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THE JOURNAL OF CHEMICAL PHYSICS **127**, 244701 (2007)

Supersonic molecular beam studies of dissociative adsorption of H_2 on Ru(0001)

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We examined reactivity of H_2 on Ru(0001) using molecular beam techniques and we compared our results to experimental results for similar systems. The dissociative adsorption of H_2 on Ru(0001) is similar to that on Pt(111) and Ni(111), although on ruthenium nonactivated adsorption is strongly suggested. However, we find no clear signature of a steering- or precursor-based mechanism that favors nonactivated reaction paths at low kinetic energy. In comparison to Pd(111) and Rh(111) our results indicate that a universal mechanism enhancing reactivity at low energy does not have a mass dependence. In addition, we have compared our results to predictions of reactivity for H_2 on Ru(0001) from six-dimensional dynamical calculations using two different generalized gradient approximation functionals. It leads us to conclude that the PW91 functional yields a more accurate value for the minimum energy path but does not impose enough corrugation in the potential. The revised-Perdew-Burke-Ernzerhof (RPBE) functional appears to behave slightly better at higher energies, but we find significant quantitative disagreement. We show that the difference is not due to different energy resolutions between experiment and theory. However, it may be due to a dependence of the reactivity on rotational state or on omission of relevant dimensions in the theoretical description. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2813413]

I. INTRODUCTION

Hydrogen dissociation on a metal surface has been recognized as an elementary step in many industrial processes. In recent decades, dissociative chemisorption of H_2 has therefore been studied intensely, both theoretically and experimentally.[1] Although many transition metals have been studied, two have traditionally been used as model systems due to the extremity of their behavior. Dissociation on Cu surfaces serves as the model system for strongly activated dissociation, whereas Pd is used for nonactivated dissociation.[2]

More recently, metal surfaces which show less extreme behavior have been the focus of detailed investigations. For example, dissociation and scattering from Pt(111) were recently addressed in a combined theoretical and experimental studies. Results from state-of-the-art calculations using a density functional theory based potential and high-dimensionality quantum dynamical calculations were compared to experimental results from supersonic molecular beam experiments.[3] The authors showed the Born-Oppenheimer approximation to be a valid assumption for the theoretical study and obtained quantitative agreement with experimental results[4] without including phonons or electronic effects. Such studies appear to indicate that the theoretical description for hydrogen dissociation on metals has progressed to a level close to completion.

The interaction of H_2 with ruthenium appears less well understood. Ruthenium has been shown to be an excellent catalyst for ammonia production from N_2 and H_2.[5,6] Although dissociative adsorption of nitrogen is rate limiting[7] and defects greatly enhance reactivity,[5,8] hydrogen dissociation on flat terraces has also found considerable attention.[9–12] A recent six-dimensional quantum dynamics study of H_2 dissociation on Ru(0001) shows that predicted initial reaction probabilities (S_0) are very sensitive to the applied generalized gradient approximations (GGAs) in constructing the potential energy surface.[13,14] In particular, use of PW91 (Ref. 15) yields lower activation barriers and, thus, higher reactivity than revised-Perdew-Burke-Ernzerhof (RPBE).[16] Previous calculations[16] suggest that the RPBE functional should

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yield results closer to experiment, since PW91 generally overestimates chemisorption energies. Here, however, the RPBE functional predicts a considerable activation barrier for adsorption, which contradicts results from earlier experiments of H_2 dissociation on Ru(0001).[10]

In addition to uncertainty regarding the use of the best functional to describe the H_2–Ru(0001) potential, electronic friction was recently suggested to explain experimental results for the reverse process of associative hydrogen desorption.[17,18] The absence of the necessity for including such effects in H_2/Pt(111) appears to indicate that a unified theory describing the interaction of hydrogen with transition metals is not yet fully developed and it remains necessary to test theoretical predictions with experiments.

In this paper, we describe a supersonic molecular beam study of the dissociative adsorption of H_2 on Ru(0001) to test the validity of assumptions in previous theoretical investigations. We determine the reaction probability as a function of kinetic energy, surface temperature and angle of impact for the vibrational ground state, and rotational ensembles resembling the molecular beam expansion temperature. We compare our results to previous experiments that investigated H_2/Ru(0001) and similar molecular beam studies for H_2 dissociation on other close-packed transition metal surfaces. The paper is organized as follows. In Sec. II we describe the experimental apparatus and methods used to determine S_0. Section III presents our results, which are then discussed in detail in Sec. IV. Section V summarizes our main conclusions.

II. EXPERIMENTAL APPARATUS AND METHODS

Experiments were carried out in a vacuum system that connects a series of five chambers, which are individually pumped by turbomolecular pumps.[19] A supersonic expansion of pure or diluted H_2 (99.9999%) or D_2 (99.8%) from 1×10^2 to 3×10^2 kPa exits a 43 μm nozzle in the first chamber. A well-defined molecular beam, created by a series of skimmers and orifices, enters the main chamber with an ultrahigh vacuum base pressure of $<1\times10^{-10}$ mbar. The ruthenium single crystal, cut and polished to within 0.1° of the (0001) face, is cleaned using standard cleaning procedures of Ar^+ bombardment and annealing. We test for surface quality using temperature programmed desorption (TPD) spectroscopy of NO, O_2, and CO, which are known to be very sensitive to impurities and defects.[20] We repeat cleaning procedures until no evidence for impurities or defects is found.

The molecular beam energy is controlled by the temperature of the expansion nozzle (room temperature to 1700 K) and seeding techniques. We determine the kinetic energy of H_2 (D_2) molecules for all expansion conditions using time-of-flight (TOF) spectrometry by varying the length of the neutral flight path. We use various wheels with different slot sizes along the edge to produce duty cycles of 0.5% for TOF purposes and 2% and 10% when measuring reaction probabilities. The TOF spectra are fitted using an appropriate form of the Boltzmann distribution for a density-sensitive detector, convoluted with the known gating function of the chopper wheel.[21] When fitting the raw data, the only important remaining adjustable parameters are the stream flight time and characteristic spread in flight time. Conversion of the data using the appropriate Jacobian allows us to plot velocity and energy distributions. Plotting the kinetic energy versus nozzle temperature yields a line, which deviates very modestly from linearity at the highest expansion temperatures. The slope equals 2.53RT, which is in reasonable agreement with molecular beam studies using similar conditions.[22]

We determine, for known kinetic energies and energy distributions, the absolute reaction probability (S_0) using the King and Wells technique.[25] It is well known that accurate determination of high reaction probabilities is complicated by convolution of the time-dependent drop in partial pressure when exposing the clean crystal to the molecular beam with the vacuum time constant. Therefore, we have verified the accurateness of our measurements using two independent means. First, for high fluxes, which yield excellent signal-to-noise ratios, we apply a fitting procedure to the King and Wells pressure trace. The fitted function consists of an exponential and a linear part, which was previously found to accurately describe coverage-dependent adsorption.[10] Extrapolating the fitted function back to the exact time when the beam impinged onto the clean surface corrects to a large extent for the convolution mentioned above. Second, for the same range of probed kinetic energies, we have systematically decreased the flux by employing chopper wheels with lower duty cycles and/or dropping the expansion pressure. We reduce the flux until we find no more increase in reactivity. These two techniques yield consistent values for S_0 in the low energy range. At high energy, the fitting and extrapolation procedure still underestimates S_0, and we only report values determined by lowering the flux.

A second complication arises from the effusive hydrogen load on the main chamber. It leads to sticking as soon as the supersonic beam is allowed into the main chamber, albeit blocked by the inert flag in front of the crystal. Since the crystal temperature is well below the onset of associative desorption, we have quantified H_2 adsorption prior to the actual measurement of S_0 using integrated TPD features with a full monolayer as reference. For all data presented here, the initial hydrogen coverage was <0.04 ML. In qualitative agreement with previous experimental studies,[10] we note that the observation of accumulating hydrogen on our Ru(0001) surface from an effusive source at room temperature implies a very low barrier to dissociation.

Using the described methods we have determined the reaction probability at a surface temperature of 180 K. At higher temperatures, associative desorption starts competing with adsorption. We have measured the reactivity also at 170 and 140 K but found no measurable differences from the data presented in Sec. III. The increasing time required to cool the crystal below 140 K does not allow for accurate measurement of S_0 since residual H_2 adsorbs to the surface while cooling.

The expansion temperatures used in this study allow for, at most, a modest fraction of vibrationally excited molecules, $f_{v>0}$, in the molecular beam ($f_{v>0}=0\%-2.4\%$ for $T_{\mathrm{nozzle}}=300-1700$ K). The reactivity that we determine is a

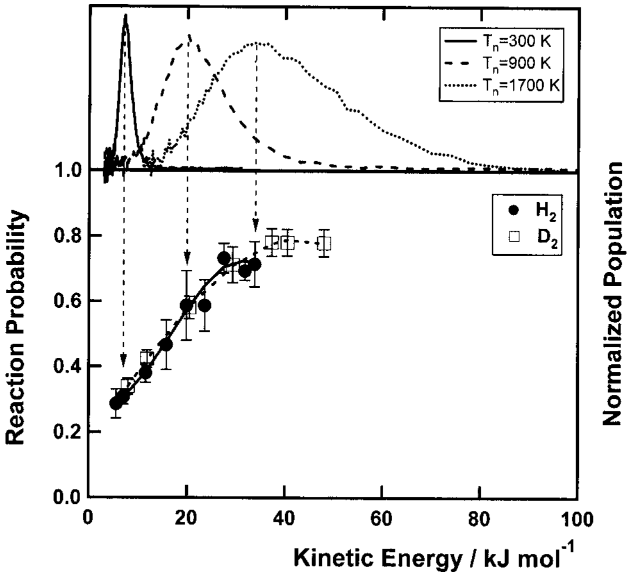

FIG. 1. Lower panel: Reaction probability of hydrogen on Ru(0001) at normal incidence. Data are fitted with fourth-order polynomials. Top panel: Convoluted energy distributions for various nozzle temperatures (see text for details).

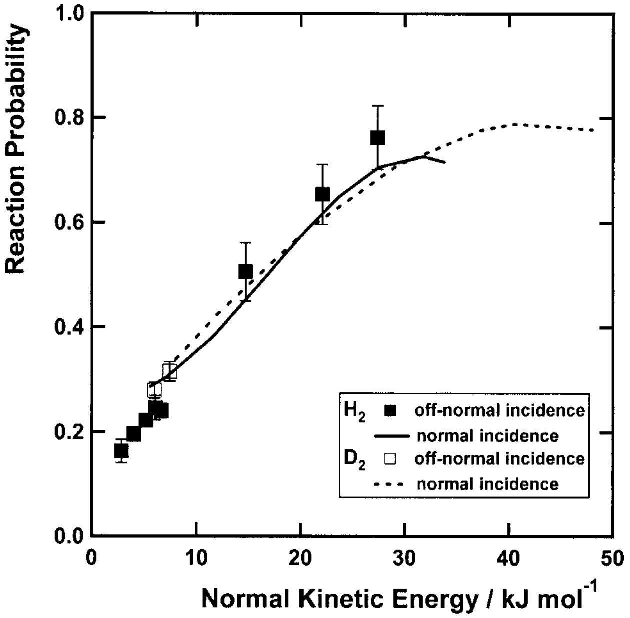

FIG. 2. Comparison of the reaction probabilities of H_2 and D_2 colliding at off-normal incidence (points) and normal incidence (lines).

weighted average of the state-resolved reactivity of each rovibrational state present in the beam. Since our results show high reactivity, the small percentage of vibrationally excited molecules does not significantly alter the measured value from the reactivity due to the dominant vibrational ground-state population. Our results may therefore be interpreted as the convoluted reactivity of the rotational population in the vibrational ground state.

Hydrogen expansions are known to exhibit poor rotational cooling.[23,24] By comparison to results from state-resolved measurements of the rotational temperature of pure n-H_2 expansions,[24] we estimate that, for our least favorable expansion conditions at room temperature ($p_0 d \sim 25$ Torr mm), the rotational distributions in our molecular beams consist of $J=0$, 1, 2, and 3 at relative intensities of approximately 15:70:10:5. Since we change both the expansion temperature and pressure in our experiments and cannot determine the exact rotational composition of our beam, we do not attempt to deconvolute the measured weighted average and attribute reactivity to individual rotational states. In addition, we have no control over rotational alignment or impact parameter. Therefore our data, indicated as S_0 in this paper, may be interpreted as the reaction probability for $\nu=0$, averaged across the unit cell, averaged over the angle between the H–H internuclear axis and the surface normal, and averaged over the lowest rotational states.

III. RESULTS

The absolute reaction probabilities for H_2 and D_2 are shown as a function of kinetic energy in Fig. 1 (lower panel) for a surface temperature of 180 K. Also shown are various beam energy distributions, which are not deconvoluted from the finite width in time of the gating function of the chopper wheel (upper panel). Therefore, the width of the distribution, especially at higher kinetic energy, overestimates the energy spread in the beam. Since the energy spread within the molecular beam is not symmetrical at high nozzle temperatures, we have chosen to position the symbols at the most probable kinetic energy determined using TOF measurements. The vertical error bars reflect one standard deviation of repeated measurements. Every indicated data point was measured in separate experiments at least 5 times and at most 15 times. The solid lines are fourth-order polynomials with no other purposes than to guide the eye and provide a reference without showing individual data in following graphs. The reaction probability appears mostly isotope independent.

We observe an almost linear increase in the reaction probability with kinetic energy up to ~30 kJ/mol. When extrapolating a line through this linear regime back to zero kinetic energy, a reaction probability of 0.19 is found. Beyond 30 kJ/mol, S_0 seems to saturate at ~0.8. Due to convolution of S_0 with the broader energy distribution inherent to the supersonic expansion at high temperature, this value might be slightly underestimated. In Sec. IV we discuss the convolution of theoretical results for S_0 with the measured energy distribution of the beam.

Figure 2 shows measured reaction probabilities for H_2 and D_2 taken at off-normal incident angles, combined with the fourth-order polynomial fits from Fig. 1. In these experiments the crystal is rotated relative to the molecular beam axis. The nearest C_{3v} symmetry plane orthogonal to the surface is rotated 10° azimuthally from the plane defined by the molecular beam axis and the surface normal. For a nozzle temperature of 300 K, incident molecular beam angles between 10° and 50° were used, corresponding to the set of data at low kinetic energy. For a nozzle temperature of 1700 K, incident angles of 15°, 30°, and 45° were used yielding the upper three data points. We have verified that rotation to positive or negative angles of the same magnitude yielded the same results.

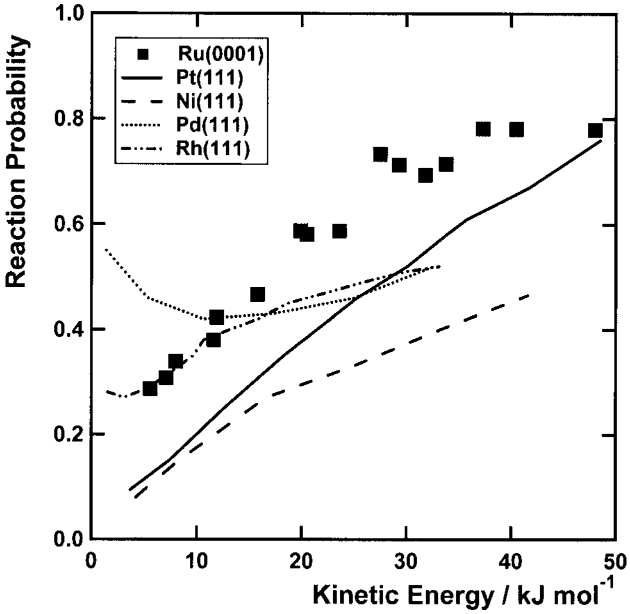

FIG. 3. Comparison of the reaction probabilities of H_2 and D_2 for various metals.

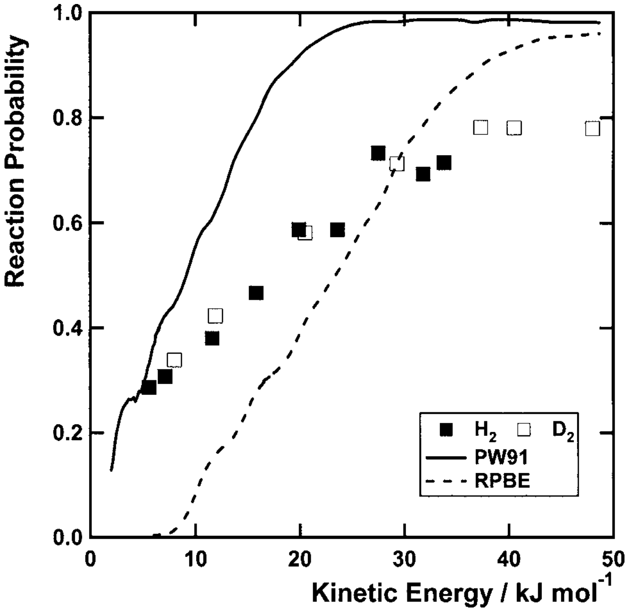

FIG. 4. Comparison of experimental data with predictions from a theoretical study using two different functionals (Ref. 14).

IV. DISCUSSION

From our data in Fig. 1 it can be concluded that the behavior of the reaction probability of H_2 on Ru(0001) is characteristic of direct activated adsorption. No strong isotope effect is observed, although there might be a minor effect at low kinetic energy for the data points taken at off-normal incidence (see Fig. 2). Normal energy scaling is observed both at high and low kinetic energies. There is no measurable dependence of the reaction probability on surface temperature within the probed range.

When comparing our results to earlier experiments of hydrogen on the Ru(0001) surface, several similarities are found. Our TPD results (not shown) compare well in terms of peak shape and desorption temperature with those of Shimizu *et al.*,[25] Kostov *et al.*,[11] Schwarz,[12] and Feulner and Menzel.[10] The results of Feulner and Menzel[10] indicate nonactivated pathways for H_2 adsorption on Ru(0001), a finding that our results corroborate.

When comparing our data to similar transition metals that have been studied with the same techniques we find several striking similarities and differences. We compare our data to surfaces of the same surface structure only, e.g., Pt(111),[4] Ni(111),[26] Pd(111),[27] and Rh(111).[28] The results are shown in Fig. 3. In the regime of kinetic energy higher than 15 kJ/mol, activated adsorption dominates for all metal surfaces shown. The fact that the slopes are similar and that (near) normal energy scaling is generally observed indicates similar shapes of barrier distributions for these metals. Almost consistently no isotope effect is observed: tunneling is not important.

Extrapolation of the linear part of the reaction probability data to $E_{\mathrm{kin}}=0$ kJ/mol yields for Pt and Ni $S_0 \sim 0$. For Pd, Rh, and Ru this procedure yields S_0 on the order of 0.2–0.4. This implies that a significant fraction of accessible phase space provides nonactivated reaction paths. The similarly shaped barrier distributions for all metals are obviously characterized by a different center value.

For Pd, in the low incident energy regime (<15 kJ/mol) some mechanism (steering or precursor based) clearly operates to favor the nonactivated paths leading to enhanced reactivity. We note that on the basis of their state-resolved measurements Gostein and Sitz[29] disputed the accuracy of the absolute values, but there is agreement regarding the presence of a mechanism leading to increasing reaction probability with decreasing kinetic energy. Rh might be slightly affected by these mechanisms as indicated by a slight upward curve and isotope effect. In this case it is attributed to a steering mechanism. We find no clear evidence for such a mechanism for Ru down to ~ 7 kJ/mol, even though 19% of phase space yields nonactivated reaction. We note that, if there is a universal mechanism that operates at low kinetic energies leading to enhanced reactivity ("finding the nonactivated reaction path"), the difference in strength of this mechanism for Pd, Rh, and Ru, which have very similar masses, indicates that the mass and motion of the metal atoms are not a significant part of this universal mechanism. The study on Rh(111) shows an isotope effect at low kinetic energy ($E_{\mathrm{kin}} < 15$ kJ/mol), which is attributed to different rotational state distributions for H_2 and D_2 expansions. Our data do not exclude nor corroborate such an effect, although in our experiments we likely have rotational state distributions that are significantly different when comparing H_2 and D_2. For D_2, the expected rotational state distribution exhibits $n(J=2) > n(J=1) \sim n(J=0)$, while for H_2 $n(J=1) \gg n(J=0) > n(J=2)$.

Figure 4 shows a comparison between our results and those of dynamics calculations for the same system.[14] When comparing the results, we observe that the absolute values are of the right order of magnitude. At low kinetic energy our results match the dynamics calculations using PW91 best, while at higher energies they are in better agreement with those using RPBE.

From the comparison, we conclude that there are three major differences between theory and experiment. First, the onset of reaction varies significantly. Both PW91 and RPBE yield activated minimum energy paths (approximately 1.5 and 8.5 kJ/mol, respectively). In earlier experimental work, significant dissociation using an effusive source at room temperature was observed.[10,25] These results imply that, at most, a very modest activation barrier, such as predicted using the PW91 functional, may be present. However, our results strongly suggest that nonactivated dissociation also takes place. As mentioned, when extrapolating our data linearly to zero kinetic energy, we find a reactivity of 0.19. Although single crystals used in experiments always suffer from defects due to a minor misorientation in the crystallographic plane, the defect concentration on our Ru(0001) crystal is too low to explain this value. Therefore, it appears that either the excited rotations of H_2 present in our molecular beam at low kinetic energy ($f_{J=1}\approx 70\%$, $f_{J=2}\approx 10\%$, $f_{J=3}\approx 5\%$) couple efficiently to an activated reaction coordinate or the theoretical description of this system using the PW91 functional overestimates the barrier to reaction. Since PW91 is generally considered to overestimate bond strengths,[16] we find the former explanation more likely.

The second difference between theoretical and experimental results is the observed maximum reactivity. Both sets of calculations indicate that S_0 goes to unity for high kinetic energy (25 kJ/mol for PW91 and 45 kJ/mol for RPBE), whereas our data suggest a maximum of approximately 0.8. This second difference is coupled to the third difference, namely, the slope of the data. Vincent *et al.*[14] pointed out that the results from the calculations using RPBE indicate more corrugation than PW91, resulting in a less steep rise in the dissociation probability. The slope of our data suggests even more corrugation. However, as we have pointed out, our data suffer from a convolution with fairly broad energy distributions at higher kinetic energies due to incomplete cooling in the supersonic expansion (see Fig. 1, upper panel). Since the data from theoretical calculations are energy resolved, we have verified whether convolution of the theoretical data with our measured energy distributions for a pure hydrogen beam at various conditions makes the difference disappear. For PW91, we find no significant changes when applying the convolution. This is not surprising since S_0 scales linearly with energy in the range where our energy distributions are fairly symmetrical. The convoluted data using the RPBE functional differ more from energy resolved data above 28 kJ/mol. The reaction probability no longer goes to unity within the probed range, but has a value of 0.76 at 34 kJ/mol. However, the curvature is still positive and the reaction probability will not stabilize around 0.8. We conclude that a significant difference between the experimental data and the predictions using the RPBE functional including the energy convolution persists.

We consider three possible origins for the discrepancy at higher energy. First, in our experiments the rotational distribution in the molecular beam becomes broader with increasing kinetic energy, whereas the theoretical study discusses results for $J=0$ only. For our conditions, the rotational temperature of the beam will be close to the nozzle temperature[23,24] and peaks around $J=3$ at the highest kinetic energy. Since we observe that the measured reactivity has a lower slope than the predicted reactivity for $J=0$, the difference between theory and experiment may be caused by differences in rotational states if the higher J states in our molecular beam are less reactive than lower J states. Such rotational effects have been observed previously both in experiment and theory on, among others, Pd(111),[27] Pt(111),[30] and Cu(111).[22,31] For Pd(111), state-resolved experiments[29] show that reactivity decreases from $J=0$ and 1 to $J=2$ and 3 at fixed kinetic energy. Reactivity increases again for higher J states. The difference is strongly reduced by increasing kinetic energy and is essentially gone at 10 kJ/mol, except for $J=0$ which remains more reactive than other rotational states. In a recent theoretical study of the J dependence on H_2 dissociation on Pt(111),[31] $J=4$ was also shown to be less reactive at intermediate kinetic energies than $J=0$. However, the difference disappeared at higher kinetic energies and rotational effects due to the quantum number J alone were claimed not to explain the similar differences between theory and experiment. In contrast, the authors pointed to the potential energy surface and, in particular, the GGA, as likely culprits. Finally, on Cu(111) also an initial decrease in reactivity with J has been observed experimentally.[22,31] Apart from the J dependence, a detailed theoretical study[32] also observed strong effects due to m_J. Especially at J states and kinetic energies similar to those present in our molecular beams, cartwheeling H_2 molecules were found to be much less reactive than helicopters. Since our experiments yield the weighted average reactivity of the rotational distribution present in the molecular beam, the observed discrepancy between our data and predictions for Ru(0001) can therefore be the result of a rotational effect, but only if $J=0$ is at least 20% more reactive than all other J states at high kinetic energies.

A second possible origin of the discrepancy is the existence of phonon and electron-hole pair excitations in the experiment, which are ignored by the dynamical calculations. Inclusion of these could lead to lower reaction probabilities if they mainly act as energy-loss mechanisms for the incoming H_2 molecule, thereby lowering the available energy to overcome activation barriers. Recent experimental studies employing femtosecond laser pulses to desorb H_2 from Ru(0001) indicate that the desorption process involves nonadiabatic coupling of vibrational degrees of freedom to *e*-*h* pair excitations.[17,18] However, the authors also observe strong isotope effects and a dependence on adsorbate-adsorbate interactions. These observations make it questionable whether the requirement of inclusion of *e*-*h* pairs in the description of desorption transfers to adsorption in the zero-coverage limit. In addition, at the highest kinetic energies, our measured reaction probabilities are constant (i.e., independent of kinetic energy), whereas any effect on the reactivity due to friction would be energy dependent.[18]

Our final consideration regarding differences between experiments and theory at high energy involves the final state of dissociating molecules on the surface. In experiments, high energy molecules that have dissociated might leave the surface through associative desorption before arriving at an equilibrium position. In calculations, reactivity is generally defined by a cutoff value for the bond length of the dissociating molecule, without considering possible recombination outside the unit cell. This difference may also explain why at high energies, experiments do not yield unit sticking probability, whereas theory does. Scattering experiments could provide insight whether recombination of nonequilibrated atoms must be taken into account.

To our knowledge, unit sticking probability on metal surfaces has never been observed experimentally for H_2 dissociation at kinetic energies accessible by supersonic molecular beam techniques.[4,26–28] The same holds true for the dissociative adsorption of CH_4 on transition metals, even for vibrationally excited molecules with large quantities of vibrational and kinetic energies.[33] Theoretical studies of these systems generally predict that unit sticking probability should be reached within the same energy regime. We express our concern about this discrepancy between theory and experiment and hope that it will receive proper attention.

V. SUMMARY

We have measured the reaction probability of the dissociative adsorption of H_2 and D_2 on Ru(0001) as a function of kinetic energy, incidence angle, and surface temperature. Our results show an increasing reaction probability for increasing kinetic energy and imply significant nonactivated dissociation without a signature of steering or precursor-based mechanisms. Normal energy scaling is obeyed and the reaction probability is independent of surface temperature. No strong isotope effect is observed. The picture for dissociation of hydrogen on Ru(0001) that emerges from these results is that direct dissociative adsorption occurs on a wide distribution of barriers. The barrier distribution is similar for Pt(111) and Ni(111), but is centered at such a low value that nonactivated dissociation occurs. However, nonactivated reaction paths are not favored at low kinetic energies by a steering or precursor-based mechanism. Comparison to Pd(111) and Rh(111), where signatures of such a mechanism is present, leads us to conclude that a universal mechanism enhancing reactivity at low energy lacks a dependence on the mass of the metal atoms.

Comparing our experimental data to results from dynamical calculations using the PW91 and RPBE functionals, we find disagreement with both sets of results. Whereas PW91 yields a more accurate minimum energy barrier than RPBE, it results in too little corrugation in the potential. Although RPBE appears to behave better in short-range interactions, quantitative disagreement at the high kinetic energies remains. The differences cannot be ascribed to poor energy resolution at high kinetic energy in molecular beam experiments. We suggest that its origin reflects a reduced reactivity of rotationally excited molecules or the lack of phonon, *e-h* pair excitation, and hydrogen recombination in the theoretical treatment.

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