Eigenstate-Resolved Studies of Gas-Surface Reactivity: CH₄ (ν_3) Dissociation on Ni(100)

L. B. F. Juurlink, P. R. McCabe, R. R. Smith, C. L. DiCologero, and A. L. Utz

Department of Chemistry and W. M. Keck Foundation Laboratory for Materials Chemistry, Tufts University,
Medford, Massachusetts 02155
(Received 26 March 1999)

A new experimental technique uses state-resolved infrared laser excitation to probe a polyatomic molecule's dissociative chemisorption dynamics with previously unattainable detail. Methane molecules excited to $\nu = 1$ of the ν_3 C-H stretching vibration are up to 1600 times more reactive on a clean Ni(100) surface than are molecules in the ground vibrational state. Over a translational energy range of 27 to 54 kJ/mol, their absolute reaction probability increases from 3×10^{-4} to 6×10^{-3}, which indicates that ν_3 is responsible only in part for the vibrational activation reported in previous studies.

Energized molecules frequently dominate reactivity in activated chemical systems, but for many important gas-surface reactions, the mechanistic basis for activation remains controversial. In the gas phase, experiments routinely probe the reactivity of energized reagents as a function of their translational energy (E_{trans}) and internal quantum state. Such studies reveal key features of the potential energy surface governing reactivity and serve as stringent tests of chemical reaction theory [1]. In contrast, few techniques exist for obtaining similarly detailed data in gas-surface reactions, particularly those involving polyatomic reagents [2,3]. Without such data, it is difficult to test existing models and theories, or to direct the development of improved theories of gas-surface reactivity.

This Letter describes a new experimental technique for studying gas-surface reactions that provides detailed, state-resolved data, and it shows how these data can help unravel the mechanism for methane dissociation on Ni(100). We combine infrared laser excitation of molecules in a supersonic molecular beam and spectroscopic quantification of the surface-bound reaction products to obtain translational energy dependent, vibrational eigenstate-resolved, absolute reaction probabilities for dissociative chemisorption. Our approach provides independent control over the internal quantum state of reagents, their translational energy and angle of incidence onto the surface, and the chemical composition and temperature of the surface. These are the first beam-surface experiments to provide direct experimental evidence for vibrational activation by a specific vibrational mode in a polyatomic molecule. Specifically, we find that excitation of the ν_3 antisymmetric C-H stretching vibration in CH₄ dramatically enhances reactivity. The enhancement is significantly less than has been suggested in previous models of methane dissociation [4,5], but is consistent, in part, with predictions of a recent quantum calculation of methane dissociation on a nickel surface [6].

Methane dissociation on catalytically active transition metal surfaces is highly activated and has been the focus of many studies. Early work on polycrystalline W [7] and

Rh [8] surfaces yielded evidence for both vibrational and translational activation, but attempts to promote methane dissociation on Rh(111) [9] and Rh thin films [10] via laser excitation of the ν_3 [9,10], $2\nu_4$ [9], and $2\nu_3$ [10] vibrations failed to achieve a measurable degree of activation. The most detailed mechanistic evidence to date comes from molecular beam experiments. Beam-surface studies of methane dissociation on Ni(100) [4,11] and Ni(111) [12] reveal that reactivity increases exponentially with increasing E_{trans} and that high vibrational temperatures (T_{vib}) promote reactivity.

The high dimensionality of the potential energy surface governing methane dissociation has complicated attempts to identify the reaction mechanism. The efficacy of vibrational energy (E_{vib}) suggests a "late" barrier to reactivity [1], but controversy persists over which of the many vibrational coordinates in methane most resembles the reaction coordinate. Collision induced dissociation experiments by Beckerle *et al.* on Ni(111) suggest an important role for bending vibrations [13,14], while a number of theoretical calculations suggest an important role for the C-H stretching coordinates [5,6,15–18]. The reaction coordinate may also be a linear combination of two or more translational and vibrational coordinates. Our experiments shed light on this controversy by revealing how specific internal coordinates couple to the reaction coordinate.

A brief description of our experimental approach follows; a full description will appear elsewhere [19]. Gas mixtures ranging from 1% to 25% methane (99.99%) in H₂ (99.9999%) expand into vacuum through a 25 μm orifice in an inconel 600 nozzle. The pressure behind the orifice is 370 kPa, and the nozzle temperature is 400 ± 2 K. Time-of-flight measurements verify that methane kinetic energies range from 27 to 57 kJ/mol with $\Delta E / E \leq$ 15%. The beam is triply differentially pumped prior to entering an ultrahigh vacuum chamber (base pressure 8 × 10^{-11} Torr), where it impinges on a clean Ni(100) crystal. Standard cleaning procedures [4] reduce C, S, and O impurity levels below the 0.5% detection limit of our Auger electron spectrometer. Approximately 2 mW of infrared light from a continuous wave (cw), single mode, color

center laser (Burleigh FCL-20, $\Delta \nu < 1$ MHz) enters the first differential pumping stage and makes 16 orthogonal crossings through the molecular beam in a multipass cell [20]. We excite methane to ν_3, $v = 1$, $J = 2$ via the $R(1)$ transition at 3038.4985 cm^{-1}. A pyroelectric bolometer in the second differential chamber quantifies infrared absorption [21], and a computer-controlled laser frequency stabilization system maintains resonance with the desired methane transition.

To obtain an absolute sticking probability for ν_3, we must know the flux of state-selected molecules impinging on the Ni(100) surface. We first quantify total methane flux. Our quadrupole mass spectrometer measures the steady-state partial pressure of methane in the chamber with the molecular beam on for each gas mixture. This partial pressure, when multiplied by the experimentally determined pumping speed and divided by the beam's area gives total methane flux. Typical fluxes range from $(2.5-10.7) \times 10^{15}$ CH$_4$ molecules/(cm^2 sec) at the surface. Next, we determine the fraction of molecules excited by the laser. Infrared absorption measurements confirm that rotational relaxation in the beam is essentially complete, so 9/16 of the $v = 0$ population is in $J = 1$ and is available for excitation via the $R(1)$ transition [22]. We measure absorption as a function of laser power with a bolometer placed in the beam path, and we fit these data with the known functional form for a saturated optical transition to obtain the fraction of $v = 0$, $J = 1$ molecules excited to ν_3 [23]. Depending on the beam velocity, and hence the transit time of molecules through the laser light, we excite 12%–16% of the total methane flux to ν_3, $v = 1$. This measured fractional excitation efficiency agrees well with calculated values [23,24]. Radiative and collisional deactivation of ν_3 in the molecular beam is insignificant during the 100 μs flight time from multipass cell to surface [24,25], so the molecules we excite reach the Ni(100) surface in their initially prepared state.

Carbon deposition on the nickel surface signifies methane's dissociative chemisorption. Following a timed dose, the ratio of carbon's areal density to the integrated flux of methane is the sticking probability, S_0. We measure surface carbon coverage using Auger electron spectroscopy and calibrate our measurements with the known 0.50 ML C coverage resulting from a saturated dose of C$_2$H$_4$ on Ni(100) [26]. Dose times are chosen to give carbon coverages of about 0.08 ML. The surface temperature is held at 475 K to promote rapid recombinative desorption of hydrogen carrier gas that dissociatively adsorbs to the surface and to facilitate a direct comparison with the results of Holmblad et al. [4].

We verify that carbon deposition arises only from methane's dissociative chemisorption. Extended exposures of the crystal to a pure methane beam, whose normal kinetic energy is too low to result in measurable dissociation, do not yield a detectable Auger signal, indicating that the beam is free of carbonaceous impurities with sig-

nificant sticking probabilities. Adsorption of carbon from background sources is also insignificant. We position our 1 cm diameter Ni(100) crystal so that the molecular beam impinges only on its top half and verify after each dose that the portion of the surface not directly imaged by the molecular beam is free of carbon.

To obtain a state-resolved sticking probability, we measure the average sticking probability for molecules in the beam with and without laser excitation of the ν_3, $v = 1$, $J = 2$ eigenstate. The solid circles in Fig. 1 show the absolute sticking probability for the thermally excited distribution of vibrational states emerging from a 400 K nozzle source without laser excitation. The data are collected at incident angles ranging from 0° to 31° with respect to the surface normal. Each point is the average of at least three, but no more than twelve individual measurements and is plotted as a function of the beam's normal component of kinetic energy, $E_\perp$. The data indicate that normal energy scaling holds at $T_{\mathrm{vib}} = 400$ K over the energy range investigated. These sticking probabilities agree well with those reported by Holmblad et al. for a similar vibrational temperature [4]. The open circles in Fig. 1 are sticking probabilities measured at normal incidence for doses in which infrared light resonant with the ν_3, $R(1)$ transition irradiates a molecular beam from a 400 K nozzle source. Error bars are 95% confidence limits based on the standard deviation of replicate measurements.

We extract state-resolved sticking probabilities by analyzing the contribution of various subsets of molecules in the beam to the average sticking probabilities we measure. The average sticking probability measured with the laser off is the sum of a contribution from the ground vibrational state ($v = 0$) and an average contribution from all thermally excited vibrational states.

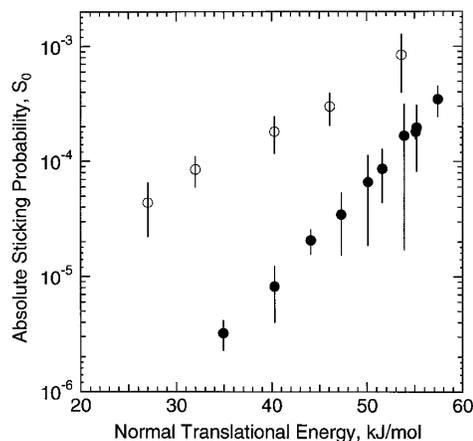$$S_0^{\mathrm{laser\text{-}off}} = f_{\nu=0} S_0^{\nu=0} + (1 - f_{\nu=0}) S_0^{\nu>0}. \quad (1)$$

FIG. 1. Vibrationally averaged sticking probabilities for CH$_4$ on a clean Ni(100) surface with (open circles) and without (solid circles) laser excitation of the $J = 2$, ν_3 C-H stretching eigenstate.

The population of $v = 0$ in the beam is $f_{v=0}$, the sticking probability for molecules in $v = 0$ is $S_0^{v=0}$, and the average sticking probability for the ensemble of thermally excited vibrational states emerging from the 400 K molecular beam source is $S_0^{v>0}$. The measured sticking probability for laser-on experiments is the sum of contributions from $v = 0$, thermally excited vibrational states, and the laser-excited ν_3 state.

$$S_0^{\text{laser-on}} = (f_{v=0} - f_{\text{exc}})S_0^{v=0} + (1 - f_{v=0})S_0^{v>0}$$
$$+ f_{\text{exc}}S_0^{\nu_3}. \quad (2)$$

Here, f_{exc} is the fraction of molecules in the beam excited from $v = 0$ to ν_3, and $S_0^{\nu_3}$ is the state-resolved sticking probability for the laser-excited state. Since the laser-on and laser-off experiments are performed at the same nozzle source temperature, the thermal distribution of vibrational states, and hence $f_{v=0}$ and $S_0^{v>0}$, are identical for the two experiments. The difference between the laser-on and laser-off measurements at a fixed translational energy is therefore

$$S_0^{\text{laser-on}} - S_0^{\text{laser-off}} = -f_{\text{exc}}S_0^{v=0} + f_{\text{exc}}S_0^{\nu_3}. \quad (3)$$

This difference depends only on the fraction of molecules excited by the laser and on the absolute, state-resolved sticking probabilities for $v = 0$ and ν_3. It is independent of the distribution of vibrational states emerging from the nozzle expansion and does not require any assumptions regarding the details of that vibrational state distribution. Rearranging Eq. (3) yields Eq. (4), which we use to calculated state-resolved sticking probabilities.

$$S_0^{\nu_3} = \frac{S_0^{\text{laser-on}} - S_0^{\text{laser-off}}}{f_{\text{exc}}} + S_0^{v=0}. \quad (4)$$

We rely on the model of Holmblad et al. for values of $S_0^{v=0}$ [4]. $S_0^{\text{laser-off}}$, which is an experimentally measured upper bound on $S_0^{v=0}$, is less than 2% of $S_0^{\nu_3}$ at all translational energies investigated, so the value of $S_0^{v=0}$ contributes minimally to our calculated reaction probabilities.

Figure 2 displays our computed values of $S_0^{\nu_3}$ as a function of $E_\perp$. Error bars are 95% confidence limits and include the standard deviation from replicate measurements of $S_0^{\text{laser-off}}$ and $S_0^{\text{laser-on}}$ and the uncertainty in f_{exc}. The figure also displays our laser-off data, as well as predictions for the sticking probability for $v = 0$ and $v = 1$ of the C-H stretch from three prior studies. An examination of the data and comparison with the models reveal key features of methane's dissociative chemisorption dynamics and test theoretical treatments of methane dissociation.

Excitation of ν_3 promotes methane dissociation dramatically at all translational energies studied. The enhancement relative to $S_0^{v=0}$ ranges from 1600 to 80 as E_{trans} increases from 27 to 54 kJ/mol. Thus, the internal motion associated with the ν_3 eigenstate is coupled, at least in part, to the reaction coordinate for methane dissociation.

Our experiments also permit the first direct comparison of how equivalent amounts of translational and vibrational energy deposited into a single reagent molecule affect re-
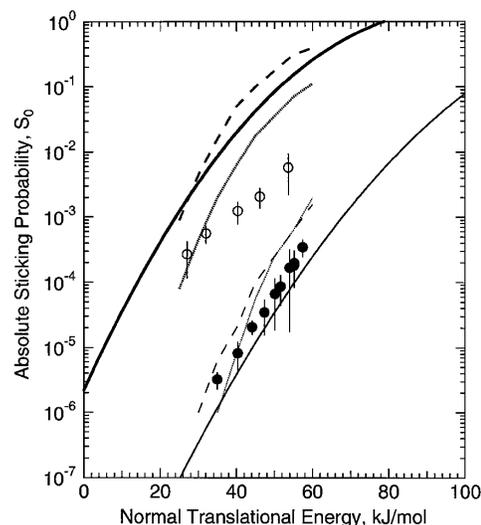

FIG. 2. Calculated sticking probabilities for the $J = 2$, ν_3 $v = 1$ C-H stretching eigenstate (open circles). The models of Holmblad et al. (solid lines) [4], Luntz (dashed lines) [5], and Carré and Jackson (dotted lines) [6], as well as our own laser-off data (solid circles) are shown for comparison. Light lines model $v = 0$, while heavy lines model $v = 1$.

activity. At all energies studied, we find that E_{trans} is more effective than $E_{\text{vib}}^{\nu_3}$. At low E_{trans}, where ν_3 is maximally effective, 36 kJ/mol of $E_{\text{vib}}^{\nu_3}$ increases sticking by a factor of 1600 relative to $v = 0$ while an equivalent amount of E_{trans} leads to a 2700-fold increase in reactivity. As E_{trans} increases, the efficacy of ν_3 decreases further. These results show that sticking probability does not scale with the total (translational plus internal) energy of the incident methane molecule and rule out a statistical model for methane dissociation on Ni(100) [27]. They also indicate that from 27 to 54 kJ/mol, the normal component of incident kinetic energy is better coupled to the reaction coordinate than is ν_3.

The efficacy of translational energy varies with methane's vibrational state. For our $T_{\text{vib}} = 400$ K sample, whose reactivity is dominated by $v = 0$ and low-lying thermally populated vibrational states, 11 kJ/mol of E_{trans} increases the sticking probability tenfold. In contrast, nearly 20 kJ/mol of E_{trans} along the surface normal is needed to achieve the same enhancement for the ν_3 molecules. A similar trend was reported by Holmblad et al. [4], whose data at higher T_{vib} exhibited a lower efficacy for translational activation.

Several models of methane dissociation have attributed vibrational activation to thermally populated C-H stretching eigenstates [4,5]. Holmblad et al. report sticking probabilities as a function of E_{trans} for a broad range of T_{vib} [4]. Our state-resolved sticking probabilities allow us to assess the contribution of ν_3 to sticking probabilities averaged over a thermal population of vibrational states. At $T_{\text{vib}} = 1050$ K, the fractional populations of $v = 1$ and $v = 2$ of ν_3 are 0.02 and 7×10^{-4}, respectively. We find that for $30 \leq E_{\text{trans}} \leq 51$ kJ/mol,

molecules in $\nu = 1$ contribute less than 2% to the measured sticking probabilities. Even if every $\nu = 2$ molecule reacted with unit probability, the experimental data for $E_{\text{trans}} > 30$ kJ/mol cannot be explained solely by the reactivity of the ν_3 C-H stretching mode. We conclude that vibrational modes other than ν_3 must play a significant role in the vibrational activation of methane on Ni(100). This finding supports the contention by Kratzer *et al.* [17] that both bending and C-H stretching motions may prove to be important in vibrational activation and calls into question the neglect of bending excitation in theoretical treatments of methane dissociation. Investigations into the reactivity of other vibrational eigenstates in methane are underway in our laboratory.

Figure 2 compares our state-resolved sticking probabilities with three models of methane dissociation. Holmblad *et al.* treat methane as a pseudodiatomic molecule and optimized state-resolved S curves to model their beam-surface data [4]. The results of their model for $\nu = 0$ agree well with our laser-off data, whose 400 K thermal distribution should be somewhat more reactive than a vibrationally cold beam. Their $\nu = 1$ model, though, significantly overestimates our measured reactivity. It is likely that other more reactive vibrationally excited modes account for their observed reactivity at high T_{vib}. Luntz applied a reduced dimensionality, thermally assisted tunneling model to methane dissociation on Ni(100). His model, which predicts the reactivity of a pseudodiatomic C-H stretching local mode state, also overestimates the reactivity of ν_3. Carré and Jackson's quantum dynamics study investigated the effect of molecular orientation on methane dissociation. Their study used Yang and Whitten's potential for methane dissociation on Ni(111) [15] and included effects of molecular rotation. Their results agree with our data at low translational energies, but overestimate the data at high E_{trans}. Since sticking probabilities on Ni(100) are typically tenfold higher than those on Ni(111), quantitative comparison of their model with our data is not entirely justified.

In summary, we describe an experimental method for measuring eigenstate-resolved absolute sticking probabilities of polyatomic molecules on surfaces. Excitation of the ν_3 antisymmetric C-H stretching eigenstate in methane dramatically enhances sticking. Despite this enhancement, translational energy remains more effective at promoting reactivity than does vibrational excitation of ν_3. This observation rules out a statistical model of methane dissociation on Ni(100). The measured reactivity of ν_3, $\nu = 1$ is much too low to account for the vibrational activation observed in previous studies, and indicates that other vibrationally excited modes contribute significantly to the reactivity of thermal samples. Finally, a comparison of our data with models of methane dissociation suggests that additional efforts are needed to quantitatively model methane dissociation on Ni(100).

[1] R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University Press, New York, 1987).
[2] D. C. Jacobs, J. Phys. Condens. Matter **7**, 1023–1045 (1995).
[3] P. L. Houston and R. P. Merrill, Chem. Rev. **88**, 657–671 (1988).
[4] P. M. Holmblad, J. Wambach, and I. Chorkendorff, J. Chem. Phys. **102**, 8255–8263 (1995).
[5] A. C. Luntz, J. Chem. Phys. **102**, 8264–8269 (1995).
[6] M.-N. Carré and B. Jackson, J. Chem. Phys. **108**, 3722–3730 (1998).
[7] H. F. Winters, J. Chem. Phys. **64**, 3495–3501 (1976).
[8] C. N. Stewart and G. Ehrlich, J. Chem. Phys. **62**, 4672–4682 (1975).
[9] J. T. Yates, Jr. *et al.,* J. Chem. Phys. **70**, 2266–2272 (1979).
[10] S. G. Brass, D. A. Reed, and G. Ehrlich, J. Chem. Phys. **70**, 5244–5250 (1979).
[11] A. V. Hamza and R. J. Madix, Surf. Sci. **179**, 25–46 (1987).
[12] M. B. Lee, Q. Y. Yang, and S. T. Ceyer, J. Chem. Phys. **87**, 2724–2741 (1987).
[13] J. D. Beckerle *et al.,* J. Chem. Phys. **86**, 7236–7237 (1987).
[14] J. D. Beckerle *et al.,* J. Chem. Phys. **91**, 5756–5777 (1989).
[15] H. Yang and J. L. Whitten, J. Chem. Phys. **96**, 5529–5537 (1992).
[16] A. C. Luntz and J. Harris, Surf. Sci. **258**, 397–426 (1991).
[17] P. Kratzer, B. Hammer, and J. K. Nørskov, J. Chem. Phys. **105**, 5595–5604 (1996).
[18] R. Milot and A. P. J. Jansen, J. Chem. Phys. **109**, 1966–1975 (1998).
[19] P. R. McCabe, L. B. F. Juurlink, and A. L. Utz (to be published).
[20] T. E. Gough, D. Gravel, and R. E. Miller, Rev. Sci. Instrum. **52**, 802–803 (1981).
[21] R. E. Miller, Rev. Sci. Instrum. **53**, 1719–1723 (1982).
[22] G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1945).
[23] R. B. Bernstein, *Chemical Dynamics via Molecular Beam and Laser Techniques* (Oxford, New York, 1982).
[24] L. S. Rothman *et al.,* J. Quant. Spectrosc. Radiat. Transfer **60**, 665–710 (1998).
[25] P. Hess and C. B. Moore, J. Chem. Phys. **65**, 2339 (1976).
[26] C. Klink *et al.,* Phys. Rev. Lett. **71**, 4350–4353 (1993).
[27] V. A. Ukraintsev and I. Harrison, J. Chem. Phys. **101**, 1564–1581 (1994).