# Energetics and dynamics of GaAs epitaxial growth via quantum wave packet studies

Fedor N. Dzegilenko

NAS Technical Report NAS-99-001 March 1999

MRJ Technology Solutions, Inc.
Information Technology Modeling and Simulation group at NAS,
NASA Ames Research Center, M/S T27-A1, Moffett Field, CA 94035
http://www.nas.nasa.gov/NAS/TechReports/NAS-99-001

**ABSTRACT**

The dynamics of incorporation of $As_2$ molecule into the flat GaAs(100) surface is studied computationally using the combination of density functional theory and quantum wave packet dynamics. The two-dimensional potential energy surface (PES) describing the interaction of incoming $As_2$ molecular beam with the GaAs surface is calculated using the density functional theory. Two coordinates include the internuclear As-As distance and the distance between the $As_2$ center of mass and Ga atom of GaAs surface. The GaAs surface is represented by a cluster of 36 atoms. The computed PES shows a significant barrier (around 1 eV) in the entrance channel and a strongly bound molecular chemisorption site indicating the importance of quantum effects. The time-dependent Schrödinger equation is solved on a 75 X 751 rectangular grid by expanding the wave packet in a discrete variable representation basis and propagating it in time using the Chebyshev expansion algorithm. The probabilities of trapping and subsequent dissociation of the molecular $As_2$ bond are calculated as a function of beam translational energy and the vibrational quantum number of $As_2$.

**Keywords:** MBE growth, gallium arsenide, density functional theory, wave packet dynamics

email:fedor@nas.nasa.gov

## 1. INTRODUCTION

The molecular beam epitaxial (MBE) technique remains to be the major method to produce gallium arsenide, an important optoelectronic material. In this method, the GaAs surface, which is kept at $\approx$ 600 K, is irradiated by the gallium atomic beam and arsenic molecular beam composed mainly of $As_2$ and $As_4$ molecules.[1–4] For the Ga-terminated GaAs surface, the dissociative chemisorption of $As_2$ molecules leads to growth of an As layer. The probability of this process depends on the initial conditions of the molecular arsenic beam. This work aims to elucidate this dependence based on first principles calculations.

Several groups have studied the reaction mechanisms of GaAs MBE growth. Arthur,[1] Foxon and Joyce,[2] Tok *et al.*,[3] and Ott *et al.*[4] have proposed various kinetic schemes based on the assumption of the molecular precursor-mediated reaction. The incorporation kinetics of Ga, $As_2$, and $As_4$ species into the GaAs(100) and (110) surfaces is modeled by a series of microscopic steps such as adsorption, desorption, chemisorption, and migration. These and another popular GaAs MBE growth modeling technique, the kinetic Monte-Carlo method,[5–8] requires the detailed knowledge of energetics and microscopic rate constants of adsorption, desorption, and migration steps which is often is not available.

The chemisorption of $As_2$, $As_4$, and $GaAs_2$ clusters on a flat and step site of GaAs(100) surface was studied by Fukunishi *et al.*[9] using the Hartree-Fock method. The GaAs surface was modeled by a cluster and the total energy of the combined molecule-surface system was computed at several geometries. For the $As_2$ molecule, the results indicate that dissociative adsorption is more favourable at a step site than on a flat surface.

No *quantum wave packet* calculations have been reported so far for the incorporation dynamics of $As_2$ into the GaAs(100) surface. The major difficulty lies in the absence of a reliable interaction potential for the Ga-As system, though several empirical potentials have been proposed over the years.[10,11] The quality of these potentials, which contain a number of fitting parameters, needs to be further tested.

## 2. THE MODEL

In our study, the flat Ga-stabilized GaAs(100) surface is represented by the $Ga_8As_8H_{18}$ cluster similar to the one used in Ref. 9. The "excessive" dangling bonds of Ga and As atoms are saturated by H atoms. The geometry optimization is performed using the density functional theory (DFT)[12] method with B3LYP hybrid functional.[13] The double-zeta LANL2DZ[14] basis set is used throughout the calculations. The calculations are performed using the Gaussian 94 program.[15] The $As_2$ molecule approaches the cluster and further chemically reacts with it. The two quantum molecular degrees of freedom considered in our model are $Z$ - the distance between the $As_2$ center of mass and the central Ga atom of the surface cluster, and r, the $As_2$ internuclear coordinate (Fig. 1). The conservation of $C_{2v}$ symmetry is assumed in the simulations. After optimizing the geometry of the bare GaAs cluster, the chemical interaction with the approaching $As_2$ molecule is turned on and the resulting potential energy surface (PES) for the combined system is computed on a two-dimensional (Z,r) grid. The geometry of the surface cluster is held fixed at its previously optimized value which corresponds to the rigid surface approximation. The rectangular grid spans from 1.74 to 8.34 $\AA$ for the $As_2$ internuclear distance and from 0.16 to 9.16 $\AA$ for the translational coordinate Z. The size of the grid is $35 \times 46$. The neighbouring grid points are separated by 0.2 $\AA$ for each coordinate. The values of the potential in between the grid points are computed by using the bicubic interpolation method.[16]

## 3. RESULTS AND DISCUSSION

The resulting PES is shown for the chemically significant region in Fig. 2. The potential exhibits two minima and two saddle points. The global minimum (which is assigned the zero of energy for the fitted potential) is located at r = 2.43 $\AA$ and Z = 2.17 $\AA$ and corresponds to the *molecular* adsorption of the $As_2$ molecule on the surface. The second minimum with an energy of 4032 $cm^{-1}$ is located at r = 4.09 $\AA$ and Z = 1.56 $\AA$ and corresponds to the dissociation of the $As_2$ molecule into two As atoms on the surface. The effective locations of the saddle points in the incoming and dissociative channels are found by minimizing the potential over one of the coordinates while keeping track of the remaining one. The saddle point in the incoming channel occurs at r = 2.31 $\AA$, Z = 2.88 $\AA$ with an energy of 10644 $cm^{-1}$. The "vacuum" (i.e at large Z distances) energy of the $As_2$ molecule is 2776 $cm^{-1}$. This gives an activation energy, $E_{act}$, of 7868 $cm^{-1}$, which is close to 1 eV. The large desorption barrier of 10644 $cm^{-1}$ (=1.32 eV) is consistent with the experimental value of $> 0.92$ eV[3] for $As_2$ on GaAs(110). The barrier in the dissociative coordinate r occurs at r = 3.36 $\AA$, Z = 1.73 $\AA$ and has an energy of 6122 $cm^{-1}$. We conclude that the

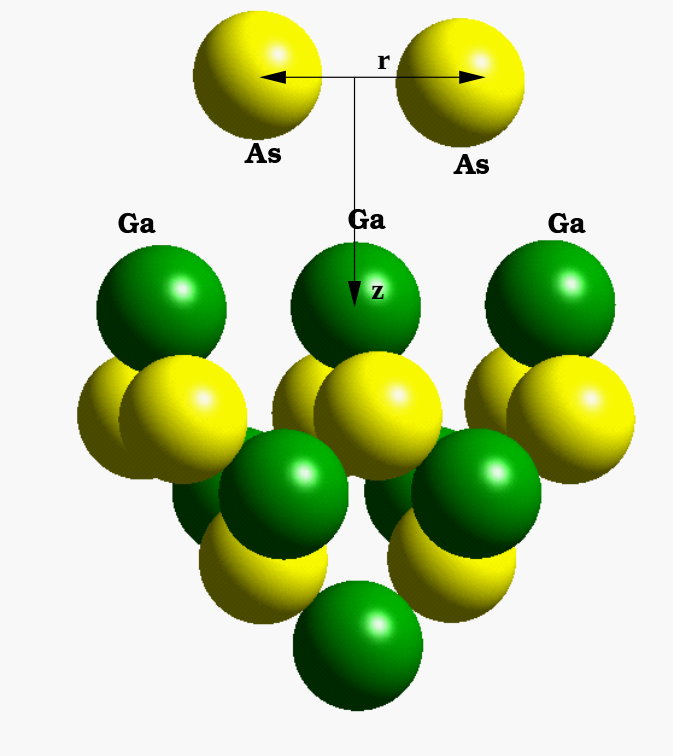



**Figure 1.** The interaction of $Ga_8As_8H_{18}$ cluster, representing the flat Ga-stabilized GaAs surface, with the incoming $As_2$ molecule

chemisorption of $As_2$ is strongly activated and that the molecular adsorption site is energetically more favourable than the dissociative one. This, however, does not preclude the population of the latter site, provided that the total initial energy of the beam is larger than the energy of the atomic chemisorption minimum. The computed PES in Fig 2 underlines the importance of dynamical treatment via *quantum* techniques.

The two-dimensional time-dependent Schrödinger equation (TDSE) for the $As_2$ - GaAs surface system is solved for the molecular Hamiltonian, $\hat{H}$, given by:

$$\hat{H}(Z,r) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial Z^2} + V(Z,r), \tag{1}$$

where $m = \frac{m_{As}}{2}$ is the reduced mass for the $As_2$ stretching coordinate r, $\mu = 2m_{Ar}$ is the appropriate mass for the translational coordinates Z, and $V(Z,r)$ is the $As_2$ - surface interaction potential.

A method based on the expansion of the wave function in a discrete variable representation (DVR) basis has been used for solving the TDSE.[17–19] For both the Z and r coordinates we employ a plane wave original basis.[17] The DVR basis set is constructed from the original basis set using a standard procedure.[17–19] We have varied the number of DVR basis functions $N_Z$ and $N_r$ at each coordinate to ensure the convergence of the results. For the Z coordinate we determined that $N_Z = 751$ with $Z_{min} = 0.5\mathring{A}$ and $Z_{max} = 8\mathring{A}$ was adequate to obtain the converged results. Similarly, $N_r = 75$ with $r_{min} = 2\mathring{A}$ and $r_{max} = 5\mathring{A}$ was shown to be adequate for the internuclear coordinate r. A two dimensional DVR direct-product basis of order 56325 was used for wave function propagation.

The initial wave function is chosen as a product of a vibrational eigenfunction of the $As_2$ molecule, $\phi_v(r)$, and a Gaussian in translational coordinate Z.

$$\Psi(Z,r,t=0) = (2\pi\sigma^2)^{-\frac{1}{4}} exp(-\frac{(Z-Z_0)^2}{4\sigma^2} - ik_0 Z)\phi_v(r), \tag{2}$$

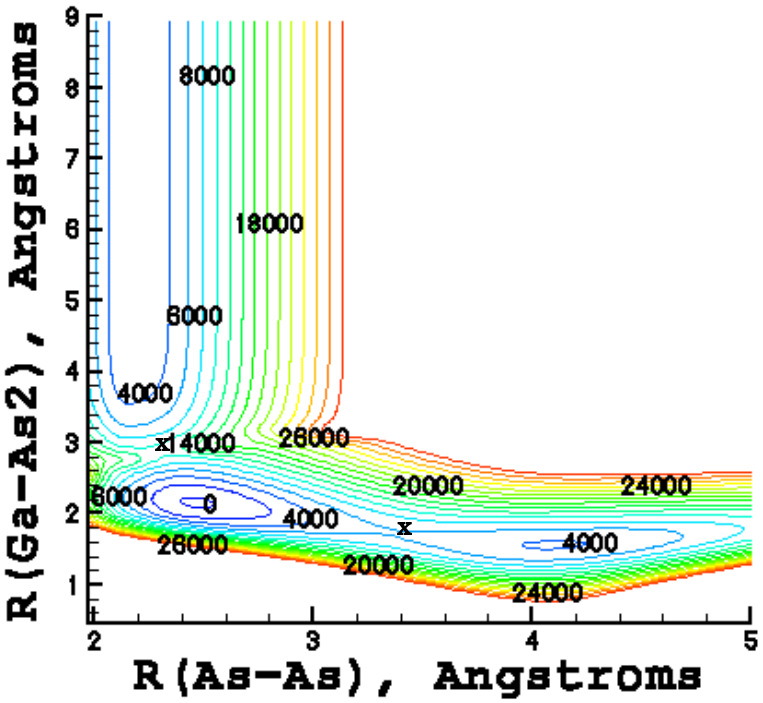



**Figure 2.** The two-dimensional interaction potential (in $cm^{-1}$) describing the interaction of $As_2$ with the flat GaAs surface. Saddle points are marked with crosses

which is a wave packet centered on $Z_0$ with the average translational momentum in Z direction given by $k_0$ and the width of the coordinate (and momentum) distribution determined by $\sigma$. The average translational energy of the initial wave packet is:

$$< E_{tr} >= \hbar^2(k_0^2 + 0.25/\sigma^2)/2\mu. \tag{3}$$

Time evolution of the wave packet is achieved by expanding the propagator in a series of *modified* Chebyshev polynomials[20–23] which allows us to include a large time step and the absorbing potential into the original Chebyshev expansion.[24] The wave-packet has been exponentially absorbed starting at $Z = 7.5$ $\AA$, in order to destroy the outgoing amplitude in the larger Z region before it could be unphysically reflected. In the present study we use 30000 Bessel functions for a total integration time of 3 ps.

Desorption was monitored by computing the outgoing probability flux through a dividing surface near the large Z boundary of the grid at a point before the absorbing boundary condition is applied. The large Z boundary of the grid is far away from the potential well of the adsorbate-surface complex so that the probability flux through the dividing surface corresponds to the scattering of the $As_2$ molecule off the surface. If we define Z=S as the dividing surface, then the probability flux through this surface in the positive Z direction is given by

$$J(S,t) = \frac{\hbar}{\mu} Re \frac{1}{i} < \Psi^*(S,r,t) \mid [\frac{\partial}{\partial Z}\Psi(Z,r,t)]_{Z=S} >, \tag{4}$$

and the quantum desorption probability is defined as

$$P_d(t) = \int_0^t J(S,t')dt'. \tag{5}$$

We have used S = 7 $\AA$. The integral over time in Eq. 5 is evaluated numerically with the intermediate fluxes stored each 5 fs. This is accomplished by recomputing the time-dependent coefficients in modified Chebyshev expansion

along with the values of the wave function and its derivative over the Z coordinate at Z=S only, so that no storage of the full wave function and its derivative at each time step is required. We have also performed integration with a smaller time step of 0.5 fs and found the results similar to the 5 fs time step case. The reaction probability, $P_r$, is given by 1 - $P_d(t)$. $P_r$ corresponds to the combined probability of sticking (molecular adsorption) and dissociation. The code was parallelized on 32 processors of SGI Origin2000 using High Performance Fortran. Almost linear scaling with the number of processors has been achieved.

The existence of the large activation barrier and the strongly bound molecular state significantly affects the dissociation dynamics by trapping $As_2$ near the GaAs surface and causing multiple reflections of the wave function. The trapped molecule can live for some time as a resonant state, it can further dissociate into the atoms, or it can scatter back into the gas phase. Fig. 3 shows snapshots of $|\Psi|^2$ at four different times. The initial state has v = 0 and the initial translational energy of 10113.7 $cm^{-1}$.

The average initial value of As-As stretching coordinate r is 2.18 $\AA$ and the average initial value of the Z coordinate is 6.05 $\AA$. The wave packet is localized in both Z and r coordinates at t = 0. At t = 1 ps, the wave packet has significant amplitude both at large and small values of Z. The former corresponds to the nonreactive part of the wave packet which was reflected off the barrier in Z coordinate and is heading towards large Z values corresponding to desorption. The build up of amplitude at small Z values corresponds to the molecular adsorption (sticking) of the $As_2$ molecule on the GaAs surface. Further dissociation of the $As_2$ molecule into individual As atoms is evident as there is some amplitude at larger r values. This process becomes even more prominent at t = 2 and 3 ps, which shows gradual leakage of the amplitude into the area of large r values, which corresponds to the dissociation of $As_2$. At the same time, the amplitude of the reflected part of the wave packet at larger values of Z diminishes, meaning that almost no desorption is taking place anymore.

The reaction probabilities at t = 3 ps are shown in Fig. 4 as a function of the translational energy of the incoming wave packet for the ground and first two excited vibrational states of $As_2$.

The activation energy in Z coordinate ($E_{act}$ = 7868 $cm^{-1}$) is marked with the cross on the Z axis. In all the cases, there is a translational energy threshold below which the reaction does not occur. This reaction threshold is equal to $\approx$ 7300 $cm^{-1}$ for the ground vibrational state which is lower than $E_{act}$. The reaction in the range of translational energies between 7300 and 7868 $cm^{-1}$ occurs as a result of tunneling through the barrier into the molecular chemisorption well.

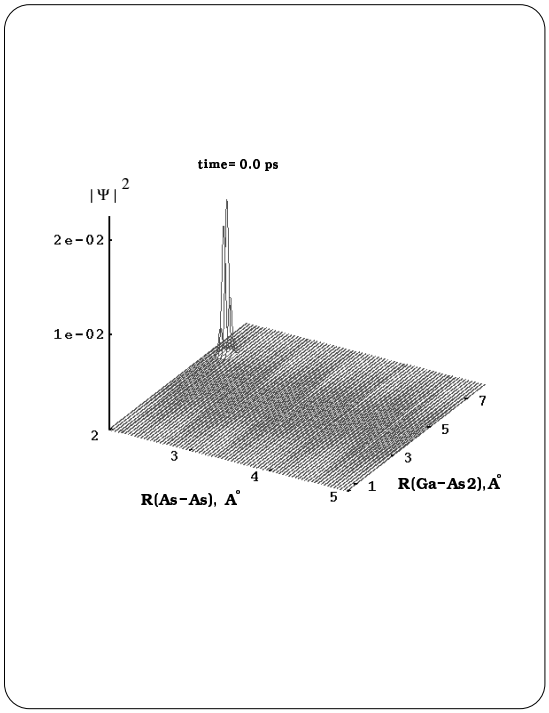
For the ground vibrational state, the reaction probability steadily increases with the initial translational energy, reaches a maximum value of around 17% at $E_{tr}$ = 9779 $cm^{-1}$ and decreases afterwards. For the excited vibrational states, the maximum of $P_r$ is observed at translational energies below $E_{act}$, and the reaction probability slightly decreases with $E_{tr}$ afterwards. We conclude that for $E_{tr}$ below $E_{act}$, vibrations accelerate dissociation. In contrast, at translational energies above $E_{act}$, vibrations promote scattering rather than dissociation.

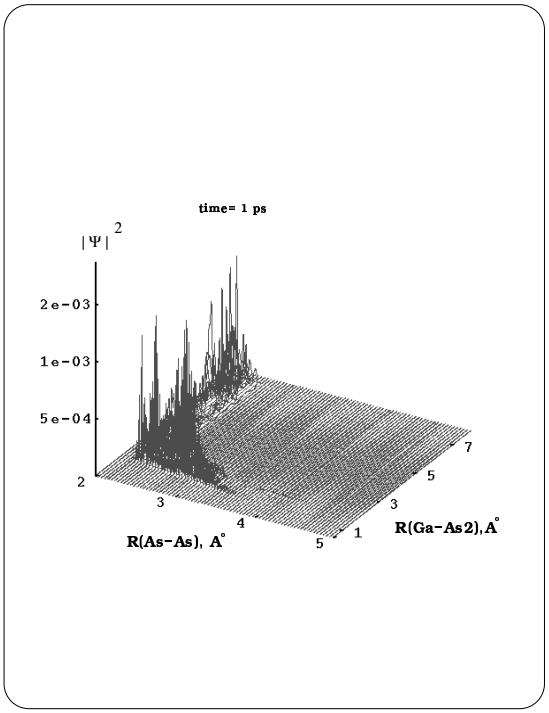
The phenomenological explanation of the observed dependence is the following. At translational energies below $E_{act}$, the effective energy transfer from the low frequency ($\approx$ 400 $cm^{-1}$) vibrational coordinate r to the translational coordinate Z facilitates tunneling through the barrier in the incoming Z-channel for the initially excited vibrational states. This increases the overall probability of $As_2$ dissociation for the excited vibrational states as compared to the ground vibrational state.

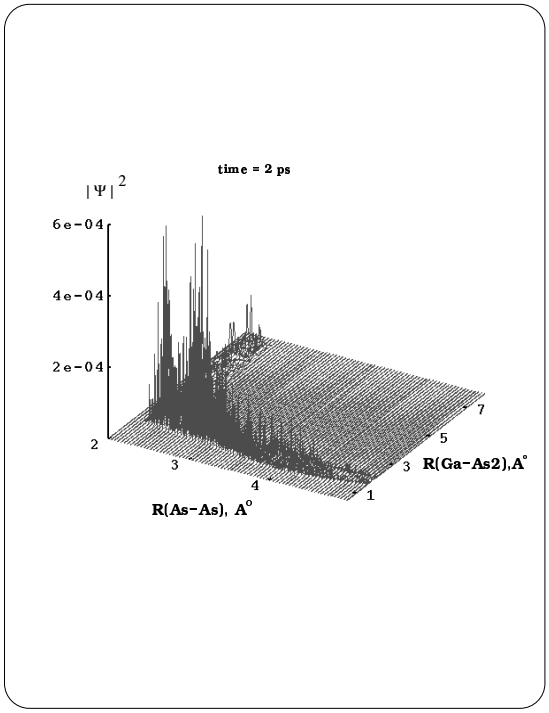
For the translational energies above $E_{act}$, the incoming wave function still feels the barrier and breaks into two pieces in its vicinity. One piece continues to move towards the surface into the molecular precursor state, while the second one is reflected back into the gas phase. The same picture holds for the wave function reflected off the repulsive wall of $As_2$ - surface potential at small Z. The r-coordinate is stretched in the vibrationally excited states as compared to the ground state (which has r = 2.18 $\AA$), and its value is close to that of the entrance transition state (r = 2.31 $\AA$). As a result, the vibrationally excited wave function efficiently "penetrates" the Z-coordinate activation barrier both on the way in and out of the surface. After several reflections, the overall result for the vibrationally excited wave function is an increased probability of scattering at the expense of dissociation. The barrier in the dissociation channel occurs at a significantly larger r = 3.36 $\AA$ so that none of the initial vibrational wave functions have significant amplitude in this region.

## 4. CONCLUSION

In conclusion we have calculated, for the first time, the DFT-based PES describing the dissociation of the $As_2$ molecule on the flat Ga-terminated GaAs(100) surface. Based on this PES, we have calculated the probabilities



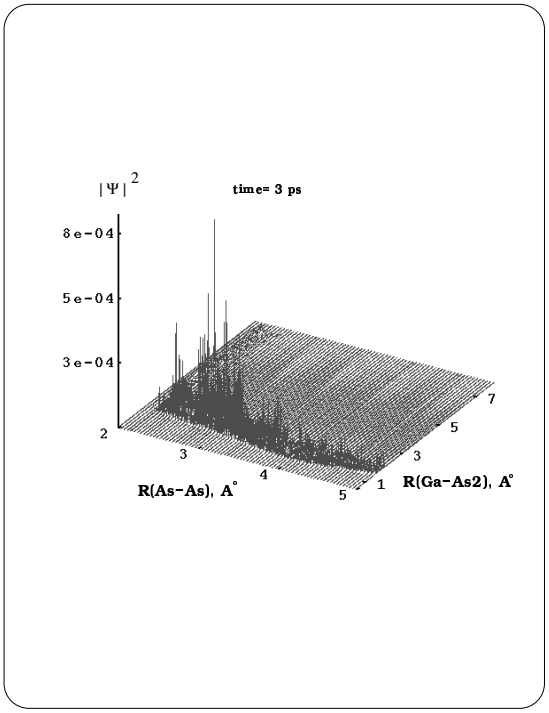




**Figure 3.** Snapshots of modulus squared of quantum wave function for the ground vibrational state v = 0, and initial translational energy $E_{tr}$ = 10113.7 $cm^{-1}$ at t = 0, 1, 2, and 3 ps respectively

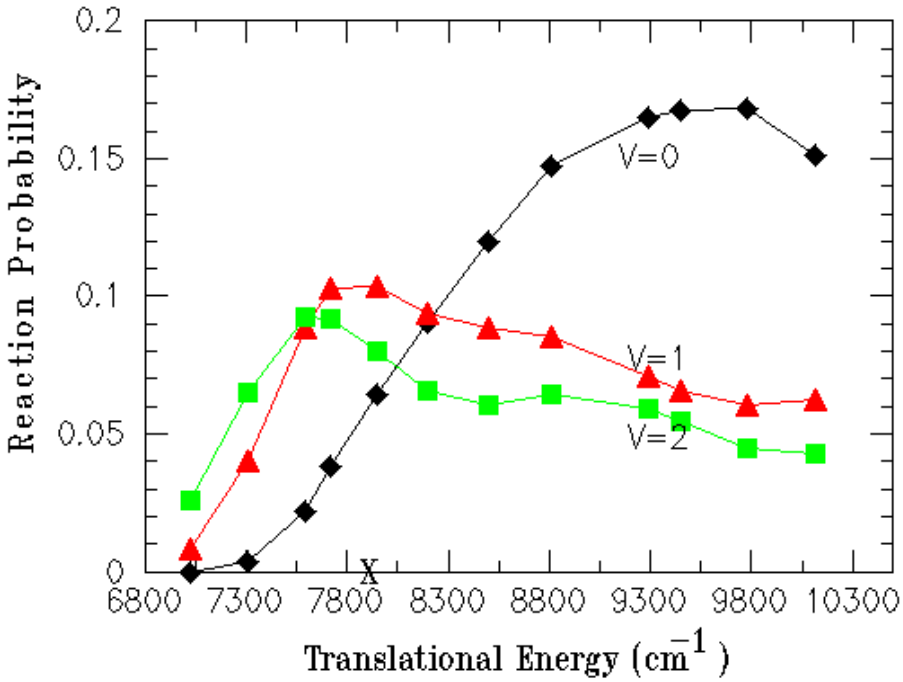



**Figure 4.** Combined probability of sticking and dissociation of $As_2$ as a function of the initial translational energy for the ground and first two excited vibrational states of $As_2$

of $As_2$ sticking and dissociation as a function of beam translational and vibrational energy using a quantum wave packet technique. The existence of the significant activation barrier and the strongly bound molecular chemisorption site indicates the importance of quantum effects in MBE growth of GaAs.

## ACKNOWLEDGMENTS

We thank M. Frumkin for help with parallelization and J. Musaev, D. Srivastava, and B. Biegel for useful discussions. This work was supported by MRJ, Inc. under NASA contract NAS2-14303.

## REFERENCES

1. J. R. Arthur, Surf. Sci. **43**, 449 (1974).
2. C. Foxon and B. Joyce, Surf. Sci. **50**, 434 (1975); *ibid* **64**, 293 (1977).
3. E. Tok, J. Neave, F. Allegretti, J. Zhang. T. Jones, B. Joyce, Surf. Sci. **371**, 277 (1997).
4. A. Ott, S. Casey, A. Alstrin, S. Leone, J. Vac. Sci. Technol. B **14**, 2742 (1996).
5. A. Madhukar, Surf. Sci. **132**, 344 (1983); S. V. Ghaisas and A. Madhukar, Phys. Rev. Lett. **56**, 1066 (1986).
6. S. Clarke and D. Vvedensky, Phys. Rev. Lett **58**, 2235 (1987); T. Shitara, D. Vvedensky, M. Wilby, J. Zhang, J. Neave, and B. Joyce, Phys. Rev. B **46**, 6815 (1992); P. Smilauer and D. Vvedensky, Phys. Rev. B **48**, 17603 (1993).
7. Ch. Heyn and M. Harsdorf, Phys. Rev. B **55**, 7034 (1997)
8. J. LePage, M. Alouani, D. Dorsey, J. Wilkins, P. Blochl, Phys. Rev B **58**, 1499 (1998).
9. Y. Fukunishi and H. Nakatsuji, Surf. Sci. **291**, 271 (1993); *ibid* 281; *ibid* 291.
10. K. E. Khor and S. Das Sarma, Phys. Rev. B **38**, 3318 (1988).
11. D. Conrad and K. Scheerschmidt, Phys. Rev. B **58**, 4538 (1998).
12. W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

13. A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
14. P. Hay and W. Wadt, J. Chem. Phys. **82**, 270 (1985); W. Wadt and P. Hay, *ibid* 284 (1985); P. Hay and W. Wadt, *ibid*, 299 (1985).
15. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, GAUSSIAN 94, Revision D.1, Gaussian, Inc., Pittsburg PA, 1995.
16. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in FORTRAN*, (Cambridge University Press), p. 120 (1992).
17. J. Muckerman, Chem. Phys. Lett **173**, 200 (1990).
18. J. Lin and J. Muckerman, Comp. Phys. Comm. **63**, 538 (1991); Y. Guan and J. Muckerman, J. Phys. Chem. **95**, 8293 (1991).
19. F.N. Dzegilenko and E. Herbst, J. Chem. Phys. **104**, 6330 (1996); F.N. Dzegilenko, E. Herbst, and T. Uzer, J. Chem. Phys. **102**, 2593 (1995).
20. V. A. Mandelstam and H. S. Taylor, J. Chem. Phys. **102**, 7390 (1995); *ibid* **103**, 2903 (1995).
21. S.K. Gray and G.G. Balint-Kurti, J. Chem. Phys. **108**, 950 (1998); S. K. Gray, J. Chem. Phys. **96**, 6543 (1992).
22. G.-J. Kroes, E.J. Baerends, and R.C. Mowrey, Phys. Rev. Lett. **78**, 3583 (1997); G.-J. Kroes, M. Wall, J. Pang, and D. Neuhauser, J. Chem. Phys. **106**, 1800 (1997)
23. Y. Huang, D. J. Kouri, and D. K. Hoffmann, J. Chem. Phys. **101**, 10493 (1994); Y. Huang, S. Iyengar, D. J. Kouri, and D. K. Hoffmann, J. Chem. Phys. **105**, 927 (1996).
24. H. Tal-Ezer and R. Kosloff, J. Chem. Phys. **81**, 3967 (1984).