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LETTERS

Spectroscopic Constants for $GaAs_2^-$, $GaAs_2$, Ga_2As^-, and Ga_2As

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Low-lying electronic states of Ga_2As^-, Ga_2As, $GaAs_2^-$, and $GaAs_2$ are investigated using complete active space multiconfiguration self-consistent field technique followed by multireference singles + doubles configuration interaction calculations that included 5.5 million configurations. Our computations reveal the existence of two excited states of the Ga_2As^- anion close to the neutral ground state of Ga_2As, which also exhibits two nearly degenerate states of C_s and C_{2v} geometries. Assignments to the recently observed anion photodetachment and far-IR spectra are suggested.

I. Introduction

The current investigation was stimulated by a recent observation of Ga_2As and $GaAs_2$ molecules and their anions in Neumark's laboratory[1] using the anion photoelectron spectroscopy in the 1.5−3.5 eV binding energy region. Computational studies of the electronic states of both anions and neutral species would be very valuable in aiding the assignments of the observed spectra and in the interpretations. Weltner and co-workers[6] have reported the far-infrared spectra of Ga_2As and $GaAs_2$ among other species in Ar and Kr gases condensed on Au surfaces at 4 K. As we show here, the Ga_2As cluster and its anion are particularly exciting species due to potentially overlapping excited states of the anion and nearly degenerate neutral ground states with distorted (C_s) and isosceles triangular (C_{2v}) structures. Because of the shallow bending potential energy surfaces and the possibility of distortion to a lower symmetry due to the interaction of two nearly degenerate states, Ga_2As is very challenging for computational studies as different levels of theories tend to yield different results.

In general, generation and spectroscopic constants of the group III−V and group IV semiconductor clusters have been the topic of several experimental and theoretical studies in recent years.[1−13] The group III−V compounds are used in fast microelectronic devices and light-emitting diodes. Our comprehension of mechanisms of fabrication processes such as chemical etching depends on the thermodynamic and kinetic data of the chemical species, which in turn require elucidation of the low-lying states of these species. Furthermore, theoretical and experimental studies of such clusters provide significant insight into the properties of these species as a function of their sizes, as these species exhibit significant variations in their properties as a function of their sizes.

In recent years a number of experimental techniques[1−8] have been employed to probe the low-lying electronic states of these clusters. In particular, Neumark and co-workers[1,3,4,7] have harnessed the anion photoelectron spectroscopic method to investigate the electronic states of In_xP_y, Ga_xP_y, and Al_xP_y clusters among other species.

There is very little known on the low-lying electronic states of Ga_2As^- and Ga_2As. In a previous study, Das and the author[13] have studied a bent state of Ga_2As ($^2B_1$) and a linear state ($^2\Pi_u$), which was located 0.12 eV above the bent $^2B_1$ state. The electronic states of the Ga_2As^- anion have not been studied at all. As shown here, even the ground state of Ga_2As is ambiguous in that there are two nearly degenerate states with a distorted C_s geometry and a C_{2v} geometry. There are other low-lying states, some of which are not minima but saddle points. Moreover, the Ga_2As^- anion is shown to exhibit several excited states among which at least two states fall in the region of the low-lying states of the neutral Ga_2As. There are previous studies

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on $GaAs_2$,[10,11] which have revealed bent low-lying states. In the current study, the electronic states of the title anions and their neutral molecules are investigated using relativistic ab initio CASSCF/MRSDCI techniques that included 5.5 million configurations.

II. Method of Investigation

While the low-lying electronic states of $GaAs_2$ are relatively simple, Ga_2As is far more complex due to nearly degenerate $^3\Pi_u$ and $^3\Sigma_g^-$ states of Ga_2[10,20] which combine with the ^4S ground state of As[17] resulting in doublet and quartet electronic states for Ga_2As. The $GaAs_2^-$ anion is quite simple in that electron attachment to a single open-shell orbital in the low-lying doublet states of $GaAs_2$ would always yield the same closed-shell $^1A_1$ state, but Ga_2As^- could exhibit both closed-shell $^1A_1$ and open-shell triplet states.

The computations were made with relativistic effective core potentials (RECPS) for the Ga and As atoms with the outer $4s^24p^1$ and $4s^24p^3$ shells retained in the valence space, respectively. The RECPS together with the valence (3s3p) Gaussian basis sets[14] were augmented with an additional set of diffuse s and p functions and two sets of six-component 3d functions with $\alpha_{d1} = 0.2910$ and $\alpha_{d2} = 0.09$ for Ga and $\alpha_{d1} = 0.3880$, $\alpha_{d2} = 0.1185$ for As.

In the CASSCF computations, 4s and 4p orbitals of Ga and 4p orbitals of As were included in the active space spanning four a_1, three b_2, two b_1, and one a_2 orbitals, which we label 4321-CAS for $GaAs_2$. Nine electrons of $GaAs_2$ (and 10 for $GaAs_2^-$) were distributed in all possible ways among these orbitals at the CASSCF level. For the Ga_2As and Ga_2As^- species, we carried out a 4321-CASSCF in which all 11 electrons of Ga_2As (12 electrons of Ga_2As^-) were distributed in all possible ways.

The MRSDCI calculations included all configurations in the CASSCF with absolute values of coefficients ≥ 0.045 as reference configurations. These computations included single and double excitations from up to 25 reference configurations. Multireference Davidson corrections to the MRSDCI energies for uncoupled quadruple clusters were calculated and the energy separations thus computed were labeled as MRSDCI + Q results. The MRSDCI included up to 5 530 172 configurations, and full geometry optimizations were carried out at the MRSDCI level. The CASSCF/MRSDCI calculations were carried out using a modified version[15] of the ALCHEMY II codes[16] to include RECPs. The vibrational frequencies and infrared intensities (IR) were computed at the density functional theory (DFT;B3LYP) level together with analytical gradients and the same RECPs and basis sets as the ones used in CASSCF/MRSDCI computations. The computations of the distorted structure were considered in the C_s symmetry.

III. Results and Discussions

A. Electronic States of $GaAs_2$ and $GaAs_2^-$. Table 1 shows the optimized geometries and energy separations of the low-lying electronic states of $GaAs_2^-$ and $GaAs_2$ at the MRSDCI level. The $^2B_2$ state is unequivocally the ground state of $GaAs_2$, while the closed-shell $^1A_1$ state is the ground state of $GaAs_2^-$. The equilibrium geometries of both neutral and anionic clusters are isosceles triangles with very acute apex angles. The Ga−As bond lengths tend to become longer as the apex angle becomes more acute, while the As−As bond length contracts. Accordingly, the Ga−As bond lengths are significantly contracted to 2.586 Å for the anion from 2.80 Å for the neutral. The Ga−As bond contraction upon electron attachment is consistent with significant Ga−As character of the open-shell orbital of the neutral $GaAs_2$.

TABLE 1: MRSDCI Geometries and Energy Separations of the Electronic States of $GaAs_2^-$ and $GaAs_2$

species	state	θ^a (deg)	Ga−As	As−As (Å)	E (eV)	μ_e (D)[b]
$GaAs_2^-$	$^1A_1$	52.7	2.586	2.296	−1.50 (−1.61)[c]	
$GaAs_2^-$	$^3B_1$	51.5	2.651	2.303	−0.91 (−1.29)[c]	
$GaAs_2^-$	$^3A_2$	66.9	2.37	2.613	−0.59 (−0.84)[c]	
$GaAs_2$	$^2B_2$	45.9	2.80	2.184	0.0	1.449
$GaAs_2$	$^2A_1$	60.7	2.40	2.425	0.71 (0.65)	1.271
$GaAs_2$	$^2A_2$	46.5	2.90	2.290	1.09 (1.09)	3.20
$GaAs_2$[d]	$^4B_1$	58.2	2.496	2.429	1.26	1.267
$GaAs_2$	$^2B_1$	51.4	2.76	2.394	2.13 (2.08)	0.46

[a] θ = apex angle, Ga−As = two equal sides of the isosceles triangle. [b] Ga^+As^- polarity. [c] Numbers in parentheses are MRSDCI+Q values. [d] DFT level.

The $^2A_1$ excited state is 0.71 eV above the $^2B_2$ ground state at the MRSDCI level, while the $^4B_1$ and $^2B_1$ electronic states are 1.26 and 2.13 eV above the ground state, respectively. As seen from Table 1, We also find a $^2A_2$ electronic state around 1.25 eV above the ground state. However, the optimized geometry is a saddle point due to distortion into a more stable asymmetric structure. The optical transition to this state from the ground state of the neutral cluster is dipole-allowed and hence this state should be observable in its distorted form in optical spectroscopy of $GaAs_2$. There exists a Ga−As−As linear permutational isomer with a $^2\Pi$ state.[13] However, this state is a saddle with an electronvolt higher energy than the ground state of $GaAs_2$, and it rearranges to the bent structure.

The first $^3B_1$ excited state with a very acute isosceles triangular geometry has an energy separation of 0.59 eV from the ground state. A $^3A_2$ state is found at 0.86 eV above the ground state of the anion. Thus, there is no excited-state degenerate with the ground state of the anion.

Table 3 shows the vibrational frequencies, IR intensities, and zero-point corrections for the low-lying electronic states of $GaAs_2^-$ and $GaAs_2$ obtained at the DFT(B3LYP) level of theory. The DFT equilibrium geometries are found to be close to the MRSDCI geometries with bond lengths within 0.01−0.06 Å and bond angles within 5°. The bond lengths differ typically by 0.01 Å with the exception of the $^2A_1$ state for which the As−As base bond length differs by 0.06 Å. Thus, the vibrational frequencies shown in Table 3 should have reasonable accuracy. As seen from Table 3, both symmetric and asymmetric stretches have comparable IR intensities and the $\nu_2(A_1)$ modes are more intense. This is comprehensible in view of the strong As−As bonding at the base of the isosceles triangle which would offer large resistance for bending leading to both large and strong $\nu_2(A_1)$ frequency modes for the electronic states of $GaAs_2$. The $^2A_2$ state with a stationary point shown in Table 1 has an imaginary B_2 frequency and thus it is not a minimum along the asymmetric stretch, although it is a minimum for bending and symmetric stretching modes.

Weltner and co-workers[6] have obtained the far-infrared spectra of small gallium arsenide molecules obtained by laser vaporization into Ar and Kr gases followed by condensation on a Au surface at 4 K. The two natural isotopes of Ga would produce two topomers for $GaAs_2$, thus Li et al. assigned the strong doublet structure at 174 cm^{-1} to a symmetric stretch of $GaAs_2$ with a very acute geometry and an apex angle of 38.2°. As seen from Table 3, indeed we compute the $\nu_2(A_1)$ symmetric stretch at 162.5 cm^{-1} with a strong IR intensity (20.37) for $GaAs_2$ consistent with Li et al.[6] A weak band at 160 cm^{-1} was tentatively assigned to the ν_1 mode of $GaAs_2$ by Li et al. However, as we see from Table 3, the $\nu_1(A_1)$ mode occurs at a considerably higher frequency (382.5 cm^{-1}) and with a too small intensity and thus it cannot be due to the $\nu_1(A_1)$ mode of $GaAs_2$. The origin of this band is puzzling.

The leading configuration for the ground state of $GaAs_2$ is $1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_2^2 1b_1^2 2b_2^1$, while the $^2A_1$ state arises from the promotion of an electron from $4a_1$ to $2b_2$. The compositions of these orbitals are analogous to the isovalent species described before.[12,13] While the ground state of the $GaAs_2^-$ anion is a closed-shell $^1A_1$ state, the $^3B_1$ electronic state of the $GaAs_2^-$ anion is formed from $^1A_1$ through promotion of an electron from $2b_2$ to $1a_2$. The higher $^3A_2$ state is formed through promotion of an electron from $4a_1$ to $1a_2$. Since the $4a_1$ orbital is energetically lower, the $^3B_1$ state is lower than the $^3A_2$ state. Both $^3B_1$ and $^3A_2$ states are considerably complex in that 25 reference configurations make nonnegligible contributions.

The Mulliken populations of the electronic states for $GaAs_2$ and $GaAs_2^-$ shown in Table 4 reveal that the gross populations of Ga are between 2.53 and 2.75 for the doublet states, while the total As populations are between 5.13 and 5.24. The excess populations of 0.126−0.236 on As are due to charge transfer from Ga to As consistent with the dipole moments of $GaAs_2$. The $^2B_2$ ground state is composed of Ga ($s^{1.831}p^{0.771}$) and As ($s^{1.840}p^{3.150}$), while the gross populations for $^2A_1$ are Ga ($s^{1.229}p^{1.318}$) and As($s^{1.839}p^{3.163}$). The primary difference in the populations between the two states arises from the s and p populations on Ga atoms. The Ga (4s) population is 1.831 in $^2B_2$, which is obviously larger than the corresponding population in $^2A_1$ (1.229), while the Ga (4p) population is 0.771 in $^2B_2$, which is noticeably smaller than the corresponding population in $^2A_1$ (1.318). The Mulliken populations are consistent with the nature of the orbitals. The difference between the two states lies in the occupancies of the $4a_1$ and $2b_2$ orbitals. The $4a_1$ bonding orbital is fully occupied in the $^2B_2$ ground state with significant s participation from Ga, and it thus increases the Ga (4s) population. The doubly occupied $2b_2$ orbital in $^2A_1$ is composed of Ga (p_y) and As$_1$ (p_z)−As$_2$(p_z) resulting in a larger p population of 1.318 on Ga.

The Mulliken populations of the $^1A_1$ ground state of $GaAs_2^-$ are Ga($s^{1.79}P^{1.11}$) and As($s^{1.96}P^{3.43}$) compared to the Ga ($s^{1.83}p^{0.81}$) and As ($s^{1.84}p^{3.13}$) populations of the neutral $^2B_2$ ground state. Consequently, the two As atoms receive 78% of the attached electronic charge.

We restrict comparison of our work to the recently observed photodetachment spectra to qualitative details, as the spectra are yet to be published.[1] Our computed MRSDCI +Q electron affinity of the $GaAs_2$ molecule is in good agreement with the measured electron affinity considering the complexity of the electron correlation treatment. As seen from Table 1, the first excited state of the $GaAs_2^-$ anion is a $^3B_1$ state and it is well above the ground state (0.6 eV). Therefore, the possibility of electronic transitions originating from another state of the anion close to the ground state is ruled out, and the anion detachment spectra should clearly originate from a single closed-shell ground state of the ion. The anion detachment spectra confirm the existence of a low-lying excited state for $GaAs_2$ that we have computed at 0.7 eV shown in Table 1. On the basis of the computed results, we assign the lowest vibrational progression to the X^2B_2 ground state of the neutral $GaAs_2$, while the second vibrational progression should be assigned to the A^2A_1 excited state.

As seen from Table 1, there is a $^4B_1$ excited state for the neutral $GaAs_2$ at 1.3 eV above the ground state at the DFT-(B3LYP) level. The state has a stable minimum at the geometry shown in Table 1, consistent with the vibrational frequencies reported in Table 3. However, the $^2A_2$ excited state at 1 eV above the ground state has an imaginary B_2 asymmetric stretch frequency suggesting that it would distort to a C_s geometry resulting in a $^2A''$ state. While it is not clear if these states are observable in the anion photodetachment spectra, both states are observable in optical spectra, but the quartet state would exhibit lower intensity since it is spin-forbidden.

TABLE 2: MRSDCI Geometries and Energy Separations (MRSDCI+Q in parentheses) of Ga_2As^- and Ga_2As

species	state	Ga−As−Ga (deg)	Ga−As[a] (Å)	Ga−Ga (Å)	E (eV)[c]	μ_e (au)[b]
Ga_2As^-	$^1A_1$	98.5	2.37	3.591	−2.20 (−2.17)	
Ga_2As^-	$^3B_2$	65	2.456	2.639	−1.15 (−1.30)	
Ga_2As^-	$^1B_2$	65	[2.50]	2.686	−0.87	
Ga_2As^-	$^3B_1$				−0.5	
Ga_2As^-	$^3A_2$				−0.4	
Ga_2As^-	$^1B_1$	72	2.58	3.032	−0.33 (−0.37)	
Ga_2As	$^2A'$	90.3	2.283 2.534	3.41	0.0 (0.025)	(0,0.989, −1.624)
Ga_2As	$^2B_2$	79.9	2.407	3.091	0.09 (0.0)	−1.703
Ga_2As^-	$^3A_1$	74	2.62	3.154	0.27 (0.19)	
Ga_2As	$^2B_1$	108.2	2.52	4.083	0.16 (0.22) 0.03 (DFT)	−1.334
Ga_2As	$^2A_1$	118.5	2.47	4.245	0.24 (0.19)	−0.653
Ga_2As	$^4B_2$	68.0	2.43	2.718	1.00 (0.94)	−1.202
Ga_2As	$^4B_1$	120.6	2.45	4.256	2.2 (DFT)	

[a] Ga−As side bond lengths. [b] Negative polarity means Ga^+As^- polarity. For $^2A'$ state this is a vector with two non-zero components. [c] Numbers in parentheses are MRSDCI+Q results.

B. Electronic States of Ga_2As and Ga_2As^-. As seen from Table 2, while the ground state of the anion is unambiguously a closed-shell $^1A_1$ state, the neutral Ga_2As is far more complicated. We find two nearly-degenerate states, one with an unsymmetrical triangular structure with a C_s geometry, while the other has a symmetrical isosceles triangular structure, which calls for further analysis. As seen from Table 2, the $^2B_2$ state and the $^2A_1$ states exhibit stationary points at the MRSDCI level. However, at the DFT level both states exhibit imaginary B_2 vibrational frequencies but the DFT method predicts too long a base (Ga−Ga) bond. The imaginary B_2 frequency suggests distortion into a C_s structure. Both the states correlate into a $^2A'$ state in the C_s group and thus the C_s minimum originates from this distortion. As seen from Table 2, the MRSDCI method confirms the existence of the $^2A'$ minimum. However, it should be mentioned that the $^2B_2$ state has a strong multireference character with 15 reference configurations contributing to this state. As a result, the DFT method yields a different optimized geometry for the $^2B_2$ state, especially with respect to the Ga−Ga base bond length, which comes out to be too long (0.5 Å), and therefore the DFT frequencies cannot be considered as very reliable due to the multireference character of this state. The Ga−As bond lengths of the C_s structure are not too far off at the two levels, but the Ga−Ga bond is again longer at the DFT level. As seen from Table 2, in fact, the $^2B_2$ state is only 0.09 eV above the $^2A'$ state at the MRSDCI level, although at the MRSDCI+Q level, the symmetrical $^2B_2$ state seems to be favored. On the other hand, at the DFT level, the $^2A'$ state is clearly favored. This suggests that the electron correlation effects from other reference configurations seem to be important in stabilizing the symmetrical structure.

TABLE 3: Vibrational Frequencies and Zero-Point Energies of the Electronic States of $GaAs_2^-$, $GaAs_2$, Ga_2As^-, and Ga_2As

system	state	$\nu_1(A_1)$ (IR intens)	$\nu_2(A_1)$ (IR intens)	$\nu_3(B_2)$ (IR intens)	ZPC (kcal/mol)
$GaAs_2^-$	$^1A_1$	329.6 (5.60)	198.1 (10.86)	152.1 (6.24)	0.97
$GaAs_2$	$^2B_2$	382.5 (0.59)	162.5 (20.37)	80.3 (0.68)	0.89
$GaAs_2$	$^2A_1$	311.6 (0.15)	238.7 (3.55)	161.9 (0.27)	1.02
$GaAs_2$	$^4B_1$	271.7 (0.31)	204.3 (9.39)	77.8 (0.14)	0.79
Ga_2As^-	$^1A_1$	240.5 (9.00)	46.5 (0.05)	275.3 (85.38)	0.80
Ga_2As	$^2A'$ (C_s)	182.7 (14.14)	50.4 (0.059)	265.6 (12.49)	0.71
Ga_2As	$^2B_1$	194.5 (7.88)	43.0 (0.029)	225.0 (91.4)	0.66
Ga_2As	$^4B_1$	172.8 (2.51)	35.9 (0.335)	169.2 (31.8)	0.54

As seen from Table 2, the $^2B_1$ state is nearly degenerate with both $^2A'$ and $^2B_2$ states at both DFT and MRSDCI levels. In fact, allowing for the computation in C_s symmetry leads to an optimized structure with C_{2v} symmetry in this case. This is consistent with the real vibrational frequencies for this state shown in Table 3. This state is only 0.03 eV above the $^2A'$ state at the DFT level, but at the MRSDCI level this state is 0.16 eV higher than the $^2A'$ state. Clearly this state should be observable, as it exhibits a minimum at all levels. Another very interesting feature is that the $^1B_1$ excited state of the Ga_2As^- anion is below and close to the neutral ground state of Ga_2As. We also find a $^3A_1$ excited state of the anion but this state is above the neutral ground state. The next excited $^4B_2$ state lies an electronvolt above the ground state. The next excited $^4B_1$ state, which has a stable minimum (Table 3), is 2.2 eV above the ground state and is thus not observable in the photodetachment spectra. As seen from Table 3, in contrast to $GaAs_2$, the electronic states of Ga_2As exhibit smaller $\nu_2(A_1)$ bending vibrational frequencies, consistent with weaker bonding at the Ga−Ga base.

Electronic transitions from the C_s unsymmetrical $^2A'$ state are dipole-allowed to the $^2B_2$ and $^2B_1$ states. Likewise, electronic transitions from the symmetrical $^2B_2$ electronic state are dipole-allowed to the $^2A_1$ and $^2A_2$ states but not to the $^2B_1$ state. Thus, optical spectroscopy could contrast the unsymmetrical and symmetrical structures, as transition to the $^2B_1$ state is allowed in the former case but forbidden in the latter case.

As seen from Table 2, the $^2A'$ state has an equilibrium geometry that differs from the ground state of the anion especially with respect to one of the Ga−As bond lengths, which is very long. The $^2B_2$ and $^2B_1$ electronic states too exhibit geometry variations from the ground state of the anion, the former exhibiting a smaller apex angle, thus a shorter Ga−Ga bond but comparable Ga−As distances, while $^2B_1$ exhibits an obtuse triangular geometry with elongated Ga−As bonds and no Ga−Ga bonding. Consequently, we predict considerable vibrational progression in the anion photodetachment spectra due to these geometry variations.

Li et al.[6] have observed a strong triplet at 205.4, 204.7, and 204.0 cm^{-1} in the far-infrared spectra of gallium arsenide molecules. On the basis of three topomers for Ga_2As due to two natural isotopes of Ga, the strong triplet was assigned by Li et al. to Ga_2As $\nu_3(B_2)$ asymmetric stretch. As seen from Table 3, the most consistent mode for this band is the $\nu_3(B_2)$ mode computed at 225 cm^{-1} with the strongest IR intensity for any mode of Ga_2As. Furthermore, the obtuse bond angle estimated by Li et al. (99.7°) is not too far from our computed bond angle of 108.2°. Considering that the $^2B_1$ state is nearly degenerate with the ^2A’ state, this assignment is supported by our computations. The weak band at 160 cm^{-1} is either due to the $\nu_1(A')$ stretching mode of Ga_2As (C_s) or the $\nu_1(A_1)$ mode of the $^2B_1$ state.

The leading configurations for the electronic states of Ga_2As and their orbital compositions are qualitatively analogous to the isovalent species considered before.[12,13] Briefly, the ground state originates from the $(1a_1^2 2a_1^2 3a_1^2\ 1b_2^2)1b_1^2 2b_2$ configuration, while the $^2B_1$ state arises from the $^1b_1^1 2b_2^2$ configuration. The $^2A_1$ state arises from the promotion of an electron from $3a_1$ to $2b_2$ relative to the ground state.

TABLE 4: Mulliken Population Comparison for the Low-Lying Electronic States of $GaAs_2$, Ga_2As, and Their Ions

		gross population							
		total		Ga			As		
species	state	Ga	As	s	p	d	s	p	d
$GaAs_2^-$	$^1A_1$	2.968	5.516	1.788	1.11	0.065	1.960	3.425	0.129
$GaAs_2^-$	$^3B_1$	2.888	5.556	1.808	1.008	0.072	1.975	3.455	0.126
$GaAs_2$	$^2B_2$	2.747	5.126	1.848	0.813	0.086	1.838	3.128	0.161
$GaAs_2$	$^2A_1$	2.612	5.194	1.879	0.682	0.051	1.847	3.188	0.159
$GaAs_2$	$^2A_2$	2.383	5.309	1.811	0.532	0.039	1.968	3.211	0.130
$GaAs_2$	$^2B_1$	2.528	5.236	1.781	0.707	0.04	1.815	3.13	0.251
Ga_2As^-	$^1A_1$	3.132	5.736	1.819	1.219	0.094	1.824	3.779	0.133
Ga_2As	$^2A'$	2.643 2.867	5.490	1.794 1.683	0.774 1.093	0.075 0.091	1.852	3.519	0.119
Ga_2As	$^2B_2$	2.652	5.697	1.802	1.562	0.07	1.936	3.634	0.128
Ga_2As	$^2B_1$	2.769	5.463	1.778	0.905	0.09	1.90	3.439	0.124
Ga_2As	$^2A_1$	2.710	5.581	1.806	0.828	0.076	1.871	3.604	0.101
Ga_2As	$^4B_2$	2.86	5.280	1.622	1.157	0.081	1.880	3.265	0.136

As seen from Table 4, all the electronic states of Ga_2As exhibit reduced Ga (s) and As(s) Mulliken populations compared to the atoms, while the As (p) populations are between 3.26 and 3.63 due to charge transfer from Ga to As (4p). The $^2B_2$ state of Ga_2As is composed of As($s^{1.94}p^{3.63}$) and Ga($s^{1.80}p^{0.78}$) Mulliken populations. The corresponding populations for the $^2B_1$ state are As ($s^{1.90}p^{3.44}$) and Ga ($s^{1.78}p^{0.91}$). The Mulliken populations of the ground state of the Ga_2As^- anion reveals that only 4% of the attached electron resides on As, while 96% of the charge density is on the Ga atoms. The Ga atoms should primarily determine the electron affinity of Ga_2As.

Our computed results are in overall agreement with the anion photodetachment spectra to be reported by Taylor et al.[1] The spectra seem to exhibit an intense peak near 2.5 eV followed by a progression in the 2.7−3 eV region. Both X($^2A'$, $^2B_2$) and $^2B_1$ states have geometry differences from the ground state of the anion and thus either state would exhibit vibrational progression predicted by our computations. While there is ambiguity with respect to the ground state of Ga_2As, we believe that the vibrational progression near 2.7−3 eV could be assigned to the $^2B_1$ state, which has real vibrational frequencies, as seen from Table 3. This is also complicated further by the fact that the spin−orbit coupling, which is nonnegligible for Ga and As, could couple the $^2B_1$ state (spin up) with $^2A_1$ (spin down) and $^2B_2$ (spin up).[19] It is not clear if the $^4B_2$ states computed in Table 2 would be observable in the detachment spectra, but the higher $^4B_1$ state is too high, although it has a stable minimum as confirmed by the vibrational frequencies in Table 3.

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References and Notes

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