

Dissociative chemisorption of methane on Ni(100): Threshold energy from $\text{CH}_4(2\nu_3)$ eigenstate-resolved sticking measurements

H. L. Abbott, A. Bukoski, D. F. Kavulak, and I. Harrison^{a)}

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319

(Received 16 June 2003; accepted 6 August 2003)

A three-parameter microcanonical theory of gas-surface reactivity is used to model the dissociative sticking of vibrationally excited methane with two quanta of energy in the ν_3 antisymmetric C–H stretch. An apparent threshold energy for C–H bond cleavage of CH_4 incident on Ni(100) of 65 kJ/mol is found, in quantitative agreement with *ab initio* quantum chemistry calculations but 38 kJ/mol less than GGA-DFT calculations. Successful microcanonical analysis and prediction of recent thermal equilibrium and various nonequilibrium dissociative chemisorption experiments for methane on Ni(100) provide no evidence for mode-specific reactivity. © 2003 American Institute of Physics. [DOI: 10.1063/1.1613935]

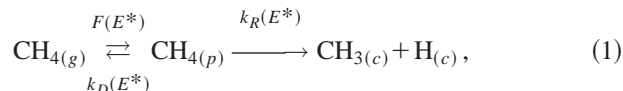
I. INTRODUCTION

Activated dissociative chemisorption of methane on the Ni(100) surface is an important model reaction for the rate-limiting step in the industrial steam reforming of methane over supported Ni catalysts.¹ The exceptionally diverse range of experimental studies^{2–6} and electronic structure calculations^{7,8} available for CH_4 dissociation on Ni(100) makes this reaction an excellent proving ground for kinetic theories and models of gas-surface reactivity involving polyatomic molecules. Although tunneling across a barrier located along a C–H reaction coordinate was at one time considered to be the dominant reactive mechanism,^{9–11} methane dissociative chemisorption is currently believed to proceed primarily in “over-the-barrier” fashion.^{12,13} Semiempirical analysis^{14,15} of supersonic molecular beam experiments in which the translational and vibrational energies of methane impinging on Ni(100) could be independently varied have suggested that vibrational energy is not quite as effective as translational energy in promoting dissociation.^{4,6} Several theoretical studies on reduced dimensionality potential energy surfaces have indicated that the dissociative chemisorption should be mode-specific—displaying a dynamical propensity to react from favored vibrational^{16,17} or rotational¹¹ quantum states. Arguing against such mode specificity, a full dimensionality microcanonical unimolecular rate theory (MURT) applied to methane on Ni(100),¹⁸ whose three free parameters were fixed by fitting the varied supersonic molecular beam experiments of Holmblad *et al.*,² was able to recover the 67 ± 4 kJ/mol apparent threshold energy for dissociation calculated by *ab initio* electronic structure theory,⁷ and “adequately” predict the sticking of the vibrationally excited ($1\nu_3, J=2$) eigenstate of methane as a function of translation energy,⁴ as well as the thermal equilibrium sticking of mbar pressure thermal bulb experiments.³ In this Communication, new vibrational overtone excited ($2\nu_3, J=2$)

eigenstate-resolved molecular beam experiments⁶ are used to refine the MURT parameters and extract an improved estimate of the threshold energy for dissociation. The mode-nonspecific MURT is shown to be capable of qualitatively, or arguably quantitatively, accounting for all of the most recent experimental results.

II. THEORETICAL MODEL

We assume the methane dissociative chemisorption kinetics can be described microcanonically as,^{18,19}



where the E^* zero of energy occurs with methane at infinite separation from the surface when all species are at 0 K. Methane incident on the surface from the gas phase is assumed to form a transient gas/surface collision complex consisting of a molecule, in the neighborhood of the physisorption potential well minimum, that interacts with a few immediately adjacent surface atoms. These collisionally formed “physisorbed complexes” (PC) or “local hot spots” are energetic and transient intermediate species that are not in thermal equilibrium with the surrounding substrate. Physisorbed complexes formed at some total energy E^* [i.e., $\text{CH}_{4(p)}$ in Eq. (1) where surface coordination numbers are suppressed] can go on to desorb or react dissociatively with the surface to yield chemisorbed fragments with Rice–Ramsperger–Kassel–Marcus (RRKM) rate constants $k_D(E^*)$ and $k_R(E^*)$. Initial dissociative sticking coefficients, S , are experimentally derived from the ratio of the deposited C coverage, typically measured by Auger electron spectroscopy, to the incident fluence of methane molecules, extrapolated backwards to zero net fluence. The steady state approximation applied to the $\text{CH}_{4(p)}$ coverage of Eq. (1) yields a PC-MURT that predicts

$$S = \int_0^\infty S(E^*) f(E^*) dE^*, \quad (2)$$

^{a)}Phone: (434) 924-3639; Fax: (434) 924-3710. Electronic mail: harrison@virginia.edu

where

$$S(E^*) = \frac{W_R^\ddagger(E^* - E_0)}{W_R^\ddagger(E^* - E_0) + W_D^\ddagger(E^*)} \quad (3)$$

is the microcanonical sticking coefficient, W_i^\ddagger is the sum of states for transition state i , E_0 is the apparent threshold energy for dissociation, and

$$f(E^*) = \int_0^{E^*} f_t(E_t) \int_0^{E^* - E_t} f_v(E_v) \int_0^{E^* - E_t - E_v} f_r(E_r) \times f_s(E^* - E_t - E_v - E_r) dE_r dE_v dE_t \quad (4)$$

is the probability distribution for creating a physisorbed complex at E^* . The $f(E^*)$ is formed by convolution over the distribution functions for the flux weighted translational energy, vibrational energy, and rotational energy of the incident methane, along with the surface energy distribution for s oscillators vibrating at the mean Ni phonon frequency, $\nu_s = (3/4)k_b T_{\text{Debye}}/h$, of 235 cm^{-1} .

The molecular beam studies of methane dissociative chemisorption on Ni(100) find that the dissociative sticking coefficient scales with the translational energy directed along the surface normal, $E_n = E_t \cos^2 \vartheta$. Discounting parallel molecular translational energy as a spectator or inactive form of energy over the course of the reactive gas-surface collisions, we assume that only normal translation will contribute to E_t in the expressions above (i.e., set $E_t = E_n$ alone). Following common practice, we further assume that the molecular beam nozzle temperature, T_n , sets the vibrational and rotational temperatures of the beam molecules as $T_v = T_n$ and $T_r = 0.1 T_n$, respectively.

Once the transition state characteristics have been defined through iterative simulation of varied experimental data or by electronic structure theory calculations, any experimental sticking coefficient can be predicted using Eq. (2) to average the microcanonical sticking coefficient over the probability for creating a physisorbed complex at E^* under the specific experimental conditions of interest. In the absence of definitive guidance from electronic structure calculations, and in the spirit of employing a surface kinetics theory with a minimum number of adjustable parameters, we assume the transition states for desorption and dissociation are loose and share as many common mode frequencies with each other as possible. The transition state for desorption is taken to occur when methane is freely rotating and vibrating in the gas phase, far from the surface. The dissociation transition state is characterized by the nine vibrational modes of methane in the gas, s vibrational modes of the surface oscillators, four vibrational modes at a single lumped frequency ν_D representative of the three frustrated rotations and the vibration along the surface normal of methane at the dissociation transition state, and one of the triply degenerate antisymmetric C-H stretching vibrations [$\nu_3(\text{CH}_4) = 3020 \text{ cm}^{-1}$] of methane is sacrificed as the reaction coordinate. The resulting PC-MURT has only three adjustable parameters, E_0 , ν_D , and s , that can be fixed by comparative simulation to varied experimental data.

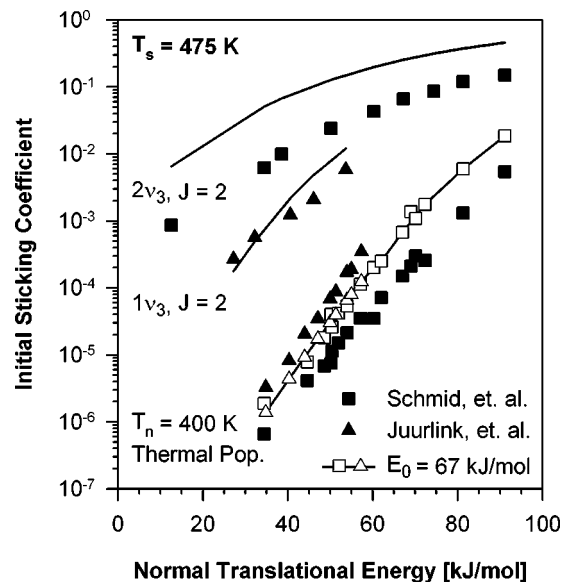


FIG. 1. The filled points are experimentally derived initial dissociative sticking coefficients as a function of mean translational energy for methane impinging on Ni(100) from a supersonic molecular beam with a nozzle temperature of $T_n = 400 \text{ K}$, and for the $(1 \nu_3, J=2)$ (Ref. 4) and $(2 \nu_3, J=2)$ (Ref. 6) methane eigenstates. The open points and lines are theoretical predictions of the PC-MURT based on a $E_0 = 67 \text{ kJ/mol}$, $\nu_D = 100 \text{ cm}^{-1}$, and $s = 2$ parameter set.

III. RESULTS AND DISCUSSION

As mentioned briefly above, an earlier PC-MURT analysis of methane dissociative chemisorption on Ni(100) extracted a parameter set of ($E_0 = 67 \text{ kJ/mol}$, $\nu_D = 100 \text{ cm}^{-1}$, $s = 2$) by fitting the varied molecular beam sticking data of Holmblad *et al.* and this could be used to quantitatively predict other experimental data relatively well.¹⁸ Figure 1 puts the PC-MURT with this parameter set to the test and compares its predictions to the thermal beam and vibrationally excited eigenstate-resolved experimental sticking coefficients reported by Juurlink *et al.* and Schmid *et al.* Although the theoretical predictions are reasonable for the thermal beam and $(1 \nu_3, J=2)$ sticking they substantially overpredict the $(2 \nu_3, J=2)$ sticking. A useful measure when comparing theory to experiment is the average relative discrepancy,

TABLE I. Average relative discrepancy (ARD) between experimental dissociative sticking coefficients and the predictions of the PC-MURT are compared for theoretical parameter sets with different threshold energies for dissociation, E_0 . The experimental sticking coefficients were only rescaled in ARD calculations for the $E_0 = 65 \text{ kJ/mol}$ parameter set, as appropriate for Fig. 2.

Reference	Type of Expt.	ARD (%) $E_0 = 67$ kJ/mol	Scaling divisor for Expts.	ARD (%) $E_0 = 65$ kJ/mol
Schmid <i>et al.</i> (Ref. 6)	$2 \nu_3$ and $T_n = 400 \text{ K}$	350	1	33
Juurlink <i>et al.</i> (Ref. 4)	$1 \nu_3$ and $T_n = 400 \text{ K}$	103	5.9	64
Holmblad <i>et al.</i> (Ref. 2)	Mol. Beam	25	4.5	43
Nielsen <i>et al.</i> (Ref. 3)	Thermal	232	1	33

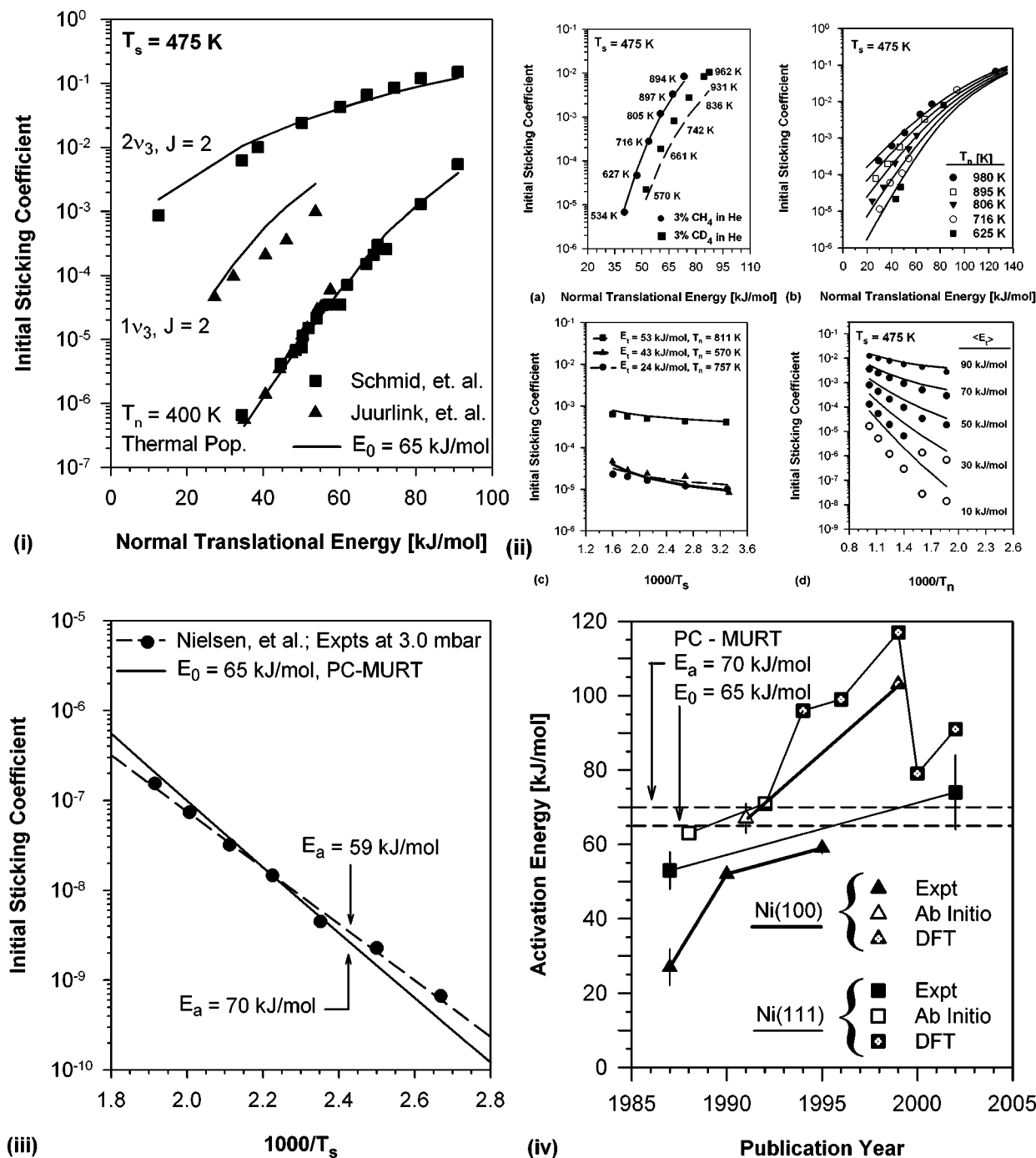


FIG. 2. (i)–(iii) Comparison of the most recent experimentally derived initial dissociative sticking coefficients (points) for methane impinging on Ni(100) with the theoretical predictions of the PC-MURT (lines) based on $E_0 = 65$ kJ/mol, $\nu_D = 170$ cm $^{-1}$, and $s = 2$. (i) Molecular beam experiments for $T_n = 400$ K and for single eigenstates ($1\nu_3, J = 2$) and ($2\nu_3, J = 2$). The Juurlink *et al.* sticking coefficients have been divided by 5.9. (ii) Molecular beam derived sticking coefficients of Holmblad *et al.* (Ref. 2) have been divided by 4.5. (iii) Thermal equilibrium bulb experiments (Ref. 3) at 3 mbar pressure. (iv) Activation energies for CH_4 dissociative chemisorption, E_a , derived experimentally (Refs. 3,20,22,23) and apparent threshold energies, $E_0 (= E_a \text{ at } 0 \text{ K})$, derived from *ab initio* (Refs. 7,21,24) or density functional theory (Refs. 8,25–28) electronic structure calculations are compared to the predictions of the PC-MURT.

$$\text{ARD} = \left\langle \frac{|S_{\text{theory}} - S_{\text{expt}}|}{\min(S_{\text{theory}}, S_{\text{expt}})} \right\rangle, \quad (5)$$

which is reported in Table I for several experimental data and theoretical parameter sets. Figure 1 shows that for nominally identical experimental scans of methane supersonic molecular beams with $T_n = 400$ K over mean translational energy, the calculated sticking coefficients derived from the two different laboratories differ by a factor of ~ 7.5 . The PC-MURT

predicts that all the $T_n = 400$ K experimental data from both laboratories should fall on essentially the same curve. Unfortunately, order of magnitude differences in sticking coefficients as a function of E_t [i.e., $S(E_t; T_n, T_s)$] reported by different molecular beam laboratories are not uncommon,¹ albeit that almost invariably there are differences in the T_n and T_s experimental conditions that makes direct comparisons difficult to assess in the absence of a well agreed upon

theoretical model that can accurately predict the results of such non-equilibrium experiments. Although experimental reproducibility from a particular laboratory may be excellent, precise calibration of absolute sticking coefficients is undoubtedly very difficult to achieve, especially when sticking coefficients are small (e.g., $S < 10^{-3}$). Consequently, it may not be unreasonable to introduce scaling factors to renormalize sticking coefficients derived from some laboratories, in an effort to recover a common "absolute" sticking scale, when comparing experimental results to theoretical predictions.

When the Schmid *et al.* $2\nu_3$ and $T_n=400$ K sticking data were separately simulated using the PC-MURT an optimal parameter set of ($E_0=65$ kJ/mol, $\nu_D=170$ cm $^{-1}$, $s=2$) was found to minimize the ARD at 33%. Although this $E_0=65$ kJ/mol parameter set can equally well predict the thermal equilibrium sticking measured at ten orders of magnitude higher pressure in thermal bulb experiments,³ it only qualitatively reproduces the sticking behavior reported for the molecular beam experiments of Juurlink *et al.* and Holmblad *et al.* However as discussed above and as pointed out in Fig. 1, quantitative agreement between laboratories running identical experiments has sometimes been lacking at order of magnitude levels. To most effectively illustrate that the PC-MURT can qualitatively or, perhaps quantitatively, reproduce the reported experimental behavior we worked to optimally overlay the theoretical predictions with the experimental sticking as shown in Figs. 2(i)–2(iii) where the Juurlink and Holmblad sticking data have been rescaled to minimize their ARD with theory. The Fig. 2 and Table I comparisons of theory and experiment indicate that the $E_0=65$ kJ/mol parameter set is an improvement over the $E_0=67$ kJ/mol set, if indeed the Schmid and Nielsen data are accurate and the Juurlink and Holmblad data require rescaling. Certainly, the PC-MURT is capturing, at the very least, the qualitative behavior of the dissociative sticking of methane on Ni(100). Nevertheless, additional experiments will be needed to evaluate and confirm the absolute accuracy of the experimentally reported sticking coefficients if definitive further theoretical progress is to be made.

Figure 2(iv) reviews how experimentally determined activation energies and theoretically predicted apparent threshold energies for CH₄ dissociative chemisorption on Ni(100) and Ni(111) surfaces have evolved over the past 25 years. Siegbahn and co-workers⁷ calculated $E_0=67\pm 4$ kJ/mol for CH₄ on Ni(100) using *ab initio* quantum chemistry methods, in quantitative agreement with our PC-MURT finding of $E_0=65$ kJ/mol based on simulating the Schmid *et al.* experiments. Figure 2(iv) shows that activation energies reported from thermal bulb experiments have been increasing over the years, and this correlates with the implementation of several experimental refinements over time.¹ Most recently, the activation energy for CH₄ dissociation on the Ni(111) surface was reported as $E_a=74\pm 10$ kJ/mol,²⁰ which is nominally 3 kJ/mol higher than the most sophisticated *ab initio* calculation²¹ of 71 kJ/mol for E_0 on the Ni(111) surface.

Assuming that the methane transition states are similar on both the Ni(100) and Ni(111) surfaces, the PC-MURT prediction of $E_a=70$ kJ/mol on the Ni(100) surface seems quite reasonable given that $E_0=65$ kJ/mol, E_a should be slightly higher than E_0 ,¹⁹ and the ARD of 33% between the predicted thermal sticking coefficients and the Nielsen *et al.* results is excellent. Important to point out is that the GGA-DFT estimate⁸ of $E_0=103$ kJ/mol for CH₄ on Ni(100) is incompatible with our PC-MURT modeling of the existent experimental data displayed in Fig. 2, regardless of whether or not some of the data needs to be rescaled.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation (NSF), Grant #0078995. H.L.A. and A.B. gratefully acknowledge fellowship support under NSF IGERT Grant #9972790, and D.F.K. under NSF REU Grant #0097659. The authors thank Rainer Beck for generously providing updated and extended experimental data prior to their publication elsewhere.

- ¹J. H. Larsen and I. Chorkendorff, *Surf. Sci. Rep.* **35**, 165 (1999).
- ²P. M. Holmblad, J. Wambach, and I. Chorkendorff, *J. Chem. Phys.* **102**, 8255 (1995).
- ³B. O. Nielsen, A. C. Luntz, P. M. Holmblad, and I. Chorkendorff, *Catal. Lett.* **32**, 15 (1995).
- ⁴L. B. F. Juurlink, P. R. McCabe, R. R. Smith, C. L. DiCologero, and A. L. Utz, *Phys. Rev. Lett.* **83**, 868 (1999).
- ⁵L. B. F. Juurlink, R. R. Smith, and A. L. Utz, *Faraday Discuss.* **117**, 147 (2000).
- ⁶M. P. Schmid, P. Maroni, R. D. Beck, and T. R. Rizzo, *J. Chem. Phys.* **117**, 8603 (2002); R. D. Beck (private communication).
- ⁷O. Swang, K. Faegri, O. Gropen, U. Wahlgren, and P. Siegbahn, *Chem. Phys.* **156**, 379 (1991).
- ⁸H. S. Bengaard, I. Alstrup, I. Chorkendorff, S. Ullmann, J. R. Rostrup-Nielsen, and J. K. Nørskov, *J. Catal.* **187**, 238 (1999).
- ⁹C. T. Rettner, H. E. Pfnur, and D. J. Auerbach, *Phys. Rev. Lett.* **54**, 2716 (1985).
- ¹⁰J. Harris, J. Simon, A. C. Luntz, C. B. Mullins, and C. T. Rettner, *Phys. Rev. Lett.* **67**, 652 (1991).
- ¹¹M. N. Carre and B. Jackson, *J. Chem. Phys.* **108**, 3722 (1998).
- ¹²V. A. Ukraintsev and I. Harrison, *J. Chem. Phys.* **101**, 1564 (1994).
- ¹³A. C. Luntz, *J. Chem. Phys.* **102**, 8264 (1995).
- ¹⁴H. A. Michelsen, C. T. Rettner, D. J. Auerbach, and R. N. Zare, *J. Chem. Phys.* **98**, 8294 (1993).
- ¹⁵A. C. Luntz, *J. Chem. Phys.* **113**, 6901 (2000).
- ¹⁶R. Milot and A. P. J. Jansen, *Phys. Rev. B* **61**, 15657 (2000).
- ¹⁷L. Halonen, S. L. Bernasek, and D. J. Nesbitt, *J. Chem. Phys.* **115**, 5611 (2001).
- ¹⁸A. Bukoski and I. Harrison, *J. Chem. Phys.* **118**, 9762 (2003).
- ¹⁹A. Bukoski, D. Blumling, and I. Harrison, *J. Chem. Phys.* **118**, 843 (2003).
- ²⁰R. C. Egeberg, S. Ullmann, I. Alstrup, C. B. Mullins, and I. Chorkendorff, *Science* **497**, 183 (2002).
- ²¹H. Yang and J. L. Whitten, *J. Chem. Phys.* **96**, 5529 (1992).
- ²²T. P. Beebe, D. W. Goodman, B. D. Kay, and J. T. Yates, *J. Chem. Phys.* **87**, 2305 (1987).
- ²³I. Chorkendorff, I. Alstrup, and S. Ullmann, *Science* **227**, 291 (1990).
- ²⁴A. B. Anderson and J. J. Maloney, *J. Phys. Chem.* **92**, 809 (1988).
- ²⁵H. Burghgraef, A. P. J. Jansen, and R. A. Vansanten, *J. Chem. Phys.* **101**, 11012 (1994).
- ²⁶P. Kratzer, B. Hammer, and J. K. Nørskov, *J. Chem. Phys.* **105**, 5595 (1996).
- ²⁷V. Ledentu, W. Dong, and P. Sautet, *J. Am. Chem. Soc.* **122**, 1796 (2000).
- ²⁸H. S. Bengaard, J. K. Nørskov, J. Sehested, B. S. Clausen, L. P. Nielsen, A. M. Molenbroek, and J. R. Rostrup-Nielsen, *J. Catal.* **209**, 365 (2002).