Molecular Dynamics Simulations of the Influence of Surface Temperature on the Trapping of Methane on Iridium Single-Crystalline Surfaces[†]

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Classical molecular dynamics simulations have been performed to model the temperature dependence on trapping of methane on the (111) and the reconstructed (110) surfaces of iridium. Methane is modeled as a monatomic particle of mass 16 amu. The simulations suggest that on the (110)−(1 × 2) surface that the trapping probability scales nearly with total energy and that close to normal energy scaling is prevalent on the (111) surface, consistent with what is known from experimental measurements. Further, the simulations are in reasonable quantitative agreement with the measured trapping probabilities at a surface temperature of 65 K. For the highest surface temperature that we employed in the simulations, $T_s = 1465$ K, methane molecules that trapped appeared to be thermalized with the surface as determined by the translational energies and the angular distribution of the desorbing molecules. Additionally, the trapped molecules had calculated surface lifetimes that corresponded well with the physical adsorption well depth and surface temperature. The effect of surface temperature on the value of the trapping probability is complicated and strongly dependent upon the initial translational energy of the impinging particle; the trapping can both increase and decrease with increasing surface temperature. However, the values for trapping that we calculate from our simulations do not deviate markedly from their low-temperature values.

Introduction and Background

Methane is an important molecule in several industrial catalytic processes and as such it has been the subject of several important investigations in surface chemical dynamics.[1−4] The results of these experimental studies strongly suggested that a direct mechanism to dissociation is dominant for incident kinetic energies exceeding ∼0.2 eV. That is, it is thought that the molecule dissociates directly upon impact with the surface due to the high translational and/or the vibrational energy of the molecule.

Recently, it has been postulated that a precursor mechanism (trapping-mediated dissociative chemisorption) is dominant for the reactive adsorption of methane on the (110) and (111) surfaces of iridium for translational energies less than ∼0.1 eV.[5−7] In these studies the precursor is thought to be a trapped, physically adsorbed methane molecule that is thermalized with the surface. In a trapping-mediated dissociative chemisorption mechanism the impinging molecule collides with the surface and either scatters off directly or exchanges sufficient translational energy to fall into a physical adsorption well.[8−11] This last process is frequently referred to as trapping and it is the initial step in the binding and thermal accommodation of the molecule with the surface. In the trapping-mediated mechanism picture the thermally accommodated molecule has "forgotten" its gas-phase origins. In this scenario, the molecule is thought to be mobile on the surface and can either chemically react with the surface at selected sites or desorb back into the gas phase. In simple quantitative modeling of trapping-mediated chemi-

sorption, trapping is assumed to be independent of surface temperature and dependent only upon incidence kinetic energy and angle. Concomitantly, once the molecule is trapped and thermally accommodated, desorption and surface reaction are modeled by simple temperature-dependent rate coefficients. Thus, the dissociative chemisorption probability S_o in the trapping-mediated mechanism can be mathematically stated as the following:

$$S_o(E_i,\theta_i,T_s) = \alpha(E_i,\theta_i)[k_c(T_s)/(k_c(T_s) + k_d(T_s))]$$

in which k_c is the rate coefficient for dissociative chemisorption from the physically adsorbed state, k_d is the rate coefficient for desorption from the physically adsorbed state, α is the trapping probability, E_i is the incidence kinetic energy, θ_i is the incidence angle, and T_s is the surface temperature. It is clear from many previous studies[8,12−14] that the trapping probability α is dependent upon incidence translational energy E_i and incidence angle θ_i; what is less clear is the effect of surface temperature on trapping.

The trapping-mediated chemisorption model discussed above has proven to be quite useful in studies of initial chemisorption for facile adsorption systems (in which the barrier to chemisorption is below the vacuum zero level and the chemisorption probabilities are high) but much less is known about the utility of such a model for activated adsorption systems. In facile chemisorption systems the effect of T_s on the value of the trapping probability may not be so important since the highest dissociation rates occur at the lowest temperatures.[10,11,15] However, for trapping-mediated chemisorption in activated systems the probability for dissociative surface reaction increases as the substrate temperature increases.[16] For the case of methane, which is known to be activated on all single-crystalline transition metals that have been studied, the surface temperatures that

would be required for activation from a physically adsorbed precursor state would be expected to be very high (on Ir, surface temperatures well above 600 K are typically required for detection of dissociation). At such elevated temperatures the lifetime of the physically adsorbed precursor on the surface is expected to be very short and it is not known whether the precursor can accommodate thermally on such a short time-scale.[17-20] These considerations prompted the computational studies discussed in this paper.

It would be especially useful to determine the effect of surface temperature on trapping for activated chemisorption systems so that the trapping-mediated contribution to reactive adsorption could be better understood. The trapping-mediated component to dissociative chemisorption in gas−surface systems in equilibrium could, in principle, be substantial since, for example, a relatively large number of gas-phase molecules in a Maxwell−Boltzmann distribution at a temperature of 1000 K or less have translational energies in a regime in which the trapping probability could be significant.

Rettner and co-workers have previously studied the trapping-mediated dissociative chemisorption of nitrogen on W(100).[9] In this facile adsorption system the value of the trapping-mediated chemisorption probability was measurable by the King and Wells method (i.e., the values exceeded 0.05) even at surface temperatures as high as 800−1000 K and this prompted this group to perform a scattering study of the effect of surface temperature on trapping.[15] In this investigation of nitrogen scattering from W(100) the authors concluded that the trapping probability of nitrogen into the precursor state was relatively insensitive to surface temperature (accounting for 20% or less of the differences observed in scattering at 400 K and 800 K). Mullins, Rettner, and co-workers later studied the surface-temperature dependence of the trapping of Ar on Pt(111) by scattering measurements[21] and found that the trapping probability at the lowest energy kinetic employed (∼ 0.02 eV) decreased by approximately 25% upon increasing the surface temperature from 80 to 273 K. In a later paper Head-Gordon, Tully, and others showed that some of the decrease in trapping probability at higher kinetic energies was due to "quasi-trapped" Ar atoms that had accommodated their normal velocity component but not the parallel component.[22] The time scale for accommodation of the parallel momentum component for glancing incidence, high kinetic energy Ar atoms was longer than the average residence time of the atom on the surface at relatively high temperatures.

Finally, Madix and co-workers have investigated the effect of surface temperature of the trapping of ethane on Pt(111) employing classical molecular dynamics simulations[23] and determined that the value of the trapping probability decreases by no more than a factor of 2 over the surface temperature range from 100 to 700 K. Here we expand on these previous studies by presenting results of molecular dynamics simulations of the trapping of methane on iridium single crystals.

Computational Methods

The trajectory simulations performed and reported on in this paper employed a computer code developed by J. C. Tully.[22,24] Details regarding the algorithms and methods employed in the code have been discussed previously,[24] thus, only specific information regarding the simulations reported here will be discussed further.

The Ir(110) and Ir(111) surfaces were simulated using a 6 × 6 × 3 slab. The lattice constants and surface atom geometries match the surface being simulated. In the case of Ir(110) we assume the (1 × 2) "missing row" reconstructed surface. Forces between Ir atoms in the slab are harmonic with nearest and next nearest neighbors included. Periodic boundary conditions parallel to the surface are employed to simulate a larger surface. Dissipation and fluctuation are included at the bottom of the slab. Force and friction constants were chosen on the basis of the bulk Debye temperature.[24]

We model the methane molecule as a monatomic gas (we refer to this subsequently as "methon") with a mass of 16 amu. Thus, we are ignoring rotational and vibrational energy transfer in the collision dynamics. These degrees of freedom do not contribute much to the trapping dynamics and thus, the essential physics of the problem is captured by our calculations. If anything, we would expect the trapping to increase with these additional degrees of freedom available.

A pairwise sum of Morse potentials was used to describe the methon−slab interaction:

$$V = \sum_{j=1}^{108} D(\exp(-2\delta(r_j - r_o)) - 2\exp(-\delta(r_j - r_o)))$$

Here we are summing the interaction of methon with each Ir atom in the slab where $r_j - r_o$ is the distance from the "methon atom" to slab atom j. The parameters used for the methon/Ir(110) and methon/Ir(111) potentials are determined from experimental thermal desorption data[6] and trapping at 65 K on the Ir(110) surface. The binding energy, D, employed was 0.023 eV, the Morse range parameter used was $\delta = 1.13/$ Å, and the minimum separation distance r_o was taken to be 3.8 Å.

Simulation of Trapping at 65 K. In addition to simulations of trapping at temperatures far in excess of the nominal desorption temperature for methane on Ir we conducted simulations of the trapping of methane on both the Ir(110) and Ir(111) surfaces at lower temperatures (see Figure 1). These simulations were conducted employing a slab temperature of 65 K since this allowed a direct comparison of the calculated results with experimental data for the case of Ir(110)[5,6] (a direct comparison with Ir(111) at 65 K was not possible because experimental data could not be acquired at 65 K; the desorption temperature of methane on the Ir(111) surface is below 65 K). For these low-temperature simulations, trajectories were allowed to continue until the methon atom either (i) escaped ($Z > 10$ Å or (ii) the maximum number of integration steps had been completed (30 ps). The integration step size was 1 fs. For these low-temperature simulations the output from the code was sorted into two categories: scattered trajectories and trapped trajectories. Methon atoms that escaped from the surface in a time less than the maximum number of integration steps were categorized as scattered. A trajectory was considered trapped if the particle remained on the surface for 30 ps or longer.

As shown in Figure 1 the comparison of the simulation and the experimental data for the low-temperature case of trapping on Ir(110) is reasonable and this gave us confidence to employ the computer code for cases in which the surface temperature exceeded the desorption temperature.

Determination of Trapping at Surface Temperatures in Excess of the Desorption Temperature. A different criterion from that employed above must be used to determine the trapping probability from the results of simulations of methon scattering at surface temperatures in excess of the desorption temperature of methane from iridium. Here we will define trapping probability to mean the fraction of trajectories in a group of simulations that lead to a "fully thermalized" methon

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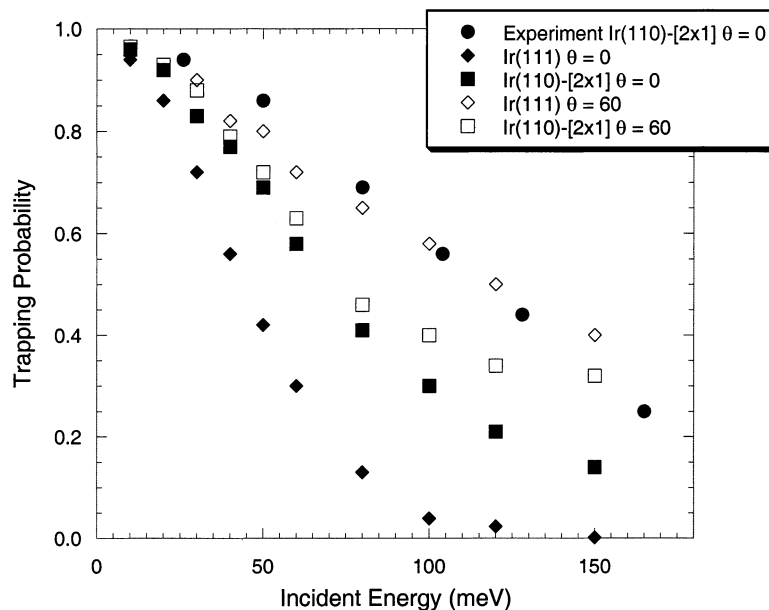*J. Phys. Chem. B, Vol. 106, No. 33, 2002* **8351**

Figure 1. Computed and measured trapping probabilities at a surface temperature of 65 K. Each calculated point represents the results from 1000 trajectories.
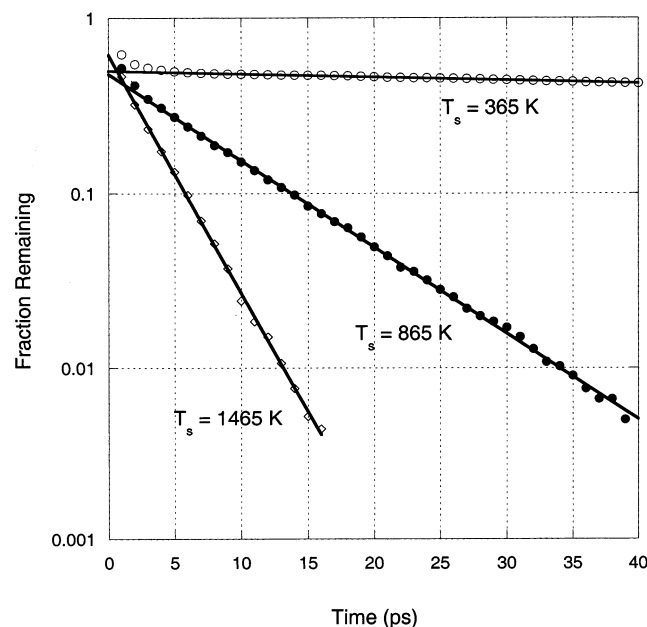

Figure 2. Fraction of particles remaining on the surface as a function of time parametric in surface temperature. The incidence energy was 50 meV on Ir(110) at normal incidence. Each decay curve is the result of that 10 000 trajectories. The solid line is a fit to an exponential decay function ignoring the first couple of points.

Figure 3. An expansion of Figure 2 at early times. [Fraction of particles remaining on the surface as a function of time parametric in surface temperature. The incidence energy was 50 meV on Ir(110) at normal incidence.]

atom on the simulated Ir slab. We employ the method of Adams and Doll[25] to determine the fraction of thermalized methon atoms. In this method the logarithm of the number of particles still bound to the surface is plotted versus methon residence time. Extrapolating back to time zero employing the slope at long times yields the initial "thermalized" trapping probability (e.g., see Figures 2 and 3). Head-Gordon and Tully[22] have criticized this method noting that for energetic, glancing incidence argon atoms impinging on a Pt(111) surface the time scale for accommodation in the parallel direction is much longer than the time scale in the normal direction. Thus, treatment of data by the Adams and Doll method would be misleading because the Ar atoms are not truly thermalized since many of the atoms, particularly at higher surface temperatures, desorb
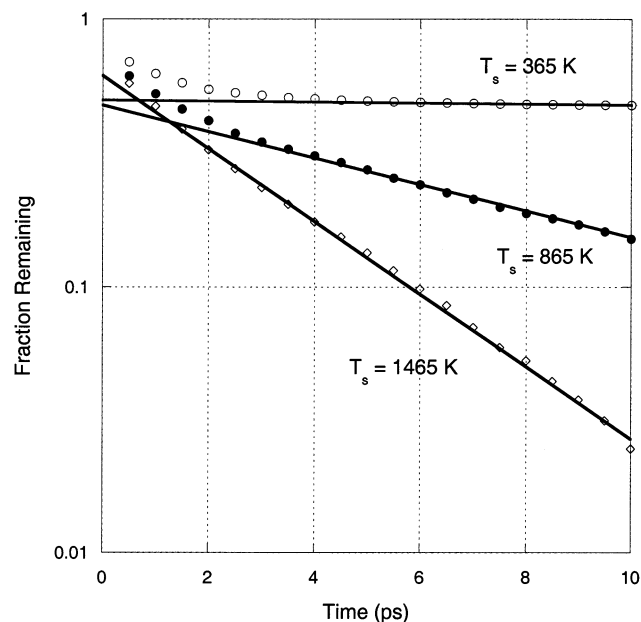
prior to parallel momentum accommodation. However, we have found that such issues are not relevant for lower translational energy particles (i.e., incidence energies that are smaller than or comparable to the binding energy of the particle) and especially those at normal incidence angles. Here we report on calculations in which the Adams and Doll method can be used accurately by checking the time scale of parallel momentum accommodation to ensure thermalization. Thus, we have exclusively studied very low translational energy particles in our simulations. As mentioned above, perhaps it is the lowest energy particles that are of most importance since under equilibrium conditions, even at relatively high temperatures, the vast majority of methane molecules would have translational energies less than the binding energy.

Results and Discussion

In Figure 1 the calculated trapping probabilities for methon on Ir(110) at two different incidence angles are shown as a function of incidence translational energy and compared to experimental measurements of the trapping of methane.[5,6] In both the experiments and the simulations, adsorption (at angles other than normal incidence) is azimuthally against the rows (i.e., normal to the rows) of the Ir(110) reconstructed surface. Experimentally the trapping of methane scales almost perfectly with total energy;[6] in the simulations we see an energy-angle scaling intermediate between total energy and normal energy but much closer to total energy scaling.

Experimental measurements regarding the simulations of trapping from the Ir(111) surface are not available because the desorption temperature of methane from this surface was less than 65 K and this was the lowest temperature attainable experimentally. However, it is still instructive to study the calculated results. The trapping simulations shown in Figure 1 suggest a much stronger effect of incidence angle on Ir(111) than on Ir(110). Careful examination of the results indicate that the energy-angle scaling parameter that would best fit the trapping values on Ir(111) is between $n = 1.0$ and $n = 1.6$ (i.e., $\alpha = \alpha \ (E_i \cos^{0.35} \theta_i)$; recall that $n = 0$ would describe total energy scaling and $n = 2$ would describe normal energy scaling); much closer to normal energy scaling. The dissociative chemisorption data for methane on Ir(111)[7] in the low kinetic energy regime (i.e., trapping-mediated chemisorption regime) also suggest a scaling close to normal energy scaling.

Figures 2 and 3 display the logarithm of the fraction of methon particles remaining on the simulated Ir(110) surface as a function of time, parametric in surface temperature for an incidence kinetic energy of 50 meV at normal incidence. As seen most easily in Figure 3, there is a deviation between the line fit to the long-time data and the early (i.e., less than 4 ps) portion of the trajectories. This deviation is a result of methon particles that scatter from the surface within the first few picoseconds without thermalizing. Particles that remain on the surface beyond this point have thermalized to the surface temperature as evidenced by determination of the average translational energy of the desorbing particles as a function of time and their angular distribution of desorption (these results are not shown). The average translational energy of the desorbing particles is thermal and, within computational uncertainties, the angular distribution is an equilibrium distribution. If we extrapolate these data back to time zero the vertical axis intercept can be interpreted as the initial fraction of particles that trap, i.e., the trapping probability. With careful examination of this procedure we note two things: first, the values that we extrapolate to as intercepts of the fraction remaining do not vary drastically with temperature and second, these values lead to calculated trapping probabilities that are quite comparable with the value of the trapping probability computed at 65 K. We also note that by considering the desorption process to be first order, a time constant for desorption, or the mean lifetime on the surface can be determined from these plots as a function of temperature. These results, for both the Ir(110) and Ir(111) surfaces are plotted in an Arrhenius construction in Figure 4 and the apparent activation energy from this plot can be interpreted as the physical adsorption well-depth. For the Ir(110) case the activation energy, as determined from these simulations, has a value of 0.182 eV, in reasonable agreement with the experimental value of the well-depth based on thermal desorption measurements (0.15 eV). For the Ir(111) case the value is
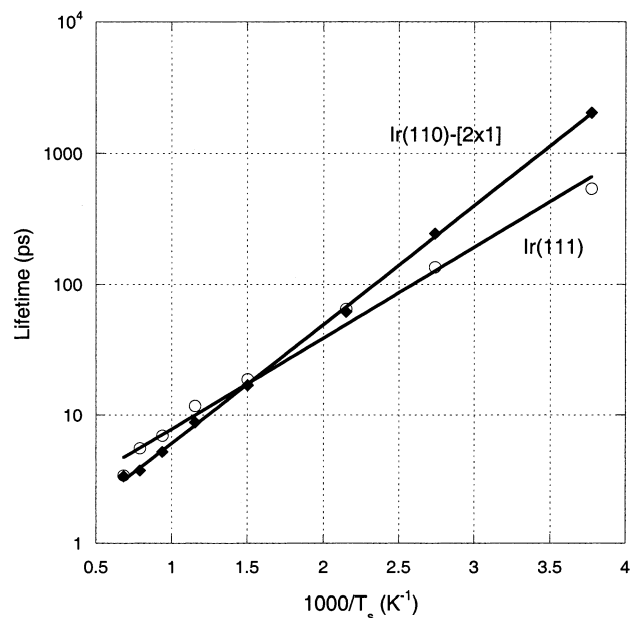

Figure 4. Methon mean lifetime on Ir(111) and Ir(110)$-$(1 $\times$ 2) as a function of inverse temperature. The lifetime is taken as the reciprocal of the slope of decay curves similar to those shown in Figure 2.
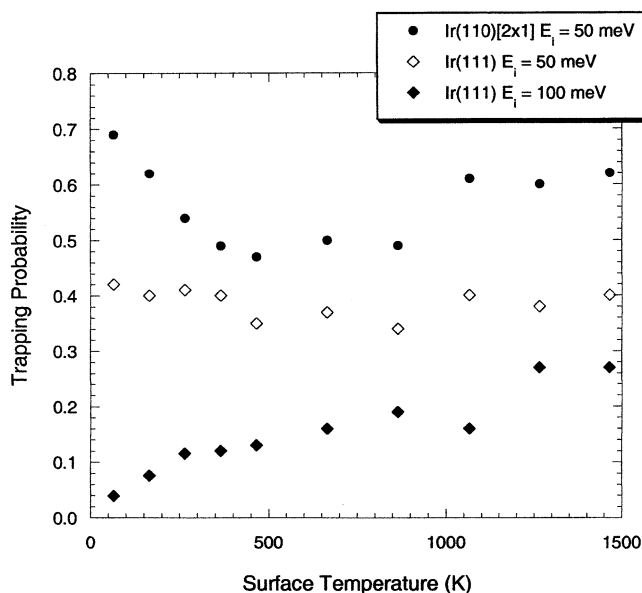

Figure 5. Computed trapping probability at normal incidence as a function of surface temperature. Each point represents 1000 trajectories except for the three points associated with the results shown in Figure 2 (365, 865, and 1465 K).

0.129 eV. We do not have an experimental value for comparison but we know that it should be less than that for Ir(110).

Finally, in Figure 5 we display trapping probabilities as a function of surface temperature determined from trajectory calculations as described above for both the Ir(111) and Ir(110) surfaces. In two of the cases the incidence angle is normal and the incidence kinetic energy is 50 meV. The other case has an initial translational energy of 100 meV and is also at normal incidence. For the case of incidence energy of 50 meV on Ir(110), the trapping probability decreases slightly with increasing surface temperature from a value of approximately 0.69 at 65 K. For the case of incidence energy of 50 meV on Ir(111), the trapping probability remains nearly constant with increasing surface temperature from an a value of approximately 0.42 at 65 K. For the higher incidence energy (100 meV) trapping data

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on Ir(111) the value of the trapping probability increases noticeably from a value of approximately 0.04 at 65 K as the surface temperature increases. These results are consistent with results from simple hard cube models[26,27] which also indicate only small deviations in the trapping probability as a function of surface temperature. Hard cube models also show similar trends, with the trapping probability increasing with increasing surface temperature for small values of the trapping probability and vice versa for high values.

These results suggest that for activated dissociative chemisorption systems (i.e., methane on transition-metal single-crystal surfaces) a trapping-mediated precursor mechanism is likely to play a dominant role in the reactive adsorption for systems either in equilibrium (i.e., a Maxwell−Boltzmann distribution of kinetic energies) or for low translational energy molecules in molecular beam experiments regardless of the surface temperature. Indeed, it is likely that detection of adsorption under such conditions will be enhanced by increased surface temperature.

Summary

Classical trajectory calculations of methane physical adsorption on two different Ir surfaces capture the essential physics of the process and the simulations are in reasonable quantitative agreement with the experimental measurements available. The energy-angle scaling behavior of trapping on both the corrugated Ir(110) surface and the smooth Ir(111) surface is predicted adequately. Further, the values of the trapping probability as a function of translational energy and incidence angle for the Ir(110) surface are in reasonable agreement with the experimental measurements. Finally, our simulations suggest that surface temperature affects the value of the trapping in complicated ways: for conditions in which the value of the trapping probability is relatively high then increasing surface temperature slightly decreases the value of the trapping probability slightly and vice versa.

Our results strongly suggest that for activated dissociative chemisorption systems that a trapping-mediated mechanism is likely to be a dominant component of the reactive adsorption for systems in equilibrium or for low translational energy molecules in molecular beam experiments.

References and Notes

(1) Rettner, C. T.; Pfilur, H. E.; Auerbach, D. J. *Phys. Rev. Lett.* **1985**, *54*, 2716.

(2) Ceyer, S. T. *Annu. Rev. Phys. Chem.* **1988**, *39*, 479 and references therein.

(3) Luntz, A. C. *J. Chem. Phys.* **1989**, *90*, 1274; Schoofs, G. R.; Arumainayagam, C. R.; McMaster, M. C.; Madix, R. J. *Surf. Sci.* **1989**, *215*, 1.

(4) Larsen, J. H.; Chorkendorf, I. *Surf. Sci. Rep.* **1999**, *35*, 163 and references therein.

(5) Seets, D. C.; Wheeler, M. C.; Mullins, C. B. *Chem. Phys. Lett.* **1997**, *266*, 431.

(6) Seets, D. C.; Wheeler, M. C.; Mullins, C. B. *J. Chem. Phys.* **1997**, *107*, 3986.

(7) Seets, D. C.; Reeves, C. T.; Ferguson, B. A.; Wheeler, M. C.; Mullins, C. B. *J. Chem. Phys.* **1997**, *107*, 10299.

(8) Mullins, C. B.; Weinberg, W. H. *J. Chem. Phys.* **1990**, *92*, 3986; *J. Chem. Phys.* **1990**, *92*, 4508; *J. Vac. Sci. Technol. A* **1990**, *8*, 2458.

(9) Rettner, C. T.; Stein, H.; Schweizer, E. K. *J. Chem. Phys.* **1988**, *89*, 3337; Rettner, C. T.; Schweizer, E. K.; Stein, H. *J. Chem. Phys.* **1990**, *93*, 1442; Rettner, C. T.; Stein, H.; Schweizer, E.; Auerbach, D. J. *J. Vac. Sci. Technol. A* **1989**, *7*, 1863.

(10) Soulen, S.; Madix, R. J. *Surf Sci.* **1995**, *323*, 1.

(11) Wheeler, M. C.; Seets, D. C.; Mullins, C. B. *J. Chem. Phys.* **1996**, *105*, 1572; Davis, J. E.; Nolan, P. D.; Karseboom, S. G.; Mullins, C. B. *J. Chem. Phys.* **1997**, *107*, 943.

(12) Rettner, C. T.; Bethune, D. S.; Auerbach, D. J. *J. Chem. Phys.* **1989**, *91*, 1942.

(13) Rettner, C. T.; Mullins, C. B.; Bethune, D. S.; Auerbach, D. J.; Schweizer, E. K.; Weinberg, W. H. *J. Vac. Sci. Technol. A* **1990**, *8*, 2699.

(14) Arumainayagam, C. R.; Madix, R. J. *Prog. Surf. Sci.* **1991**, *38*, 1.

(15) Rettner, C. T.; Schweizer, E.; Stein, H.; Auerbach, D. J. *Phys. Rev. Lett.* **1988**, *61*, 986.

(16) King, D. A. *CRC Critical Rev. Solid State Mater. Sci.* **1978**, *7*, p 167.

(17) Chakravarty, C.; Metiu, H. *J. Chem. Phys.* **1995**, *102*, 8643.

(18) Weinberg, W. H. *J. Vac. Sci. Technol. A* **1992**, *10*, 2271.

(19) Walker, A. V.; King, D. A. *J. Chem. Phys.* **2000**, *112*, 4739.

(20) Luntz, A. C.; Winters, H. F. *J. Chem. Phys.* **1994**, *101*, 10980.

(21) Mullins, C. B.; Rettner, C. T.; Auerbach, D. J.; Weinberg, W. H. *Chem. Phys. Lett.* **1989**, *163*, 111.

(22) Head-Gordon, M.; Tully, J. C.; Rettner, C. T.; Mullins, C. B.; Auerbach, D. J. *J. Chem. Phys.* **1991**, *94*, 1516.

(23) Stinnett, J. A.; Weaver, J. F.; Madix, R. J. *Surf. Sci.* **1997**, *380*, 489.

(24) Tully, J. C. *J. Chem. Phys.* **1980**, *73*, 1975; Muhlhausen, C. W.; Williams, L. R.; Tully, J. C. *J. Chem. Phys.* **1985**, *83*, 2594.

(25) Adams, J. E.; Doll, J. D. *Surf. Sci.* **1981**, *103*, 472.

(26) Logan, R. M.; Stickney, R. E. *J. Chem. Phys.* **1966**, *44*, 195.

(27) Logan, R. M.; Keck, J. C. *J. Chem. Phys.* **1968**, *49*, 860.