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An *ab initio* study of potassium chemisorption on the GaAs(110) surface

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Abstract. Different possible adsorption sites of potassium atoms on a gallium arsenide (110) surface have been investigated using *ab initio* self-consistent unrestricted Hartree–Fock total-energy cluster calculations with Hay–Wadt effective core potentials. The effects of electron correlation have been included by invoking the concepts of many-body perturbation theory and are found to be highly significant. We find that the K atom adsorption at a site modelled with a $\text{KGa}_5\text{As}_4\text{H}_{12}$ cluster is most favoured energetically, followed by K adsorption at the site modelled with the $\text{KGa}_4\text{As}_5\text{H}_{12}$ cluster. For molecular potassium, a parallel approach positron modelled by a $\text{K}_2\text{Ga}_5\text{As}_4\text{H}_{12}$ cluster is most favoured energetically followed by a vertical approach position modelled by a $\text{K}_2\text{Ga}_4\text{As}_5\text{H}_{14}$ cluster. The effects of charge transfer from K and K_2 to the GaAs surface as well as the possibilities of metallization are also analysed and discussed.

1. Introduction

The physics of the Schottky barrier formation at a metal–semiconductor interface has been pursued with great intensity due to the extensive applications [1, 2]. Metal–GaAs(110) has been considered as a prototype interface and a sizable number of experimental data, e.g., by core level photoelectron spectroscopy (CLPS), scanning tunnelling microscopy (STM), electron energy loss spectroscopy (EELS) etc, on these systems have recently been acquired that highlight the effects of band bending and the shift of the Fermi level, E_F [3–13]. Theoreticians have split the analysis of the band bending and the shift of the Fermi level in two groups, one for small metal coverage, θ ($\theta \leq 1$ monolayer), for which the Fermi level movement exhibits a logarithmic dependence on θ , independent of the metal [14] and large metal coverages for which $\theta > 1$ and the final pinning position depends explicitly on the specific interactions at the metal–GaAs interface [15]. Even as one concentrates on the small- θ range, several methods emerge, which emphasize different aspects of the interface structure and dynamics. In particular, self-consistent *ab initio* electronic structure calculations are needed to judge the validity of the different models. In this paper, we examine the adsorption of K and K_2 on a GaAs(110) surface and we first comment on some relevant experimental and theoretical literature.

Kendelewicz *et al* [16] studied the chemisorption and Fermi level pinning at the Cs/GaAs(110) and K/GaAs(110) interfaces by using soft-x-ray photoemission. They found that Cs and K overlayers deposited on the GaAs(110) surface produced band bending of 0.7 eV, comparable with band bendings produced by more electronegative metals. Inasmuch as Cs chemisorbed in two sites on the GaAs(110) surface, no definite conclusion was arrived at for K chemisorption. Also, in direct contrast with Cs, K was found to react with GaAs. Ortega *et al* [17] studied the behaviour of charge transfer and oxidation

of GaAs(110) substrates, covered with potassium and/or oxygen by Auger photoelectron spectroscopy, work function measurements and low-energy electron diffraction. Though no direct experimental evidence of the preferred adsorption sites of K on GaAs was found, it was nevertheless implied that K adsorption should take place in the vicinity of the Ga atoms, possibly forming one-dimensional chains, up to a coverage of 0.5 monolayer (ML). The adsorption of K atoms onto the GaAs surface also resulted in a charge transfer, estimated to be 0.15 electrons per K adatom at 0.5 ML coverage, to the semiconductor substrate, indicated by a strong work function decrease. The minimum in work function was found to occur at 0.5 ML for K adsorption at 300 K onto both p type and n type doped samples. Magnusson and Reihl [18] studied the development of the electronic structure of K-GaAs(110) by low-energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS) and angle resolved inverse photoemission techniques. For the completed monolayer, the work function change was 3.25 eV and the K induced band bending was found to be 0.3 ± 0.1 eV, about half the bending reported by Kendelewicz *et al* [16]. They also found that the GaAs(110) 1×1 -K surface at room temperature was non-metallic, in disagreement with jellium model slab calculations [19] of the alkali metal overlayer on a GaAs surface. This study was immediately followed by a study by the same authors [20] of the surface electronic structure of submonolayer to full monolayer coverages of K and Cs on GaAs(110). The behaviour was found to be different for K and Cs, in that K induced one filled and one empty surface states. The surface was again found to be non-metallic. Ventrice and DiNardo [21] carried out a LEED I - V study of the K/GaAs(110) interface. In agreement with a theoretical study by Ortega and Flores [22], it was concluded that multiple sites had comparable energies and that no strong site preference was expected. However, they found that K did not intermix with GaAs. Ventrice and DiNardo [23] also studied the evolution of the electronic excitation spectra of the metal-semiconductor interface and the interfacial metallization as a function of K coverage. They found the state of the interface to be non-metallic for all K coverages through saturation at room temperature. This is consistent with a picture of the interface as a correlated system i.e. a Mott insulator [24].

As far as theoretical calculations are concerned, Ortega and Flores [22] used a first-principles tight-binding approach to analyse the K-GaAs interface. For the cases of K bonded to Ga and K bonded to As, almost identical chemisorption energies of ~ 0.85 eV were obtained, at distances of 4.2 Å between K and Ga and K and As. The induced density of states for a monolayer in the semiconductor gap was not zero and the Fermi energy was found to be about 0.49 eV for both cases. The same authors then used a different theoretical analysis, termed 'a consistent molecular-orbital theory', to analyse the early stages of the K-GaAs(110) interface formation. Here, they found that, for 0.5 ML coverage, the minimum in the chemisorption energy appeared for K bonded on Ga at a K-Ga distance of ~ 3.5 Å. The energy was ~ 0.8 eV/atom. For full monolayer coverage, they found that the minimum in the chemisorption energy is obtained by locating half of the K monolayer atoms bonded to Ga and the other half in an intermediate position. Pankratov and Scheffler [25] applied density functional theory with the local density approximation for the exchange correlation functional for potassium adsorbed on GaAs(110). They concluded that the system can be well described by a Mott-Hubbard system with a large charge transfer. The calculated value of the Hubbard correlation energy (~ 0.56 eV) was found to be a property of the Ga dangling orbital. Finally, Khoo and Ong [26] used the complete neglect of differential overlap (CNDO) method to study the characteristics of potassium diffusion and adsorption on perfect and stepped GaAs(110) surfaces. They found that the stable site for K was the bridge site encompassing one Ga and two As surface atoms. In the equilibrium geometry for diatomic K, the second K atom occupied the next-nearest-neighbour bridge site. This

suggested the formation of an open linear structure parallel to the surface atomic zigzag chains.

The above results indicate that, in spite of a series of experimental and theoretical studies, there exist significant controversies about K adsorption on GaAs(110). In our work, we propose to use an alternative formalism, namely *ab initio* unrestricted Hartree–Fock (UHF) theory, to study the chemisorption of K and K₂ on GaAs by simulating the surface with finite hydrogen bonded GaAs (GaAsH) clusters. It is well known that clusters are well suited for the study of semiconductor surfaces [27], and in general can yield accurate results of such properties as the chemical nature of a bond, bond length and other geometrical data [28]. Inasmuch as the effects of electron correlation can be very significant, we have studied these by invoking the concepts of fourth-order many-body perturbation theory, as in our previous works on chemisorption of alkali atoms on Si surfaces [29], of Na on the GaAs(110) surface [30] and of H and O atoms on Li surfaces [31].

This paper is organized as follows: in section 2 we discuss the basic theory and the computational method used; the cluster models and results of potassium chemisorption on these clusters are presented in section 3. Finally, conclusions are presented in section 4.

2. The theory and the computational method

Both the unrestricted Hartree–Fock (UHF) theory and the many-body perturbation theory (MBPT), as used in this work, are well documented in the literature [32–36]. Here we present only a basic equation to define some terms. In MBPT, the energy is given by the linked diagram expansion

$$\Delta E = E - E_0 = E_1 + E_{\text{corr}} = \sum_{n=0}^{\infty} \langle \Phi_0 | V [(E_0 - H_0)^{-1} V]^n | \Phi_0 \rangle_L \quad (1)$$

where Φ_0 is taken to be the UHF wavefunction, H_0 is the sum of one-electron Fock operators, E_0 is the sum of UHF orbital energies and $V = H - H_0$ is the perturbation, where H is the usual electrostatic Hamiltonian. The subscript L indicates the limitation to linked diagrams. Though one can include various categories of infinite-order summations from equation (1), the method is usually limited by termination at some order of perturbation theory. For most of the bare clusters, we have carried out complete fourth-order calculations (MP4), which consist of all single-, double-, triple- and quadruple-excitation terms [30]. For the chemisorbed systems, due to severe demand on available computational resources, usually only MP2 (up to second-order perturbation theory) calculations have been carried out.

Now one of the primary considerations involve in *ab initio* HF/MBPT calculations is the determination of the type of basis set to be used [37]. Basis sets used in *ab initio* molecular orbital computations usually involve some compromise between computational cost and accuracy. Keeping in mind the tremendous cost of *ab initio* calculations, specifically for large systems such as K, Ga and As, we have elected to represent them by effective core potentials (ECPs) or pseudopotentials (PPs). In particular, we have used the Hay–Wadt effective core potential (HWECP) [38–39] which is known to provide almost exact agreement with all electron results. However, to improve the accuracy of our calculation further, one d function was added to all the HW basis sets. The exponent of the d function was chosen to provide the minimum energy for the K₂, Ga₂ and As₂ dimers, with the bond lengths fixed at experimental values. For H a (4s/1p) basis set was used. All computations were done using the programs GAMESS [40] and GAUSSIAN 92 [41] on the Cray Y-MP8/864 at the University of Texas Center for High Performance Computing and on the Cray Y-MP C90 at the National Science Foundation Pittsburgh Supercomputing Center.

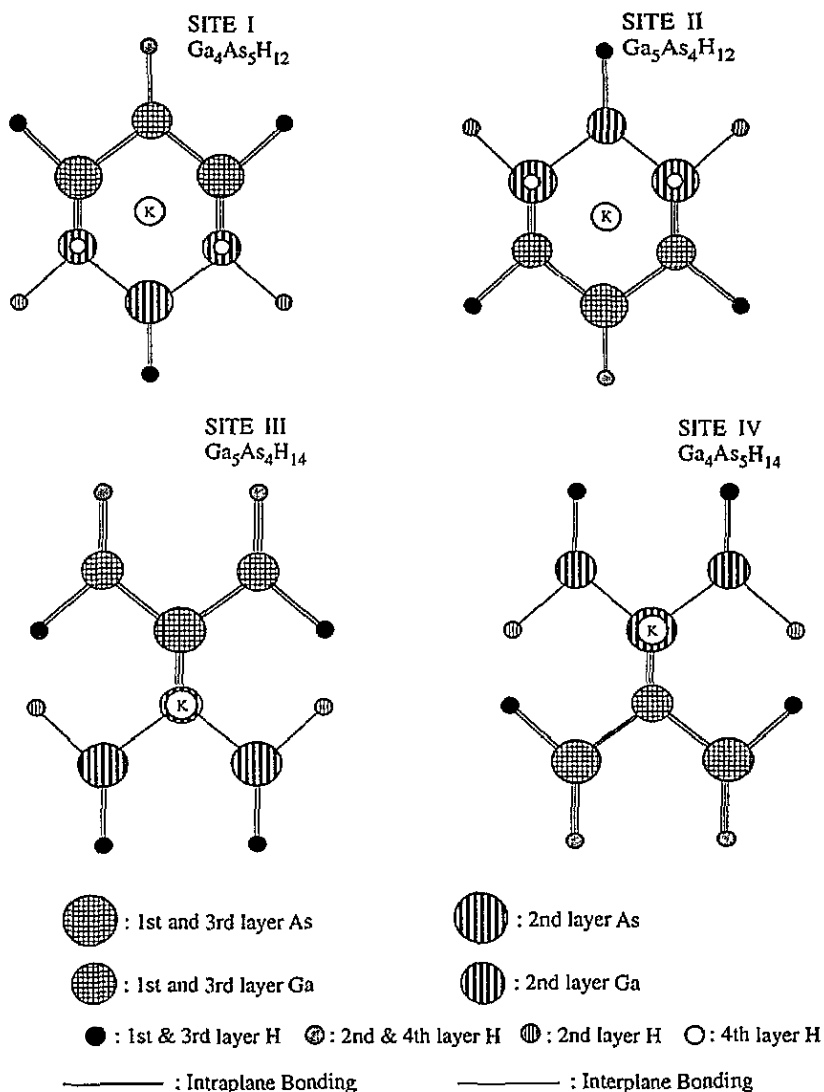


Figure 1. K adatom locations on the GaAs(100) surface.

Table 1. Optimum vertical heights of the K adatom from the ideal GaAs surface (lattice constant = 5.65 Å), and the total energies (au) and the chemisorption energies (eV) of K + GaAs clusters.

Cluster	Site	Height (Å)	Bond length (Å)		Total energy (au)		Chemisorption energy (eV)	
			K-Ga	K-As	SCF	MP2	SCF	MP2
Ga ₄ As ₅ H ₁₂	I	0.99	3.67	3.08	-43.7937	-44.7790	0.14	1.50
Ga ₅ As ₄ H ₁₂	II	2.67	3.40	3.41	-39.8896	-40.8038	0.45	2.02
Ga ₅ As ₄ H ₁₄	III	2.33	4.17	2.73	-40.7122	-41.7163	-1.69	1.02
Ga ₄ As ₅ H ₁₄	IV	2.66	3.01	4.37	-44.5045	-45.6736	-3.07	1.49

3. K and K₂ adatom interactions with the GaAs(100) surfaces

The basic clusters used to represent the GaAs(110) surface have been presented before and will not be discussed in detail again. In brief, we studied GaAs clusters up to three layers and since, at the second-order MBPT level, Ga₅As₄H₁₂, followed by Ga₄As₅H₁₁, has the most stable configuration, these units were chosen for further study. To study potassium chemisorption on the GaAs(110) surface, we then considered the four sites used by Fong *et al* [42] and in our studies of Na chemisorption on GaAs(110) [30]. Top views of all these four K+GaAs systems are shown in figure 1 and the clusters corresponding to these sites are represented by Ga₄As₅H₁₂, Ga₅As₄H₁₂, Ga₅As₄H₁₄, respectively. A single adatom K was then placed at all fixed sites, and for each system the total energy as a function of the vertical height z from the surface plane was calculated. The HF energy was then plotted against z (negative z representing position of the adatom below the surface) and the minimum-energy z value, z_{eq} , was taken to be the equilibrium position of the adatom. A single-point MP2 calculation was then performed at the z_{eq} value. To examine the relative stability of chemisorption at the different sites, the chemisorption energies E_c are calculated from

$$E_c(\text{K}/\text{Ga}_x\text{As}_y\text{H}_z) = E(\text{K}) + E(\text{Ga}_x\text{As}_y\text{H}_z) - E(\text{KGa}_x\text{As}_y\text{H}_z) \quad (2)$$

and table 1 shows the values of E_c and z_{eq} . This technique has been applied before by us, for example, to Li atom chemisorption on a Si surface [29] to clearly identify the chemisorption site that a STM study [43,44] had proposed. At this point, surface reconstruction possibilities are not allowed, based on some evidence that at low alkali metal coverages, the reconstruction and relaxation of the GaAs(110) surfaces may be lifted [45–47].

Table 2. Chemisorption energies from the results of total optimization.

Site	Lattice constant (Å)	Height (Å)	Bond length (Å)		Total energy (au)		Chemisorption energy (eV)	
			K–Ga	K–As	SCF	MP2	SCF	MP2
I	5.09	1.20	3.40	2.89	–43.9596	–44.9069	0.43	1.76
II	5.11	2.72	3.33	3.33	–40.0548	–40.9373	1.29	2.48
III	5.01	2.42	3.91	2.72	–40.9197	–41.8980	–2.03	1.00
IV	4.98	2.80	3.07	4.14	–44.7475	–45.7874	–2.51	–0.43

Before we discuss the results, we note first that the stable atomic site of K on GaAs(110) is not known experimentally. From the results of table 1, we note first that all sites are stable at the MP2 level but, at the self-consistent field (SCF) level, sites III and IV have negative chemisorption energy. This again illustrates the importance of correlation for an AM– (AM = alkali metal) GaAs system [30,48]. Site II has the highest chemisorption energy at both the SCF and MP2 levels. Sites I and IV have nearly identical chemisorption energies at the MP2 level, but the results at the SCF level are quite different. This is in some contrast with the results for Na–GaAs systems [30], where sites I and II were found to be most stable with site II having significantly higher chemisorption energy. Comparing our results to the bond lengths of K–Ga (3.12 Å) and K–As systems (2.67 Å), we find that the nearest-neighbour distance between K and Ga or As, in general, increases as a result of the competition of all the neighbouring atoms. For site II, the optimum vertical height of the K adatom from the

topmost layer is found to be 2.67 Å. Orgtega and Flores [22] found a chemisorption energy of ~ 0.8 eV for the most stable site. This is significantly less than the value of 2.02 eV for our chemisorption energy. Also, their K–Ga distance of 3.5 Å matches fairly well with our distance of 3.4 Å but their value of 3.3 Å for the distance of the K layer to the surface GaAs layer is significantly larger than our value of 2.67 Å. On the other hand, Khoo and Ong [26], based on their CNDO calculations, found that, for the most stable site, the distance of the K atom from the surface layer is 0.73 Å and the K–Ga bondlength is 2.53 Å.

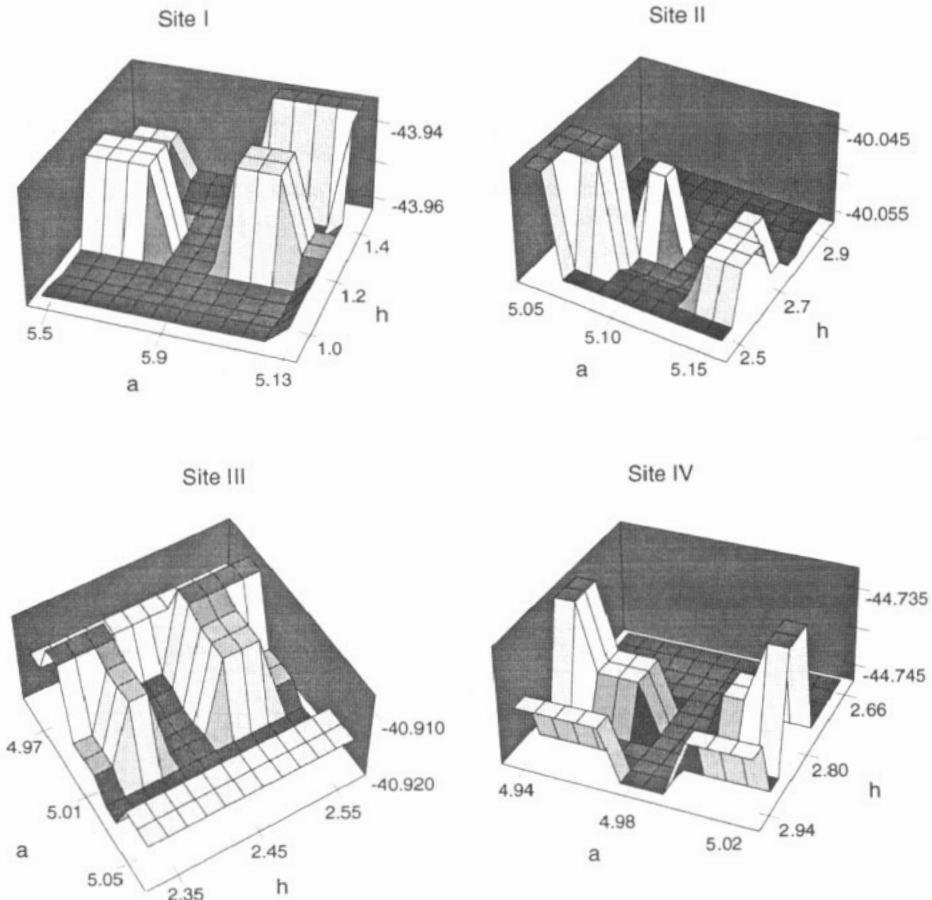


Figure 2. Total energies (au) vs. lattice constant (Å) and adatom height (Å) from the surface for each site.

In the next stage of the calculations, we studied the possibilities of surface reconstruction. The adatom was then again allowed to approach the clusters and a simultaneous optimization of the adatom distance and the cluster lattice constant was carried out. Table 2 summarizes the results of such a total optimization process and figure 2 shows three-dimensional plots of the total energy versus lattice constants and adatom heights for all the four sites. If we compare the results in table 2 to those in table 1, we first note that the atoms in the reconstructed surface move closer compared to an ideal surface but the adatom moves away from the surface. The K–Ga and K–As distances, in general, decrease. The same general

conclusions prevailed also for Na. The total energies of the chemisorbed clusters also decrease, as expected, after optimization but, as for Na, the chemisorption energies do not indicate any consistent pattern. At the SCF level, compared to the ideal surface, E_c increased for sites I, II and IV but decreased for site III; at the MP2 level, E_c increased for sites I and II but decreased for sites III and IV. Site II still remains the most preferred site followed by site I and III respectively; site IV becomes unstable after optimization.

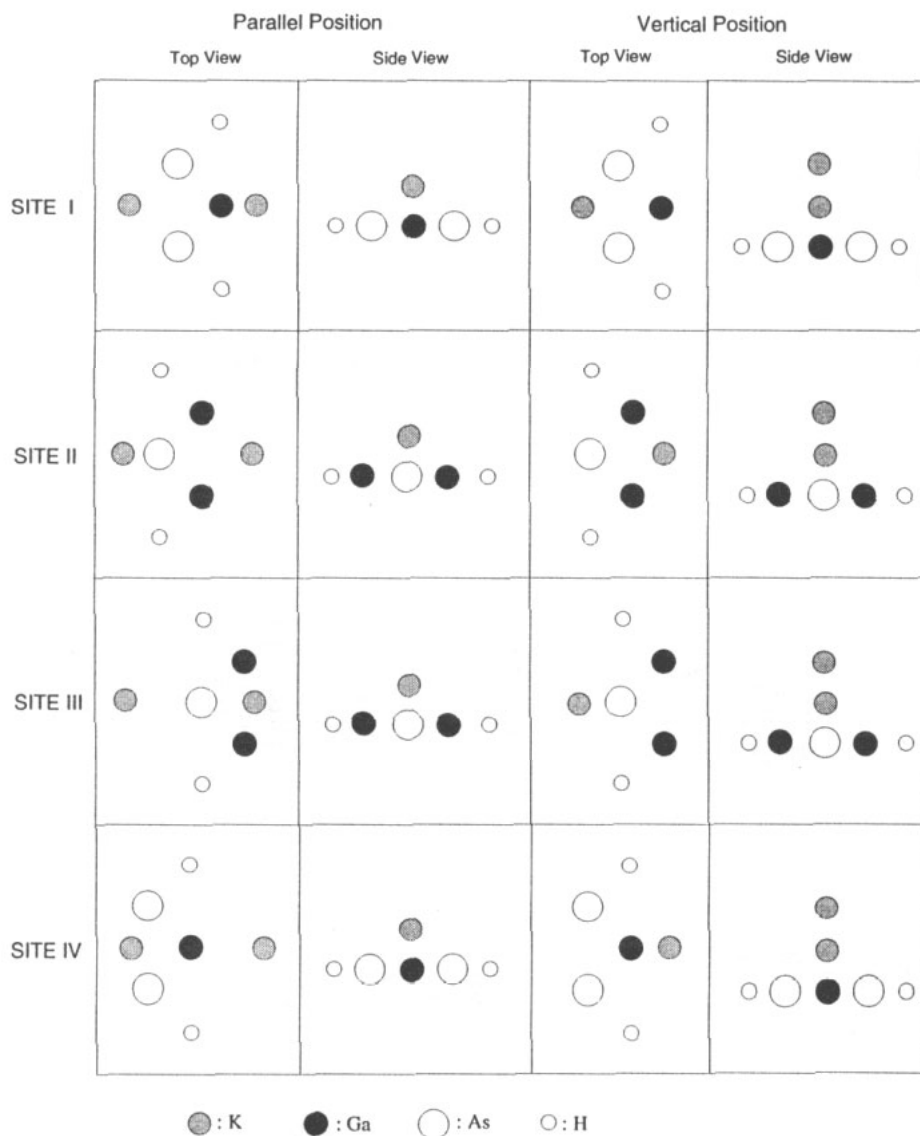


Figure 3. Schematic Drawings of GaAs(110)/K₂ for four sites.

We now discuss some preliminary results on molecular potassium adsorption on GaAs(110). Noting again that no experimental information on site preferences is available, we tried approach positions along the four sites mentioned above for molecular potassium.

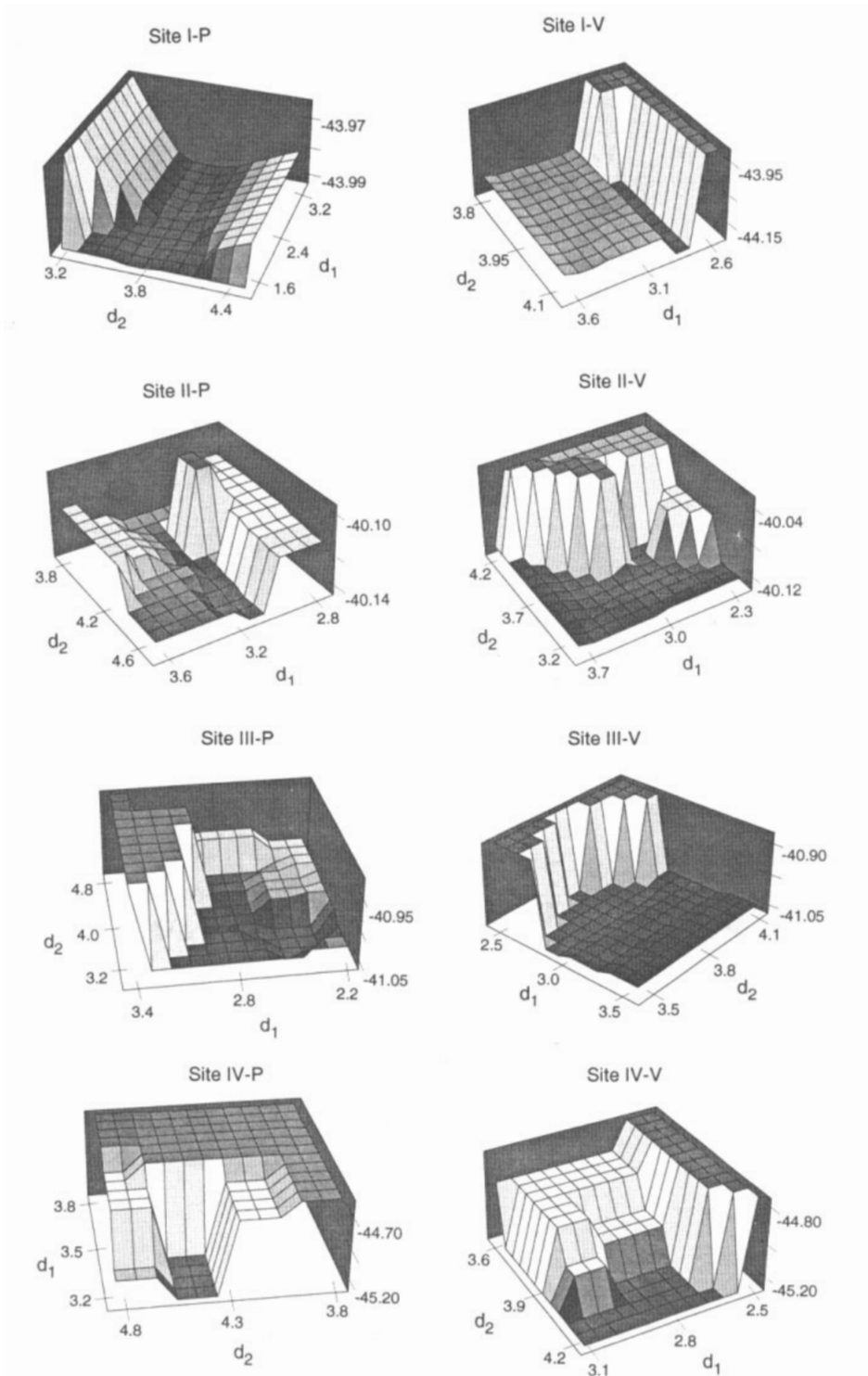


Figure 4. UHF total energies (au) vs. d_1 and d_2 . Here d_1 refers to the distances (\AA) between the surface and the adatoms for the parallel configurations or the first adatom heights (\AA) for the vertical configurations and d_2 refers to the interatomic distances of K_2 .

Table 3. Chemisorption energies for the $K_2 + GaAs$ clusters.

Site	Adatom distance (Å)		Total energy au		Chemisorption energy (eV)	
	d_1	d_2	SCF	MP2	SCF	MP2
I-P	1.80	3.60	-43.9928	-44.9794	0.42	1.63
I-V	2.80	3.93	-44.1996	-44.9373	6.05	0.48
II-P	3.05	4.50	-40.1448	-41.0266	2.26	2.75
II-V	2.80	3.80	-40.1197	-41.0006	1.58	2.05
III-P	2.50	3.50	-41.0854	-41.9693	3.33	2.57
III-V	2.80	3.80	-41.0585	-41.9455	2.60	1.93
IV-P	3.20	4.50	-45.2370	-45.8845	11.72	1.89
IV-V	2.80	4.00	-45.2533	-45.8997	12.17	2.30

Figure 3 shows schematic drawings of GaAs(110)/ K_2 for the four sites and table 3 shows the results for the chemisorption energies for these clusters. K_2 was allowed to approach both parallel and perpendicular to the GaAs(110) surface and a three-dimensional optimization of the total energy against the height of the first adatom from the GaAs(100) surface and the interatomic distance was carried out. In table 3, d_1 is the height of the first adatom from the surface and d_2 is the separation distance between the two K atoms. Figure 4 shows a plot of the SCF total energies against the parameters d_1 and d_2 . As can be seen from the results of table 3, including correlation has a drastic effect on site preferences and the values of chemisorption energies. The chemisorption energies are calculated from

$$E_c(K_2/Gd_xAs_yH_z) = E(K_2) + E(Ga_xAs_yH_z) - E(K_2Ga_xAs_yH_z). \quad (3)$$

Here $E(K_2)$ is the total energy of the potassium dimer at the optimized interatomic distance. At the SCF level, site IV has unusually high chemisorption energy compared to all the other sites. Considering also that the optimized interatomic separation of diatomic potassium is 3.53 Å, dissociative chemisorption is certainly a possibility. At the MP2 level, all sites are competitive, with site II-P and site IV-V being most stable among the parallel (P) and vertical (V) approach positions, respectively. Again, dissociative chemisorption is a possibility, specifically for site II-P where $d_{K-K} = 4.50$ Å. We point out also that MP2 level energies, in general, decreased (compared to the SCF level chemisorption energies) except for site II and this site appears to be most stable for atomic as well as molecular chemisorption, if the molecule is allowed to approach parallel to the GaAs(110) surface. Using the CNDO method, Khoo and Ong [26] studied the possibility of K atom location at different sites and found the minimum-energy configuration to be one in which the atoms are separated by 8.02 Å. The large difference between the two calculations might simply be due to the different theoretical methods and the different sites used.

We have also studied the atomic charge distributions for the ideal and optimized clusters. In all cases, we find significant charge transfer from the K atom to Ga and As atoms, with the Ga atoms losing charge and the As atoms gaining charge. This is true for all the sites as expected; however, the charges on the particular atoms, as expected, vary. Figure 5 shows the charge density plots for different coverages of chemisorbed systems at site II. It can be seen that there are no significant changes in the GaAs surface upon the adsorption of K. Also, while the charge density around K has a comparatively low-density distribution, clearly, the K charge density is not totally depleted. This is because there is only a partial charge

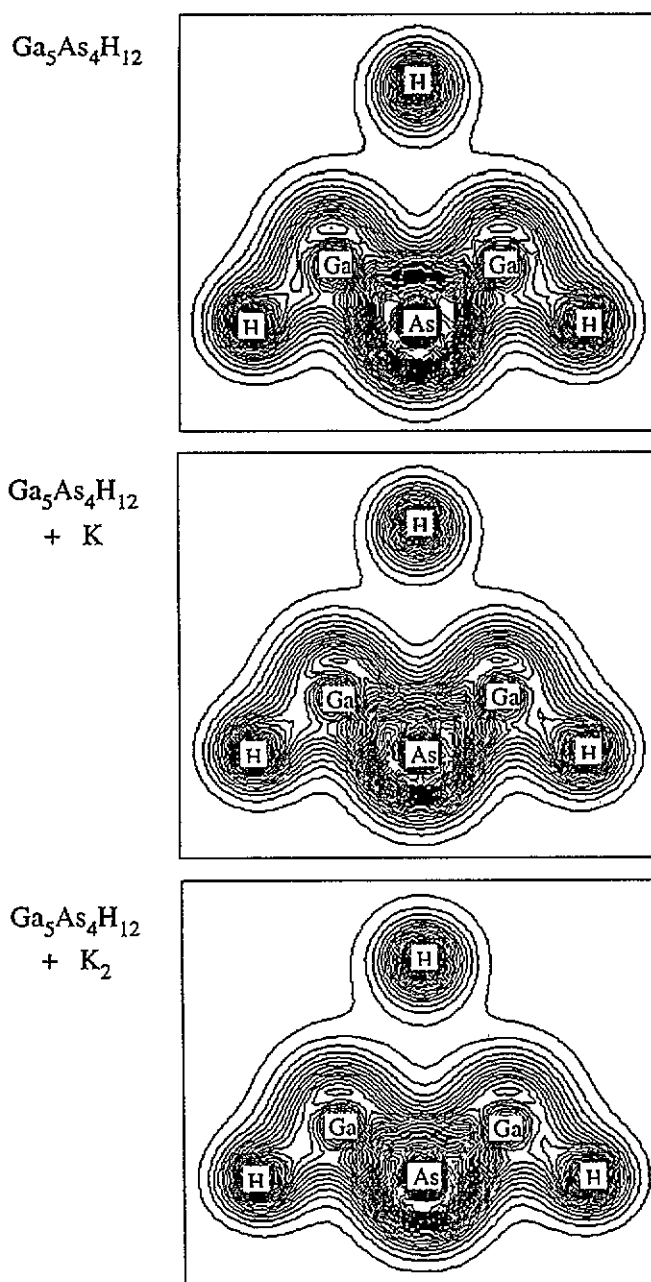


Figure 5. Charge density plots of GaAs/ K_m clusters for the (110) surfaces at site II.

transfer, Δq , of $0.83e$ and $0.84e$ for sites I and II, respectively. For GaAs/ K_2 systems, again, in general, Ga atoms lose charge and the As atoms gain charge. All the parallel positions have more charge transfer than the vertical positions because, in this position, the K atoms have much more possibility of interaction with GaAs(110) surfaces. For site II, an analysis of the wave-function coefficients shows that the highest occupied molecular orbital

and the lowest unoccupied molecular orbital (HOMO–LUMO) states of the surface layer atoms of the cluster before K adsorption consist principally of s and p states. Upon the adsorption of K, the GaAs HOMO–LUMO states retain their characteristics and the K states are basically s and p. Also, the HOMO states are pushed up in energy ($\Delta E = 0.66$ eV) and the HOMO–LUMO gap decreases significantly, from 0.257 au to 0.128 au. Thus, the gap decreases by 1.06 eV. Similar analysis shows a general reduction of HOMO–LUMO gaps for K and K_2 adsorption (table 4), indicating the possibilities of eventual metallization.

Table 4. HOMO–LUMO gaps for $Ga_xAs_yH_z$ and $K_mGa_xAs_yH_z$ clusters.

Clusters	Site	Gap (eV)
Ideal surface	II	4.98
	IV	4.69
Ideal surface/K	II	5.27
Ideal surface/ K_2	II-P	3.34
	IV-V	5.03
Optimized surface	II	6.99
Optimized surface/K	II	5.93

4. Conclusions

We can summarize the results for potassium chemisorption on GaAs(110) surface as follows. Different possible adsorption sites of K atoms on a GaAs surface have been investigated using *ab initio* self-consistent unrestricted Hartree–Fock total-energy cluster calculations with Hay–Wadt effective core potentials. The effects of electron correlation have been included by invoking the concepts of many-body perturbation theory and are found to be highly significant. For the K adsorption on the ideal surface, site II is the most stable site at both the SCF and MP2 levels, with E_c values of 0.45 eV and 2.02 eV respectively. The height of the K atom from the surface is found to be 2.67 Å. For total optimization of GaAs + K clusters site II is also the most stable site at both the SCF and MP2 levels with E_c of 1.29 eV and 2.48 eV respectively. Quasihexagonal symmetry and coordination among the surrounding atoms are expected to be the primary reasons for the stability of site II, followed by site I. Chemisorption energy data of molecular potassium show that for a parallel position of K_2 , a site II-P modelled by a $K_2Ga_5As_4H_{12}$ cluster is most favoured energetically with an E_c of 2.75 eV at the MP2 level, and for a vertical position of K_2 , a site IV-V modelled by a $K_2Ga_4As_5H_{14}$ cluster is most favoured energetically with an E_c of 2.30 eV at the MP2 level. The diatomic potassium distance of 4.50 Å at site II-P suggests possible dissociative chemisorption of K_2 on the GaAs(110) surface. There is also significant charge transfer to the GaAs surface upon the adsorption of K and K_2 . In general, Ga atoms lose charge and As atoms gain charge. Comparisons of the HOMO–LUMO gaps upon the adsorption of K and K_2 show distinct possibilities of metallization.

Acknowledgments

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