resolution is optimal for features at low electron kinetic energy according to the relationship in the experimental section. Varying the wavelength allows us to resolve spectral features as seen for feature X in the top two panels of Fig. 1.

4 Analysis and discussion

In a previous study [1] we obtained low-resolution (~ 30 meV) anion photoelectron spectra of $Ga_xP_y^-$ $(x, y \leq 9)$ at 266 nm. As a result we were able to identify the electronic states of the smaller Ga_xP_y clusters based on the calculations of Balasubramanian and coworkers [6–9]. In our previous study, we were only able to compare changes in vertical detachment energies with the term energies calculated by Balasubramanian. The electronic state assignments made in our previous paper [1] are assumed here. However, the new spectra are vibrationally resolved allowing us to estimate the adiabatic electronic affinities and term values. Table 1 compares the results of the present and the previous studies. The assignment of the vibrational structure depends heavily on the previous results of the ZEKE/PES spectra taken of the InP_2^-/InP_2 and In_2P^-/In_2P systems [3].

4.1 GaP_2

Figure 1 shows the photoelectron spectra of GaP_2^- taken at 266, 355, and 498 nm and at a polarization angle of $\theta = 90°$. Spectra taken at other polarization angles show no overlapping electronic transitions, so this polarization optimally represents these electronic states. The top panel shows the entire spectrum taken at 266 nm. Three electronic states are visible labeled X, A, and B. In accordance with our previous study [1] we assign features X, A, and B to the $^2B_2$, $^2A_1$, and $^2B_1$ states. At the appropriate wavelength each electronic state shows resolved vibrational structure. Feature A is similar in appearance to feature X having a FWHM of 319 and 291 meV, respectively, indicative of a large geometry change. Feature B shows the most clearly resolved structure.

The $^2B_2$ ground state is calculated [7] to have a C_{2v} geometry with an acute ∠P−Ga−P bond angle of 43.9°. A preliminary Franck-Condon analysis allows us to estimate the origin to occur at 1.726 eV, yielding an electron affinity of the same value. The vibrational structure reveals a progression with an average spacing of 240 cm^{-1}. In analogy to the ground state we are able to estimate

Table 1. Vibrational fundamentals, term values, and electron affinities of GaP_2^-/GaP_2 and Ga_2P^-/Ga_2P.[1]

Molecule	State	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Term value (eV)	Previous[2] (eV)
GaP_2^-	$\tilde{X}\,^1A_1$	589			−1.726	−1.78
GaP_2	$\tilde{X}\,^2B_2$		240		0.000	
		(322)	(220.9)			
	$\tilde{A}\,^2A_1$		329		1.250	0.99
					(1.07)	
	$\tilde{B}\,^2B_1$	500	234		2.598	2.34
					(2.33)	
Ga_2P^-	$\tilde{X}\,^1A_1$	403			−2.507	−2.42
Ga_2P	$\tilde{X}\,^2B_1$		64		0.000	
				(280.5)		
	$\tilde{A}\,^2B_2$	331			0.251	0.27
					(0.09)	

[1] Frequencies and term values in parenthesis are from [2] and [7], respectively.
[2] Ref. [1].

the vibrational frequency and the origin of the first excited $^2A_1$ state to be 329 cm^{-1} and 2.976 eV, respectively. This affords a term value of 1.250 eV. Balasubramanian [7] calculates this splitting to be 1.07 eV, a difference of ∼ 250 meV. The ZEKE spectra of InP_2^- taken by Arnold *et al.* [3] show progressions in the $\tilde{X}$ and $\tilde{A}$ states having frequencies of 190 and 287 cm^{-1} and they were assigned to the ν_2 bending modes of each state, respectively. We make the same assignment to the observed progressions in the $\tilde{X}$ and the $\tilde{A}$ states of GaP_2. This gives a bending frequency of 240 and 329 cm^{-1} for these states, respectively. The assignment of the ground state frequency is also in accord with the frequency of 220.9 cm^{-1} reported by Li *et al.* [2].

Feature B is much less congested than the two bands previously discussed, allowing us to see more detail. The most intense peak, B2, represents the origin of the $^2B_1$ state and is located at 4.324 eV, affording a term value of 2.598 eV. The calculated value [7], 2.33 eV, is also ∼ 250 meV below the experimental value. The most intense progression incorporating peaks B2, B4, and B6 exhibits a comparatively large frequency of 500 cm^{-1}. This mode most likely corresponds to P-P motion and we assign it to ν_1. Peak B1 is a hot band corresponding to the same mode in the ion with a frequency of 589 cm^{-1}. Combination bands with a frequency of 234 cm^{-1} are indicated by peaks labeled B3, B5, and B7. This frequency is similar to the ground state ν_2 mode, and we assign it to the ν_2 bending mode. Electron affinities, term values, vibrational frequencies, and spectroscopic assignments for the triatomic species are given in Table 1.

4.2 Ga_2P

Figure 2 shows the photoelectron spectra of Ga_2P^- taken at the wavelengths of 355 and 416 nm and at the polariza-

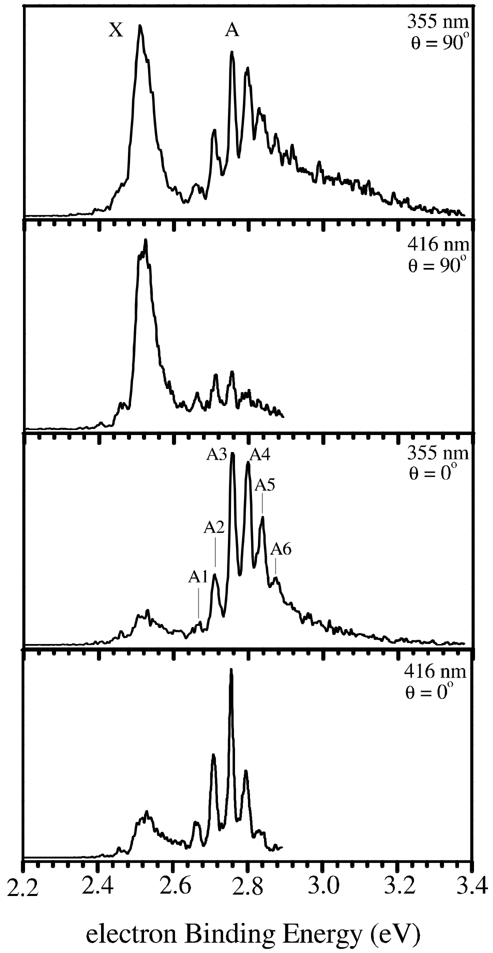

Fig. 2. Photoelectron spectra of Ga_2P^- taken at the photodetachment wavelengths of 355 and 416 nm. Laser polarization angles are $\theta = 0°$ and 90° with respect to the direction of electron collection.

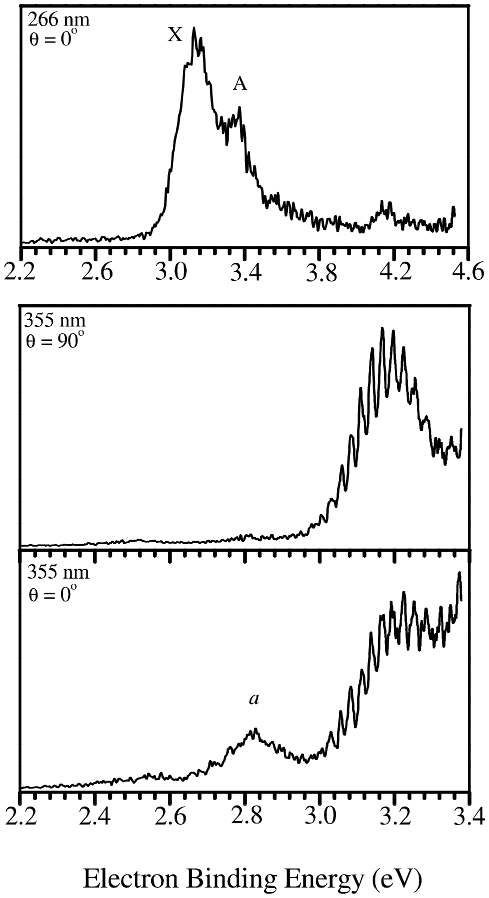

Fig. 3. Photoelectron spectra of Ga$_2$P$_3^-$ taken at the photodetachment wavelength of 266 and 355 nm. Laser polarization angles are $\theta = 0°$ and 90° with respect to the direction of electron collection.

tion angles of $\theta = 0°$ and 90° for each wavelength. These spectra show two electronic states having very different polarization dependences. Feature X is an intense feature showing several barely resolved peaks in the 416 nm spectrum taken at $\theta = 90°$. Both features X and A are strongly polarization dependent and are well separated. The transition to the first excited state results in an extended progression labeled A1-A6. We were previously [1] able to assign features X and A to the ^{2}B$_1$ and ^{2}B$_2$ states, respectively.

The ^{2}B$_1$ ground state is calculated [7] to have a C$_{2v}$ geometry with a ∠Ga–P–Ga bond angle of 111.0°. Li *et al.* [2] observe a vibrational transition of 280.5 cm^{-1}, assign it to the asymmetric stretch, ν_3, and estimate the bond angle to be 85.7°. The higher resolution spectrum taken at 498 nm barely resolves vibrational structure spaced by 64 cm^{-1}. This yields an electron affinity of 2.507 eV. Again we compare our spectra with the previously studied In$_2$P$^-$/In$_2$P system. The appearance of the 266 nm In$_2$P$^-$ and Ga$_2$P$^-$ anion photoelectron spectra are very similar [3]. Both show a single intense transition to the ground state and a broader Franck-Condon profile in the first excited state. Arnold *et al.* [3] observe two active modes in the $\tilde{X}$ state of In$_2$P. They reported the most active mode to be the ν_2 bend with a frequency of 47 cm^{-1}. A less intense combination band involving the symmetric stretch ν_1 was measured to be 204 cm^{-1}. By analogy, we assign the 64 cm^{-1} frequency to the neutral bending mode, ν_2.

Peak A3 is the most intense peak of the first excited state and is identified as the origin of the ^{2}B$_2$ state located at 2.758 eV. This gives a term value of 0.251 eV. Balasubramanian's value [7] of 0.09 is not in accord with our measurement. Peaks A3-A6 form a progression in the neutral of 331 cm^{-1}. A progression of hot bands, A1 and A2 afford an anion frequency of 403 cm^{-1}. The transition to the $\tilde{A}$ state was not observed in the ZEKE spectrum of In$_2$P$^-$ because it is not allowed. The photoelectron spectrum of In$_2$P$^-$ does not show resolved structure either. However, peaks A3-A6 in our spectra show a progression of 331 cm^{-1} in the first excited state of the neutral. The vibrational frequency of diatomic GaP is 283.6 cm^{-1} as reported by Li *et al.* [2]. The frequency we measure is therefore too high to be a bending mode. According to photoelectron selection rules we expect to preferentially see activity in the totally symmetric modes. Therefore we assign the frequency of 331 cm^{-1} to the totally symmetric mode, ν_1.

4.3 Ga$_2$P$_3$

The top panel of Fig. 3 contains a 266 nm spectrum of Ga$_2$P$_3^-$ taken at a polarization angle of $\theta = 0°$. The lower two panels show photoelectron spectra taken at 355 nm with polarization angles of $\theta = 0°$ and 90°. The 266 nm spectrum clearly shows two electronic states, labeled X and A, centered at 3.14 and 3.35 eV, respectively. The 355 nm spectra show an extended vibrational progression that follows a polarization dependence. In addition, the 355 nm spectrum taken at $\theta = 0°$ reveals another feature labeled *a* located at 2.84 eV which is absent in the same polarization of the 266 nm spectrum.

Analysis of the final cluster, Ga$_2$P$_3$, is less straightforward. No experimental data is available for comparison. Current *ab initio* results [8] show a trigonal bipyramidal (D$_{3h}$) ^{2}A$_2''$ state is calculated to lie only 0.05 eV above the distorted trigonal bipyramidal ^{2}B$_1$ state, resulting from Jahn-Teller distortion of a ^{2}E$''$ state. The polarization dependence indicates that feature X and A are two overlapping electronic states. In our spectra they appear to be separated by much more than the calculated value of 0.05 eV. However we can not confidently identify features X and A. Based on Franck-Condon simulations we estimate the origin of feature X to be at 3.004 eV. Vibrational analysis of feature X shows a frequency of 223 cm^{-1} which most likely involves Ga–P stretching motion. The identity of feature *a* is also uncertain. It only appears in the 355 nm spectra, most dominantly at $\theta = 0°$. The possibility of a two-photon process involving photodissociation and subsequent photodetachment of a daughter ion is unlikely.

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