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## Multidimensional Effects on Dissociation of N<sub>2</sub> on Ru(0001)

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The applicability of the Born-Oppenheimer approximation to molecule-metal surface reactions is presently a topic of intense debate. We have performed classical trajectory calculations on a prototype activated dissociation reaction, of N<sub>2</sub> on Ru(0001), using a potential energy surface based on density functional theory. The computed reaction probabilities are in good agreement with molecular beam experiments. Comparison to previous calculations shows that the rotation of N<sub>2</sub> and its motion along the surface affect the reactivity of N<sub>2</sub> much more than nonadiabatic effects.

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The Born-Oppenheimer (BO) approximation is a standard tool of the chemical physicist aiming to compute rates of chemical reactions. Transition state theory, which is the standard theory for computing reaction rates for complex systems, depends on its validity [1]. The BO approximation has been used successfully in the description of many gas phase reactions [2]. However, its applicability to molecule-metal surface reactions has been questioned, due to the possibility of electron-hole pair excitations. These reactions are relevant to heterogeneous catalysis [3,4], which is of enormous relevance: about 90% of the chemical manufacturing processes employed worldwide use catalysts in one form or another [5].

Direct evidence for nonadiabatic effects on molecule-surface scattering comes from experiments showing electron-hole pair excitation accompanying chemisorption of atoms and molecules [6], and showing ejection of electrons from low work function metal surfaces accompanying scattering of highly vibrationally excited molecules with high electron affinity [7]. Also, it has recently been shown that nonadiabatic [diabatic with [8] or without [9] couplings] models describe the dissociation of O<sub>2</sub> on Al(111) well, whereas an adiabatic description fails. It has even been argued that indirect evidence exists that nonadiabatic effects decrease the reactivity of N<sub>2</sub> on Ru(0001) (a low spin molecule with low electron affinity reacting on a general type transition metal surface) by more than an order of magnitude [10,11].

The N<sub>2</sub> interaction with Ru(0001) has been intensively studied [10–15] because N<sub>2</sub> dissociation is considered the rate-limiting step in the industrial synthesis of ammonia over Ru catalysts. Most of the ammonia produced is used for fertilizers, making ammonia indispensable for our society [5]. Recent research [4,16] has shown that Ru steps are much more important to N<sub>2</sub> dissociation than the (0001) terraces, but the N<sub>2</sub> + Ru(0001) system has emerged as a system of high fundamental interest. It exhibits properties that make it fundamentally different from the well-studied H<sub>2</sub>/Cu system [17], such that the N<sub>2</sub>/Ru(0001) system can be considered as another proto-

type system of dissociative chemisorption [18]. For N<sub>2</sub>/Ru(0001) the reaction barrier is located much more in the exit channel than for H<sub>2</sub>/Cu. The value of the intramolecular distance at the minimum barrier geometry ( $r_b$ ) is greater than the equilibrium bond distance by  $1.3a_0$  for N<sub>2</sub>/Ru(0001) ( $r_b \approx 3.4a_0$ ) [13] and by  $0.8a_0$  for H<sub>2</sub>/Cu ( $r_b \approx 2.2a_0$ ) [19]. The barrier  $V^*$  to reaction is much higher for N<sub>2</sub> + Ru(0001) ( $\approx 2$  eV) [13] than for H<sub>2</sub> + Cu ( $\approx 0.5$  eV) [19]. In contrast to H<sub>2</sub>/Cu [17] comparison between adiabatic theory and experiment for N<sub>2</sub> reaction on Ru(0001) has so far presented major discrepancies, for dissociative chemisorption, associative desorption [11], and inelastic scattering [18], supporting the idea of a large influence of nonadiabatic effects.

An unusual feature of reaction of N<sub>2</sub> on Ru(0001) is that the dissociation probability ( $S_0$ ) saturates at a very small value ( $10^{-2}$ ) for incidence energies ( $E_i$ )  $\gg V^*$  [10,14]. To understand the surprisingly low reactivity a combination of experiment and modeling analysis was applied [11]. The first model applied was a 2 + 1D( $r, Z; q$ ) adiabatic model, in which, besides the N-N distance ( $r$ ) and the molecule-surface distance ( $Z$ ) [Fig. 1(a)], a coupling to surface phonons ( $q$ ) was included. This adiabatic model failed to reproduce the experimental  $S_0$ , overestimating it by 2 orders of magnitude at high  $E_i$  (Fig. 2). In the second 2 + 2D( $r, Z; q, \Gamma$ ) model an additional coupling to electron-

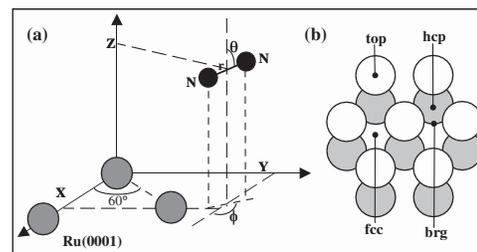


FIG. 1. (a) Coordinate system used. (b) High symmetry points of the Ru(0001) surface. White (gray) spheres denote atoms in the first (second) layer. Atoms in the third (fourth) layer are directly below the atoms in the first (second) layer.

hole pair excitation ( $\Gamma$ ) was introduced leading to much better agreement with experiment (Fig. 2). However, to obtain this level of agreement a very large nonadiabatic coupling was required, i.e., 12 times larger than required for the description of vibrational damping of  $O_2(v=1)$  adsorbed on Pt(111) [11].

Here we show that the description of multidimensional effects through the inclusion of the other 4 degrees of freedom (DOFs) of  $N_2$  in the dynamics is essential to account for the experimental reactivity. A very good quantitative description of the reaction dynamics can already be obtained with a model treating all molecular degrees of freedom but neglecting electron-hole pair excitation and phonons. The results and comparison to previous calculations show that nonadiabatic coupling affects the reaction of  $N_2$  on Ru(0001) to a much smaller extent than previously assumed, and provide further justification for the application of adiabatic models to most molecule-surface reactions relevant to heterogeneous catalysis.

A detailed description of theoretical methods used in this work is presented elsewhere [20]. We take the ruthenium surface as frozen. Although  $N_2$  is a heavy molecule and some energy exchange to phonons could be expected, experiments on Ru(0001) show  $S_0$  to be independent of surface temperature ( $T_s$ ) in the range of collision energies here considered [ $E_i = 2.5$  eV [10]], justifying our neglect of the phonons to some extent. The BO approximation is made, neglecting electron-hole pair excitations. Our model considers motion in all six DOFs of  $N_2$  [Fig. 1(a)].

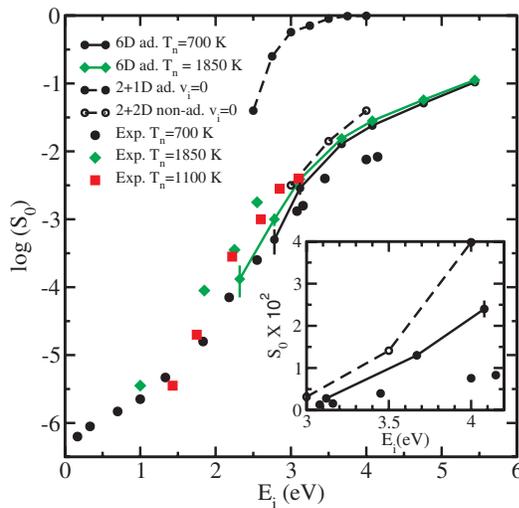


FIG. 2 (color). The log of the probability of  $N_2$  dissociation on Ru(0001) is plotted vs normal translational energy  $E_i$ . Continuous lines with full symbols represent 6D adiabatic calculations, the dashed line with full symbols represents 2 + 1D adiabatic calculations from [11], and the dashed line with open symbols 2 + 2D nonadiabatic calculations from [11]. Experimental measurements: full circles from [10]; full green diamonds from [10]; full red squares from [14]. The inset shows  $S_0$  times  $10^2$  vs normal translational energy. Results are shown for different nozzle temperatures ( $T_n$ ).

We assume that density functional theory (DFT), with the use of the generalized gradient approximation (GGA) for the exchange-correlation energy, gives an accurate description of a molecule-surface reaction if it proceeds adiabatically [17]. In applying the GGA we have used the RPBE (revision of Perdew-Burke-Ernzerhof) functional [21], which is accurate for molecular chemisorption [21] and performed well in modeling ammonia production [4]. The ion cores were described using Vanderbilt pseudopotentials [22] (with core cutoff radii of:  $r_c^N = 0.6$ ,  $r_c^{Ru} = 0.9a_0$ ) and a plane wave basis set is used for the electronic orbitals. With the selected number of Ru layers (3) and the size of the unit cell ( $2 \times 2$ ), the plane wave energy cutoff (350 eV), the amount of  $k$  points used, and the other selected input parameters [20], the molecule-surface interaction energies are converged to within 0.1 eV of the plane wave—pseudopotential RPBE results. The DFT calculations were performed with the DACAPO code [23].

To obtain a potential energy surface (PES), the DFT data were interpolated using a modified Shepard (MS) method [24,25]. This method is here applied to a molecule-surface reaction with a direct interface to DFT for the first time. The interpolated PES is given by a weighted series of second-order Taylor expansions centered on *ab initio* data points. The gradients are computed analytically by DACAPO, and second derivatives from the gradients using forward differencing.

Reaction probabilities were computed using the quasi-classical trajectory (QCT) method [26], the initial vibrational energy of the molecule including zero-point energy. Dissociation is defined to take place whenever  $r$  reaches  $5.0a_0$  with a positive radial velocity. To include the effect of nozzle temperature ( $T_n$ ), reaction probabilities are computed for the  $N_2$  vibrational states  $v_i = 0-2$ , and the results weighted assuming the vibrational temperature to equal  $T_n$ . This implies that  $P_v = 1$  for  $v_i = 0$  at  $T_n = 700$  K, and 0.83, 0.145, 0.025 for  $v_i = 0, 1$ , and 2, respectively, at  $T_n = 1850$  K. All calculations were performed for normal incidence, and for the initial rotational state  $J_i = 0$ , because the reaction probabilities do not depend significantly on  $J_i$  [20] for  $J$  states with significant population at the rotational temperatures relevant to the molecular beams used in the experiments [27].

Figures 3(a) and 3(b) show 2D ( $r, Z$ ) cuts through the DFT PES. For  $N_2$  approaching the surface with its bond parallel to the surface ( $\theta = 90^\circ$ ) and its center of mass over a top site [Fig. 3(a)] and halfway between a top site and a fcc site [Fig. 3(b)], the 2D cuts present very high barriers. The second geometry is close to the lowest barrier geometry at  $(X, Y, Z, r, \theta, \phi) = (1.4a_0, 2.20a_0, 2.53a_0, 3.40a_0, 86.23^\circ, -29.33^\circ)$ ,  $X$  and  $Y$  being the Cartesian coordinates associated with motion parallel to the surface [Fig. 1(a)], and the barrier height  $V^*$  being 2.27 eV [the PW91 barrier was 1.70 eV, but this is very likely too low: PW91 [28] fails [4] to predict the 0.4 eV barrier found experimentally for stepped Ru [16], which is accurately described by the

RPBE functional [16]]. Figures 3(c) and 3(d) show that the  $N_2 + Ru(0001)$  PES exhibits a very large anisotropy and corrugation near the minimum barrier geometry, much larger than for a representative  $H_2/Cu$  system [19]. The  $N_2 + Ru(0001)$  system presents a much narrower bottleneck towards dissociation than  $H_2/Cu$ . The effect is largest for the anisotropy, which is greater for  $N_2$  because its interatomic distance is larger at the barrier, making it more difficult to rotate it to a tilted geometry.

The  $S_0$  obtained from the 6D QCT calculations for  $T_n = 700$  K for  $E_i$  in the classical regime ( $E_i > V^*$ ) are in good agreement with the experimental  $S_0$  for the same  $T_n$  (Fig. 2). Remarkably, inclusion of the four rotational and parallel translational degrees of freedom with the two molecular degrees of freedom ( $r$  and  $Z$ ) also considered in the 2 + 1D model [11] discussed above lowers the reaction probability obtained with this model by about 2 orders of magnitude. The reason that the inclusion of the rotations and parallel translations lowers the reactivity much more for  $N_2/Ru(0001)$  than for  $H_2/Cu$  [17], and that  $S_0$  is so small for  $E_i \gg V^*$ , is that the barrier is a much narrower bottleneck for  $N_2/Ru(0001)$  than for  $H_2/Cu$ , as discussed above [Figs. 3(c) and 3(d)].

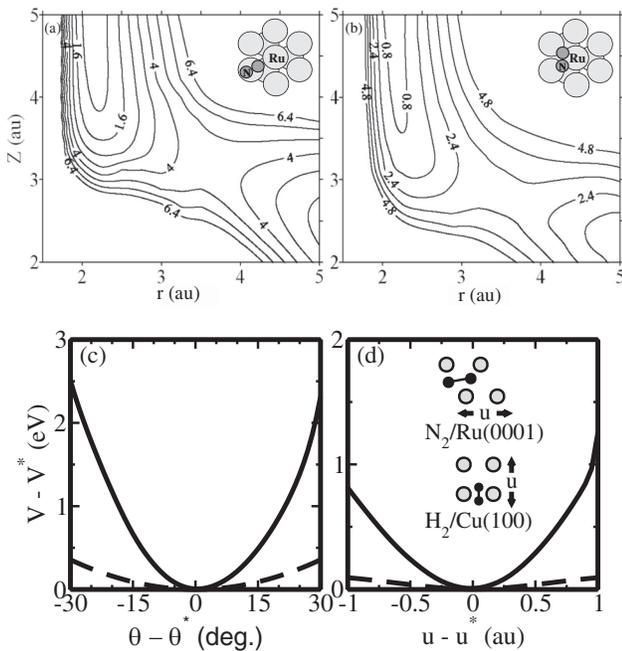


FIG. 3. Two-dimensional cuts through the potential energy surface for (a) the molecule approaching the top site with the N-N bond parallel to the surface ( $\theta_i = 90^\circ$ ) and (b) the molecule approaching a site halfway between the top and fcc sites with  $\theta_i = 90^\circ$ . The potential is for the molecule oriented as indicated by the inset. The spacing between contour levels is 0.8 eV. The anisotropy and corrugation of the  $N_2/Ru(0001)$  (solid line) and  $H_2/Cu(100)$  [19] (dashed line) potentials near the minimum barrier is illustrated by plotting their dependence on  $\theta$  (c) and  $u$  (d), keeping all other coordinates fixed to the barrier geometry  $Q^*$ . Here,  $u$  is the coordinate for motion along a straight line parallel to the surface, such that  $V$  varies the least.

The 6D QCT dynamics overestimates  $S_0$  by about a factor 3 at  $E_i \approx 4$  eV, the agreement being better than for the nonadiabatic 2 + 2D model [11] (inset Fig. 2). This level of agreement between adiabatic theory and experiment suggests a much smaller role for nonadiabatic effects than previously assumed on the basis of the comparison of experiment to adiabatic 2 + 1D results [11]. The remaining disagreement with experiment can be due to the (i) approximations made in the implementation of the adiabatic frozen surface model, or to the exclusion of (ii) phonons and (iii) electron-hole pair excitations from the model. Concerning (i), the exact exchange-correlation functional is not yet known, but the use of the GGA with DFT has allowed the calculation of accurate dissociation probabilities for  $H_2/metal$  systems [17]. The QCT method has been shown to provide accurate results for dissociation of  $H_2$  ( $v = 0$  and 1) on  $Cu(100)$  [29],  $H_2$  presenting a much greater challenge to the classical approximation than  $N_2$ . Concerning (ii), the inclusion of phonons in low-dimensional models lowers the reactivity [11] as also found for (iii) electron-hole pair excitations (Fig. 2) [11]. The experiments on laser assisted associative desorption and vibrationally inelastic scattering referred to above [18], and our finding that the 6D adiabatic model does overestimate energy transfer to molecular vibration in scattering [20], suggest that the discrepancy that remains between 6D adiabatic theory and experiment (inset Fig. 2) is in part due to nonadiabatic effects. The finding that inclusion of phonons also reduces the reaction probability suggests that the factor 3 discrepancy observed at the highest  $E_i$  (inset Fig. 2) is an upper bound to the effect that electron-hole pair excitations might have on the reactivity.

Our results show that late barrier reactions, like  $N_2 + Ru(0001)$  but also  $CH_4 + Ni(111)$  [30], require a treatment of all molecular DOFs: the exclusion of part of these can change the reactivity by 2 orders of magnitude. Discrepancies of this size between experimental reactivity and reactivity obtained in low-dimensional simulations cannot be taken as evidence for nonadiabaticity. Our results suggest that the BO approximation yields a good description of nitrogen dissociation at metal surfaces, even for the high  $E_i$  here considered. Explanations discussed in detail in Ref. [20] are that  $N_2$  has zero electronic spin, so that nonadiabatic spin quenching cannot affect the reactivity [9], and that  $N_2$  has a low electron affinity, so that the transfer of an electron to the molecule cannot lead to electronic excitations in the metal [7,8]. For  $Ru(0001)$ , a contributing factor may be that the molecular chemisorption well in front of the barrier is shallow, and that a reacting molecule is not likely to pass through it [the  $N_2$  orientations at the barrier and in the well differ [12]], so that no energy will be lost to electron-hole pair excitation passing through such a well [6]. More research on reactions involving  $N_2$ ,  $NO$ , and  $O_2$  is needed to determine the importance of these factors, and to establish if and by how much the large charge rearrangement implied in the

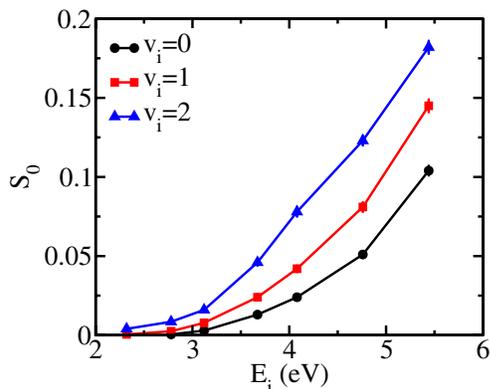


FIG. 4 (color online). Computed dissociation probability vs incidence energy for several initial vibrational states  $v_i$  and  $J_i = 0$ .

breaking of multiple bonds in  $\pi$ -bonded molecules implies nonadiabaticity [31].

The vibrational efficacy  $\eta(S_0) = [\epsilon_{v=0}(S_0) - \epsilon_{v=1}(S_0)] / [E_{\text{vib}}(v=1) - E_{\text{vib}}(v=0)]$  is a measure of the importance of molecular vibration for promoting reaction. Here  $\epsilon_v(S_0)$  is the energy required to obtain a reaction probability  $S_0$  for the molecule initially in the state  $v$ , and  $E_{\text{vib}}$  the molecule's vibrational energy. The  $\eta$  we compute from 6D QCT results (Fig. 4) for  $E_i > 2.3$  eV and for a range of  $S_0$  values ( $5 \times 10^{-4} - 0.1$ )  $\approx 1.6$ . Thus, in our adiabatic model vibrational excitation promotes reaction more efficiently than increasing  $E_i$ . This is in agreement with an analysis of the previous experiments [10] for  $E_i < 2.55$  eV and  $T_n = 700$  and 1850 K (Fig. 2). Taking  $S_0(T_n = 700 \text{ K}) = S_{0v=0}$  and  $S_0(T_n = 1850 \text{ K}) = (1 - c)S_{0v=0} + cS_{0v=1}$ , with  $c$  the fraction of molecules in  $v = 1$  at 1850 K assuming that only  $v = 0$  and 1 are populated, we compute vibrational efficacies greater than 3 from the data. Our calculations suggest that neglect of the  $v = 2$  contribution [the experiments [10] were done for only 2  $T_n$  values] should lead to overestimation of the experimental  $\eta$  by no more than 0.5. Both the present adiabatic theory and previous experiments [10] thus show a large effect of  $N_2$  vibration on dissociation on Ru(0001), in contrast to a previous statement [14] that the effect should be less than for  $H_2/Cu$  ( $\eta \approx 0.5$ ).

We have performed QCT calculations on dissociative chemisorption of  $N_2$  on Ru(0001) based on a DFT adiabatic PES and treating all six molecular DOFs. The multi-dimensional effects of  $N_2$  rotations and translations parallel to the surface dramatically lower the reactivity of  $N_2$  on Ru(0001), leading to good agreement between adiabatic theory and experiment, and suggesting a much smaller role for nonadiabatic effects than previously assumed. The dramatic lowering of the reactivity is due to the large anisotropy and corrugation that the molecule sees when approaching the barrier, the  $N_2/Ru(0001)$  barrier presenting a much narrower bottleneck to reaction than found in the  $H_2/Cu$  prototype system.

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