

**Ring Polymer Molecular Dynamics Approach to Quantum Dissociative
Chemisorption Rates**

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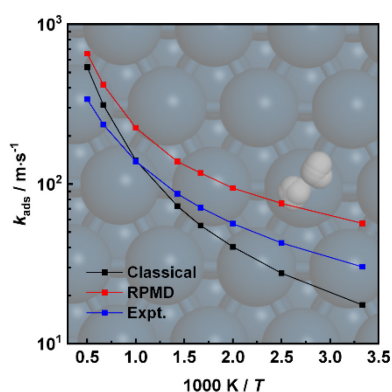
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Abstract

A ring polymer molecular dynamics (RPMD) method is proposed for the calculation of dissociative chemisorption rate coefficient on surfaces. The RPMD rate theory is capable of handling quantum effects such as the zero-point energy and tunneling in the dissociative chemisorption, while relies on classical trajectories for the simulation. Applications to H_2 dissociative chemisorption are demonstrated. For the highly activated process on $\text{Ag}(111)$, strong deviations from the Arrhenius behavior are found at low temperatures and attributed to tunneling. On $\text{Pt}(111)$, where the dissociation has a barrierless pathway, the RPMD rate coefficient is found to agree with the experimentally derived thermal sticking coefficient within a factor of two over a large temperature range. Significant quantum effects are also found.

TOC graphic



There is strong experimental evidence of nuclear quantum effects in reactions involving light atoms, in both the gas phase¹ and extended systems.^{2, 3} Recently, the rates for recombinative desorption of H₂ on Pt surfaces were accurately measured for the first time and found to exhibit strong nuclear quantum effects even at the temperature of 1000 K.⁴ These new experiments challenge theory to provide a first principles interpretation. In principle, the quantum rate coefficient can be computed by directly solving the Schrödinger equation. However, a quantum dynamical characterization of an elementary chemical reaction at the gas-solid interface is quite challenging,⁵⁻⁷ due to the large number of surface degrees of freedom (DOFs). The conventional wave packet method based on an explicit solution of the time-dependent Schrödinger equation becomes impractical and there is strong desire to find a numerically efficient method to incorporate quantum effects in rate calculations for surface reactions.

An alternative way to rate calculations is the statistical approach such as the transition-state theory (TST), which, due to the ease of implementation, has become a popular method for bimolecular reactions in the gas phase.⁸ The basic assumption is that the rate is determined by the thermal population of the activated complex, which once reached decays irreversibly to products.^{9, 10} As a result, the rate coefficient can be obtained from the flux passing through a dividing surface between reactants and products, often placed near the reaction barrier. In a typical implementation,¹¹ the partition functions used in TST calculations are evaluated using the harmonic oscillator approximation. However, such approximations could drastically fail due to strong

anharmonicity in low-frequency modes, which are especially abundant in surface processes. When quantum tunneling is important, TST typically relies on a semiclassical treatment,¹² which might miss important multidimensional effects. Finally, TST does not rigorously take recrossing of the dividing surface into consideration, which can be quite important in some cases.¹³ Dynamical corrections using classical trajectories have been suggested for high temperatures.¹⁴

The ring polymer molecular dynamics (RPMD) approach proposed by Manolopoulos and coworkers¹⁵ represents a promising alternative to TST in computing the rate coefficient.¹⁶⁻¹⁹ The basic premise of RPMD is to take advantage of the isomorphism for statistical properties in a quantum and a fictitious classical system,²⁰ in which a quantum particle is replaced by a necklace of harmonically connected beads.¹⁵ It is well suited to include quantum effects such as zero-point energy and tunneling.¹⁹ In addition to the linear scaling law with respect to the number of particles in the system, the RPMD rate theory has a number of desirable properties. First, it is reduced to the classical limit when only one bead is used, which offers a convenient way to examine the impact of quantum effects.¹⁵ Second, it is independent of the definition of the dividing surface,¹⁷ which is very difficult to achieve in the conventional TST calculations.

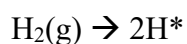
The rate theory based on RPMD has been formulated by the *ad hoc* replacement of the classical Hamiltonian with the RPMD one.^{16, 17} Its implementation to gas-phase bimolecular reactions^{18, 19, 21} has been applied to many systems with great success.¹³

Surface reactions present additional challenges due to the large number of surface DOFs. So far, some applications of the RPMD approach have been reported for surface processes,²²⁻²⁷ but none has been applied to chemical reactions where bond breaking and forming are present.

Recently, there is also significant interest in treating multidimensional tunneling using the quantum instanton theory (QI).²⁸ Applications of QI to dissociative chemisorption have been reported for several systems.²⁹⁻³¹ However, it has been shown for gas phase bimolecular reactions that RPMD outperforms QI in rate calculations.^{19,}³² Furthermore, it is not clear how QI can be applied to a nominally barrierless process.

In this work, we present the adaptation of the RPMD rate theory to the dissociative chemisorption (DC) of H₂ using a rigid surface model. We investigated two special cases, one is the activated DC on Ag(111) and the other is the barrierless DC on Pt(111). Our results demonstrate reasonable agreement with the available experimental sticking rates in the latter case, and strong quantum effects in both cases.

We start with defining the rate equation for a DC process of a homonuclear diatom (e.g., H₂) on an infinite surface:



where * indicates the adsorbed state for the dissociated atomic fragments. The extension to a polyatomic system is trivial. The rate equation can be defined either in terms of the molecular concentration in the gas phase or by the coverage on the surface.

$$-\frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{H}^*]}{dt} = k(T)[\text{H}_2]. \quad (1)$$

Experimentally, it is more convenient to measure the coverage on the surface (with the unit of $1/\text{m}^2$) so the rate coefficient $k(T)$ is often given in the unit of m/s .⁴

Quantum mechanically, the rate coefficient can be written as,³³

$$k(T) = \frac{1}{Q_r^\square(T)} c_{fs}^\square(t \rightarrow \infty), \quad (2)$$

where $Q_r^\square(T)$ is the reactant quantum mechanical partition function per unit volume and $c_{fs}^\square(t)$ the flux-side correlation function defined in the N -particle phase space $\{\mathbf{p}, \mathbf{q}\}$:

$$c_{fs}^\square(t) = \frac{1}{(2\pi\hbar)^{3N}} \int d^{3N}\mathbf{p} \int d^{3N}\mathbf{q} e^{-\beta H(\mathbf{p}, \mathbf{q})} \delta[\xi(\mathbf{q})] v_\xi(\mathbf{p}, \mathbf{q}) h[\xi(\mathbf{q}_t)], \quad (3)$$

where the reciprocal temperature is given by $\beta = 1/k_B T$. The dividing surface is defined by $\delta[\xi(\mathbf{q})]$ along the reaction coordinate $\xi(\mathbf{q})$ and $h[\xi(\mathbf{q}_t)]$ is a Heaviside function, which counts the fraction of trajectories $(\mathbf{p}_t, \mathbf{q}_t)$ passing through the dividing surface to the product side at time t . The initial velocity along the reaction coordinate $\xi(\mathbf{q})$ is,

$$v_\xi(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^N \frac{\partial \xi(\mathbf{q})}{\partial \mathbf{q}_i} \frac{\mathbf{p}_i}{m_i}. \quad (4)$$

With the ring polymer ansatz,¹⁵ the Hamiltonian in Eq. (3) is replaced by the ring polymer counterpart:

$$H_n(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^N \sum_{j=1}^n \left(\frac{|\mathbf{p}_i^{(j)}|^2}{2m_i} + \frac{m_i}{2} \omega_n^2 \left| \mathbf{q}_i^{(j)} - \mathbf{q}_i^{(j-1)} \right|^2 \right) + \sum_{j=1}^n V(\mathbf{q}_1^{(j)}, \dots, \mathbf{q}_N^{(j)}), \quad (5)$$

where each atom is replaced by a ring polymer consisting of n beads that are interconnected via harmonic springs with the spring frequency of $\omega_n = \frac{1}{(\beta_n \hbar)}$, $\beta_n = \frac{1}{nk_B T}$ is the n -bead reciprocal temperature, $\mathbf{p}_i^{(j)}$ and $\mathbf{q}_i^{(j)}$ are momentum and position vectors of the j^{th} bead of the i^{th} atom, respectively, m_i is the atomic mass of the i^{th} atom,

V is the potential energy surface (PES) of the N -atom system. The corresponding ring polymer rate theory assumes an analogous form to Eq. (3), with the ring polymer Hamiltonian in Eq. (5) and $n \times 3N$ phase space.^{16, 17}

For DC, two dividing surfaces are introduced in terms of the ring polymer centroid variables, analogous to the case of a bimolecular reaction in the gas phase.¹⁹ The first dividing surface is located in the asymptotic reactant valley where the molecule is high above the surface,

$$s_0(\bar{\mathbf{q}}) = Z_\infty - Z, \quad (6)$$

where Z is the vertical distance between the center of mass (COM) of the dissociating molecule and the surface and Z_∞ is an adjustable parameter that is chosen to be sufficiently large to make the interaction between the molecule and the surface negligible. It can be readily shown (Appendix I) that the corresponding rate coefficient has the unit of m/s. The second dividing surface is located in the transition-state region and can be defined as,

$$s_1(\bar{\mathbf{q}}) = (Z^\ddagger - Z) - (r^\ddagger - r), \quad (7)$$

where r is the distance between two dissociation fragments, $Z^\ddagger$ and $r^\ddagger$ are the corresponding distances at the saddle point of the PES.

A suitable interpolating reaction coordinate $\xi(\bar{\mathbf{q}})$ that connects two dividing surfaces is given by,¹⁹

$$\xi(\bar{\mathbf{q}}) = \frac{s_0(\bar{\mathbf{q}})}{s_0(\bar{\mathbf{q}}) - s_1(\bar{\mathbf{q}})}, \quad (8)$$

such that $\xi \rightarrow 0$ as $s_0 \rightarrow 0$ and $\xi \rightarrow 1$ as $s_1 \rightarrow 0$. Here the overline notation $\bar{\mathbf{q}}$ indicates that we have taken the dividing surfaces $s_0(\bar{\mathbf{q}}) = 0$ and $s_1(\bar{\mathbf{q}}) = 0$ to be

functions of the centroid coordinate,

$$\bar{\mathbf{q}} = \frac{1}{n} \sum_{j=1}^n \mathbf{q}^{(j)} \quad (9)$$

of a ring polymer composed of n beads.

In practice, the RPMD rate coefficient is presented^{18, 19} in the Bennett–Chandler factorization form,^{34, 35}

$$k^{\text{RPMD}}(T) = k^{\text{QTST}}(T; \xi^\ddagger) \kappa(t \rightarrow t_p; \xi^\ddagger). \quad (10)$$

Here, the first term, $k^{\text{QTST}}(T; \xi^\ddagger)$, is the centroid-density quantum transition state theory (QTST) rate coefficient¹⁷ evaluated at the peak ($\xi^\ddagger$) of the potential of mean force (PMF) along the reaction coordinate:

$$k^{\text{QTST}}(T) = \left(\frac{1}{2\pi\beta\mu_Z} \right)^{\frac{1}{2}} e^{-\beta[W(\xi^\ddagger) - W(0)]}, \quad (11)$$

where μ_Z is the molecular mass and $W(\xi)$ is the PMF calculated by using umbrella integration.^{21, 36, 37}

$$W(\xi^\ddagger) - W(0) = \int_0^{\xi^\ddagger} \sum_{i=1}^{N_{\text{windows}}} \left[\frac{N_i P_i(\xi)}{\sum_{j=1}^{N_{\text{windows}}} N_j P_j(\xi)} \left(\frac{1}{\beta} \frac{\xi - \bar{\xi}_i}{(\sigma_i)^2} - k_i(\xi - \bar{\xi}_i) \right) \right] d\xi, \quad (12)$$

with the probability distribution

$$P_i(\xi) = \frac{1}{\sigma_i \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\xi - \bar{\xi}_i}{\sigma_i} \right)^2 \right]. \quad (13)$$

Here N_{windows} is the number of biasing windows placed along the reaction coordinate with a specific value $\bar{\xi}_i$ assigned to each window, N_i is the total number of steps sampled for window i , $\bar{\xi}_i$ and σ_i^2 are the mean value and the variance calculated for the i th window from the trajectory generated by the modified ring polymer Hamiltonian,

$$H_n^\xi(\mathbf{p}, \mathbf{q}) = H_n(\mathbf{p}, \mathbf{q}) - \frac{1}{\beta_n} \ln f_\xi(\bar{\mathbf{q}}) + 1/2 k_i(\xi(\bar{\mathbf{q}}) - \bar{\xi}_i)^2, \quad (14)$$

where k_i is the force constant which defines the strength of the bias in window i and

$$f_{\xi}(\bar{\mathbf{q}}) = \left\{ \sum_{i=1}^N \frac{1}{2\pi\beta m_i} \left[\frac{\partial \xi(\bar{\mathbf{q}})}{\partial \bar{\mathbf{q}}_i} \right]^2 \right\}^{\frac{1}{2}}. \quad (15)$$

The second factor in Eq. (10), $\kappa(t \rightarrow t_p; \xi^{\ddagger})$, is the long-time limit of the time-dependent ring polymer transmission coefficient. This is a dynamical correction to centroid density QTST that accounts for recrossing of the reaction coordinate $\xi(\bar{\mathbf{q}}) = \xi^{\ddagger}$ at $t \rightarrow t_p$, t_p is a “plateau” time, and ensures that the resulting RPMD rate coefficient $k_{\text{RPMD}}(T)$ will be independent of any choice of the dividing surface.¹⁹ It is given by¹³

$$\kappa(t \rightarrow t_p; \xi^{\ddagger}) = \lim_{t \rightarrow t_p} \frac{\langle f_{\xi}(\bar{\mathbf{q}})^{-1} v_{\xi}(\mathbf{p}, \mathbf{q}) h[\xi(\bar{\mathbf{q}}_t) - \xi^{\ddagger}] \rangle_{\xi^{\ddagger}}}{\langle f_{\xi}(\bar{\mathbf{q}})^{-1} v_{\xi}(\mathbf{p}, \mathbf{q}) h[v_{\xi}(\bar{\mathbf{p}}, \bar{\mathbf{q}})] \rangle_{\xi^{\ddagger}}}, \quad (16)$$

where the subscripts on the brackets indicate that the averages are over the constrained ensemble at $\xi(\bar{\mathbf{q}}) = \xi^{\ddagger}$ and the factor of $f_{\xi}(\bar{\mathbf{q}})^{-1}$ is a metric tensor correction for the effect of the constraint.³⁸

In this work, we applied the RPMD rate theory for DC to two systems, one with a high barrier and the other with a null barrier. For simplicity, we have assumed a rigid surface approximation, which has been widely used in dynamics studies of H₂ DC thanks to the large mass disparity.⁵ In addition, this constraint can be readily relaxed in RPMD calculations, thanks to the linear scaling laws.¹⁵

For the highly-activated H₂ + Ag(111) system, we employed the six-dimensional PES constructed by Jiang and Guo³⁹ using the permutation invariant polynomial neural network (PIP-NN) approach.^{40, 41} The lowest dissociation barrier for H₂ on Ag(111) is at the bridge site, associated with a high and “late” barrier of 1.15 eV. A contour plot for the PES at this site is shown as a function of Z and r with the angular coordinates optimized in Fig. 1(a). Additional contour plots of the PES (Figs. S1 and S2) can be

found in Supporting Information (SI).

For the non-activated system, namely H₂ dissociation on Pt(111), there have been many previous theoretical calculations.⁴²⁻⁴⁶ We choose to construct a new six-dimensional PIP-NN PES based on 1457 density functional theory (DFT) points generated by a trajectory-free active learning strategy.^{47, 48} All DFT calculations were performed by the Vienna *Ab-initio* Simulation Package (VASP).^{49, 50} The ionic core-electron interactions were described by the projector-augmented wave (PAW) method,⁵¹ and the Kohn-Sham valence electronic wave function was expanded in a plane-wave basis set with a kinetic energy cutoff at 400 eV. The surface of Pt(111) was modelled by a five-layer slab with a vacuum region of 15 Å in the vertical direction within a 2×2 (1/4 ML coverage) surface unit cell. The Brillouin zone was sampled using a $9 \times 9 \times 1$ Γ -centered k -points grid mesh. The exchange–correlation effects were represented within GGA using the PBE α -vdW-DF2 functional.⁴⁶ A total root mean squared error (RMSE) of 6.73 meV was obtained using the PIP-NN method. A two-dimensional PES cut of the non-activated reaction path is shown in Fig. 1(b) for comparison, where the COM of H₂ is fixed on the top site and the angular coordinates optimized. Additional contour plots of the PES can be found in SI.

All calculations were performed using a home-made FORTRAN code in Cartesian atomic coordinates with the ring polymer Hamiltonian in Eq. (5), thus imposing no restriction on the overall rotational or translational motion of the system. For the calculation of the PMF, the reaction coordinate (-0.05 to 1.10) was divided by an equal size ($d\xi = 0.01$) with the force constant of the biasing potential of 2.72 (T/K) eV using

the umbrella sampling technique as described above. In each sampling window, 60 constrained sampling trajectories of 100 ps were carried out, before which the system was equilibrated for 20 ps with the Andersen thermostat⁵² for thermalization. After determining the PMF at each temperature, the transmission coefficient was computed. Specifically, a long (2 ns) parent trajectory was carried out with the ring-polymer centroid constrain at the peak of PMF via the SHAKE algorithm⁵³ after an initial equilibration period of 20 ps, constrained configurations were sampled once every 2 ps. For each of these configurations, 150 separate unconstrained ring polymer trajectories were spawned with different initial momenta sampled from a Boltzmann distribution. These trajectories for Ag(111) and Pt(111) were then propagated for 150 fs and 120 fs, respectively, which is long enough for the transmission coefficients to reach plateau values. The time step is selected to be 0.1 fs in all RPMD calculations. The classical rate coefficients were also calculated for comparison by setting the number of beads to one.

For H₂ DC on Ag(111), the thermal rate coefficients were calculated at a number of temperatures ranging from 300 to 1000 K. The convergence was tested with up to 32 beads, as shown in Fig. S3 at the representative temperature of 500 K. The parameter Z_∞ in Eq. (6) was set to 7 Å for all of the temperatures considered and the s_1 dividing surface was placed at the barrier at the bridge site ($\xi = 1.0$ or $Z=1.10$ Å and $r=1.27$ Å). The converged RPMD PMFs along the reaction coordinate ζ are displayed in Fig. 2(a). As shown, the free-energy barrier increases from low to high temperatures due to the negative entropy change from reactants to the transition state. In Figs. 2(b) and 2(c),

the classical and RPMD PMFs are compared at two representative temperatures (500 and 1000 K), which shows the RPMD free-energy barrier is significantly lower than the classical counterpart. This trend becomes more pronounced at lower temperatures. At high temperatures, the difference can be attributed to the inclusion of ZPE in RPMD, while at low temperatures, both tunneling and ZPE contribute and it is difficult to distinguish the contributions from the two quantum effects.

The time-dependence of the converged RPMD transmission coefficient, $\kappa(t; \xi^\ddagger)$, the dynamical factor, is shown in Fig. 3(a). Clearly, all the transmission coefficients reach plateau values after initial drops from one. The transmission coefficient increases slightly with decreasing temperature. This temperature dependence shows that the less available thermal energy at lower temperatures leads to less recrossing of the dividing surface.

The final RPMD rate coefficients are compared with the classical ones in Fig. 4(a) and listed in Table 1. It is clearly shown that the rate coefficients from converged RPMD simulations are larger than those from classical limit at all temperatures, owing to tunneling. It also shows that the difference in the rate coefficients between the classical and RPMD simulations increases with decreasing temperature, which is to be expected from the larger contribution of tunneling to the centroid-density QTST rate at the lower temperature as shown in Figs. 2(b) and 2(c). Unfortunately, there has been no experiment on this system and a comparison is thus not possible.

The calculation for the H₂ DC on Pt(111) follows the same protocol as Ag(111)

described above. In particular, Z_∞ was set to 7 Å and the s_1 dividing surface was placed at the second submerged saddle point ($\xi = 1.0$ or $Z = 1.55$ Å and $r = 1.10$ Å). The convergence was also tested with up to 32 beads, as shown in Fig. S4 at the representative temperature of 500 K. The converged RPMD PMFs are shown in Fig. 2(d) at a number of temperatures ranging from 300 to 2000 K. There is a free-energy barrier near the first submerged saddle point in the entrance channel. Despite the barrierless minimum energy path at the top site, the dissociation pathways at other surface sites all have non-negligible barriers, as shown in Fig. S2. The PMF thus represents an effective barrier for the impinging molecule. In the meantime, the second submerged saddle point shown in Fig. 1(b) does not lead to a free-energy barrier and has no impact on the kinetics. This is due to the fact that dissociation pathways in other surface sites possess no such a saddle point, as shown in Fig. S2. In addition, the free-energy barrier on Pt(111) decreases with temperature and is much lower than Ag(111). Interestingly, there are still some small differences between the classical and quantum PMFs at two representative temperatures (500 and 2000 K), as shown in Fig. 2(e) and (f), suggesting the presence of quantum effects even for such lower barrier process. The quantum-classical difference in the barrier height becomes smaller at higher temperatures, as the system approaches the classical limit where the quantum effect is dominated by the ZPE.

As shown in Fig. 3(b), the transmission coefficients are smaller on Pt(111) than on Ag(111), indicating more recrossing, presumably due to the low effective barrier of the system. The recrossing is also more prominent at higher temperatures.

In Fig. 4(b) and Table 1, the calculated classical and quantum rate coefficients are compared with the experimental thermal sticking coefficients at several temperatures. The latter were derived in Ref. ⁴ from previous experimental data. It can be seen from the figure that the experimental data do not follow the Arrhenius behavior, namely a straight line in the $\log k - 1/T$ plot. This curvature of the temperature dependence is reproduced by both the classical and quantum results. The deviation from the Arrhenius behavior in the classical limit suggests that the curvature in the temperature dependence of the rate coefficient is not due to quantum effect. On the other hand, the difference between the classical and quantum rate coefficients is not large (a factor of three), and nearly independent with temperature. The RPMD rate coefficients are in reasonably good agreement with the experimental counterparts, within a factor of two, supporting the accuracy of the RPMD calculations.

The theory-experimental discrepancy, while small, might be attributable to a number of factors. First, the PES might contain errors due to the uncertainty associated with the functional. Second and perhaps more prominently, the rigid surface approximation used here might be inadequate. Although the mass of the H atoms is low compared with that of the metal, the fluctuation of the surface atoms might change the PES significantly to affect the kinetics. The impact of surface motion can in principle be included in RPMD calculations and we plan to explore this in future work.

In this work, the RPMD rate theory is extended to DC of gas phase molecules on surfaces and applied to two prototypical systems. The main advantage of the RPMD

approach is its ability to include quantum effects such as zero-point energy and tunneling, albeit approximately. In addition, it is numerically efficient for extended systems as the computation is based on classical trajectories. Although the numerical examples discussed in this work were based on rigid surface models, the inclusion of the surface atoms is straightforward.

The application of this RPMD rate theory to the highly activated H_2 DC on $\text{Ag}(111)$ revealed strong nuclear quantum effects at low temperatures, resulting in a significant deviation from the Arrhenius behavior. This is attributed to tunneling of the impinging H_2 over the dissociative barrier. It is also demonstrated that the RPMD theory can be applied to systems where the dissociation minimum energy pathway involves no activation barrier, namely the DC of H_2 on $\text{Pt}(111)$. Here, the calculated rate coefficient follows the same non-Arrhenius temperature dependence of the experimentally derived sticking coefficient within a factor of two. Moderate quantum effects are also seen. The favorable comparison with the experiment offers strong evidence for the reliability of the RPMD rate theory.

As discussed in Introduction, the RPMD rate theory has many advantages over other theoretical approaches including TST. It naturally avoids the harmonic oscillator approximation and is capable of handling soft modes. It treats the recrossing dynamics and the results are independent of the choice of the dividing surface, which is hard to define properly in a multidimensional space. Most importantly, it includes quantum effects such as tunneling and zero-point energy, thus ideally suited for studying nuclear

quantum effects. Finally, it scales linearly with the dimensionality of the system, which is important for extended systems.

Finally, we emphasize that further applications of the RPMD to surface reactions can be expected. For instance, the observed strong high-temperature quantum effects in the recombinative desorption of H_2 and D_2 reported in the recent experiment⁴ is amenable to an RPMD characterization. Both Eley-Rideal and Langmuir-Hinshelwood reactions can also be treated within the same framework. Such progress will complement the recent advances in accurate rate measurements of elemental surface reactions.⁵⁴

Supporting information: Additional results on the PES and convergence.

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Appendix I

It is well established that $c_{fs}^{\square}(t; s)$ is a real and odd function of t which is discontinuous at $t = 0$ and has a positive limit as t tends to zero from above.³³ This leads to a well-defined TST approximation to the rate coefficient,

$$k^{QTST}(s) = \frac{1}{Q_r^{\square}(T)} c_{fs}^{\square}(t \rightarrow 0_+; s), \quad (I1)$$

where

$$c_{fs}^{\square}(t \rightarrow 0_+; s) = \prod_{i=1}^{3N} \left(\frac{m_i}{2\pi\beta\hbar^2} \right)^{1/2} \int d^{3N} \mathbf{q} e^{-\beta V(\mathbf{q})} \delta[s(\bar{\mathbf{q}})] f_s(\bar{\mathbf{q}}), \quad (I2)$$

with

$$f_s(\bar{\mathbf{q}}) = \left\{ \sum_{i=1}^N \frac{1}{2\pi\beta m_i} \left[\frac{\partial s(\bar{\mathbf{q}})}{\partial \bar{\mathbf{q}}_i} \right]^2 \right\}^{\frac{1}{2}}. \quad (I3)$$

When using the dividing surface $s_0(\bar{\mathbf{q}}) = Z_{\infty} - Z = 0$, it becomes

$$f_{s_0}(\bar{\mathbf{q}}) = \left(\frac{1}{2\pi\beta\mu_Z} \right)^{\frac{1}{2}}, \quad (I4)$$

and therefore

$$c_{fs}^{\square}(t \rightarrow 0_+; s_0) = \left(\frac{1}{2\pi\beta\mu_Z} \right)^{\frac{1}{2}} Q_r^{\square}(T), \quad (I5)$$

where the reactant partition function is given as

$$Q_r^{\square}(T) = Q_{trans}^{\square}(T) Q_{int}^{\square}(T), \quad (I6)$$

with

$$Q_{trans}^{\square}(T) = \left(\frac{\mu_Z}{2\pi\beta\hbar^2} \right)^{1/2}, \quad (I7)$$

and

$$Q_{int}^{\square}(T) = \left(\frac{\mu_r}{2\pi\beta\hbar^2} \right)^{3n/2} \int d^3 \mathbf{r} e^{-\beta V_{int}(\mathbf{r})}. \quad (I8)$$

Finally, substituting Eq. (I5) into Eq. (I1) gives

$$k^{QTST}(s_0) = \left(\frac{1}{2\pi\beta\mu_Z} \right)^{\frac{1}{2}}, \quad (I9)$$

which is in the unit of m/s.

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Table 1 Summary of centroid-density QTST rate coefficients, transmission coefficients and RPMD rate coefficients for H₂ DC on Ag(111) and Pt(111) in the temperature interval between 300 and 1000 K. The centroid-density QTST and RPMD rate coefficients are given in m/s and the numbers in parentheses denote powers of 10.

	T (K)	N_{bead}	k_{QTST}	κ	k_{RPMD}
Ag(111)	300	32	4.30(-16)	0.905	3.89(-16)
	400	32	7.56(-12)	0.899	6.80(-12)
	500	32	3.47(-09)	0.882	3.06(-09)
	600	32	2.51(-07)	0.875	2.20(-07)
	700	16	5.67(-06)	0.865	4.90(-06)
	1000	16	2.05(-03)	0.845	1.73(-03)
Pt(111)	300	32	9.71(+01)	0.584	5.67(+01)
	400	32	1.34(+02)	0.565	7.57(+01)
	500	32	1.73(+02)	0.546	9.45(+01)
	600	32	2.17(+02)	0.540	1.17(+02)
	700	16	2.59(+02)	0.534	1.38(+02)
	1000	16	4.05(+02)	0.555	2.25(+02)
	1500	8	7.09(+02)	0.589	4.18(+02)
	2000	8	1.07(+03)	0.612	6.55(+02)

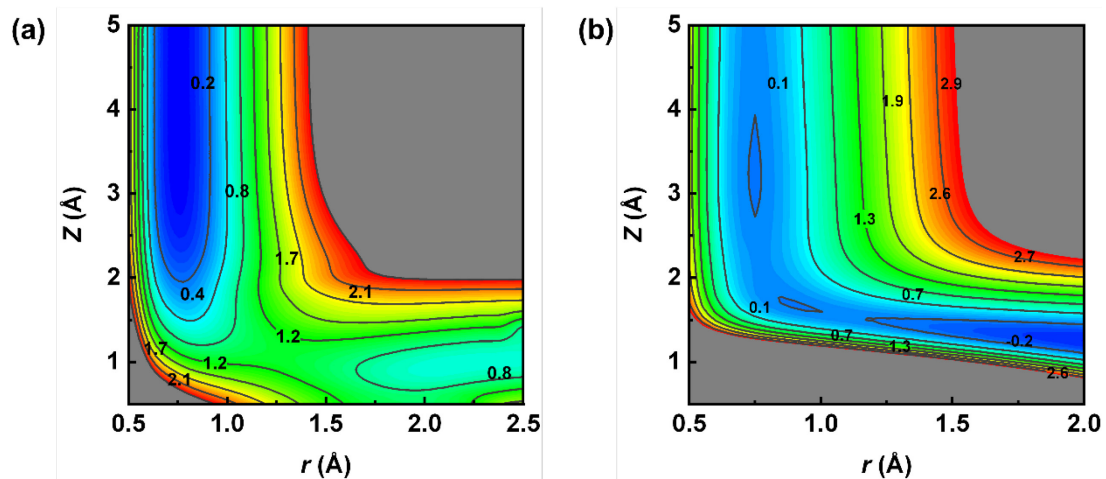


Fig. 1. Two-dimensional contour plots with the COM of H₂ fixed on the bridge site of Ag(111) (a) and the top site on Pt(111) (b), with the angular coordinates optimized. There is a substantial barrier height of 1.15 eV for H₂ dissociation on Ag(111), while H₂ dissociation on Pt(111) has no intrinsic barrier, but contains two submerged saddle points.

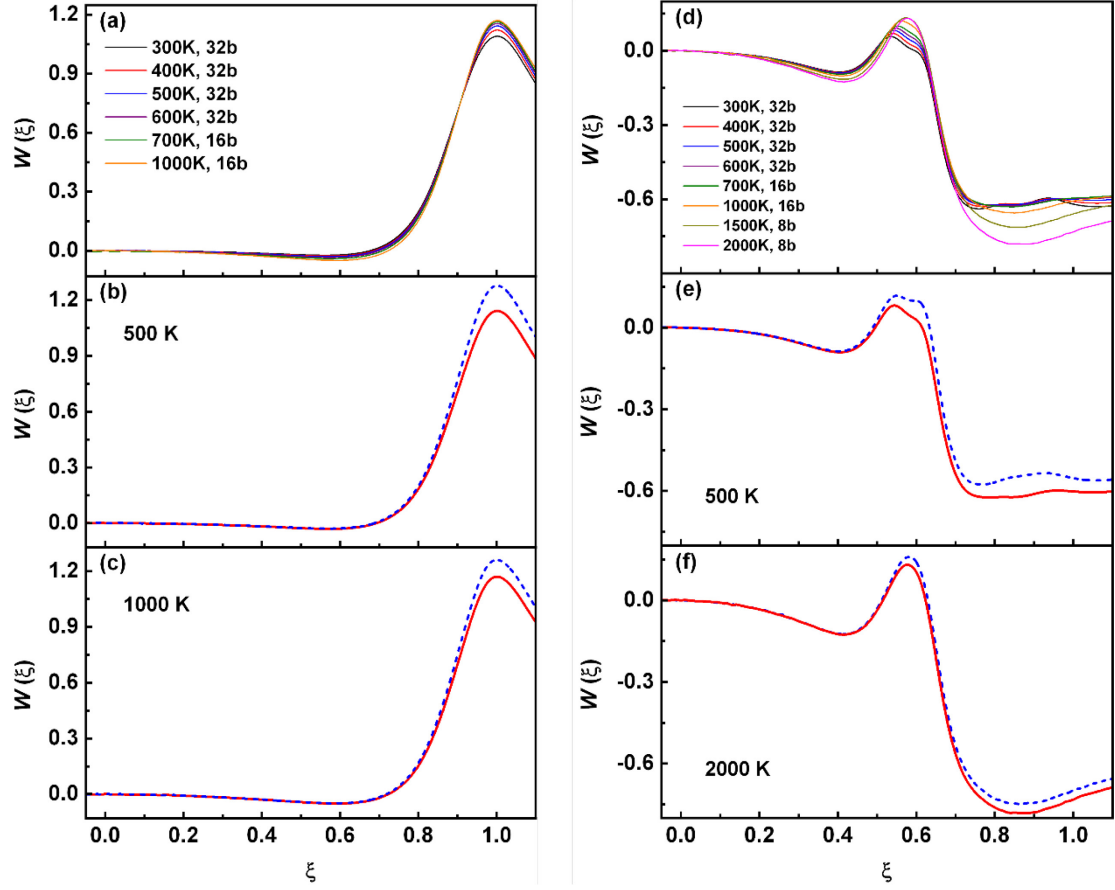


Fig. 2. Converged RPMD PMFs ($W(\xi)$ in eV, with the number of beads marked) for the H_2 DC (a and d) and comparison of the classical (dashed blue line) and RPMD (solid red line) PMFs at two temperatures (b, c and e, f). The left and right panels are for Ag(111) and on Pt(111), respectively.

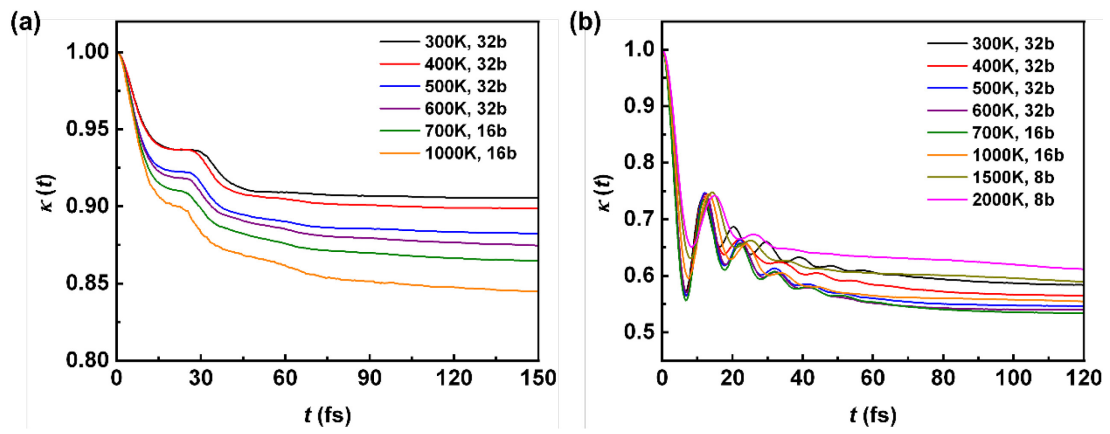


Fig. 3. Converged RPMD transmission coefficients (with the number of beads marked) for the H_2 DC. The left and right panels are for Ag(111) and on Pt(111), respectively.

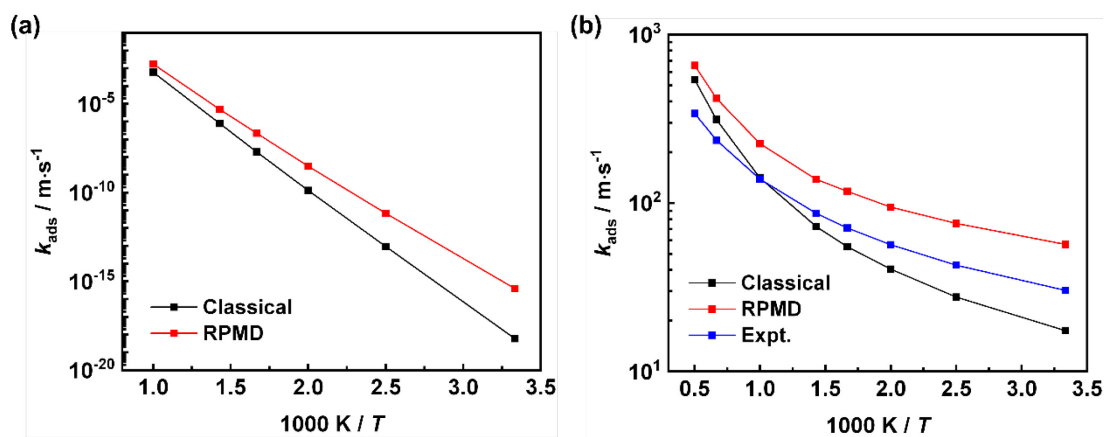


Fig. 4. Arrhenius plots of classical, RPMD and available experimental rate coefficients for the H_2 DC. The left and right panels are for Ag(111) and on Pt(111), respectively.