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The effect of surface relaxation on the \( \text{N}_2 \) dissociation rate on stepped Ru: A transition state theory study

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The dissociation of \( \text{N}_2 \) on stepped Ru is the rate limiting step in the industrial synthesis of ammonia on Ru catalysts (see Refs. 1–4). In a preceding paper,\(^5\) we have examined the effect of tunneling on the reaction rate for \( \text{N}_2 \) on a stepped Ru surface with \((0001)\) terraces. The positions of the surface atoms were frozen, in order to reduce the computational effort. The strong tunneling effect found in previous model calculations\(^6–11\) is not found. In contrast, the tunneling effect was very small above room temperature. The thermal rate constant obtained from harmonic transition state theory (TST) therefore agrees very well with the accurate quantum-mechanical result. In this note we further examine the accuracy of the harmonic TST rate constant and consider the effect of surface motion. Different models to take the effect of surface motion in account are employed. The best theoretical result for the thermal sticking coefficient, which is proportional to the thermal rate constant, is then compared with experiment.

Density-functional theory (DFT) calculations are performed to localize the transition state and to determine energies and vibrational frequencies at the transition state. Technical details are the same as in Ref. 5, except that the present work also includes relaxations of the Ru atoms in the topmost two layers. The transition state of \( \text{N}_2 \) dissociation is localized by constraining the N–N distance and relaxing both the other nitrogen degrees of freedom and the positions of the Ru atoms in the topmost two layers. By varying the N–N distance we localized the saddle point. The calculated barrier height for a relaxed surface is 0.65 eV. It should be noted that this barrier is higher than the one reported by Logadóttir and Nørskov.\(^1\) They used the same \((4 \times 2)\) unit cell and the same relaxed surface model. The difference is mainly due to the more accurate localization of the saddle point in the present work.

The relaxation of the surface has a considerable effect on the barrier height, lowering it from 1.0 to 0.65 eV. Therefore, it is obvious that surface degrees of freedom cannot be neglected. In principle, harmonic TST would require that all relaxed degrees of freedom are included in to the dynamical treatment. This requires lots of computer time but does not necessarily change results. Thus we include only selected atoms in the dynamical treatment.

The expression for the thermal rate constants \( k \) in transition state theory is given as

\[
    k = \frac{k_B T}{2 \pi h} \frac{Q^{\uparrow}}{Q_{\text{reactants}}} e^{-\Delta E/k_B T},
\]

where \( \Delta E \) is the vibrationally adiabatic barrier height and \( Q^{\uparrow} \) and \( Q_{\text{reactants}} \) are the partition functions of the activated complex and reactants (per unit volume), respectively. \( \Delta E \), \( Q^{\uparrow} \), and \( Q_{\text{reactants}} \) are defined according to the specific reduced dimensional model employed. Here, the harmonic approximation is used to evaluate \( \Delta E \) and the partition functions. The thermal rate constant \( k \) is related to the sticking coefficient \( S \) according to

\[
    S = \sqrt{\frac{2 \pi m}{k_B T}} n_{\text{active}} k,
\]

where \( m \) is mass of a \( \text{N}_2 \) molecule, and \( n_{\text{active}} \) the density of active sites on the surface. For \( n_{\text{active}} \) we use the value estimated by Logadóttir and Nørskov \((n_{\text{active}} \approx 1.57 \times 10^{17} \text{ m}^{-2})\).\(^1\)

The simplest approximation to include the motion of the surface atoms into the rate constant is to calculate the barrier height and the vibrational harmonic frequencies of \( \text{N}_2 \) at the transition state on a relaxed surface but neglect the vibrations of the surface atoms. Here, we call this model the “relaxed/ \( \text{N}_2 \) model.” This type of modeling is frequently used in the literature. To investigate the role of surface vibrations a more advanced model is needed. In a “relaxed/\( \text{N}_2+2\text{Ru} \)” model the vibrations of two-step Ru atoms next to the upper \( \text{N} \) atom are included, see Fig. 1. Due to the interaction between a dissociating \( \text{N}_2 \) molecule and the surface, the Ru atoms at the step relax upwards compared to the clean surface positions. In the relaxed/\( \text{N}_2+2\text{Ru} \) model we consider the motion of both Ru atoms in all three dimensions. Thus, the vibrational motion at the transition state involves six nitrogen and six ruthenium degrees of freedom. The harmonic frequencies for the different models are given in Table I. For the \( \text{N}_2+2\text{Ru} \) model, modes 1–5 and the mode corresponding to the imaginary frequency mainly involve motion of the nitrogen atoms.
and modes 6–11 mainly involve motion of the Ru atoms. By comparing the frequencies of the relaxed/N₂ and relaxed/N₂+2Ru models we can conclude that the small differences in frequencies are probably due to the coupling between nitrogen and ruthenium degrees of freedom in the relaxed/N₂+2Ru model.

The surface vibrations do not change the vibrationally adiabatic barrier height significantly, as can be seen in Table I. The coupling changes only the factor \( Q^1/Q_{\text{reactants}} \), and therefore has only a small effect on the sticking probability. The thermal sticking coefficients are presented in Fig. 2. The results of the two models considered differ by less than 10%.

This suggests that the relaxed/N₂ model, which only takes relaxation of the surface into account but neglects Ru frequencies explicitly, can be used to reliably predict the sticking probability or rate constant. Figure 2 shows that the sticking coefficient obtained using the relaxed surface models with an activation energy of 0.65 eV is two to four orders of magnitude smaller than the experimental result of Dahl et al. Previous work shows that the tunneling effect is mainly determined by the imaginary frequency \( \omega_i \) and is adequately described by the Wigner tunneling theory. According to this theory, the ratio between the rate constants with and without tunneling is given by the tunneling factor \( \kappa = 1 + \frac{\hbar}{2 \pi} (\hbar |\omega_i|/k_B T)^{1/2} \).
For example, at room temperature (300 K), the tunneling factors are 1.16 and 1.22 for the frozen and relaxed surface models, respectively. Although the tunneling effect is somewhat stronger for the relaxed surface, it still has a marginal effect on the rate constant. At temperatures relevant to ammonia synthesis, the difference is even less: at 750 K, it is 1.03 and 1.04 for the frozen and relaxed surface models, respectively. The effect of surface relaxation is thus predominantly an energy shift. Due to this energy shift the frozen surface model cannot yield quantitative reaction rates, as is clearly demonstrated in Fig. 1. However, the quantum dynamics at the transition state region is correctly described in the frozen surface model.

The present work shows that the effects of surface motion are adequately accounted for in the relaxed/N\textsubscript{2} model. In a previous study we have shown that tunneling effects are negligible.\textsuperscript{5} Thus, harmonic TST employing the relaxed/N\textsubscript{2} model is an accurate approach to calculate the rate constants from DFT data. The applicability of this model in first-principles study of the ammonia synthesis rate\textsuperscript{2} is therefore confirmed by the present results. The main source of error are the DFT calculations itself. Fortunately, the results of the overall ammonia production are quite insensitive to the DFT errors due to the compensation effect.\textsuperscript{13}

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