raperly and cleanly neutralized. The reaction mixture obtained after the incubation for 48 hours at 25°C showed in DLS a marked increase in apparent hydrodynamic diameter from 11 to 82 nm (Fig. 4J). Therefore, we carried out tapping-mode AFM of an aliquot of the reaction mixture on mica and found that long cylindrical objects are reconstructed (Fig. 4F). These observations indicate that reduced nanorings FeCNR1 are equilibrated with their uniaxially “merged” nanotubular assembly of FeCNT4 (Fig. 1E). The uniaxial merging event of FeCNR1 appears rather sluggish, certainly due to its large entropic loss. When the reaction mixture, incubated for 0.5 hours after the complete reduction of the ferrocene units of FeCNR1, was air-dried on mica and analyzed with tapping-mode AFM, only toroidal objects were visualized (Fig. 4E). Analogous to the case of FeCNT4, we attempted oxidative cutting of larger-diameter FeCNT5 by using Cl2FcBF4. However, a mixture of ill-defined structures resulted. We consider that FeCNT4 cannot satisfy a requisite for the selective attenuation of noncovalent forces, most likely because of an insufficient structural robustness originating from its large and thin-wall dimensions.

Considering a possible entropic penalty for the formation of giant nanotubulres through the direct self-assembly of small molecules, we suppose that the Ag(I)-mediated nanotubular assembly of FeL1 (Fig. 1C) probably occurs stochastically, without preceding formation of the corresponding nanorings (FcNR). In the crystalline state, tetraylferrocene derivatives are known to adopt an eclipsed geometry (29, 30). By means of 1H nuclear magnetic resonance (NMR) spectroscopy in CD3CN, we confirmed that the geometry of FeL1 in solution is more biased to the eclipsed form at lower temperatures. However, even at -40°C 1H NMR spectral feature was still dynamic (Fig. S5). Meanwhile, when FeL1 is bound to Ag(I) ions a metallophilic interaction may occur, so that its tendency to form the eclipsed geometry is enhanced. The resultant Ag(I)-bound bent-shaped ligands are connected together to form a doubly bridged metal-organic oligomer (Fig. 1B, bottom center). Such oligomers may start to stack up bilaterally via amplified r-stacking and metallophilic interactions. Consequently, curvy sheet-like intermediates would form and grow up stochastically to furnish nanotubular FeCNT4 at the final stage. In regard to the stochastic assembling mechanism thus proposed, neither nanotubes nor nanorings were detected with AFM when oxidized FeL1 (FcL1)1 with an attenuated stacking ability was likewise treated with AgBF4 (Fig. S19). As highlighted in the present work, 200-membered metal-organic decagonal nanorings (Fc10NR1), obtained by oxidative cutting of the nanotube, are unlikely to form directly with conventional self-assembling protocols. Together with the results of electrosclatic pasting (Fig. 1G) and reductive merging (Fig. 1E) of FeCNR1, we believe that the stepwise noncovalent synthesis—involved cutting, pasting, and merging operations—may open additional routes for nanoscale synthesis.

References and Notes
24. Materials and methods are available as supplementary materials on Science Online.

Vibrationally Promoted Dissociation of Water on Ni(111)

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Water dissociation on transition-metal catalysts is an important step in steam reforming and the water-gas shift reaction. To probe the effect of translational and vibrational activation on this important heterogeneous reaction, we performed state-resolved gas/surface reactivity measurements for the dissociative chemisorption of D2O on Ni(111), using molecular beam techniques. The reaction occurs via a direct pathway, because both the translational and vibrational energies promote the dissociation. The experimentally measured initial sticking probabilities were used to calibrate a first-principles potential energy surface based on density functional theory. Quantum dynamical calculations on the scaled potential energy surface reproduced the experimental results semi-quantitatively. The larger increase of the dissociation probability by vibrational excitation than by translation per unit of energy is consistent with a late barrier along the O-D stretch reaction coordinate.

Water dissociation on transition-metal surfaces (1, 2) is an essential part in the steam reforming process used on a large scale by the chemical industry to convert natural gas [methane (CH4)] to H. In the first step, CH4 and water vapor (steam) react on a Ni catalyst to produce a mixture of CO and H2 (syngas). The CO is reacted again with water, and this water-gas shift reaction produces additional H2 and CO2. The H2 is used as a clean fuel and for the industrial production of important chemicals such as ammonia and methanol. In both reactions, the dissociative chemisorption of H2O on the catalyst surface to form chemisorbed OH(ads) and H(ads) is an essential fundamental step, so an in-depth understanding of the adsorption and dissociation of water on a transition-metal catalyst surface is highly desirable. Although the dissociative chemisorption of CH4 has been extensively studied by quantum-state-resolved experiments (3–9), until now, few experimental studies of water dissociation on transition metals have been available (2). We report a quantum-state-resolved study for D2O dissociative chemisorption on Ni(111), jointly with a quantum-dynamical
Dissociative chemisorption of both water and CH$_4$ on Ni surfaces occurs via a direct mechanism in which the incident molecules either dissociate on the surface on initial impact or are scattered back to the gas phase intact. For CH$_4$, earlier experiments have shown that the dissociative chemisorption is activated by both the translational and vibrational energy of the incident molecule [(3) and references therein]. Quantum-state–resolved experiments for CH$_4$ have later revealed several signatures of nonstatistical reaction dynamics. The dissociation reaction of several isotopologues of CH$_4$ on Ni and Pt surfaces was observed to be both mode-specific (4–6) and bond-selective (7, 8). Furthermore, the vibrational efficacy $\eta(v)$, which compares reactivity enhancement for vibrational excitation of a specific quantum state $v$ with the effect of increasing the incident translational energy by an equivalent amount, took values both above and below unity, depending on the vibrational state of CH$_4$ and the type of metal surface. Finally, experiments with laser-aligned incident CH$_4$ molecules uncovered a hitherto unexplained steric effect in the CH$_4$ reactivity on several different Ni surfaces (9, 10). All these observations show the inadequacy of statistical models (11, 12) for a realistic microscopic description of CH$_4$ chemisorption and provide stringent tests for classical and/or quantum-dynamics calculations on multidimensional PESs (13–16).

Recently, theoretical studies of water dissociative chemisorption have predicted strong mode specificity (17), bond selectivity (18), and steric effects (19, 20) for water on Cu(111) and Ni(111) (21). In addition, experiments have demonstrated mode specificity and bond selectivity in bimolecular reactions of water with H (22–24) and Cl atoms (25) in the gas phase. The strong vibrational enhancement in these gas-phase processes has been attributed, according to Polanyi’s rules (26), to the “late” barrier along the reaction path, a characteristic that is shared by the dissociative chemisorption of both CH$_4$ and water. Challenged by the theoretical predictions, we investigated the effects of translational and vibrational excitation on the dissociation probability of water on the Ni(111) surface. We used single- and double-resonance excitation by infrared (IR) laser pumping in a molecular beam (27) to prepare surface-incident D$_2$O selectively either with one or two vibrational quanta of antisymmetric O-D stretch excitation ($v_2$ or $2v_2$) in order to measure its state-resolved dissociation probability on a Ni(111) single-crystal surface. Such a selective quantum-state preparation by population inversion only became feasible recently for D$_2$O because of the availability of tunable high-power IR laser sources that emit light in the O-D stretching region. To better understand the experimental results, a six-dimensional (6D) PES was developed based on a large number of DFT points on Ni(111), and the dissociative chemisorption dynamics of D$_2$O were investigated with a 6D quantum wave-packet method. As demonstrated below, the synergistic interplay between state-resolved experiment and high-level quantum theory leads to a much deeper understanding of this prototypical surface reaction.

Details of the experimental setup have been described in previous publications (28, 29). Briefly, a continuous molecular beam of D$_2$O was generated by skimming a supersonic expansion of a gas mixture of 3% D$_2$O in He obtained by bubbling He gas through a reservoir containing liquid D$_2$O. The beam was passed through an IR source (two optical parametric oscillators) and 27% of the IR sources only allowed the preparation of O-D stretch quantum states of the D$_2$O reactant as a function of incident translational energy ($E_i$) for the $v_3$ and $2v_3$ states, as well as without laser excitation by quantifying the coverage of the surface-bound OD(ads) product with Auger electron spectroscopy (AES) resulting from a known dose of incident D$_2$O (additional experimental details can be found in the supplementary materials (SM) (30)).

For a theoretical description of water dissociation on Ni(111), we developed a 6D flat rigid surface model (Fig. 1), following our earlier work on Cu(111) (17). The 6D global PES was constructed from ~22,000 spin-polarized DFT points on a three-layer slab with a 2 × 2 unit cell, using the PW91 functional (31) implemented in VASP (the Vienna Ab-initio Simulation Package) (32, 33). These points were fit using the permutation-invariant polynomial approach (34), with a root mean square deviation of 2.0 kJ/mol for the dynamically relevant region (points below 145 kJ/mol). The resulting PES reproduces the geometries, energies, and frequencies for stationary points obtained in the DFT calculations quite well and are also consistent with earlier electronic structure calculations (30). The quantum dynamics were represented in Jacobi coordinates (shown in Fig. 1) by a 6D Chebyshev real wave-packet method (20, 35). Specifically, an initial wave packet was launched for a rovibrational state of reactant (D$_2$O) above the surface and propagated on the PES using the Chebyshev three-term recursion formula. The total reaction probability was computed with a flux method on a dividing surface placed beyond the saddle point. The effects of surface corrugation, impact site, and lattice motion are approximately treated based on the approaches of Jackson and co-workers (14, 36, 37). A more detailed description of the theoretical calculations is given in the SM (30).
Figure 2 shows a comparison of the AES-detected OD coverage on the Ni(111) surface resulting from two D₂O depositions at $E_t = 36.5$ kJ/mol with and without laser excitation of the incident molecular beam. For the laser-off deposition, the absence of substantial OD coverage in the region where the molecular beam struck the Ni(111) surface (Fig. 2, right, labeled laser-off) shows that $36.5$ kJ/mol of translational energy normal to the surface was insufficient for the incident D₂O to overcome the reaction barrier and to dissociate to produce OD(ads). For the laser-on deposition (Fig. 2, left, labeled laser-on), rovibrational excitation of $30\%$ of the incident D₂O in the molecular beam with two quanta of the antisymmetric O-D stretch normal mode ($2\nu_3$) added $66.8$ kJ/mol of vibrational energy to the reactant molecules and led to dissociation of $0.05\%$ of the incident vibrationally excited D₂O ($2\nu_3$) as detected by the AES signal. The data presented in Fig. 2 show that water dissociation on Ni(111) is strongly activated by vibrational energy, which is consistent with the results of earlier simulations for the H₂O/Cu(111) system (17).

In order to probe for translational activation and to compare the effect of translational and vibrational energy, we performed reactivity measurements at several incident energies $E_t$ in the range of $36.5$ to $75$ kJ/mol for $\nu_3$ and $2\nu_3$ excitation of the incident D₂O and in the range of $55$ to $75$ kJ/mol without laser excitation. The average $E_t$ of the molecular beam was controlled by changing the temperature of the expansion nozzle $T_n$ in steps of $100$ K from $373$ to $773$ K. Figure 3 shows a summary of our state-resolved D₂O reactivity measurements on a Ni(111) surface at a surface temperature of $300$ K. Because we varied $E_t$ by increasing $T_n$, and vibrational relaxation in a supersonic expansion is inefficient, the measured laser-off D₂O reactivity contained an unknown contribution from the dissociation of vibrationally excited D₂O from the hot nozzle. Thus, the measured laser-off reactivity can only be taken as an upper limit to the $\nu = 0$ reactivity, which, depending on the fraction of vibrationally excited D₂O and the vibrational efficacies, may be substantially lower. The experimental state-resolved $\nu_3$ and $2\nu_3$ reactivities were not affected by the effect of heating the expansion nozzle, because they were obtained from the difference between laser-on and laser-off measurements, where the contributions of thermally excited vibrations cancel.

For comparison of the effect of translational and vibrational excitation, we parameterized the state-resolved data by fitting S-shaped reactivity curves, initially suggested by Luntz (38), to each of the $\nu_3$ and $2\nu_3$ data sets. For the laser-off data, which represent an average of different vibrational states populated at a given $T_n$, the same analysis is not suitable. These S-shaped curves are based on the assumption of a Gaussian distribution of reaction barrier heights of width $W$ about an average barrier $E_B$. The width of the barrier reflects the combined effect of different initial orientations of the incident D₂O, the distribution of impact sites of D₂O within the unit cell of the Ni(111) surface lattice, and the distribution of thermal surface atom displacement along the surface normal. The fitted curves are represented by the dotted lines in Fig. 3. The horizontal shift of $37$ kJ/mol between the state-resolved S-shaped reactivity curves for $\nu_3$ and $2\nu_3$ excitation along the $E_t$ axis can be used to compare the effects of translational and vibrational energy on the reaction probability. The ratio of the translational energy shift to the vibrational energy of $33.2$ kJ/mol gives the vibrational efficacy $\eta(2\nu_3,\nu_3)$. For the second quantum of $\nu_3$ excitation, the efficacy is $1.1 \pm 0.05$, indicating that vibrational excitation from $\nu_3$ to $2\nu_3$ is more efficient in promoting reactivity than is adding an equal amount of translational energy to the incident molecule. Because the efficacy for the second quantum of $\nu_3$ excitation is expected to be lower than that of the first (3), we would expect $\eta(\nu_3)$ to be larger than $1.1$, although we cannot determine it directly from the laser-off data for the reasons stated above. Given such a large effect of vibrational energy on the reactivity, we can conclude that the laser-off reactivity is dominated by thermal vibrationally excited molecules, which is consistent with the theoretical results presented below.

The state-resolved reactivity data for $\nu_3$ and $2\nu_3$ excitation reported here provide stringent tests for theoretical models. The 6D model used here contains all important degrees of freedom for water dissociative chemisorption, including all three vibrational modes of D₂O. Although the theoretical sticking probabilities calculated on the PW91 PES display appreciable mode specificity, they were systematically larger than the experimental results. The discrepancy was attributed to the underestimation of the barrier height ($64.6$ kJ/mol relative to free H₂O) by the PW91 functional. Indeed, a higher ($99.1$ kJ/mol) barrier was found with
Reactivity can be understood by the recently proposed decay parameter of the reaction coordinate at the transition state. Such coupling can be estimated by the projection of the reactant mode vector onto the reaction coordinate vector at the transition state. The high vibrational efficacy for D₂O dissociative chemisorption can be rationalized by the fact that the SVP projection for the antisymmetric stretching mode (0.65) is substantially larger than that for the translation (0.34). As discussed elsewhere, the stronger coupling between the reactant vibration and the reaction coordinate is related to the lower barrier and thus consistent with Polanyi’s rules (26). Indeed, it is shown in Figure 1 that the classical outer turning point of the v₁ = 0, 1, or 2 state progressively approaches the saddle point, allowing better access of the transition state.

There has been substantial progress in understanding dissociative chemisorption of diatomic molecules on metal surfaces in recent years (45). The theory-experiment agreement in these systems has reached an unprecedented level, thanks to the chemical accuracy (<1 kcal/mol) of the PESs (41). However, it is still extremely challenging to repeat such success for heterogeneous reactions involving polyatomic molecules. The in-depth understanding of the reaction dynamics for water dissociation provided by the present synergistic experimental-theoretical work has important implications in advancing our understanding and control of prototypical polyatomic surface reactions beyond their well-understood diatomic counterparts. The mode specificity demonstrated in the dissociative chemisorption of water on Ni(111) suggests that such a phenomenon is not restricted to CH₄ and might be quite prevalent in many surface reactions. A key determinant of mode specificity and bond selectivity is the slow rate of surface-induced intramolecular vibrational energy redistribution of the reactant, which is related to its sparse density of states (46). Both CH₄ and H₂O, and many other molecules, obviously possess these properties. More interestingly, the results presented here suggest that water dissociation in high-temperature (700° to 1100°C) steam reforming is dominated by Boltzmann populated excited vibrational states, thanks to their high vibrational efficacies. Further experimental and theoretical work will be needed to investigate mode specificity, bond selectivity, and steric effects in water chemisorption, with the goal of developing a predictive understanding of this important gas/surface reaction.

References and Notes

30. Materials and methods are available as supplementary materials on Science Online.

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Supplementary Materials

www.sciencemag.org/content/344/6183/504/DC1 Materials and Methods
Figs. S1 to S8
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References (47–82)
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