Eley-Rideal Dynamics of the Reaction of Gas-phase H(D) with D(H) on Cu(111)

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Abstract. We present an overview of our theoretical studies of the Eley–Rideal dynamics of the reaction of gas-phase H(D) with D(H) adsorbed on Cu(111). The studies are based on a three-dimensional flat-surface model and an empirical potential energy surface. Results for reactive cross sections and rovibrational HD product state distributions are presented. The pronounced isotope effects on the vibrational state distribution are shown to have a simple dynamical origin. Our predictions for these product distributions are in semi-quantative agreement with experiments, whereas the calculated and measured reactive cross section disagree.

1. Introduction

Most gas-surface reactions that have been studied occur via the Langmuir-Hinschelwood (LH) mechanism, in which both reactants are adsorbed and thermally equilibrated with the surface. A much less common pathway, for which strong evidence has only recently appeared from state-resolved molecular beam experiments [1–7], is the Eley–Rideal (ER) mechanism where the gas-phase species reacts directly with an adsorbed species. Prime examples are provided by the reactions of gas-phase H atoms with Cl adsorbed on Au(111) [1,4,5] and of gas-phase H(D) atoms with adsorbed D(H) atoms on Cu(111) [3,6,7]. In these cases, the experimental evidence for the ER mechanism is based on two characteristic dynamical features; the sensitivity to the initial state of the incident atom, and the relatively large translational and internal energy of the product. The latter feature is due to the large exothermicity for the ER mechanism, in which only a single adsorbate-substrate bond has to be broken, compared to the LH mechanism where two such bonds are broken. However, many possible pathways lie between these limiting ER and LH mechanisms, such as the hot atom mechanism proposed by Harris and Kasemo [8]. To distinguish the ER mechanism from the LH mechanism is not a trivial matter because an hot atom that is introduced by the trapping of a gas-phase atom on a surface may retain a major part of its incident energy and lateral momentum.

Support for the ER reaction mechanism has also been produced by theoretical dynamics studies based on fully quantum-mechanical models [9–16]. Most of these studies are based on a simple two-dimensional collinear geometry and treat the reactions of gas-phase hydrogen atoms with either hydrogen or chlorine atoms adsorbed on metal surfaces [9–11]. These studies have revealed several dynamical features that are in qualitative agreement with experiments, such as a large vibrational excitation of the product molecule [9,10], the importance of the relative masses of the reactants on the product state [10,11], and the strong dependence on the vibrational state of the adsorbed atom that leads to a low apparent thermal activation energy [11].

The collinear studies have been revealing but do not fully account for the dynamics, and can at best be viewed as qualitative. A more realistic description of the ER dynamics has been achieved by the application of a three-dimensional flat-surface model [13–15] to the reaction of H(D) with D(H) on Cu(111). The model is based on a flat-surface approximation for the potential energy surface, so it does not restrict the motion of the reactants and the product. This enables us to calculate reaction cross sections and detailed rovibrational product state distributions. The interaction of Hydrogen with Cu(111) is relatively well-characterized from theoretical and experimental studies of the dynamics of dissociative adsorption [16–17], helping us to construct a reasonable potential energy surface. Another appealing feature of this system is the possibility of probing the ER dynamics by studying the effects of isotopic substitution on the product state, and comparing with detailed state-resolved atomic beam experiments performed very recently by Rettner and Auerbach [6,7].

In this paper we present an overview of our studies, based mainly on the flat-surface model of the ER mechanism for the reaction of a gas-phase H(D) atom with an adsorbed D(H) atom on Cu(111). Results are presented for the isotope dependence of the reactive cross section and the vibrational and rotational state distributions. The model is assessed by a comparison of our predictions with experiment.

A detailed description of the model and the method of implementation is given in our paper [13], which henceforth will be referred to as PJ. We present the main assumptions and ingredients of the model in Section 2, the results are discussed in Section 3 and compared with experiment in Section 4, and we make some concluding remarks in Section 5. For easy reference, the initially adsorbed and incident atoms will be referred to as the targon and the incidon, respectively. Moreover, we shall use the terminology H-on-D, D-on-H and so on to describe the different isotopic combinations of the incidon and the targon.

2. Theory

The recombination of two atoms involves six degrees of freedom, assuming both electronic adiabaticity and a rigid substrate. The latter assumption is justified by the relatively small masses of H and D. At present, a full quantum-mechanical treatment including all these degrees of freedom is intractable, so it is necessary to make some physical approximations that reduce the high dimensionality of the problem. The small diffusion barriers of H atoms on a metal surface suggest a flat-surface appromixation, in which the lateral variation of the potential energy surface (PES) is neglected. The PES is then a function of only three variables ρ, z_i and z_t, which are defined in the inset of Fig. 1. This approximation reduces the dimensionality of the problem from six to three by introducing the following three constants of motion: $\mathbf{P}_\parallel$ the center-of-mass momentum parallel to the surface and J_z, the projection of the angular momentum normal to the surface. In this paper, we report results only for the case of the incidon at normal incidence, where $\mathbf{P}_\parallel = J_z = 0$. The case of off-normal incidence is a bit more complex, and was fully explored in PJ for H-on-H. We would like to stress that the flat-surface model gives a fully three-dimensional description of the free molecule.

The model is solved quantum-mechanically by propagating the wave function in time using well established pseudospectral techniques. The wavefunction is represented by its values on a three-dimensional grid of points. Initially, the wave function is a simple product of the ground state wave function for the targon-metal vibration, and a Gaussian wave packet for the incidon centered at a position far from the surface with an average momentum determined by the incident energy E_i. In this work we shall consider only $E_i = 75$ meV. The wavefunction is evolved numerically in time using a short time propagator algorithm based on the split-operator method. The product state distribution is obtained from the scattered wave function using a projection operator-correlation function approach.

We have elucidated the role of quantum effects on the dynamics by making a direct comparison with results from standard quasi-classical calculations. By using the term quasi-classical, we stress that it is important to account for the zero-point motion of the targon. The targon vibration, whose energy was set equal to its quantum-mechanical zero-point value, was sampled over its initial phase. Quantum numbers j and ν were assigned to the product HD molecule by setting $\hbar j$ and $\hbar(\nu + \frac{1}{2})$ equal to the classical angular momentum and the classical vibrational action variable, respectively. The quasi-classical reaction cross section is given by,

$$\sigma_r = 2\pi \int_0^\infty P_r(b) b db, \tag{1}$$

where the opacity function, $P_r(b)$, is determined by the relative number of reactive trajectories for each impact parameter, $b = \rho(t \rightarrow -\infty)$.

An appropriate model PES describing the rearrangement of chemical bonds between the H and D atoms and a metal surface like Cu(111) is provided by a London-Eyring-Polanyi-Sato (LEPS) potential. The two-body interactions describing the HD molecule and the H and D atoms adsorbed on Cu(111) are

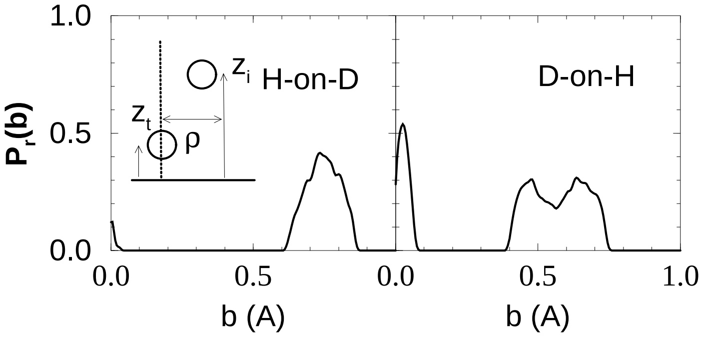

Fig. 1. Quasi-classical reaction probabilities, $P_r(b)$, as a function of impact parameter, b, for H-on-D and D-on-H. Same incidence conditions as in Table 1. The inset in the upper panel depicts the reactive scattering geometry in the flat-surface model together with the coordinates of the targon (t) and the incidon (i). The dotted line, $\rho = 0$, indicates the geometry used in the collinear model.

given by Morse potentials, whose parameters are, as discussed in PJ, readily determined from experimental and theoretical studies of H_2 and H on Cu(111). The relatively large difference between the H-D bond energy, D_m=4.745 eV, and the hydrogen chemisorption energy, D_a=2.45 eV, results in a large exothermicity $Q = D_m - D_a + E_i + \hbar\omega/2 \approx 2.44$ eV, where the isotopic differences in the zero-point energy $\hbar\omega/2$ are negligible. The Sato parameters, which determine the potential in the interaction region, are chosen to give values for the height and position of the activation barrier to dissociative adsorption that are consistent with values suggested by studies of this part of the PES [16,17]. These values, which correspond to the PES-I model in PJ, are consistent with the results from recent density functional calculations of the multi-dimensional PES for the dissociative adsorption of hydrogen [18]. This construction results in an attractive PES for the ER reaction, which means that a large part of Q is released in the entrance channel. As demonstrated for the H-on-H combination in PJ, this feature of the PES leads to a weak dependence on E_i and a highly vibrationally and rotationally excited H_2 product. In the case of the HD product, Q allows a maximum possible rotational excitation $j_{\max} = 21$ and vibrational excitation $\nu_{\max} = 5$.

3. Results and discussion

In Fig. 1, we show the calculated opacity functions, $P_r(b)$, for H-on-D and

Table 1. Comparison between calculated and measured averages of internal energies, $\langle E_{\rm int}\rangle$, vibrational quantum numbers, $\langle \nu \rangle$, and rotational quantum number, $\langle j \rangle$ and reaction cross sections σ_r for H-on-D and D-on-H. The quasi-classical results are within the parenthesis. The calculated results are for normal incidence with $E_i = 0.075$ eV while the experimental data taken from Ref. [7] are recorded at $E_i = 0.07$ eV with an angle of incidence $10°$ from the surface normal.

	H-on-D		D-on-H	
	Theory	Expts	Theory	Expts
$\langle E_{\rm int}\rangle$ (eV)	1.48 (1.48)	1.2	1.67 (1.69)	1.3
$< \nu >$	1.05 (0.51)	1.4	2.13 (1.89)	1.6
$< j >$	11.2 (14.5)	7.3	8.8 (11.7)	7.0
σ_r (Å^2)	0.27 (0.31)	$\sim$5	0.39 (0.30)	$\sim$5

D-on-H. These results look qualitatively similiar with some exceptions. For both combinations there is a relatively narrow range of reactive b close to r_0, the equilibrium HD bond length. In contrast to D-on-H, there are almost no reactive collisions for H-on-D when b is close to zero, corresponding to a collinear arrangement. This behavior is consistent with an impulsive collision argument put forward in our collinear study of this reaction [10], but due to the area element in Eq. (1) these collisions contribute negligibly to the overall behaviour. Because the detailed structure of $P_r(b)$ is quite different for the two isotopic combinations, we expect that the underlying dynamics behind this difference should also affect the HD product distributions.

As demonstrated in Table 1, there are indeed strong isotope effects in the calculated reactive cross-sections and averages of the different HD product distributions. The quasi-classical (QC) results are in good agreement with the quantum mechanical (QM) results for the average internal energy, but are less accurate for σ_r and the averages $\langle \nu \rangle$ and $\langle j \rangle$ of the HD rovibrational distributions. However, the trend of $\langle \nu \rangle$ and $\langle j \rangle$ with isotope is reproduced. As discussed in our paper [14], the impulsive collision argument fails with respect to the internal state distributions.

Strong isotope effects are also seen in the calculated detailed HD product distributions. Here we shall mainly scrutinize the HD product rovibrational state distributions. The results for the translational energy distribution have been reported and discussed in Ref. [14]. In Fig. 2, we compare the QM and QC HD product vibrational state distributions, $P(\nu)$ for the two isotopic combinations. The isotope effects on the calculated $P(\nu)$ are quite pronounced; D-on-H not only gives rise to a much larger $\langle \nu \rangle$ but also a much broader distribution than H-on-D. D-on-H gives even an appreciable population up to $\nu_{\rm max} = 5$.

The pronounced isotope effects in the calculated $P(\nu)$ are caused by changes in the relative time-scales for the motion of the reactants rather than differences

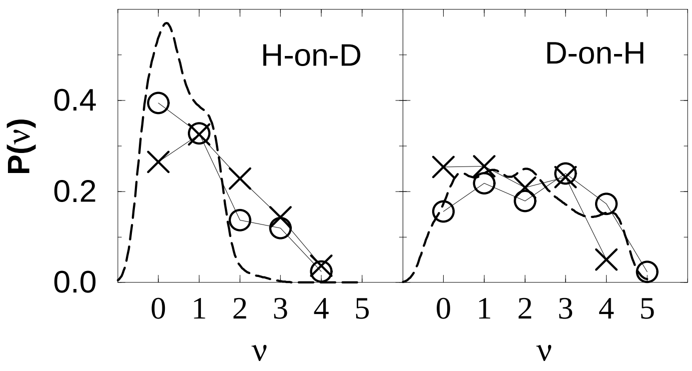

Fig. 2. Comparison between calculated and measured vibrational distributions, $P(\nu)$ for H-on-D and D-on-H. The quantum-mechanical and quasi-classical results are depicted by open symbols and dashed lines, respectively, while the experimental data taken from Ref. [6–7] are depicted by crosses. Same incidence conditions as in Table 1.

in the zero-point energy of the targon. The latter effect is consistent with $P(\nu)$ being broadest for the combination D-on-H, since this gives the larger amplitude for the targon zero-point motion. However, this explanation was disproved in paper [14] by comparing results from QC calculations using two different zero-point energies for the targon; the proper value and the value corresponding to the other isotope. Here we shall instead show that the isotope effects in $P(\nu)$ are due to a combination of two dynamical effects: (1) different ranges of reactive b in $P_r(b)$ that result from different time-scales for the relative motion of the reactants, and (2) a decrease in vibrational excitation with increasing b. These two effects will now be demonstrated in turn.

In Fig. 3, effect (1) is illustrated by the calculated results for the kinetic energy, $K_{\rm rel}$, of the relative lateral motion of the targon and the incidon for nonreactive classical trajectories as a function of b . For intermediate ranges of b, $K_{\rm rel}$ is so large that the two reactants separate too quickly to have time to form a molecule. By comparing with Fig. 1, this behavior appears to be responsible for the characteristic holes in $P_r(b)$. Furthermore, the larger values of the reactive b for H-on-D than for D-on-H is caused by a faster separation of H-on-D over a wider range of b than for D-on-H. Effect (2) is also demonstrated in Fig. 3, where QC results for the average vibrational excitation $\langle\nu\rangle$ are plotted as a function of b.

Finally, we show in Fig. 4 that the calculated rotational state probability distributions, $P(j)$, are also quite different for the two isotopic combinations. Both combinations give rise to a broad range of rotational excitations from $j = 0$ to $j_{\rm max} = 21$. H-on-D tends to populate higher j states than for D-on-H.

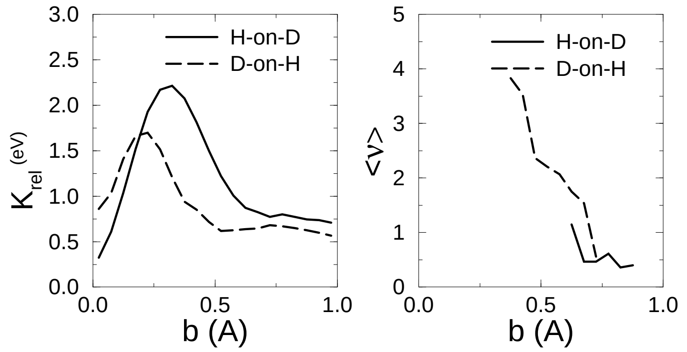

Fig. 3. Quasi-classical averages of the relative kinetic energy, K_{rel}, along the surface and vibrational quantum number, $\langle \nu \rangle$, as a function of impact parameter, b, for the two isotope combinations. Same incidence conditions as in Table 1.

This behavior is consistent with the variation of the QC reaction probability with b shown in Fig. 1, but a more detailed analysis of the QC calculation reveals that there is no simple mapping between the rotational excitations and b, as there is for the vibrational excitations. Once again we see that the QC distribution is too narrow for H-on-D but fairly good for D-on-H. In Ref. [14], we showed that these isotopic effects are not simply due to differences in the QC zero-point motion of the targon for the two isotopic combinations. In analogy with the results for H-on-H presented in PJ, the strong oscillations in the calculated $P(j)$ are probably due to interference effects, and are expected to be washed out at off-normal incidence.

4. Comparison with experiments

The recent and detailed atomic beam measurements of the internal state of the HD product for these reactions by Rettner and Auerbach [6–7] enable us to assess our flat-surface model for the reaction dynamics by making a direct comparison of our predictions with their data. We shall not attempt to make any exhaustive comparison here that will be made elsewhere.

As shown in Table 1, they observed a high rovibrational excitation of the HD product. Some of the observed rovibrational states had energies corresponding to the maximum possible energy released in this reaction. This observation provides strong experimental evidence for an ER-like pathway for the reaction. The overall magnitudes and the trend between the two isotopic combinations of the averages of the internal energy and the rovibrational state distributions

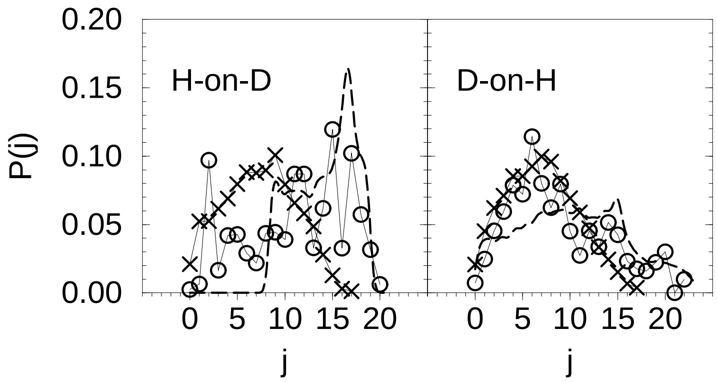

Fig. 4. Comparison between calculated and measured rotational state distributions, $P(j)$ for H-on-D and D-on-H. The quantum mechanical and quasi-classical results are depicted by open symbols and dashed lines, respectively, while the experimental data taken from Ref. [6–7] are depicted by crosses. Same incidence conditions as in Table 1.

are in good agreement with experiments, but the calculated isotope effects are more pronounced. This level of agreement suggests that our model is at least a reasonable starting point for the development of an understanding of the ER dynamics behind this reaction. This view is supported by the following comparison of the calculated vibrational and rotational state distributions with the experimental data.

We find a rather impressive agreement between the calculated and measured $P(\nu)$ for the two isotopic combinations, as shown in Fig. 2. The calculations reproduce semi-quantatitively the magnitudes of the observed $P(\nu)$ for the two cases. That the observed isotope effects of $P(\nu)$ are so well reproduced by our model suggests that the aforementioned dynamical effects behind the isotope effects in the calculated $P(\nu)$ make the latter effects rather insensitive to the details of the PES.

As shown in Fig. 4, the calculation also reproduces amazingly well the observed $P(j)$ for D-on-H, whereas the agreement for H-on-D is not as good. In the case of D-on-H, the main discrepancy shows up at high $j \sim 15$–20 where the calculation gives larger values for $P(j)$ than the experiments, whereas in the case of H-on-D, the calculation does not reproduce the shape of the observed $P(j)$ at low j and gives too much rotational excitation at high j. The isotope effects in the observed $P(j)$ are smaller than in the calculations.

A most puzzling observation, in view of the rather impressive agreement between theory and experiment for the product internal state distributions, is the disagreement between the calculated and measured reactive cross-sections, which differ by an order of magnitude. A possible explanation for this disagreement is that, as discussed by Rettner and Auerbach [7], the incidon may react with the targon after making a few bounces with the surface. They argue that the dynamics for the reaction after a few bounces is still similar to the direct one; the large mass mismatch between the H(D) atoms and the Cu atoms ensures that the energy transfer to the Cu substrate is inefficient, so the incidon retains a major part of its incidence energy and momentum, even after a few bounces. Alternatively, the disagreement could result from a too crude PES or neglect of surface corrugation in the model. In the papers [13,15], we showed that it is possible to construct a PES, called PES-V, that can give rise to values for σ_r of the same order of magnitude as the observed values, but PES-V is qualitatively different from PES-I and gives, for example, a wrong isotope effect for $\langle \nu \rangle$.

5. Summary and concluding remarks

We have presented a brief overview of our theoretical studies of the dynamics underlying the Eley–Rideal reaction between a gas-phase H(D) atom and a D(H) atom adsorbed on a Cu(111) surface that are based on a flat-surface model and an empirical potential energy surface (PES). The final state distribution of the HD product and the reaction cross section have been calculated using both fully quantum and quasi-classical methods. The predictions of the model for these quantities have been directly compared with results from very recent state-resolved atomic-beam experiments performed by Rettner and Auerbach [6,7].

The results from the QC calculations are in general agreement with the quantum-mechanical results with respect to qualitative behaviour and trends. The good agreement of the overall magnitude and the isotope effects of the rovibrational distributions with experiment suggests that the model is able to capture some essential ingredients of the reaction dynamics. The vibrational state distributions exhibit the most pronounced isotope effects. An analysis of the QC calculations reveal that these effects are caused by isotope differences in the relative timescales for the motion of the reactants rather than in the zero-point motions of the initially adsorbed atom. A most puzzling observation is the strong disagreement between the calculated and measured values of the reactive cross section. Two possible explanations of this disagreement are that the cross-section is enhanced by the gas-phase atom making a few bounces with the surface before it reacts or by steering introduced by the surface corrugation. Work is in progress to use density functional theory to construct a more accurate PES, which combined with QC calculations should be able to clarify this matter.

Acknowledgements

The work by MP has been supported by the Swedish Natural Science Research Council (NFR). Bret Jackson acknowledges support from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy, under Grant # DE-FG02-87ER13744. Allocation of computer time by the Center for Parallel Computers (PDC) in Stockholm is also gratefully acknowledged.

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