Quantum dynamics of an Eley–Rideal gas–surface reaction: Four dimensional planar model for H(D)(gas)+D(H)-Cu(111)

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We present a quantum dynamical study for the abstraction reaction of hydrogen and its isotope on Cu(111) surface by a four-dimensional planar model. The rigid surface corrugation has been explicitly treated. High vibrational and rotational excitation observed in our product–state distributions indicates that the reactions occur mainly via the Eley–Rideal mechanism as suggested earlier by experiments as well as the three-dimensional flat surface model. The four-dimensional planar model using a cut through the six-dimensional LEPS (London–Eyring–Polanyi–Sato) potential energy surface essentially reproduces the isotope effects observed in experiment in the energy distributions of the reaction product. The unreacted atoms are found either to bounce back from the surface or to diffuse on the surface as atoms. A significant concentration of diffusing atoms on the surface could result in an associative desorption pathway and contribute to the experimental measurement of HD formation.

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I. INTRODUCTION

The chemical reactions of gas molecules on a solid surface have been an active research field in both experiment and theory. In particular, the H atom(s)–Cu surface systems are serving as prototype models to understand details of gas–surface collisions due to the favorable characteristics for experiment as well as quantum simulation. Recently rigorous quantum-dynamics calculations have been performed for the dissociative adsorption of H₂ on Cu(111) (Ref. 2) and Cu(100) (Ref. 3) surfaces. Excellent agreement was obtained between the rotational alignment of the dissociation measured in high resolution experiments and calculated in the six-dimensional quantum simulation.

In addition to dissociative adsorption, another important category of gas–surface reactions is the direct abstraction reaction in which a collision between an incident atom from the gas phase and a surface-absorbed atom results in the formation of a gas molecule. The actual reaction pathway for such a reaction might be complicated, since the solid surface could play an active role which influences the reaction path. In particular the reaction could be influenced by energy dissipation of the incident reagent to the surface and temporary trapping of the atoms on the surface. The Eley–Rideal (ER) mechanism is defined as having essentially no energy lost to the surface during the reaction, i.e., the surface acts as a rigid body. In this case the total energy of the molecular system is conserved. On the other hand, the desorptive recombination mechanism in which the reaction occurs after the incident reagent has transferred significant amount of energy to the surface and has reached thermal equilibrium is called the Langmuir–Hinschelwood (LH) mechanism. The obvious distinction between these two mechanisms is the energy release to the products in the reaction, that is, the ER mechanism is more exothermic than the LH mechanism. Energy conservation in the ER mechanism also implies that the time scale of the reaction occurrence should be short enough so that the surface motion could not remove significant amounts of the initial energy. Therefore unlike the LH mechanism, the ER reaction products retain more information about the incident reagent, which typically results in an angular distribution peaked toward the specular angle.

Although the ER mechanism has been predicted for a long time by theoretical studies using quasiclassical models, experimental evidence for such a mechanism was obtained in 1991 from a proton-transfer reaction on Pt(111) surface. More recent experiments have further demonstrated that the ER mechanism plays a dominant role in some reactions on other solid surfaces. Rettner and Auerbach have performed a series of experiments to study the ER mechanism from several perspectives. The ER reaction on which they focused is the formation of HD from H atoms incident on a D atom-covered Cu(111) surface (H-on-D) and from D atoms incident on an H atom-covered Cu(111) surface (D-on-H). They observed several indications that the ER mechanism is active for the reaction. The product HD molecule was produced with a great deal of internal energy, close to the full amount permitted by the exothermicity of this reaction. The angular distribution of HD was found to be asymmetrical about the surface normal, peaked toward the specular direction on the opposite side of the normal from that of the incident atom. Furthermore, their most recent work determined the detailed quantum–state distribution of products of this reaction. A high degree of vibrational and rotational excitation of the product HD molecule was observed. For both isotope combinations, the probability of inelastic scattering of the incident atom from the surface was found to be less than 0.1, while the reaction probability to form HD via the ER mechanism is around 0.47. Therefore, they estimated that the reactive cross-section is 5.2 Å². Another energetically open arrangement is the exchange reac-
tion process in which the absorbed atom is substituted by the incident atom and consequently desorbed from the surface. Experimentally it was found that such a substitution is not probable. The final energetically open arrangement is trapping of the incident atom on the surface, and the probability for this was found to be about equal to that of the ER mechanism.

There have also been several theoretical studies for this reaction. Kratzter and Brenig\textsuperscript{20} and Jackson and Persson\textsuperscript{21} have employed two-dimensional (2D) quantum-mechanical collinear models to study the ER reaction. A feature found in the 2D model is that the product molecule tends to populate highly excited vibrational states. However, for the H/Cu system there is a discrepancy between the 2D model and experiment with respect to the isotope effect for the product internal energy. The 2D calculation\textsuperscript{21} predicted that the H-on-D reaction yields higher average internal energy than the D-on-H reaction, while experimentally the trend\textsuperscript{9} is reversed. Later Jackson and Persson employed a three-dimensional (3D) flat surface model to treat the product HD molecule as a three-dimensional rotor.\textsuperscript{22} Their 3D results, based on four different potential energy surfaces, display a high degree of rotational excitation. On one of their potential energy surfaces, the averaged internal energy for the H-on-D reaction is lower than that of the D-on-H reaction, contrary to the 2D model but consistent with the experiment. Very recently, Jackson \textit{et al.}\textsuperscript{23} have performed a full dimensional quasiclassical trajectory study for the ER reaction of hydrogen on the Cu(111) surface. They came to the conclusion that most of the products observed in the previous experiments must originate from trapping of incident atoms rather than the direct ER mechanism, since in the quasiclassical model the reactive cross-section from the direct collision between an incident atom and an absorbed atom is ten times smaller than that measured by the experiment.\textsuperscript{9}

Although theoretical research on this system has progressed rapidly, a thorough understanding of the ER reaction would require a full dimensional quantum-dynamics simulation based on an accurate \textit{ab initio} potential energy surface (PES). Currently both a full dimensional dynamical calculation as well as the construction of a very accurate PES are very difficult. However, we can extend the quantum calculation to include surface corrugation in a four-dimensional planar calculation using a PES shown to give excellent results for dissociative adsorption.\textsuperscript{2,5} In Sec. II, the PES and the formulae used in the four-dimensional dynamical calculation will be presented. In Sec. III, we will show the results and compare them with the experiments as well as the results from other theoretical models. Finally, we will conclude with a brief summary in Sec. IV.

II. THEORY

A. Potential energy surface

Even for the simplest gas–surface system such as H$_2$/Cu(111), an accurate \textit{ab initio} calculation of the ground state PES is a challenging task. So far, only the density functional theory (DFT) using the generalized gradient approximation has been used to generate some \textit{ab initio} data points for PESs involving H atoms which appear consistent with experiment.\textsuperscript{24,25} Whether the total number of those energy points is sufficient to construct a global and reliable PES is indeed questionable. At the current stage, a feasible approach is to use available \textit{ab initio} data points to construct an empirical PES\textsuperscript{26} based on the LEPS functional form London–Eyring–Polanyi–Sato (LEPS).\textsuperscript{6} By comparing experiments, this approach has been proven to be qualitatively reliable in a recent full-dimensional quantum-dynamics simulation of the dissociative adsorption of H$_2$ on the Cu(111) surface.\textsuperscript{5} The most recent theoretical confirmation of the quality of our PES for H$_2$/Cu(111) (Ref. 26) was provided by a new extensive DFT calculation for this system.\textsuperscript{27} Thus we use essentially the same PES in this work as for the dissociative adsorption reaction\textsuperscript{26} although one region of the PES is slightly modified.

The LEPS potential energy surface is written as

$$ U = U_1 + U_2 + U_3 - \left[ Q_1^2 + (Q_2 + Q_3)^2 \right] - Q_4 (Q_2 + Q_3)^{1/2}, $$

(2.1)

where $U_i$ and $Q_i$ (for $i = 1, 2, 3$) are given by

$$ U_i = \frac{1}{4(1+\Delta)} D_i [(3+\Delta) \exp[-2 \alpha_i (q_i - q_{i,0})] - (2+6\Delta) \exp[-\alpha_i (q_i - q_{i,0})]], $$

$$ Q_i = \frac{1}{4(1+\Delta)} D_i [(1+3\Delta) \exp[-2 \alpha_i (q_i - q_{i,0})] - (6+2\Delta) \exp[-\alpha_i (q_i - q_{i,0})]]. $$

(2.2)

$U_1$ and $Q_1$ describe the interaction between hydrogen atoms, and $U_{2,3}$ and $Q_{2,3}$ describe the atom–surface interactions which are periodic functions of the nonorthogonal lateral coordinates of the hydrogen atoms,\textsuperscript{26} i.e., the lattice coordinate, and $q_1$ stands for the distance between hydrogen atoms, and $q_{2,3}$ stand for the atom–surface distances.

The various parameters in Eq. (2.2) have been provided in Ref. 26. The contour of the PES for the collinear ER reaction is plotted in Fig. 1. Since we are concerned with a low initial kinetic-energy range, around 0.1 eV, the long range hydrogen–copper attractive interaction is somewhat of a problem. In order to constrain the motion of the atoms within a tractable region, we made a slight modification in the present PES in which we cut off the long-range tail of $U_{2,3}$ and $Q_{2,3}$ from $q_{2,3} = 7$ (a.u.), i.e., we assume that $U(q) = U(\infty)$ and $Q(q) = Q(\infty)$ when $q > 7$. Our numerical test showed no qualitative difference by adding this approximation.

B. A time-dependent wave-packet approach

A quantum-dynamics simulation of this gas–surface abstraction reaction is difficult. The first fundamental difficulty is the number of open asymptotic channels. The initial state, H$+$D–Cu(111), is very energetic compared to both the ER product, HD$+$Cu(111), and the channel with two adsorbed hydrogens, H–Cu(111)$+$D–Cu(111). Open asymptotic channels include many bound states H–Cu(111)$+$D–Cu(111) with lateral momenta. Second, the symmetry
variables which can be either described by Cartesian coordinates or Jacobi coordinates. This planar model has four independent degrees of freedom. The initial wave-packet in the Cartesian coordinates, down the initial wave-packet in the Cartesian coordinates, can be written as

\[ \psi(X_1, Z_1, X_2, Z_2) = \frac{1}{\sqrt{2\pi\delta_{X_1}^{1/4}}} e^{-\frac{(X_1 - X_{1i})^2}{4\delta_{X_1}}} e^{-i k_{X_1} X_{1i}} \]

\[ \times \frac{1}{\sqrt{2\pi\delta_{Z_1}^{1/4}}} e^{-\frac{(Z_1 - Z_{1i})^2}{4\delta_{Z_1}}} e^{-i k_{Z_1} Z_{1i}} \]

\[ \times \phi_r(X_2, Z_2), \] (2.4)

where \( \delta_{X_1, Z_1} \) are the widths of two Gaussian functions imposed on the plane wave of the incident atom 1. The X and Z directions, \( X_1 \) and \( Z_1 \) are their initial positions, \( k_{X_1, Z_1} \) are lateral and vertical momenta of the incident atom 1, \( \phi_r(X_2, Z_2) \) is a bound-state wave-function of the absorbed atom 2.

The Hamiltonian in the Jacobi coordinate system which will be utilized in the time-dependent wave-packet propagation can be written as

\[ H(X, Z, r, \theta) = -\frac{1}{2M} \left( \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{1}{2\mu} \left( \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) + V. \] (2.5)

The split-operator method \( 28 \) in which the exponential Schrödinger propagator is symmetrically split is employed to

In the Cartesian coordinate system, the Hamiltonian for a diatomic system is expressed as

\[ H(X_1, Z_1, X_2, Z_2) = -\frac{1}{2M_1} \left( \frac{\partial^2}{\partial X_1^2} + \frac{\partial^2}{\partial Z_1^2} \right) - \frac{1}{2M_2} \left( \frac{\partial^2}{\partial X_2^2} + \frac{\partial^2}{\partial Z_2^2} \right) + U. \] (2.3)

The initial wave-packet is chosen as

\[ \psi(X_1, Z_1, X_2, Z_2) = \frac{1}{\sqrt{2\pi\delta_{X_1}^{1/4}}} e^{-\frac{(X_1 - X_{1i})^2}{4\delta_{X_1}}} e^{-i k_{X_1} X_{1i}} \]

\[ \times \frac{1}{\sqrt{2\pi\delta_{Z_1}^{1/4}}} e^{-\frac{(Z_1 - Z_{1i})^2}{4\delta_{Z_1}}} e^{-i k_{Z_1} Z_{1i}} \]

\[ \times \phi_r(X_2, Z_2), \] (2.4)

where \( \delta_{X_1, Z_1} \) are the widths of two Gaussian functions imposed on the plane wave of the incident atom 1. The X and Z directions, \( X_1^i \) and \( Z_1^i \) are their initial positions, \( k_{X_1, Z_1} \) are lateral and vertical momenta of the incident atom 1, \( \phi_r(X_2, Z_2) \) is a bound-state wave-function of the absorbed atom 2.

The Hamiltonian in the Jacobi coordinate system which will be utilized in the time-dependent wave-packet propagation can be written as

\[ H(X, Z, r, \theta) = -\frac{1}{2M} \left( \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Z^2} \right) \]

\[ - \frac{1}{2\mu} \left( \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) + V. \] (2.5)
propagate the wave-packet. The propagation by the split exponential propagator is given by the partitioning,

\[ \Psi(t+\Delta) = \exp\left( i \left( \frac{1}{2M} \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{1}{2\mu} \left( \frac{1}{r} \frac{\partial}{\partial r} \right) \right) \frac{\Delta}{2} \] 

\[ \exp\left( i \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) \] 

\[ \exp(-iV\Delta) \exp\left( \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right) \] 

\[ \exp\left( i \left( \frac{1}{2M} \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{1}{2\mu} \left( \frac{1}{r} \frac{\partial}{\partial r} \right) \right) \frac{\Delta}{2} \Psi(t). \] (2.6)

Using Sinc DVRs for \( X, Z, r \) and Fourier DVR\(^{29,30}\) for \( \theta \), we recast the initial wave-packet \( \Psi(X_1, Z_1, X_2, Z_2) \) in the Cartesian coordinates on the four-dimensional grids \( (X, Z, r, \theta) \) through a simple coordinate transformation. Fast Fourier transformations for \( X, Z, r \), and \( \theta \) are utilized in Eq. (2.6) to propagate the wave-packet.

In this paper, we only study normal incidence, thus the lateral momentum \( k_{X_1} \) is always 0. According to the experiments, we choose the mean energy of the incident atom as 0.1 (eV) and the vibrational state of the absorbed atom as the ground state. The Gaussian width \( \delta_{\xi_1} \) is chosen as 0.1 (a.u.), narrow enough to cover the energy range in which we are interested. The Gaussian width \( \delta_{\xi_2} \) should be as wide as possible to minimize nonzero momentum components in the lateral direction; we therefore choose it as 3.0 (a.u.). Since we have artificially curtailed the H–Cu interaction to 7.0 (a.u.), we can start the initial wave-packet at \( Z_1 = 8.0 \) (a.u.). We use 149 Sinc DVR points on \( X \) to cover the range from −10.0 (a.u.) to 10.0 (a.u.) (taking the center site, the site where the absorbed atom initially resides on, as the origin), 77 Sinc DVR points on \( Z \) to cover the range from 0.5 (a.u.) to 10.0 (a.u.), 81 Sinc DVR points on \( r \) to cover the range from 0.5 (a.u.) to 13.5 (a.u.), and 76 Fourier DVR points in \( \theta \). On the edges of boundaries (left-hand side and right-hand side of \( X \), large ends of \( Z \) and \( r \)), quadratic-form absorbing potentials\(^{31}\) with length of 2.0 (a.u.) are imposed to eliminate boundary reflection. The results are converged using 10 (a.u.) as a time-step \( \Delta \), and a total propagation time is 50,000 (a.u.). The ER reaction probability is measured by the reaction flux going through the surface plane located at \( Z = 8.0 \) (a.u.). On the surface plane, the time-dependent wave-packet is projected on the rovibrational basis set of the product molecule. Then Fourier transform is utilized to extract time-independent wave-function with different energies on the surface plane. Finally the reaction probabilities to different product states are obtained using the flux formulism (refer to Ref. 32 for details).

FIG. 3. The mean lateral translational energy, mean vertical translational energy, mean vibrational energy, and mean rotational energy of the product molecule HD in the reaction of H(D)+D(H)–Cu(111) as functions of kinetic energy of the incident atom H(D). The absorbed atom D(H)–Cu(111) is initially on the ground vibrational state. The zero point energy of HD is not included.

### III. RESULTS

#### A. Energy distribution of the product

The ER reaction of hydrogen on copper surface is about 2.2 (eV) exothermic. The isotope effect in the energy distribution of the product molecule HD from the ER reaction of H(D)+D(H)–Cu(111) is an interesting issue. In the experiment,\(^9\) for the D-on-H reaction, the mean rotational energy was measured as 0.35±0.05 (eV); about 0.02 (eV) lower than that for H-on-D. The mean vibrational energy for the D-on-H reaction was found to be 0.68±0.05 (eV) which is 0.08 (eV) higher than that for H-on-D. Assuming no energy loss to the lattice, these energies imply a mean translational energy of 1.27±0.1 (eV) for D-on-H and 1.33±0.1 (eV) for H-on-D. However, in the calculation of Jackson and Persson, their collinear model (2D)\(^{21}\) demonstrated the opposite trend, that is, the H-on-D reaction yielded higher vibrational energy than that of the D-on-H reaction. Later, their 3D flat surface model\(^{22}\) correctly reproduced the experimental trend on one of their four model potential energy surfaces.

We have calculated the mean rotational energy, vibrational energy, and translational energy distributions of HD in both reactions, and plot them as functions of incident kinetic energy in Fig. 3. The four-dimensional planar model clearly shows a strong isotope effect, and the trend agrees well with the experimental observation. The mean rotational energy for the D-on-H reaction is lower than that for H-on-D, and the difference in the experimental range of incident kinetic energy [0.07 (eV)] is about 0.03 to 0.07 (eV). The mean vibra-
tional energy for the D-on-H reaction is about 0.08 to 0.14 eV higher than that for H-on-D. The overall mean translational energy for the D-on-H reaction is lower than that for H-on-D. Although the mean vertical translational energy for the D-on-H is generally lower than the one for the H-on-D, it is reversed at some energies. Nevertheless, the mean lateral translational energy for the D-on-H reaction product is uniformly lower than that for H-on-D.

The qualitative agreement between the experiment and the four dimensional planar model implies that the lateral motions of the atoms as well as the surface corrugation are playing important roles in the energy distributions of the product molecule. The accuracy of the PES is probably crucial to reproduce the experimental observation.

Mean rotational energies as functions of vibrational state are plotted in Fig. 4. As expected, the rotational energy decreases with increasing vibrational level in both the H-on-D and D-on-H reactions. A plateau observed in the D-on-H reaction in the experiment is also shown in this theoretical calculation, although it appears here at higher vibrational states. However, in contrast to the experiment, the anticorrelation behavior of vibrational and rotational excitation is found to be particularly pronounced in the low vibrational states, and to be reduced in the high vibrational states. For the H-on-D reaction, as the vibrational energy increases by 0.44 (eV) from \( v = 0 \) to \( v = 1 \), the rotational energy drops by about 0.34 (eV). But the rotational energy only drops by 0.11 (eV) when the vibrational energy increases by 0.38 (eV) (from \( v = 4 \) to \( v = 5 \)). This quantitative difference from experiment might result from treating the product molecule as a plane-rotor in the four-dimensional treatment of the six-dimensional problem.

B. Product–state distribution

The rotational-state distributions of the product HD molecules are plotted in Fig. 5. These distributions for the H-on-D and the D-on-H are quite similar, which is consistent with the experimental observation but different from the flat-surface 3D calculation which predicted a significant isotope effect. The reaction probability first increases toward increasing \( j \), then decreases to zero at about \( j = 25 \), and the maximum of the reaction probability is at \( j = 4 \). The curves show some oscillation; such oscillation is even stronger in the flat-surface 3D calculation. Since the planar-calculation does not include the azimuthal angle of the product molecule HD, except for \( j = 0 \), each rotational-state \( j \) has only twofold degeneracy instead of the \((2j+1)\)-fold degeneracy of a three-dimensional rotor. This approximation probably prevents a quantitative comparison of rotational distributions with experiment.

The vibrational-state distributions of the product molecules are plotted in Fig. 6. The two curves are in excellent agreement with the experimental observation but different from the flat-surface 3D calculation which predicted a significant isotope effect. The reaction probability first increases toward increasing \( j \), then decreases to zero at about \( j = 25 \), and the maximum of the reaction probability is at \( j = 4 \). The curves show some oscillation; such oscillation is even stronger in the flat-surface 3D calculation. Since the planar-calculation does not include the azimuthal angle of the product molecule HD, except for \( j = 0 \), each rotational-state \( j \) has only twofold degeneracy instead of the \((2j+1)\)-fold degeneracy of a three-dimensional rotor. This approximation probably prevents a quantitative comparison of rotational distributions with experiment.
agreement with the experimental observation as well as the 3D flat-surface model. For the H-on-D reaction, it was found experimentally that the most populated vibrational state is $v = 1$, while the present theoretical study identifies $v = 2$ as the most favorable state for the reaction. For the D-on-H reaction, both the experimental and theoretical studies predicted $v = 3$ is the most populated state. However, for both the H-on-D and the D-on-H reactions, we notice that the overall vibrational probability decreases more slowly with $v$ than experiment. This is not surprising, since the reduced-dimension model artificially makes the high vibrational states more statistically likely in the reaction.

Finally we plot the rovibrational-state distributions of HD in Figs. 7 and 8 for the H-on-D and D-on-H reactions respectively. A common feature in both is that the product-state distributions extend over a wide internal-energy range; in particular, they extend to the energetic thresholds of the reactions. This feature is perhaps the most important signal of the ER mechanism in the reactions. In both reactions, the high $j$, low $v$ states and the low $j$, high $v$ states yield significantly larger reaction probability than the rest of states. Such an anticorrelation between rotational and vibrational excitation was first revealed by the 3D flat-surface model. However, unlike the 3D flat-surface model, the present 4D planar model does not produce significant bimodal behavior of the rovibrational-state distributions. The turning point in the anticorrelation between rotational and vibrational excitation is at $v = 2$ where the population of low rotational states equals that of high rotational states. Starting from $v = 3$ the low rotational states are predominant. One remarkable isotope effect between the H-on-D and D-on-H reactions is that the low rotational states in $v = 3$ and 4 are highly populated in the D-on-H reaction. Figure 9 shows that the D-on-H is more
reactive than H-on-D, although the experiment found that both of the reactions yield essentially the same cross-sections.

C. Non-ER scattering

Besides forming the product molecule HD, the H-on-D and D-on-H collisions could undergo several other dynamical processes. For non-ER processes, the orientation angle, defines the asymptotic scattering angle of the scattered atoms. These nonreactive processes have been studied by analyzing the outgoing flux of the wave-function on a surface plane at a large separation distance r. In Fig. 10 we plot the probability of non-ER scattering as a function of orientation angle . The H-on-D reaction is taken as an example, since for this quantity there is no qualitative difference between H-on-D and D-on-H. Four distinct dynamical processes are given at four different orientation angles. The or angles represent the incident atom bouncing directly back from the surface; or angles show the two atoms moving on the surface in opposite directions; and the represents the exchange reaction process in which the initially absorbed atom leaves the surface, while the incident atom is absorbed on the surface. Although the four processes are all energetically accessible, Fig. 9 clearly shows that only three of them actually occur; the exchange process is indeed unlikely. The low probability of the exchange process has also been found in the experiment and in the 3D flat-surface model. Furthermore, the two peaks observed around and imply that there are sizeable probabilities for the incident atom to stick with the absorbed atoms moving apart from each other but both bound on the surface.

IV. CONCLUSIONS

We have presented a four dimensional planar model to investigate the abstraction reaction of hydrogens on the Cu(111) surface which is believed to occur mainly via the Eley–Rideal mechanism. Although the four-dimensional model neglects two lateral motions of the hydrogens, it does allow us to study quantum-mechanically the correlations among the translation, vibration, and rotation of the reaction product when the surface corrugation is included. Consistent with the experiment, the theoretical energy distributions of the product molecule demonstrate a significant isotope effect. We are still investigating in detail the fundamental mechanism which causes this isotope effect. Quantitatively, the mean vibrational energy and rotational energy in our model are higher than those found in experiment. We speculate that in a full dimensional quantum-dynamics study these energies could be lowered by including the motions of the other degrees of freedom, lateral translation, and the azimuthal rotation, and by some energy loss to the surface. As a signature of an ER reaction, the rotational and vibrational excitation of the product molecule has been observed to be high. The unreacted incident atom is found not only to bounce back from the surface but to be adsorbed with both atoms diffusing on the surface. The exchange process in which the incident atom substitutes the absorbed atom is essentially unobservable. The observation of significant sticking has implications for the experimental observation of the ER reaction. If a significant concentration of diffusing atoms are created on the surface, these will further react with each other in an associative desorption reaction. That could increase the apparent reactive cross-section observed above that for the ER reaction alone.

The role of the so-called “hot-atom” reaction pathway is not evaluated in the present quantum-dynamics study; however, it will be a topic of future research. Finally we note that a rigorous treatment for the ER reaction of hydrogens on Cu(111) should involve not only one absorbed atom on the surface but several absorbed atoms in neighboring unit cells as well as thermal motion of the surface. Such a rigorous quantum-dynamics study is beyond our current computational resources, and various reduced dimensional methods will still be useful to understand the fundamental mechanisms in ER reactions.

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