Mode-specific reactivity of CH$_4$ on Pt(110)-(1×2): The concerted role of stretch and bend excitation

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The state-resolved reaction probability of CH$_4$ on Pt(110)-(1×2) was measured as a function of CH$_4$ translational energy for four vibrational eigenstates comprising different amounts of C-H stretch and bend excitation. Mode-specific reactivity is observed both between states from different polyads and between isoenergetic states belonging to the same polyad of CH$_4$. For the stretch/bend combination states, the vibrational efficacy of reaction activation is observed to be higher than for either pure C-H stretching or pure bending states, demonstrating a concerted role of stretch and bend excitation in C-H bond scission. This concerted role, reflected by the nonadditivity of the vibrational efficacies, is consistent with transition state structures found by ab initio calculations and indicates that current dynamical models of CH$_4$ chemisorption neglect an important degree of freedom by including only C-H stretching motion.

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Methane (CH$_4$) dissociation on transition-metal surfaces is of great interest in the context of hydrogen production since it is the rate limiting step in the steam reforming process, the principal route for the transformation of CH$_4$ into H$_2$. Despite the 15 molecular degrees of freedom associated with the CH$_4$/surface system, the elementary step in the dissociative chemisorption of CH$_4$ consists of breaking a single C-H bond and C-H stretch excitation has been shown to activate CH$_4$ dissociation on transition-metal surfaces. We previously reported that the efficacy of the antisymmetric C-H stretch overtone state (2$\nu_3$) for promoting CH$_4$ dissociation is higher on Ni(111) than on Pt(111) and proposed that this difference in activation is related to the transition state structure with a larger bond length for the dissociating C-H bond on the Ni(111) surface. Ab initio calculations performed by Nave and Jackson are in agreement with this interpretation. These results imply a significant participation of C-H bond stretch in the reaction coordinate and might indicate that reduced dimensionality models including only C-H stretch motion can describe the essential feature of the reaction dynamics. Nevertheless other degrees of freedom may also contribute to the reaction coordinate. A survey of first-principles calculations of transition states for CH$_4$/metal systems shows transition state structures of CH$_4$ with the dissociating C-H bond not only stretched but also bent from the equilibrium tetrahedral angle. Therefore, a realistic reaction coordinate might be expected to contain both C-H stretch and bend excitation. However, all dynamical models of methane dissociation published to date treat CH$_4$ as a "pseudodiatomic" containing a H$_2$C-H bond that can only be stretched. State-resolved measurement by Juurink et al. find the 3$\nu_4$ bend overtone to have a lower efficacy than the $\nu_3$ stretch fundamental in activating CH$_4$ dissociation on nickel surfaces lending support to the reduced dimensionality assumption of these dynamical models but the complete neglect of bending motion is almost certainly an oversimplification.

In this Rapid Communication, we present a state-resolved study of CH$_4$ dissociative chemisorption on Pt(110)-(1×2) which measures the reaction probability of CH$_4$ prepared in four different vibrational eigenstates comprising different amounts of stretch and bend excitation. We observed that three nearly isoenergetic vibrational states each lead to significantly different dissociation probabilities whereas two states with different vibrational energy results in very similar reactivity. These observations provide clear evidence for mode-specific reactivity for CH$_4$ on Pt(110)-(1×2) which contradicts a basic assumption of statistical reaction rate theory. Furthermore, the different efficacies for promoting the reaction of these four vibrational states provide information on the relevant degrees of freedom that theoretical models should consider to give a realistic description of CH$_4$ dissociation dynamics.

State-resolved reaction probability measurements are performed in an apparatus that consists of a molecular-beam source connected to an ultra-high-vacuum chamber (base pressure 6×10$^{-11}$ mbar). We generate a pulsed molecular beam of CH$_4$ with variable translation energy ($E_t$) by expanding different mixtures of CH$_4$ in H$_2$, He, or Ar carrier gas using nozzle temperatures of 323–373 K. The $E_t$ of CH$_4$ is determined by time-of-flight measurements using a chopper wheel and an on-axis quadrupole mass spectrometer (QMS). Before CH$_4$ collides with the Pt(110)-(1×2) surface, we excite a significant fraction of the CH$_4$ molecules to a stationary molecular eigenstate by pulsed infrared (IR) laser radiation with narrow bandwidth (0.02 cm$^{-1}$) and high energy (140 mJ/pulse). The tunable IR radiation is focused by a cylindrical lens to excite a 20 mm slice of the molecular beam 25 mm from the target surface. We use cavity ring-down spectroscopy in a separate free-jet expansion to tune the excitation laser into resonance with the selected rovibrational transition, to monitor that the resonance is maintained during the deposition time, and to determine the rotational level population of CH$_4$ in the jet expansion needed to determine the fraction of excited molecules. The laser fluence is sufficient to completely saturate the first overtone transition of the IR-active C-H stretch ($\sim$6000 cm$^{-1}$) and the stretch/bend combinations and bend overtone ($\sim$4300 cm$^{-1}$) of CH$_4$, which is verified experimentally by recording the laser fluence dependence of the laser-on depo-
TABLE I. CH₄ vibrational eigenstates excited in this study and their zero-order normal-mode label, vibrational energy $E_{vib}$ (kJ/mol), fitted shift along the $E_1$ axis $\Delta E_{1}^{v}$ (kJ/mol), and calculated vibrational efficacy $\eta_{i}$ (%).

<table>
<thead>
<tr>
<th>Zero-order label</th>
<th>$E_{vib}$</th>
<th>$\Delta E_{1}^{v}$</th>
<th>$\eta_{i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1 + v_4$ (stretch/bend)</td>
<td>50.6</td>
<td>33.9 ± 1.1</td>
<td>66.9 ± 2.1</td>
</tr>
<tr>
<td>$v_3 + v_4$ (stretch/bend)</td>
<td>51.8</td>
<td>28.1 ± 1.2</td>
<td>54.3 ± 2.3</td>
</tr>
<tr>
<td>$2v_3$ (pure stretch)</td>
<td>72.1</td>
<td>33.6 ± 1.3</td>
<td>46.6 ± 1.8</td>
</tr>
<tr>
<td>$2v_2 + v_4$ (pure bend)</td>
<td>52.2</td>
<td>20.9 ± 1.3</td>
<td>40.2 ± 2.6</td>
</tr>
</tbody>
</table>

sition signal. The Pt(110) surface is cleaned by Ar⁺ sputtering/annealing cycles until impurities can no longer be detected by Auger electron spectroscopy (AES). To determine absolute reaction probabilities for CH₄, we perform a timed exposure of the clean crystal surface to the molecular beam, measuring both the incident dose of CH₄ molecules per unit area with the calibrated QMS as well as the resulting coverage of carbon reaction products on the surface by performing calibrated AES measurements across the surface in a computer-controlled scan.¹⁶

We measured the state-resolved reactivity of CH₄, prepared in the four different vibrational states shown in Table I, each containing different amounts of C-H stretch and bend excitation given approximately by their zero-order normal-mode labels (ν₁ and ν₂ are the symmetric and antisymmetric stretch modes and ν₃ and ν₄ are IR-inactive and IR-active bend vibrations, respectively). Because of the near degeneracy of the stretch fundamentals and bend overtones, the vibrational states of CH₄ can be grouped into polyads of nearly isoenergetic vibrational states¹⁷ (Fig. 1). The states $2v_2 + v_3$, $v_1 + v_3$, and $v_3 + v_4$ states are members of the octad, whereas $2v_3$ is part of the tetradecal. The zero-order normal-mode labels $2v_2 + v_3$, $v_1 + v_4$, and $v_3 + v_4$ are good descriptors of the octad states,¹⁸ while the state labeled $2v_3$ contains about 15% $v_1 + v_3$ character both of which are pure stretching modes. Therefore, we consider the four eigenstates prepared in this study as pure bend ($2v_2 + v_3$), stretch/bend combinations ($v_1 + v_4$, $v_3 + v_4$) and pure stretch states ($2v_3$).

Figure 1 shows the result of an AES analysis of carbon product coverage across the Pt(110)-(1×2) surface after two subsequent CH₄ molecular-beam exposures ($E_i$ = 22.4 kJ/mol) in different positions on the surface. For each deposition, a different vibrational eigenstate of CH₄ was excited by tuning the laser to the corresponding R(1) rotational transition. The laser fluence was sufficient to completely saturate the excitation producing identical fractions of state-prepared CH₄ because the excitation used the same initial state ($v=0$, $J=1$) in either case. The two eigenstates, $2v_2 + v_3$ and $v_1 + v_3$, have very similar vibrational energy (Table I) but lead to different reactivity as seen in Fig. 1. $v_1 + v_3$ excitation of CH₄ in the incident molecular beam produced a 50% higher carbon product coverage even though the incident dose was only half of what was used in the $2v_2 + v_3$ deposition. This and similar data where two (or more) nearly isoenergetic states result in different reaction probabilities provide clear evidence of mode-specific reactivity of CH₄ on Pt(110)-(1×2). For mode-specific reactivity, the reaction probability is not only a function of the total available energy but depends on the specific eigenstate of the reagent molecule. Mode-specific reactivity of CH₄ has been observed previously on Ni(100) for the C-H stretch fundamentals ($v_1$ and $v_3$) (Refs. 2 and 19) and for both Ni(100) and Ni(111) comparing the bend overtones $3v_4$ with the C-H stretch fundamental $v_1$.¹² The observation of mode specificity in CH₄ dissociation demonstrates the failure of the statistical rate theory¹³ to capture the microscopic dynamics of CH₄ chemisorption on nickel and platinum surfaces.

Mode-specific reactivity for states of the octad provides information regarding intramolecular vibrational redistribution (IVR) during the methane/metal collision. We note that the narrow band excitation laser prepares a stationary rotational eigenstate of the isolated CH₄ in each case, which does not undergo IVR during the 10–20 μs flight time toward the target surface. However, close to the surface IVR becomes possible when the incident CH₄ starts to interact with the metal surface. The initially prepared eigenstate of the isolated molecule is not an eigenstate of the combined molecule/surface system and therefore can undergo a time evolution as the molecule approaches the surface which is referred to as “surface-induced IVR.” Mode specificity will only be observable if surface-induced IVR is incomplete on the time scale of the molecule/surface interaction which is less than a picosecond for the range of incident speeds used here (690–2835 m/s). Halonen et al. have modeled this surface-induced IVR process within a reduced-dimensionality vibrationally adiabatic framework comprising the C-H stretch states including their first overtones. The eigenenergies of the CH₄/metal system were calculated as a function of the molecule/surface distance.²⁰ The resulting adiabatic vibrational energy curves and associated wave functions predict different vibrational energy flow and localization for different initial states. Halonen et al. suggested that mode specificity in the reaction is due to at least partially adiabatic motion along these vibrational energy curves. Nonadiabatic effects can occur near avoided curve crossings and because the number of avoided crossings increases for higher polyads, surface-induced IVR can be expected to accelerate with increasing vibrational energy. One might also expect intrapolyad surface-induced IVR to be faster than IVR between states belonging to different polyads due to smaller energy gaps. Therefore, surface-induced IVR may reduce or suppress mode specificity for states of higher poly-
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FIG. 2. (Color online) CH$_4$ state-resolved reactivity as a function of translational energy ($E_t$). $v_1+v_4$ and $2v_2+v_4$ reactivities at $E_t$=4 kJ/mol are upper limits. The error bars represent 95% confidence interval of the convoluted uncertainties. Lines are S-shaped reactivity curves fitted to data points.

A summary of $\Delta E_i^v$ values and calculated vibrational efficacies can be found in Table 1. $\eta_v<1$ indicates that it takes less than the equivalent to $h \nu_i$ in $E_i$ to raise the reactivity of CH$_4$($v=0$) by the same amount as observed for excitation of the state $\nu_i$, therefore CH$_4$ translation is more effective than the investigated CH$_4$ vibrations to increase the reaction rate on Pt(110)-(1×2). Furthermore, it can be seen that the two stretch/bend combination eigenstates have the highest vibrational efficiencies, followed by the pure stretch overtone and the pure bend overtone.

The fact that the highest vibrational efficiencies are observed for the stretch/bend combination states is striking. So far it was commonly assumed that stretch excitation is far more important in activating CH$_4$ dissociation than bend excitation, leading to reduced-dimensionality models which include only C-H stretch coordinates. In contrast to this assumption, the present results demonstrate that concerted stretch and bend excitation results in a larger efficacy than either pure stretch or pure bend excitation. This concerted role of stretch and bend excitation is reflected by the observation that the vibrational efficiencies of the stretch/bend combination states cannot simply be predicted as energy weighted averages of the efficiencies of the contributing normal modes, i.e., the efficacies are apparently nonadditive.

The observed mode specificity, expressed by the ordering of the vibrational efficiencies, is consistent with transition state structure calculations for CH$_4$ dissociation on the Pt(110)-(1×2) surface, which shows that the dissociating C-H bond is not only stretched but also bent. Our results underline the important role of ab initio calculations in defining the reaction coordinate for CH$_4$ dissociative chemisorption on metal surfaces. We suggest that dynamical calculations should consider not only the C-H stretch but include at least the bending angle between the dissociating C-H bond and the C$_3$ axis of the spectator methyl in order to more realistically describe the dynamics of CH$_4$ chemisorption.

We note that, similar to what was observed on Ni(100) and Ni(111), the pure bending state of CH$_4$ has a lower efficacy than the pure stretching state on Pt(110)-(1×2).
Previously, Juurlink et al.\textsuperscript{12} suggested that this sort of difference in efficacy might be due to different coupling of stretch vs bend quanta to low-frequency surface phonons. The fact that we observe a higher efficacy for the stretch/bend combination state $\nu_3 + \nu_4$ than for the $2\nu_3$ state, contradicts this suggestion. Finally, it is interesting that the stretch/bend combination state $\nu_1 + \nu_4$ shows a higher efficacy than the stretch/bend combination state $\nu_3 + \nu_4$. This is reminiscent of the observation of a higher vibrational efficacy for the $\nu_1$ state compared to the $\nu_3$ state of CH$_4$ on Ni(100) (Ref. 19) but further theoretical studies will be needed to understand if the observed mode specificity for these two pairs of states shares a common origin.

In conclusion, the measured state-resolved reactivity of CH$_4$ on Pt(110)-(1 × 2) for four vibrational eigenstates with different combinations of stretching and bending motion enable a detailed comparison of the role of stretch and bend excitation of CH$_4$ in its dissociative chemisorption. vibrationally mode-specific reactivity is observed both between eigenstates belonging to different polyads and between states belonging to the same polyad which confirms that surface-induced IVR is inefficient and incomplete on the time scale of the reactive methane/metal encounter. These results contradict the fundamental assumption of statistical theories for calculating the reaction rate, invalidating them from a realistic description of the chemisorption dynamics of CH$_4$ on Pt(110)-(1 × 2). Vibrational efficacies are found to be higher for the two stretch/bend combination states than for the pure stretching and pure bending states, demonstrating their non-additivity. The observation of a concerted role of stretching and bending motion in activating CH$_4$ dissociative chemisorption calls for the inclusion of both stretching and bending degrees of freedom in dynamical models, in contrast to previously reported reduced-dimensionality models that include only stretch excitations. Finally, mode-specific chemisorption of CH$_4$ is not unique to Ni surfaces and follows similar trends on Pt(110)-(1 × 2). Dynamical calculations performed on a realistic multidimensional potential-energy surface of this benchmark gas-surface system are needed to understand these trends, not only for CH$_4$ fundamental vibrational modes but also for CH$_4$ combination and overtone states.

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