"Early" and "Late" Barriers in Dissociative Attachment: Steering Surface Reaction

4 AUTHORS, INCLUDING:

Maryam Ebrahimi
University of Waterloo
13 PUBLICATIONS **73** CITATIONS

SEE PROFILE

Iain Mcnab
Sheridan College (Oakville)
**64** PUBLICATIONS **891** CITATIONS

SEE PROFILE

"Early" and "Late" Barriers in Dissociative Attachment: Steering Surface Reaction

Maryam Ebrahimi, Si Yue Guo, Iain R. McNab, and John C. Polanyi*

Lash Miller Chemical Laboratories, Department of Chemistry and Institute of Optical Science, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

ABSTRACT In gaseous or surface reactions, "early" barriers along the reaction coordinate are commonly surmounted by reagent translation, and "late" barriers are surmounted by vibration. Here, we link barrier location to the separation of the reaction products (2H or H + Cl) following dissociative attachment of H_2 and HCl at silicon. Two markedly different approximations are used to represent Si(100)-2×1, a pair of silyl radicals and a cluster of 53 silicon atoms. In both approximations, the crest of the energy barrier is found to be located early along the reaction coordinate for attachment at neighboring silicon atoms and late for attachment at more widely separated silicons. This suggests a means for steering reaction by reagent translation or vibration, to give dissociative attachment at closer or further separations on a surface.

SECTION Surfaces, Interfaces, Catalysis
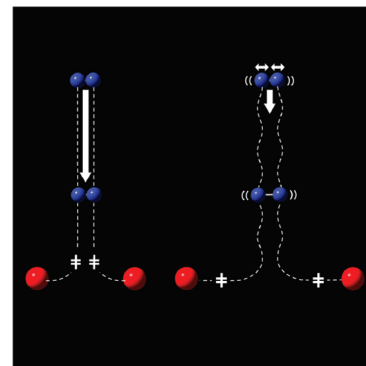
The location of the crest of the potential energy barrier along the reaction coordinate in simple atomic-transfer reactions can be a useful index of the dynamics.[1] The barrier crest is termed "early" if it lies along the approach coordinate for the reagents and "late" if it lies along the retreat (separation) coordinate for the products. Theory showed that potential energy surfaces (PESs) with an early barrier crest were most efficiently traversed by translationally excited reagents, whereas those with a late barrier crest showed a strong preference for reagent vibration. Additionally it was found that in related families of reaction, increasing barrier height correlated with shifting of the barrier crest from early to late.[2]

There is a body of experimental and theoretical literature from previous decades supporting these generalizations.[3−10] In recent sophisticated crossed molecular beam studies, Liu and co-workers examined the applicability of these rules to more complex systems.[11,12] The theory for polyatomic reactions shows that such generalizations require careful interpretation.[13,14]

The early barrier as against late barrier categorization has also been shown to be of value in rationalizing atom-transfer reactions taking place at surfaces.[15−17] To the best of our knowledge, correlation between barrier location and product separation in surface reaction has not, until now, been discussed.

Here, we have computed PESs for dissociative attachment of H_2 or HCl at Si(100)-2×1 to form a pair of chemisorbed atoms at the surface, 2 H−Si or H−Si + Cl−Si. Two different approximations were used to represent the surface atoms; in the first crude approximation, we employed (cf. earlier work)[18] a pair of silyl radicals set at a selected separation, and in the second, we used a multilayer silicon cluster terminated

by hydrogen atoms, $Si_{53}H_{44}$, providing surface silicons at various separations (details in Supporting Information).

The variable of interest in this work was the separation of the chemisorbed atoms at the surface in their final state. The variation in separation is well-known (see, for example, ref 19) and is ascribed to the existence of competing reactive pathways, even at a rigid surface. In both approximations, the minimum energy path (MEP) across the PES showed a clear correlation between increasing final-state pair separation, increased barrier height, and a shift in the barrier crest from early to late.

This shift in barrier location is expected to alter the preferred mode of motion in the reagents. Traversal of what we find to be the early barrier case, leading to reaction at a more closely neighboring pair of reagent Si-atoms, should be favored by reagent translation, whereas crossing of the late barrier leading to more widely separated pairs of chemisorbed products should be favored by reagent vibration. This suggests a means to the selective steering of surface reaction toward one or another of these outcomes, forming either closer or more distant pairs of dissociative reaction products.

The dissociative attachment of H_2 at Si(100)-2×1 is well studied and has been the subject of recent reviews.[20,21] It is a prototype for the dynamics of gas plus surface interactions on semiconductors.[22] When H_2, which has a bond length of 0.74 Å, dissociatively attaches as two H−Si at Si(100)-2×1, it does not attach at a single silicon dimer with a H-atom separation of 3.5 Å but preferentially at adjacent silicons of two silicon dimers of a dimer row, corresponding to a final

(A) DISILYL   (B) CLUSTER   (C) SITES
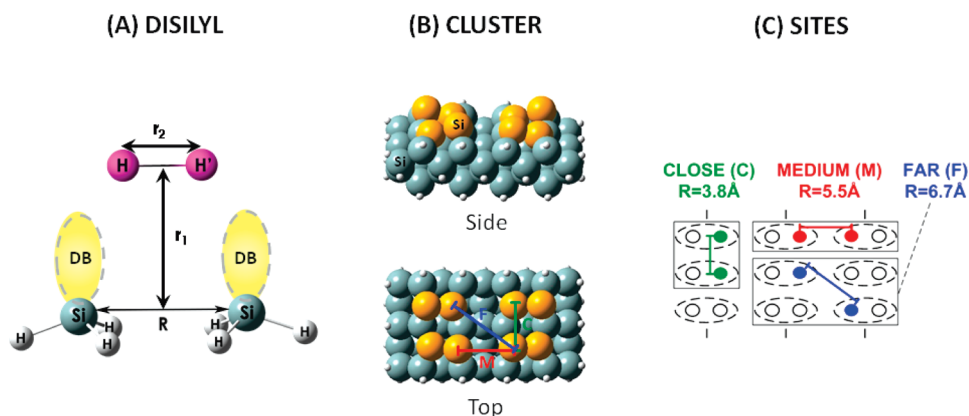
Figure 1. Schematic of the two simple models, disilyl and cluster, used in the calculations, together with the coordinate system and the three Si−Si separations being explored. (A) Two silyls placed at a distance R apart, with r_1 as the approach coordinate for dissociative attachment and r_2 as the retreat coordinate, exemplified for the case of H_2 dissociative adsorption. (B) Silicon cluster ($Si_{55}H_{44}$) comprising four silicon dimers (yellow) buckled in the c(4×2) configuration, seen from the side and the top. (C) Three pairs of reactive sites, Close, Medium, and Far.

H-atom separation of 3.8 Å. This is the separation which we characterize as "Close" in the following study, in which we seek to illuminate the contrasting molecular dynamics as compared with "Medium" and "Far" H−Si + H−Si pair formation at 5.5 and 6.7 Å, respectively.

Our second model system, the dissociative adsorption of HCl at Si(100)-2×1, has been subject to relatively little experiment or theory.[23−25] It has been selected since it would lend itself to an experimental comparison of the outcome of reaction induced by enhanced reagent translational energy (HCl from a supersonic jet) against reagent vibration (HCl excited by infrared radiation).

In this work, we examined dissociative attachment at the 2×1 reconstruction of the Si(100) silicon surface.[26] At room temperature, the repeat unit is the silicon dimer,[27] within which silicon atoms are separated by 2.28 Å.[28] Silicon dimers form dimer rows at the surface, which are separated by 7.68 Å; within the dimer rows, adjacent silicon dimers are separated by 3.84 Å.

The approach of a diatomic molecule to a surface is a six-dimensional problem.[29] Here, we reduce this to a two-dimensional problem by employing two different approximations, both of which are shown in Figure 1 (details in Supporting Information). Figure 1A shows our simple disilyl model, while Figure 1B shows the more realistic cluster model used for comparison with the disilyl model. This cluster is the smallest that contains the reaction product separations that we investigate. The uppermost layer of silicon atoms (yellow) comprises four silicon dimers in the c(4×2) configuration. For clarity, the distances used are also shown on the schematic diagram in Figure 1. In Figure 1C, the ovals shown in dashed lines represent silicon dimers, circles within the dashed ovals represent silicon atoms, and vertical lines indicate the dimer row directions.

In this work, we used the three Si−Si separations, R, indicated in Figure 1B and C, designated Close (C), Medium (M), and Far (F). The Close distance, C = 3.8 Å, corresponds to a reaction at the same side of two adjacent silicon dimers of a single dimer row. The Medium distance, M = 5.5 Å,

corresponds to dissociative attachment at two adjacent silicon atoms of two adjacent dimer rows. The Far distance pair, F = 6.7 Å, corresponds to dissociative attachment at nonadjacent silicon atoms of two silicon dimer rows, as shown in Figure 1C.

For the disilyl model, the resulting PESs were computed using density functional theory (DFT) as implemented in the program Gaussian 03[30] (UB3LYP/6-311G); the PESs are displayed in Figure 2. Internal silyl coordinates and the silyl separation, R, were held fixed while a grid of singlet energies was calculated with 0.2 Å steps in r_1 and r_2 over the ranges shown in Figure 2; the grids of energy points were mapped (using IgorPro[31]) to assigned false colors according to the energy values $E(r_1, r_2)$, and isoenergy contours were generated in IgorPro using Snyder's algorithm.[32] For the Close separation of the silicon atoms, the crest of the energy barrier occurred at the position marked **X** ($r_1 = 2.4$ Å, $r_2 = 0.8$ Å), corresponding to an early barrier reaction. As the Si−Si separation distance increased, first to Medium and then to Far, the crest of the energy barrier moved first to an intermediate position and then to a late position along the MEP. As the barrier crest got later, the barrier height increased; this is a strong correlation discussed in previous work.[2]

Figure 3A shows the energy profiles along the MEP for dissociative reaction of H_2 at the Si(100)-2×1 surface, calculated using the disilyl model at three separations, C, M, and F. The inset in Figure 3B shows energy profiles at the Close and Far separations, C and F, calculated using the cluster model.

The cluster model energies were calculated using DFT as implemented in Gaussian 03[30] (B3LYP/6-31G(d)); the atomic coordinates of the cluster were frozen, except for the silicon dimers (colored yellow in Figure 1), which were allowed to relax. We located points on the MEPs (shown in Figure 3B) by calculating cuts through the potential surface; the transition state and MEP coordinates were located to within 0.1 Å in r_1 and r_2. The results were in qualitative accord with the results of the disilyl model. For dissociative attachment occurring at a Close pair of silicon atoms, the barrier was early, while for dissociative attachment at a Far pair of silicon atoms, the
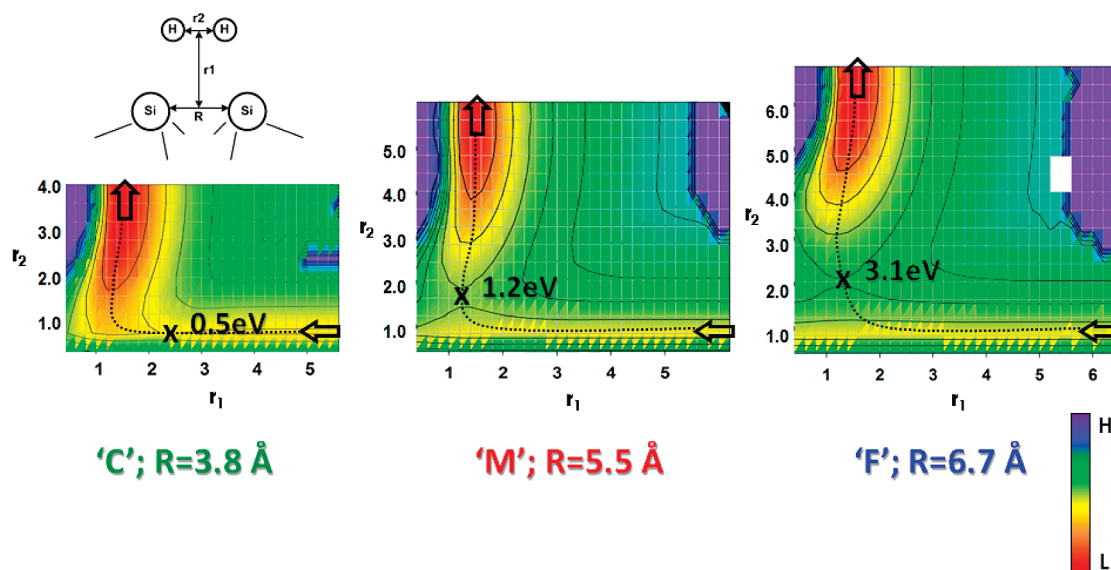
Figure 2. Three PESs calculated using the disilyl model, one for the Close separation of the product H–H atoms, one for the Medium separation, and one for the Far separation. The barrier can be seen to increase progressively and move to a later location in going from a H–H separation that is Close to Medium and Far. The three PESs exhibit early, intermediate, and late barrier crests with increasing barrier height.
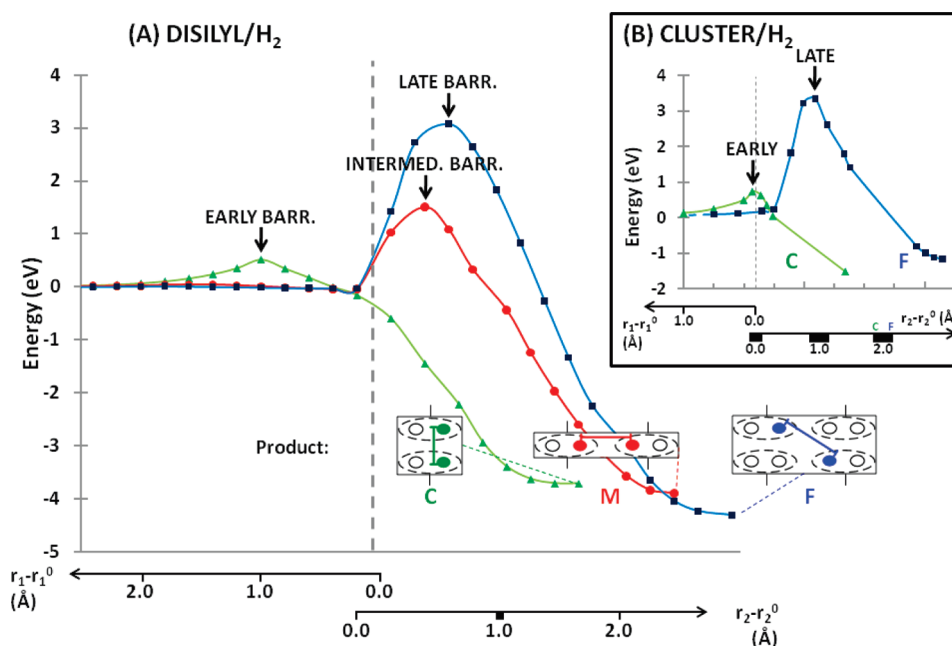
Figure 3. Energy profiles along the MEPs for H_2 dissociative attachment at Close, Medium, and Far Si–Si separations (A) for the disilyl model and (B) for the $Si_{53}H_{44}$ cluster model. The dashed line indicates the point along the reaction coordinate at which the entry valley of the PES can be regarded as giving way to the exit valley; old and new bonds are equally extended, $r_1 = r_1^0$, $r_2 = r_2^0$.

barrier was late. The calculated energy barriers, barrier crest locations, and heats of reaction obtained according to the two models are shown in Table 1. The simple disilyl model leads to exaggerated heats of reaction since the products are two gaseous silane molecules rather than a pair of more weakly bound H–Si at a silicon surface.

In the early and late barrier crest cases for H_2 (attachment at Si atoms 3.8 and 6.7 Å apart, respectively), the energy required for barrier crossing can be differently ascribed. In the

case of the early barrier, the reagents repel as the H–Si separation decreases from 5.8 to 2.8 Å (by contrast, the H–H separation remains close to its equilibrium value of 0.74 Å), whereas in the case of the late barrier, substantial work is done in stretching the H–H bond from 0.74 to 2.0 Å.

Figure 4 shows the computed energy profiles for dissociative attachment of HCl to Si(100)-2×1. The resulting barrier heights, ranging from approximately 1 eV for C to 2.5 eV for F, are expected to be upper limits, too high by some tenths of an

Table 1. Energy Barriers, Barrier Crest Locations, and Heats of Reaction for the Three Reactive Outcomes of H_2 and HCl Dissociative Attachment

molecule	Si—Si separation R (Å)	model	E_b (eV)	barrier location r_1; r_2 (Å)	$\Delta H°$ (eV)
H_2	C: 3.8 Å	disilyl	0.5	$r_1 = 2.4; r_2 = 0.8$	−3.7
		cluster	0.7	$r_1 = 1.9; r_2 = 1.0$	−1.5 (−2.0)[a]
		experiment[20]	0.6−0.7		−2.0
	M: 5.5 Å	disilyl	1.5	$r_1 = 1.2; r_2 = 1.6$	−3.9
		cluster			
	F: 6.7 Å	disilyl	3.1	$r_1 = 1.2; r_2 = 2.0$	−4.3
		cluster	3.3	$r_1 = 1.3; r_2 = 2.0$	−1.2 (−1.3)[a]
HCl	C: 3.8 Å	cluster	1.0	$r_1 = 2.1; r_2 = 1.6$	−1.2
	M: 5.5 Å	cluster	1.3	$r_1 = 1.6; r_2 = 2.0$	−1.0
	F: 6.7 Å	cluster	2.5	$r_1 = 1.6; r_2 = 2.4$	−1.0

[a] For the final state, in addition to four Si dimer atoms, H_2 atoms are also relaxed.
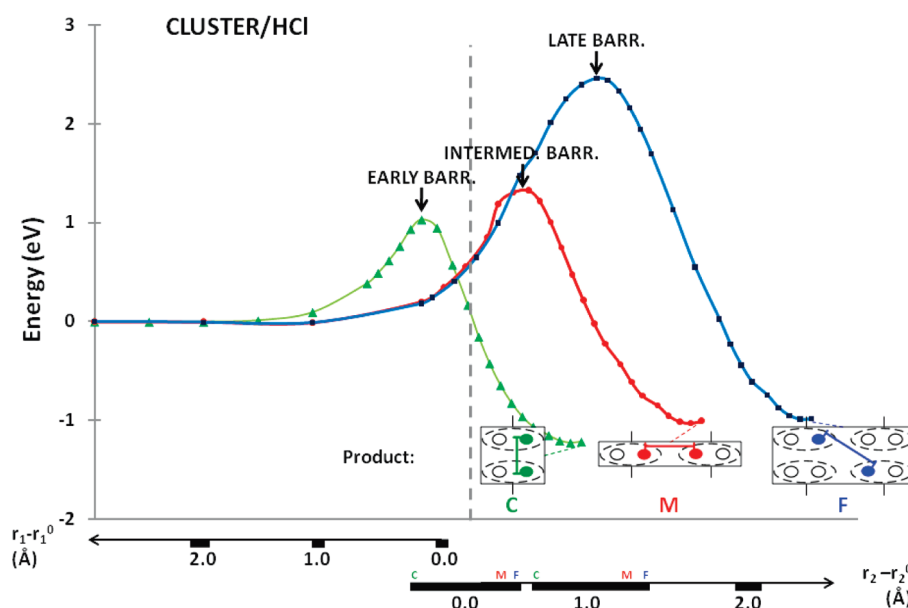
Figure 4. Energy profiles along the MEPs for HCl dissociative attachment at Close, Medium, and Far Si—Si separations for the cluster model. Due to differences in the MEPs, positions along the reaction coordinate correspond to different values of the separation coordinate in the three cases C, M, and F, as indicated by the horizontal black bars.

electronvolt due to suppression of relaxation of the silicon cluster and variation of the tilt angle of the H—Cl molecular axis as the system proceeds along the reaction coordinate.

The principal approximations used in the cluster model calculations were the cluster size (53 silicon atoms) and restriction of the reaction path to symmetric coplanar motion (implied by the use of only the two variables r_1, approach, and r_2, retreat, pictured in Figure 1A for the disilyl model). Within these approximations, we found good agreement between our calculation and available experimental data. The experimental value for the barrier height for H_2 reacting to form the experimentally observed Close H—Si pair at the surface is 0.6−0.7 eV,[20] while our computed value is 0.7 eV; see Table 1.

The approximate cluster calculation for the dissociative attachment of HCl has been included since this dipolar molecule lends itself to experimental comparison of reagent translation with reagent vibration induced by infrared excitation.

The calculations were made at a lower level of approximation — the simple disilyl representation of the silicon surface — and at a higher level — the five-layer 53 silicon atom cluster — to highlight the robustness of the principal finding; a shift in the location of the barrier crest from early to late in dissociative attachment leads to more widely separated chemisorbed reaction products.

The dynamical consequences of such a substantial change in the nature of the PES governing a single chemical reaction, whether attachment of H_2 or of HCl, is likely to be marked. Evidence from both theory and experiment supports the plausible notion that translational motion, bringing the reagents H_2 or HCl toward the surface, will be more effective in carrying the system over a barrier in the approach coordinate, r_1, whereas reagent vibration, able to produce momentum separating H from H in H_2 or H from Cl in HCl, will be more effective in carrying the system over a barrier in the retreat

coordinate, r_2. The importance of barrier location in influencing the effectiveness of reagent translation against vibration in the surface reaction has been noted by earlier workers on the grounds of both theory and experiment.[14,22] The contribution of this study is the correlation of early and late barriers with dissociative attachment to yield closer and more widely separated reaction products.

SUPPORTING INFORMATION AVAILABLE

Details of the calculations and $Si_{53}H_{44}$ cluster model coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: jpolanyi@chem.utoronto.ca.

REFERENCES

(1) Polanyi, J. C.; Wong, W. H. Location of Energy Barriers. I. Effect on the Dynamics of Reactions A + BC. *J. Chem. Phys.* **1969,** *51,* 1439–1450.

(2) Mok, M. H.; Polanyi, J. C. Location of Energy Barriers. II. Correlation with Barrier Height. *J. Chem. Phys.* **1969,** *51,* 1451–1469.

(3) Polanyi, J. C. Some Concepts in Reaction Dynamics. *Acc. Chem. Res.* **1972,** *5,* 161–168.

(4) Polanyi, J. C. Some Concepts in Reaction Dynamics. *Science* **1987,** *236,* 680–690.

(5) Heismann, F.; Loesch, H. J. Vibrational and Translational Enhancement of Endothermic Reactions: K + HCl($v = 0,1$) and K + HF($v = 0,1$). *Chem. Phys.* **1982,** *64,* 43–67.

(6) Zare, R. N. Laser Control of Chemical Reactions. *Science* **1998,** *279,* 1875–1879.

(7) Crim, F. F. Chemical Dynamics of Vibrationally Excited Molecules: Controlling Reactions in Gases and on Surfaces. *Proc. Natl. Acad. Sci. U.S.A.* **2008,** *105,* 12654–12661.

(8) Killelea, D. R.; Campbell, V. L.; Shuman, N. S.; Utz, A. L. Bond-Selective Control of a Heterogeneously Catalyzed Reaction. *Science* **2008,** *319,* 790–793.

(9) Beck, R. D.; Maroni, P.; Papageorgopoulos, D. C.; Dang, T. T.; Schmid, M. P.; Rizzo, T. R. Vibrational Mode-Specific Reaction of Methane on a Nickel Surface. *Science* **2003,** *302,* 98–100.

(10) Liu, Z.; Feldman, L. C.; Tolk, N. H.; Zhang, Z.; Cohen, P. I. Desorption of H from Si(111) by Resonant Excitation of the Si−H Vibrational Stretch Mode. *Science* **2006,** *312,* 1024–1026.

(11) Zhang, W.; Kawamata, H.; Liu, K. CH Stretching Excitation in the Early Barrier F + CHD_3 Reaction Inhibits CH Bond Cleavage. *Science* **2009,** *325,* 303–306.

(12) Yan, S.; Wu, Y.-T.; Liu, K. Tracking the Energy Flow along the Reaction Path. *Proc. Natl. Acad. Sci. U.S.A.* **2008,** *105,* 12667–12672.

(13) Liu, J; Song, K; Hase, W. L.; Anderson, S. L. Direct Dynamics Trajectory Study of Vibrational Effects: Can Polanyi Rules Be Generalized to a Polyatomic System?. *J. Am. Chem. Soc.* **2004,** *126,* 8602–8603.

(14) Barnes, G. L.; Hase, W. L. Bent out of Shape. *Nat. Chem.* **2009,** *1,* 103–104 and references therein.

(15) Hou, H.; Huang, Y.; Gulding, S. J.; Rettner, C. T.; Auerbach, D. J.; Wodtke, A. M. Enhanced Reactivity of Highly Vibrationally Excited Molecules on Metal Surfaces. *Science* **1999,** *284,* 1647–1650.

(16) Holloway, S. In *Advances in Gas-Phase Photochemistry and Kinetics: Dynamics of Gas-Surface Interactions*; Rettner, C. T., Ashfold, M. N. R., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1991; pp 113−131.

(17) Ertl, G. *Reactions at Solid Surfaces*; Wiley: Hoboken, NJ, 2009; pp 56−68.

(18) Matta, C. F.; Polanyi, J. C. Chemistry on a Peg-Board: The Effect of Adatom-to-Adatom Separation on the Reactivity of Dihalobenzenes at Si(111)-7×7 surfaces. *Phil. Trans. R. Soc. Lond. A* **2004,** *362,* 1185–1194.

(19) Lyubinetsky, I.; Dohnálek, Z.; Choyke, W. J.; Yates, J. T., Jr. Cl_2 Dissociation on Si(100)-2×1: A Statistical Study by Scanning Tunneling Microscopy. *Phys. Rev. B* **1998,** *58,* 7950–7957.

(20) Dürr, M.; Höfer, U. Dissociative Adsorption of Molecular Hydrogen on Silicon Surfaces. *Surf. Sci. Rep.* **2006,** *61,* 465–526 and references therein.

(21) Brenig, W.; Pehlke, E. Reaction Dynamics of H_2 on Si. *Ab Initio* Supported Model Calculations. *Prog. Surf. Sci.* **2008,** *83,* 263–336.

(22) Dürr, M.; Hu, Z.; Biedermann, A.; Hofer, U.; Heinz, T. F. Real-Space Study of the Pathway for Dissociative Adsorption of H_2 on Si(001). *Phys. Rev. Lett.* **2002,** *88,* 046104.

(23) Hsieh, M.-F.; Cheng, J.-Y.; Yang, J.-C.; Lin, D.-S.; Morgenstern, K.; Pai, W.-W. Determination of Dissociative Fragment-Adsorbate Interaction Energy during Chemisorption of the Diatomic Molecule HCl on Si(100). *Phys. Rev. B* **2010,** *81,* 045324.

(24) Craig, B. I.; Smith, P. V. Monolayer Chemisorption of HCl and Cl_2 on the Si(001)2×1 Surface. *Surf. Sci. Lett.* **1993,** *290,* L662–L666.

(25) Gao, Q.; Cheng, C. C.; Chen, P. J.; Choyke, W. J.; Yates, J. T., Jr. Comparison of Cl_2 and HCl Adsorption on Si(100)-(2×1). *Thin Solid Films* **1993,** *225,* 140–144.

(26) Oura, K.; Lifshits, V. G.; Saranin, A. A.; Zotov, A. V.; Katayama, M. *Surface Science — An Introduction*; Springer: Berlin, Germany, 2003; p 181, and references therein.

(27) Dürr, M.; Höfer, U. Molecular Beam Investigation of Hydrogen Dissociation on Si(001) and Si(111) Surfaces. *J. Chem. Phys.* **2004,** *121,* 8058–8067.

(28) Abukawa, T.; Wei, C. M.; Yoshimura, K.; Kono, S. Direct Method of Surface Structure Determination by Patterson Analysis of Correlated Thermal Diffuse Scattering for Si-(001)2×1. *Phys. Rev. B* **2000,** *62,* 16069–16073.

(29) Luntz, A. C. The Dynamics of Dissociative Adsorption on Metal Surfaces: "First Principles" Theory — Experiment Confrontations. *Surf. Sci.* **2009,** *603,* 1557–1563.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.;

Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02 ; Gaussian, Inc.: Wallingford, CT, 2004.

(31)   *IgorPro 5.05*. http://wavemetrics.com.

(32)   Snyder, W. V. Algorithm 531, Contour plotting [J6]. *ACM Trans. Math. Software* **1978,** *4*, 290–294.