

Exam MSc course DST, January 30, 2012.

1. Vibrational Energy Transfer (15 points)

Figures 1 and 2 below show data on the scattering of highly vibrationally excited NO scattering from two different surfaces. Fig. 1 shows the final state distribution of NO initially in the $v=15$ vibrational state after scattering from Au(111). Fig. 2 shows similar data for NO initially in vibrational state $v=12$ scattering from LiF(001).

There is obviously a much higher probability of vibrational energy transfer in the collisions with Au than in the collision with LiF.

- Estimate the fraction of molecules undergoing inelastic scattering in the two cases. (5 points)
- What is a key difference in the electronic band structure of the Au(111) target and the LiF(001) surface. (hint LiF is an insulator – Au is a metal) (5 points)
- How might this difference account for the difference in the observed differences in probability of vibrational energy transfer? (5 points)

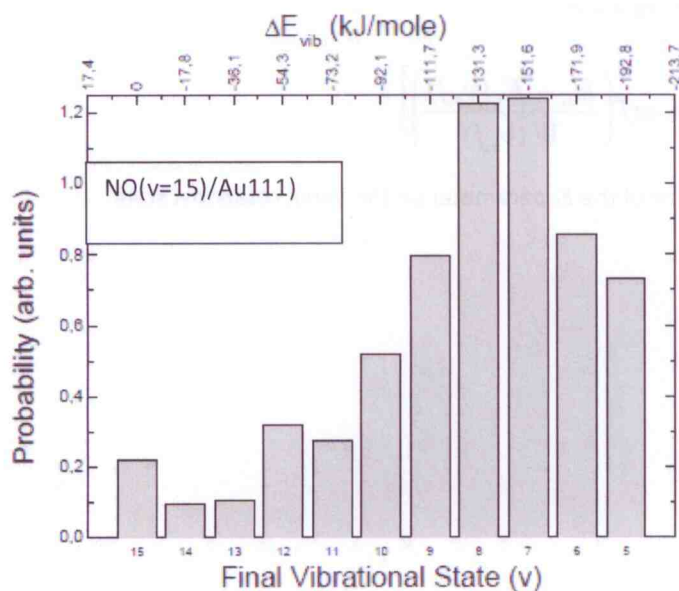


Figure 1

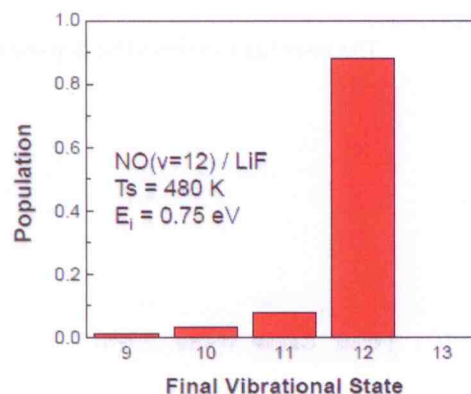
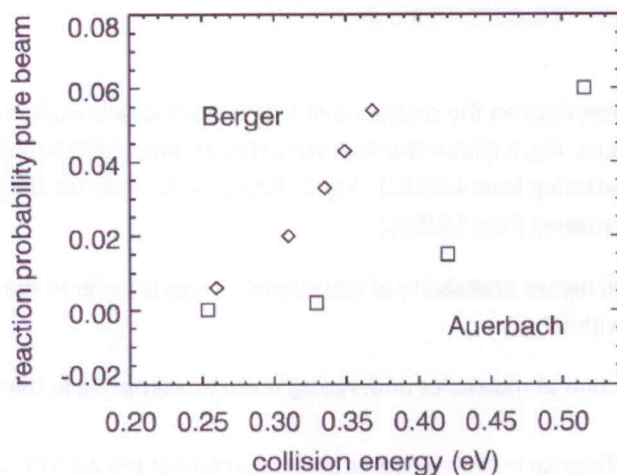


Figure 2

2. H₂-surface reactions. (20 points)

The figure below shows results of measurements of the dissociative chemisorption probability of H₂ on Cu(111), that were performed in two different groups. Both groups used molecular beams of pure H₂ to obtain their results. Later, theorists showed that both experiments could be reproduced with calculations employing the same potential energy surface.

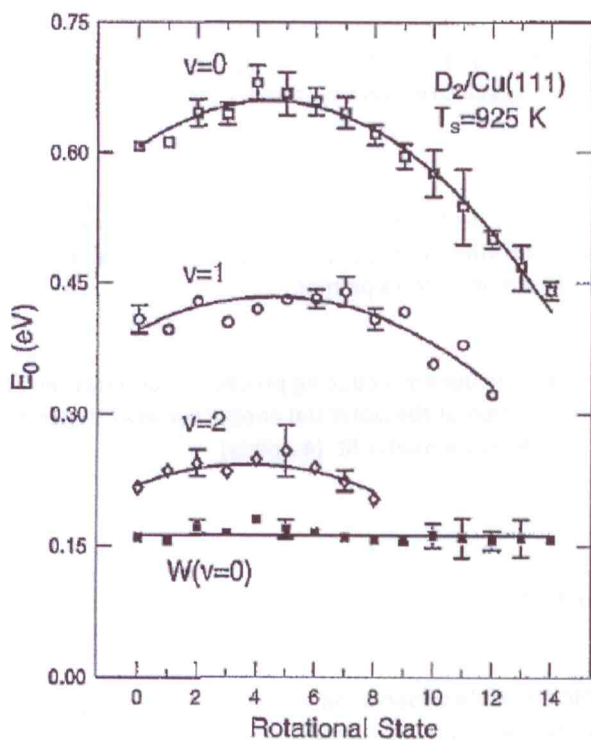


- a. What is the difference you see between the two sets of reaction probabilities? How can this difference be explained? (4 points)

It has been found experimentally that initial state resolved reaction probabilities for D₂ + Cu(111) can be well described by the equation:

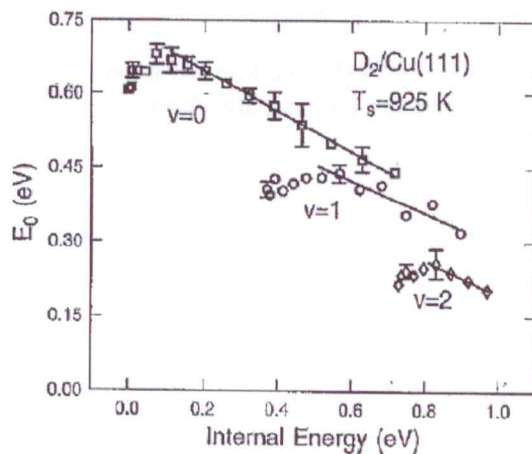
$$S_0(E_i, \theta_i, \nu, j) = \frac{A(\nu, j)}{2} \left[1 + \operatorname{erf} \left(\frac{E_i - E_0(\nu, j)}{W(\nu, j)} \right) \right]$$

The next figure shows the dependence of the E_0 parameter on the initial rotational state.



b. How does the reaction probability depend on j ? Explain the dependence on j you see in the figure. (4 points)

The next figure also shows the dependence of the E_0 parameter on the initial vibrational state, for $D_2 + Cu(111)$.



c. How does the reaction probability depend on the initial vibrational state? Give two possible explanations of this effect, based on an elbow plot of the potential energy surface and the frequency of the motion perpendicular to the reaction path in that elbow. (4 points)

In recent theoretical calculations on reactive scattering of H_2 from Cu(111), the potential energy surface for this system was computed with specific reaction parameter DFT, and fitted with the corrugation reducing procedure.

d. What are the basic ideas underlying the specific reaction parameter approach to DFT? Would you describe this method as an ab initio method, or as a semi-empirical method? Please provide arguments in favor of your answer. (4 points)

e. What is the basic idea underlying the corrugation reducing procedure, and how does this idea help to ensure an accurate interpolation of the potential energy surface? Illustrate your answer with an equation showing how the potential is fit. (4 points)

3. Models describing surface motion (15 points).

Consider a minimal model for a diatomic molecule dissociating with its bond axis aligned parallel to a metal surface, i.e. a 2D model including the molecule-surface distance and the diatomic bond length. The rigid surface and the surface mass models have the same dimensions for this problem.

(a) What are the differences between the two models? (6 points)

(b) Would you expect any difference in the dissociation probability that you compute with these models using classical dynamics? (6 points)

(c) What modification of the reaction probability would you expect to see if you change the method from classical mechanics to quantum mechanics? What quantum effect is responsible for this change? (3 points)

