Six dimensional quantum dynamics study for dissociative adsorption of H$_2$ on Cu(111) surface

Jiqiong Dai and John C. Light

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 28 April 1997; accepted 19 May 1997)

In this letter we present preliminary results of full six dimensional quantum dynamics calculations for dissociative adsorption of a hydrogen molecule on a Cu(111) surface. We utilize the time-dependent wave-packet approach to simulate the dissociation process on a full dimensional LEPS potential energy surface which has incorporated the latest ab initio data [Hammer et al. Phys. Rev. Lett. 73, 1400 (1994)]. We use a novel partitioning of the angular momentum operator in the split-operator method so that a direct product DVR can be rigorously implemented. The most interesting observation in the present rigorous quantum dynamics study is the site-averaged effect, i.e., the averaged dissociation probability of the four dimensional calculations over the three symmetric impact sites strongly resembles the exact dissociation probability of the six dimensional calculations. In accord with the low dimensional calculations, initial vibrational excitation of H$_2$ effectively reduces the translational threshold energy. The rotational orientation effect observed in the four dimensional studies remains in the present full dimensional dynamics with the cartwheel orientation yielding dramatically lower dissociative efficiency than the energetically equivalent helicopter orientation. We focus on normal incident scattering. The diffractive scattering and more detailed results will be presented in a later paper. © 1997 American Institute of Physics. [S0021-9606(97)03129-2]

The dissociative chemisorption of a hydrogen molecule on a copper surface is an ideal model for the study of chemical reaction at the gas–surface interface. The first molecular beam study of dissociative adsorption was focused on H$_2$/Cu(111). Theoretically, density functional theory has provided some benchmark ab initio information about the potential energy surface of these systems. In quantum dynamics studies, rapid progress has been made since the earliest work of Jackson and Metiu who employed a collinear two dimensional model to simulate the dissociation process of H$_2$ on Ni. The dynamical calculation for H$_2$/Cu(111) which requires far more computational effort because of the higher dissociation threshold energy has been steadily developed along the route from three dimension flat surface models, four-dimension fixed-site models, a six-dimension mixed quantum/classical treatment to the most recent reduced dimensional calculation.

These approximate calculations have clearly demonstrated many important properties of the hydrogen molecule dissociation processes on copper. Among them, the vibrational-excitation effect and the rotational-orientation effect are of most interest since they may have direct impact on control of the reaction. Holloway and Harris independently suggested that vibration of the hydrogen molecule plays a very important role in dissociative adsorption as the translational energy threshold is effectively reduced by the vibrational energy. The rotational effect was first experimentally observed by Michelsen et al. and further confirmed by the flat-surface three dimensional and fixed-site four dimensional calculations. For a specific gas–surface encounter such as H$_2$/Cu, the dissociation probability of the gas molecule usually shows a strong orientational preference. In the present system, the dissociation probability is much larger for hydrogen molecules colliding with rotation in a plane parallel to the copper surface than for those colliding perpendicularly. Thus one might dramatically enhance the dissociation rate by simply changing the orientation of reactive molecules.

Although the approximate models have achieved many important results, the most accurate study of this gas-surface reaction still requires a rigorous full dimensional quantum dynamical calculation. In this letter, we will treat the H$_2$/Cu system accurately numerically including all 6 degrees of freedom, namely, the three Cartesian coordinates of the center of mass $X$, $Y$, and $Z$, and the three internal coordinate $r$, $\theta$ and $\phi$ (see Fig. 1). To utilize the periodic surface symmetry, we replace X and Y by two coordinates $x$ and $y$ which correspond to lattice axes with skewing angle $\alpha$. Now the Hamiltonian is expressed in terms of $(x,y,Z,r,\theta,\phi)$ as,

$$H = H_{x,y} - \frac{1}{2M} \frac{\partial^2}{\partial Z^2} + \frac{1}{2m} \frac{\partial^2}{\partial r^2} + \frac{j^2}{2mr^2} + V(x,y,Z,r,\theta,\phi),$$

(1)

where $m$, $M$ and $j$ are the diatomic total mass, reduced mass and rotational angular momentum respectively. $H_{x,y}$ is defined as

$$H_{x,y} = -\frac{1}{2M} \left( \frac{1}{\sin^2 \alpha} \frac{\partial^2}{\partial x^2} + \frac{2 \cos \alpha}{\sin^2 \alpha} \frac{\partial^2}{\partial x \partial y} + \frac{1}{\sin^2 \alpha} \frac{\partial^2}{\partial y^2} \right).$$

(2)
We utilize the time-dependent wave-packet approach to simulate the gas–surface scattering. In particular, the split-operator method in which the exponential Schrödinger propagator is symmetrically split is employed to propagate the wave packet. The periodicity of the potential energy surface along \(x\) and \(y\) implies that the wave-function function should always be well represented by the superposition of the periodic functions \(e^{i k_x x}\) and \(e^{i k_y y}\) whose DVR representation is equivalent to the discrete Fourier transform. The sinc-DVR basis functions can efficiently represent both the \(Z\) and \(r\) coordinates, while the choice of basis functions to cover the remaining variables, \(\theta\) and \(\phi\), is somewhat ambiguous.

Since the spherical harmonic functions, the eigenfunctions of \(\hat{j}^2\) are a nondirect product basis set, the corresponding DVR cannot be easily constructed. In order to circumvent this difficulty, we decouple the operator \(\hat{j}^2\) so that the \(\theta\) and \(\phi\) coordinates can be separately represented by one-dimensional DVR basis functions, Legendre polynomials \(P_n(\cos \theta)\) and \(e^{im\phi}\). For instance, we separate the \(\phi\) dependency from \(\hat{j}^2\) as follows:

\[
\hat{j}^2 = \hat{j}_0^2 - \frac{1}{1 - \cos^2(\theta)} \frac{\partial^2}{\partial \phi^2},
\]

where Legendre polynomials \(P_n(\cos \theta)\) satisfy,

\[
\hat{j}_0^2 P_n(\cos \theta) = n(n + 1) P_n(\cos \theta).
\]

In Ref. 25 we showed that the direct product of Legendre DVR basis functions and \(e^{im\phi}\) serves as a good basis representation for the \(\theta\) and \(\phi\) angles. To see this more precisely, we diagonalized the \(\hat{j}^2\) operator in the two-dimensional DVR and carefully investigated the eigenvalues. First, we noticed that although \(\cos(\theta) = 1\) or \(-1\) are two singular points for \(m \neq 0\), the matrix representation of \(\hat{j}^2\) based on the direct-product DVR basis set is always nonsingular since all the Legendre DVR points are interior points. Second, the eigenvalues all converge with increasing basis size, while as expected the convergence rate is much slower for odd \(m\) blocks, particularly \(m = 1\). Thus this basis is adequate to yield converged results for the scattering calculation.

The initial wave packet (normal incidence) is chosen as

\[
\psi_{v,j}^{m}(x, y, Z, r, \theta, \phi, t = 0) = \frac{1}{\pi^{1/4}} e^{-\left(c^2 + d^2\right)^{1/4}} e^{-ikZ} Y_{j}^{m}(\theta, \phi),
\]

where the \(Y_{j}^{m}\) is a spherical harmonic function. The propagation by the split exponential propagator is given by the partitioning.

\[
\psi(t + \Delta) = \exp \left( -iH_{x, y} \frac{\Delta}{2} \right) \exp \left( i \frac{1}{2m} \frac{\partial^2}{\partial r^2} \frac{\Delta}{2} \right) \exp \left( i \frac{1}{2m} \frac{\partial^2}{\partial \phi^2} \frac{\Delta}{2} \right) \psi(t).
\]

\[
\exp \left( -i \frac{\hat{j}_0^2}{2m^2} \frac{\Delta}{2} \right) \exp \left( i \frac{1}{2m^2(1 - \cos^2 \theta)} \frac{\partial^2}{\partial \phi^2} \frac{\Delta}{2} \right) \exp \left( -iV\Delta \right) \exp \left( i \frac{1}{2m^2(1 - \cos^2 \theta)} \frac{\partial^2}{\partial \phi^2} \frac{\Delta}{2} \right) \psi(t).
\]

\[
\exp \left( -i \frac{\hat{j}_0^2}{2m^2} \frac{\Delta}{2} \right) \exp \left( i \frac{1}{2m} \frac{\partial^2}{\partial r^2} \frac{\Delta}{2} \right) \exp \left( i \frac{1}{2m} \frac{\partial^2}{\partial \phi^2} \frac{\Delta}{2} \right) \exp \left( -iH_{x, y} \frac{\Delta}{2} \right) \psi(t).
\]
In applying the operator above to the wave function, transformation matrices are applied between the exponential operators to make each diagonal in turn. For the direct product DVR used here, these matrices are both orthogonal and one dimensional.

The latest ab initio study\(^3\) provided some additional information about the potential energy surface of H\(_2/\)Cu(111) system. While the data points are too few to interpolate to form a global potential energy surface, in Ref. 11, a full dimensional potential energy surface was constructed as a LEPS function incorporating the ab initio information. Our dynamics study is based this potential energy surface.

On the numerical details, the two dimensional unit cell formed by \(x\) and \(y\) is covered by an 8×8 evenly spaced grid. 72 and 36 sinc-type DVR points are used to describe the \(Z\) and \(r\) coordinates, while the orientation angle \(\theta\) needs 28 Legendre DVR points (actually 14 points because of homonuclear symmetry) and the azimuthal angle \(\phi\) only requires 20 evenly spaced Fourier grid points. The imaginary absorbing potential\(^2\) is imposed when the interatomic distance of the hydrogen molecule, \(r\), is greater than one lattice constant 4.84 (a.u.) and the dissociation flux is calculated on the surface of \(r=4\) (a.u.). The time step for the propagation is 10 (a.u.) and the wave packets are propagated to about \(T = 10,000\) (a.u.).

We first calculate the dissociation probability from the ground rovibrational state of the hydrogen molecule. In Fig. 2(a) the present six dimensional results are compared with the four dimensional fixed-site calculations in which the center of mass (\(x\) and \(y\)) of the H\(_2\) is fixed at the bridge site, the atop site, or the center site. We notice that the difference between the full dimensional calculation and each of the fixed-site calculations is significant. The fixed-site calculations were combined by taking the average, assigning weights appropriate to the number of such sites in the unit cell [Fig. 2(a)]. The site-averaged four dimensional reaction probability and the six dimensional exact reaction probability are similar in shape, while the latter is shifted to higher energy by about 0.05 eV.

The cause of this energy shift may be the difference in zero point energy (ZPE) of the four dimensional and six dimensional calculations at the transition states since the six dimensional calculation includes the ZPE for the two lateral coordinates \(x\) and \(y\).\(^2\) The six dimensional saddle point is located at \(x = 2.42\) (a.u.), \(y = 0\), \(Z = 2.29\) (a.u.), \(r = 2.06\) (a.u.), \(\theta = 90\) (degree) and \(\phi = 90\) (degree). The zero point energy of the transition state is 0.201 (eV). When we fix the center of mass on the bridge site the position of the saddle point remains unchanged, while the zero point energy is reduced to 0.152 (eV). The zero point energies of the four dimensional transition states on the center site and the atop site are 0.132 (eV) and 0.167 (eV). Thus the differences between the ZPE’s of the transition states of the six dimensional potential and the four dimensional potentials range from 0.03 to 0.07 eV, which is qualitatively consistent with the energy shift we observe in the dissociation. To compare more precisely, we first shift both the four dimensional curves and the six dimensional curve by the corresponding ZPE’s of their transition states, then average the four dimensional results as above and compare in Fig. 2(b). Remarkably, the site-averaged reaction probability is now in excellent agreement with the exact calculation especially in the low energy region. This agreement of the site-averaged result has two important implications. First, by fixing two lateral coordinates and taking account of the differences of zero point energy, the averaged four dimensional model becomes very close to the much more expensive full dimensional model. This suggests that many important phenomena observed in the four dimensional fixed-site model\(^1\) perhaps will still be found in the rigorous six dimensional treatment.

The next issue to be addressed is whether or not the

![Dissociative adsorption of H\(_2\) (\(\nu=0, j=0\)) on Cu(111) surface](image)

FIG. 2. (a) Comparison between six dimensional calculation and four dimensional fixed-site calculations. The initial state is H\(_2\) \((\nu=0, j=0, m=0)\). The four dimensional site-averaged results are obtained by averaging the dissociation probabilities of three symmetric impact site with appropriate relative weights. (3 for the bridge site, 2 for the center site and 1 for the atop site). (b) Each curve in (a) is shifted by the appropriate ZPE. The four dimensional results are then averages as above to compare with the shifted six dimensional result.
vibrational–excitation effect still remains in the present rigorous quantum dynamics calculation. We calculate the dissociation probability from the first excited vibrational state of hydrogen molecule \((v = 1, \ j = 0, \ m = 0)\) and find that the translational threshold of \(v = 1\) is much lower than \(v = 0\) (Fig. 3), which implies that the vibrational energy is very effective in overcoming the reaction barrier and is in excellent accord with the lower dimensional calculations.

Another important issue is the role of rotational motion in the dissociative adsorption of hydrogen on copper. Both the previous flat surface and the fixed-site models\(^7\) suggested that the orientation of the initial rotational state of the incident hydrogen molecule has a dramatic effect on the dissociation process. However, the flat surface model conserves \(m\), the azimuthal quantum number. In Fig. 4, we plot the dissociation probabilities for initial states with same rotational energy but different orientation \((m)\). These results clearly demonstrate that the inclusion of two lateral degrees of freedom in \(x\) and \(y\) does not change the rotational orientation effect. The helicopter orientation \((j = 5, \ m = 5)\) gives a much bigger dissociation probability than the cartwheel orientation \((j = 5, \ m = 0)\), although they are energetically identical. The underlying mechanism of the rotational orientation effect is that dissociative adsorption is favored when both H atoms can bind simultaneously to the Cu surface. This is favored by the parallel \((m = j)\) approach. Different \(m\) states have different angular distribution. The angular distribution of the helicopter model is mainly in a plane parallel to the surface, while the cartwheel model is perpendicular. Since these two energetically equivalent incident molecules have dramatically different dissociation probabilities, one important question is whether such an orientational effect could be utilized in practice by manipulating molecular orientation in the collision process.

This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-9400379. J. D. also thanks Professor D. Neuhauser, Professor D. Clary, Dr. G. Darling and Dr. R. Mowrey for helpful communication.

References:
26. We would like to thank the referee for pointing out that ZPE differences might account for the four–six dimensional shift in energy.