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Reactive and nonreactive scattering of $\text{N}_2$ from $\text{Ru}(0001)$: A six-dimensional adiabatic study


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We have studied the dissociative chemisorption and scattering of $\text{N}_2$ on and from $\text{Ru}(0001)$, using a six-dimensional quasiclassical trajectory method. The potential energy surface, which depends on all the molecular degrees of freedom, has been built applying a modified Shepard interpolation method to a date set of results from density functional theory, employing the RPBE generalized gradient approximation. The frozen surface and Born-Oppenheimer [Ann. Phys. (Leipzig) 84, 457 (1927)] approximations were used, neglecting phonons and electron-hole pair excitations. Dissociative chemisorption probabilities are found to be very small even for translational energies much higher than the minimum reaction barrier, in good agreement with experiment. A comparison to previous low dimensional calculations shows the importance of taking into account the multidimensional effects of $\text{N}_2$ rotation and translation parallel to the surface. The new calculations strongly suggest a much smaller role of nonadiabatic effects than previously assumed on the basis of a comparison between low dimensional results and experiments [J. Chem. Phys. 115, 9028 (2001)]. Also in agreement with experiment, our theoretical results show a strong dependence of reaction on the initial vibrational state. Computed angular scattering distributions and parallel translation energy distributions are in good agreement with experiments on scattering, but the theory overestimates vibrational and rotational excitations in scattering. © 2006 American Institute of Physics. [DOI: 10.1063/1.2229197]

I. INTRODUCTION

The surface science community has taken a strong interest in the $\text{N}_2$/Ru(0001) system during the last few decades, due to the fact that ruthenium is considered a good candidate for replacing iron as a catalyst in the industrial synthesis of ammonia, and because dissociation of $\text{N}_2$ is the rate-limiting step in this process. As a consequence of this interest a large number of experimental\textsuperscript{1–13} and theoretical\textsuperscript{5,11,14} studies have been published, showing unusual and sometimes controversial results. Although recent theoretical and experimental work\textsuperscript{15–17} has proved that dissociation at Ru steps is much more efficient than at the Ru(0001) terraces, $\text{N}_2$/Ru(0001) is of much fundamental interest. This system can be considered as a new prototype system for activated dissociative chemisorption, because it exhibits properties quite different from the well studied $\text{H}_2$/Cu (Ref. 18) system. For instance, the minimum reaction barrier ($V^*$) is located further in the exit channel for $\text{N}_2$/Ru(0001) ($r_b \approx r_c + 1.3a_0$) (Ref. 7) than for $\text{H}_2$/Cu ($r_b \approx r_c + 0.8a_0$)\textsuperscript{19} and its height is much larger for $\text{N}_2$/Ru(0001) (around 2 eV)\textsuperscript{4} than for $\text{H}_2$/Cu (around 0.5 eV)\textsuperscript{19}.

One of the most striking features of the $\text{N}_2$/Ru(0001) system is that the measured reaction probability ($S_0$) increases very slowly with the incidence energy ($E_i$) for energies above the minimum reaction barrier and saturates at a very small value ($10^{-2}$) for $E_i \gg V^*$. Experimentally, it has also been found that the dissociation probability shows a very strong dependence on the initial vibrational state, vibrational energy being more efficient at promoting reaction than translational energy\textsuperscript{4} (see also Fig. 1 of Ref. 9). Isotope effects have also been investigated.\textsuperscript{5} No isotope effect has been observed in the classical regime ($E_i \gg V^*$), but for lower energies the reaction probability for $^{15}\text{N}_2$ is smaller than for $^{14}\text{N}_2$, which has been interpreted in terms of tunneling through a large barrier for dissociation.\textsuperscript{6} Another unexpected feature is the lack of vibrational excitation in molecular-beam experiments for $\text{N}_2$ scattering from Ru(0001),\textsuperscript{13} and the small amount of vibrational excitation observed in laser assisted associative desorption (LAAD),\textsuperscript{11} associative desorption being the reverse process to dissociative chemisorption. Late barrier systems (reaction barrier found for an extended vibrational coordinate) are expected to exhibit significant vibrational excitation of the molecule upon scat-
Two-dimensional (2D) nonadiabatic tunneling model was proposed in which only two-degrees of freedom (DOFs) were taken into account in the dynamics [see Fig. 1(a)]. In this model the potential energy surface (PES) includes a physisorption term ($V_{\text{phys}}$), describing the gas phase molecule attached to the surface; a chemisorption term ($V_{\text{chem}}$), describing the sum of the N-atom surface potentials; and a nonadiabatic coupling potential to account for the transition between $V_{\text{phys}}$ and $V_{\text{chem}}$. This model reproduces quite accurately the experimental $S_{0\beta}$ but introduces a number of parameters that need to be adjusted. It is not yet clear whether these parameters mostly reflect the true system dynamics or rather the restricted number of molecular DOFs treated. Two other low dimensional models were proposed in Ref. 11: (i) A $2+1\text{D}(r,Z;q)$ adiabatic model, in which not only $r$ and $Z$ are included, but also the coupling to surface phonons via a single Einstein oscillator ($q$). This low dimensional adiabatic model failed completely at reproducing the experimental value of $S_{0\beta}$ overestimating it by two orders of magnitude. (ii) A $2+2\text{D}(r,Z,q,\Gamma)$ nonadiabatic model in which an additional coupling to electron-hole (e-h) pair excitations ($\Gamma$) is included via electronic friction and fluctuating forces. Although this model gave reaction probabilities in semiquantitative agreement with experiment, this agreement was only obtained by using a very strong nonadiabatic coupling, which was 12 times larger than that required for the description of vibrational damping of O$_2$(v=1) adsorbed on Pt(111).25 The question in this case is then whether such a strong nonadiabatic coupling is physically reasonable. A recent low dimensional theoretical study,26 aiming to quantify the influence of nonadiabatic effects on the reactivity of N$_2$ + Ru(0001), suggests a smaller role of nonadiabatic effects, but the low dimensionality of the dynamical model does not allow one to reach a firm conclusion.

The low dimensional calculations were mainly focused on the influence of nonadiabatic effects and on how to include them in the dynamics. The influence of nonadiabatic effects on molecule-surface reactions has become a hot topic in the last few years, thanks to recent experiments showing direct evidence of nonadiabatic effects in molecule-surface scattering such e-h pair excitations accompanying chemisorption of atoms and molecules,27 and ejection of electrons from low work function metal surfaces accompanying scattering of highly vibrationally excited molecules with high electron affinity.28 These experiments might be viewed as questioning the validity of the Born-Oppenheimer (BO) approximation29 for molecule-surface reactions. As discussed in Ref. 30, one reason that the BO approximation could seem suspect for the scattering of molecules from metal surfaces is that the metal surface electronic states exhibit a continuum energy distribution. Nevertheless this approximation has been used successfully in modeling molecule-surface reactions for a large number of systems,30,31,32 and in modeling heterogeneous catalysis.33,34 On the other hand, recent theoretical work has shown that for some special systems, such as a high-spin molecule (O$_2$) (Ref. 35) and/or molecules of high electron affinity (O$_2$ and NO)36 reacting on a metal surface with a low density of states at the Fermi level [Al(111)], the reaction can be better described using a nonadiabatic (diabatic with 36 or without coupling35) model.

In the case of N$_2$, we have a low-spin molecule of low electron affinity, so that, in principle, nonadiabatic effects are expected to be less important. Low dimensional results seem to contradict this expectation (see discussion above), giving rise to the following questions: Is N$_2$/Ru(0001) another special system for which the adiabatic approximation fails to account for experimental results on reaction, or are the molecular DOFs associated with rotation and translation parallel...
to the surface perhaps more important for this system than for other systems. In order to give appropriate answers to these questions we present here a six-dimensional (including the six DOFs of the molecule) adiabatic (neglecting e-h pair excitations) study of N₂ interacting with a Ru(0001) surface. Assuming the system to be reasonably well described by density functional theory (DFT) and the dynamics method employed (see below), the difference between the computational results and experiments should then allow for a verdict on the importance of nonadiabatic effects for this particular system.

The paper is organized as follows: In Sec. II we describe the methodology used, i.e., the electronic structure method used to compute the molecule-surface interaction energies, the interpolation of the potential, and the quasiclassical trajectory (QCT) method used in the dynamics calculations. In Sec. III we present the main features of the six-dimensional (6D) PES obtained for N₂/Ru(0001), and then we discuss the dynamics results obtained for dissociative adsorption and scattering. A short account of some of the results obtained for dissociative adsorption has been published elsewhere. Finally, we summarize the main conclusions in Sec. IV.

II. THEORY

To build the 6D PES for the N₂/Ru(0001) system we have used the modified Shepard (MS) interpolation method adapted for molecule-surface reactions, a new feature being that for the first time we use a direct interface independent of surface temperature. We have considered the six DOFs of the molecule: r, Z, the coordinates X and Y that represent the motion parallel to the surface, and the orientation of the molecule described by the polar (θ) and the azimuthal (ϕ) angles [see Fig. 1(a)]. We have made two main approximations: (i) We take the surface as frozen, i.e., we consider the surface atoms fixed in their equilibrium positions. Although N₂ is a heavy molecule and some energy exchange with the surface could be expected, this approximation is justified, to some extent, by the experimental results showing dissociation probabilities to be independent of surface temperature (T_s). (ii) The BO approximation is applied, neglecting possible nonadiabatic effects (such as e-h pair excitations).

A. Electronic structure calculations

The electronic structure data points have been computed with DFT using the DACAPO code. The generalized gradient approximation (GGA) is used in the description of the exchange-correlation energy of the electrons. In applying the GGA we have used the RPBE functional, which gives smaller overbinding and more accurate chemisorption energies than the PW91 functional, and which has been shown to perform well in modeling ammonia production. The ion cores were described using nonlocal ultrasoft pseudopotentials (with core cutoff radii of r_core N=0.6a₀ and r_core Ru=0.9a₀) and a plane wave basis set was used for the electronic orbitals.

The adsorbate/substrate system is modeled using a three-layer slab and a 2×2 surface unit cell. The interlayer distance (c/2) was relaxed, and had a final value of 2.12 Å, slightly compressed with respect to the calculated bulk case (2.18 Å). A vacuum layer of 13.03 Å was placed between the slabs in the Z direction to avoid artifacts caused by the use of periodic boundary conditions in the direction perpendicular to the slab. To sample the Brillouin zone we have used a set of 18 Chadi-Cohen k points. The cutoff energy for the plane wave basis was set at 350 eV. Using these parameters the molecule-surface interaction energies are converged to within 0.1 eV of the RPBE results for the given USSPs. We have found a minimum energy barrier of 2.27 eV in qualitative agreement with a previous calculation, in which a value of about 2.4 eV was found for the molecule parallel to the surface and dissociating in the bridge to hollow geometry.

B. Interpolation method

In the MS interpolation method, the interpolated PES is given by a weighted series of Taylor expansions centered on DFT data points, sampled throughout the configuration space of the system. To get a physically more reasonable behavior when two atoms are close to each other, the inverse interatomic distances, Q_i=1/R_i (R_i are the interatomic distance that defines the system), are used instead of the direct interatomic distances. Thus, any configuration of the system is defined by the vector \( \mathbf{Q} = [1/R_1, \ldots, 1/R_{n(n-1)/2}] \), where \( n \) is the number of atoms needed to model the system. To model our system we use five atoms, two describing the N₂ approach the Ru(0001) surface, and three atoms, which are kept fixed, to model the frozen surface.

For each geometry \( \mathbf{Q} \) a set of 3n-6 algebraically independent linear combinations of the n(n−1)/2 interatomic distances, \( \xi_k(Q) \), can be defined in terms of the inverse distances as

\[
\xi_k = \sum_{m=1}^{n(n-1)/2} U_{mk} Q_k \quad (m = 1, \ldots, 3n-6),
\]

where \( U_{mk} \) is the transformation matrix from Cartesian coordinates to reciprocal bond lengths (see Ref. 47 for details). The potential energy at a configuration \( \mathbf{Q} \) in the vicinity of a data point \( \mathbf{Q}(i) \), can be expanded as a second-order Taylor expansion \( T_i(\mathbf{Q}) \), in these coordinates,

\[
T_i(\mathbf{Q}) = V[\mathbf{Q}(i)] + \sum_{k=1}^{3n-6} [\xi_k - \xi_k(i)] \frac{\partial V}{\partial \xi_k} \bigg|_{\mathbf{Q}=\mathbf{Q}(i)}
+ \frac{1}{2} \sum_{k=1}^{3n-6} \sum_{j=1}^{3n-6} (\xi_k - \xi_k(i))(\xi_j - \xi_j(i)) \frac{\partial^2 V}{\partial \xi_k \partial \xi_j} \bigg|_{\mathbf{Q}=\mathbf{Q}(i)}
+ \cdots,
\]

where \( V[\mathbf{Q}(i)] \), the value of the potential at \( \mathbf{Q}(i) \), and the gradients at this point are computed analytically by DACAPO. The second derivatives are computed from the gradients using forward differencing.

The total potential energy at any configuration \( \mathbf{Q} \) is then taken as...
In order to choose an appropriate data set the following iterative scheme is used.

1. We start with an initial version of the PES, which only includes a few points located along several reaction pathways. In our case, the initial PES contained 70 initial points chosen along four reaction pathways, i.e., 19 for the top, 19 for the bridge, and 19 for the hollow configuration, these three reaction pathways corresponding to the highest symmetry sites of the surface [see Fig. 1(b)] and 13 points along a minimum energy pathway. The minimum energy pathway was found by minimizing the N₂/Ru(0001) interaction energy with respect to \( \theta, \phi, X, Y, \text{and } Z \), while keeping \( r \) fixed, for several values of \( r \).

2. Using this initial PES a few classical trajectories (typically ten) are run (see below). In order to assure the accurate representation of the PES for the whole energy range in which we are interested to carry out our study, we have grown the PES using simultaneously several translational energies (only normal incidence is considered in the growth process) and two rovibrational initial states (see Table I). Along each trajectory the molecular geometries explored by the simulation are periodically stored.

3. From the stored geometries a new point is chosen (and added to the PES) according to one of the two criteria (see Refs. 39 and 48 for more details): (i) The “h-weight” criterion, which is based on the assumption that the best location for a new point would be the region most frequently visited by the trajectories. Thus, according to this criterion, the new point is added in the region of the PES most frequently visited, as long as there are not many data points already representing this region in the PES data set. (ii) The “variance” criterion, which is based on the assumption that the accuracy of the PES will be best improved if the new point is added in the region where the determination of the energy is suspected to be the most inaccurate.

4. Once the PES is updated by adding the new chosen point, we restart the growth process from (2).

5. After about 100 points are added, the accuracy of the PES is checked by computing an accurate value of the desired observable (in our case the reaction probability) from a more extensive classical trajectory simulation (10,000 trajectories). The growth process is stopped when the observable is considered to be converged, within a given tolerance. The analysis of the convergence of the reaction probability, for several incidence energies and two initial vibrational states, is shown in Fig. 2, where we have represented the reaction probability as a function of the number of data in the PES.

To obtain an accurate PES for N₂/Ru(0001) we have

![Figure 2](image-url)

**TABLE I.** Translational energies and rovibrational initial states used in the growth process. In all cases \( J_1 = 0 \).

<table>
<thead>
<tr>
<th>( v_i )</th>
<th>0 (( E_{v_i} = 0.142 ))</th>
<th>1 (( E_{v_i} = 0.427 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_i )</td>
<td>2.32</td>
<td>3.12</td>
</tr>
</tbody>
</table>

where the term \( T_{g\!i}(Q) \) represents a second-order Taylor expansion and \( w_{g\!i}(Q) \) a normalized weight function (see Refs. 41 and 48 for more details). \( N_{\text{data}} \) is the number of DFT data in the interpolation, \( G \) is the symmetry group, and \( g \!\!i \) denotes the transformation of the \( i \)th data point by the group element \( g \). To take into account the full symmetry of the system, a sum is taken over both the DFT data points and their symmetry equivalent points.

**C. Implementation of the MS method in GROW**

Unlike other interpolation schemes (see, for instance, Refs. 49 and 50), in the MS method the sampling of DFT data points is nonuniform, the density of data points being higher in the so-called dynamically important regions, which are found performing classical trajectory simulations. The idea behind the GROW method is that to calculate observables from a chemical reaction dynamics simulation, we only need to know the PES in the region of space through which the molecules pass during the dynamics.

In order to choose an appropriate data set the following iterative scheme is used.

1. We start with an initial version of the PES, which only includes a few points located along several reaction pathways. In our case, the initial PES contained 70 initial points chosen along four reaction pathways, i.e., 19 for the top, 19 for the bridge, and 19 for the hollow configuration, these three reaction pathways corresponding to the highest symmetry sites of the surface [see Fig. 1(b)] and 13 points along a minimum energy pathway. The minimum energy pathway was found by minimizing the N₂/Ru(0001) interaction energy with respect to \( \theta, \phi, X, Y, \text{and } Z \), while keeping \( r \) fixed, for several values of \( r \).

2. Using this initial PES a few classical trajectories (typically ten) are run (see below). In order to assure the accurate representation of the PES for the whole energy range in which we are interested to carry out our study, we have grown the PES using simultaneously several translational energies (only normal incidence is considered in the growth process) and two rovibrational initial states (see Table I). Along each trajectory the molecular geometries explored by the simulation are periodically stored.

3. From the stored geometries a new point is chosen (and added to the PES) according to one of the two criteria (see Refs. 39 and 48 for more details): (i) The “h-weight” criterion, which is based on the assumption that the best location for a new point would be the region most frequently visited by the trajectories. Thus, according to this criterion, the new point is added in the region of the PES most frequently visited, as long as there are not many data points already representing this region in the PES data set. (ii) The “variance” criterion, which is based on the assumption that the accuracy of the PES will be best improved if the new point is added in the region where the determination of the energy is suspected to be the most inaccurate.

4. Once the PES is updated by adding the new chosen point, we restart the growth process from (2).

5. After about 100 points are added, the accuracy of the PES is checked by computing an accurate value of the desired observable (in our case the reaction probability) from a more extensive classical trajectory simulation (10,000 trajectories). The growth process is stopped when the observable is considered to be converged, within a given tolerance. The analysis of the convergence of the reaction probability, for several incidence energies and two initial vibrational states, is shown in Fig. 2, where we have represented the reaction probability as a function of the number of data in the PES.

To obtain an accurate PES for N₂/Ru(0001) we have

![Figure 2](image-url)

**FIG. 2.** The dissociation probability as a function of the number of DFT points added to the PES data set for two incidence energies, \( E_i = 2.78 \text{ eV} \) and \( E_i = 4.76 \text{ eV} \). (a) \( v_i = 0 \) and \( J_i = 0 \); (b) \( v_i = 1 \) and \( J_i = 0 \).
D. Quasiclassical dynamics

We have performed classical dynamics to find the dynamically important regions during the growth process and to compute reaction and scattering probabilities. In both cases, we have used the so-called QCT method,54 in which the initial zero point energy (ZPE) of the molecule is included in the dynamics. Although these kinds of calculations are susceptible to the so-called ZPE violation problem (see Ref. 52), for an activated system this problem is expected to play a minor role at energies above the threshold to reaction. The QCT method generally gives accurate results for activated molecule-surface reactions.53-56 Note that the vibrational softening (adiabatic transfer of energy from internal to translational motion) that takes place when the molecule approaches the surface is taken into account in the QCT method [its absence in the classical trajectory (CT) method leads to underestimated reaction probabilities57].

To compute the reaction and the scattering probabilities we have solved the classical equations of motion using the velocity-Verlet algorithm.58 For each initial energy and initial rovibrational state, the probabilities are calculated as an average over the molecular initial conditions (internal coordinates and internal conjugated momenta). A Monte Carlo sampling method is used to simulate the molecular initial conditions for each set of initial parameters (Ei, ui, and Ji). In order to obtain low statistical errors (typically between 10% and 3% depending on the translational energy Ei), we have computed 10 000 trajectories for each value of Ei and rovibrational state of N2. We consider that dissociation has taken place whenever r reaches 5.0a0 with a positive radial velocity. The molecule is considered to be reflected whenever Z becomes equal to Zr, Zi being the initial distance between the molecule and the surface (7.5a0), with the molecule’s velocity vector pointing towards the vacuum.

III. RESULTS AND DISCUSSION

A. The N2/Ru(0001) PES

The method used to build the PES allows us to locate easily the regions of the PES important for the dynamics, by merely looking at the distribution of points in configuration space. In Fig. 3 we show the computed DFT data points projected on the (Z,r) [Figs. 3(a) and 3(b)], (X,Y) [Figs. 3(c) and 3(d)], and (sin θ, φ) [Figs. 3(e) and 3(f)] hyperplanes. Looking at Figs. 3(a) and 3(b), we can see that most of the points are added in the entrance channel (valley of reactants), which reflects the low reactivity of N2+Ru(0001). We can additionally see that for the highest energy (for both initial states u1 = 0 and u1 = 1) there are more points added around the transition state (located at r = 3.4a0 and Z = 2.53a0) than for the lowest energy, which is consistent with the fact that the reactivity is higher for higher translational energies. Figures 3(c) and 3(d) show that the added points are uniformly distributed over the (X,Y) and (sin θ, φ) planes. The (sin θ, φ) representations show slightly higher concentrations of points around sin θ = ±1, which, with the way we have defined θ in the classical dynamics, corresponds to the orientation of the molecule most favorable for dissociation.

In Fig. 4 we show two 2D (r,Z) representations of the PES. We show two configurations for which the molecule approaches the surface with its N–N bond parallel to the surface (θ = 90°). In Fig. 4(a) the center of mass (c.m.) of the molecule is located over a top site [see Fig. 1(b)], while in Fig. 4(b) the c.m. is located halfway between a top site and a fcc site, with each N atom pointing toward a hcp site. We can see that both configurations present very high barriers towards reaction, which are located far in the exit channel, i.e., at large r. The second configuration is close to the lowest barrier (V’ = 2.27 eV) geometry, which is located at (X, Y, Z, r, θ, φ) = (1.4a0, 2.20a0, 2.53a0, 3.40a0, 86.23°, −29.33°). This PES does not only present high barriers but also very large anisotropy and corrugation. In Fig. 5 we show the energy profile near the minimum barrier geometry. From this figure we can see that both the anisotropy [Fig. 5(a)] and the corrugation [Fig. 5(b)] at the barrier are much larger for N2/Ru(0001) than for the H2/Cu system50 i.e., N2/Ru(0001) presents a much narrower bottleneck towards reaction than H2/Cu.

B. Dissociative adsorption

In this section we present reaction probabilities for normal incidence obtained using the QCT method. In order to...
The potential for the molecule oriented as indicated in the inset. The spacing between the contour levels is 0.8 eV.

The potential is for the molecule approaching a site halfway between the top and fcc sites, also with \( \theta = 90^\circ \). The illustrated by plotting the dependence of we assume that the vibrational temperature \( T_n \) varies the least.

**FIG. 4.** 2D cuts through the PES for (a) the molecule approaching the top site with the \( \text{N} - \text{N} \) bond parallel to the surface (\( \theta = 90^\circ \)) and (b) the molecule approaching a site halfway between the top and fcc sites, also with \( \theta = 90^\circ \). The potential is for the molecule oriented as indicated in the inset. The spacing between the contour levels is 0.8 eV.

**TABLE II.** Initial vibrational state distributions used in our QCT simulations.

<table>
<thead>
<tr>
<th>( T_n ) (K)</th>
<th>( P_{ev0} ) (%)</th>
<th>( P_{ev1} ) (%)</th>
<th>( P_{ev2} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1850</td>
<td>83</td>
<td>14.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

**FIG. 5.** The anisotropy and corrugation of the \( \text{N}_2/\text{Ru}(0001) \) (solid line) and \( \text{H}_2/\text{Cu}(100) \) (Ref. 50) (dashed line) potentials near the minimum barrier are illustrated by plotting the dependence of \( V(V') \), \( V \) being the potential and \( V' \) the potential at the minimum barrier geometry, on \( \theta \) (a) and \( u \) (b), 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.

**FIG. 6.** (Color online) The reaction probabilities as a function of the translational energies for several initial rotational states \( J_i \) and \( v_i = 0 \).

compare our QCT results directly with the experimental ones, we have to include in our calculations the effect of the nozzle temperature (\( T_n \)), i.e., in principle we have to use the same rovibrational initial state distribution in our simulations as was presented in the experiments. To find the initial vibrational (\( v_i \)) state distribution corresponding to the different \( T_n \), we assume that the vibrational temperature \( T_{vib} \) is approximately equal to \( T_n \). The populations of the different initial vibrational states as a function of the simulated \( T_n \) are shown in Table II. To determine the initial rotational state distribu-

The agreement between theory and experiment is remarkable. From the comparison between our 6D model and the 2+1D model (results of which are also included in Fig. 7) we see that the inclusion of the remaining four molecular DOFs (associated with rotation and translation parallel to the surface) decreases the reaction probability by two orders of magnitude. This illustrates the fundamental role played by these four DOFs. In fact, the inclusion of the rotation and parallel motions lowers the reaction probability much more for \( \text{N}_2/\text{Ru}(0001) \) than for the prototype system \( \text{H}_2/\text{Cu}(100) \). This is due to the fact that, as has been shown in Sec. III A, both the corrugation and the anisotropy near the minimum barrier are much higher for \( \text{N}_2/\text{Ru}(0001) \) than for \( \text{H}_2/\text{Cu}(100) \). Thus the barrier is a much narrower bottleneck for \( \text{N}_2/\text{Ru}(0001) \) system, explaining the lower reactivity.

By looking more carefully at the comparison between 6D adiabatic theory and experiment for the higher \( E_i \) at which measurements are available (see inset in Fig. 7), we see that 6D QCT dynamics overestimates reaction probabilities by a factor of about 3 at the highest \( E_i \) for which experimental results are available (the nonadiabatic 2+2D model\(^{11} \) overestimates \( S_0 \) by a factor of about 5). In the below analy-
sis, we assume the experimental reaction probabilities4,9 to be accurate, even though there could be considerable uncertainty in their absolute value, for instance, due to the procedure comparing the temperature programmed desorption (TPD) of the small amount of N2 adsorbed to that of a monolayer N2.59,60 Other sources of error are in the determination of the collision energy and of the flux.60 These factors should, however, lead to an error of no more than a factor of 2 in the reaction probability (\(=0.01\)) measured at the highest \(E_i (=4 \text{ eV})\).60

In the theory, several factors can then be responsible for the remaining disagreement between experiment and 6D adiabatic theory: (i) approximations made in the implementation of the adiabatic frozen surface model, (ii) exclusion of phonons, and (iii) exclusion of e-h pair excitations. Concerning (i), although DFT is, in principle, an exact theory and has allowed the calculation of quite accurate dissociation probabilities for H2-metal systems,18,32 in practice its use requires some approximations. For instance, the exact form of the exchange-correlation functional is unknown, and the use of pseudopotentials to describe the ion cores is also a source of possible inaccuracies. These approximations lead to some uncertainties in the barrier heights of the system61 and, therefore, also in the reaction probabilities. We have chosen to use the RPBE GGA functional15 instead of the, at present, most used PW91 functional.62 The RPBE functional has been selected because of the following: (a) The PW91 functional fails54 to predict the barrier found experimentally (0.4 eV) for N2+ stepped Ru, which is, however, accurately described by the RPBE functional.15 (b) The RPBE functional more accurately describes atomic and molecular chemisorptions on metal surfaces than the PBE functional, which gives values close to the PW91 functional.43 (c) A recent systematic study63 of the accuracy of several functionals for barrier heights in small gas phase systems shows a better agreement between RPBE results and results of more accurate hybrid functionals than between these hybrid functionals and the PW91 functional. The QCT method, as discussed above, has been shown to provide accurate results for activated dissociation of H2 on metal surfaces,33,35 H2 presenting a much greater challenge to the classical approximation than N2.

Concerning (ii), although experimentally a minimal influence of \(T_e\) on reaction was found (for \(T_e\) between 500 and 850 K) within the classical regime \((E_i \geq V^*))4,9 this does not exclude the possibility that N2 (which is rather heavy compared to H2, for which the frozen surface approximation works quite well51,64) transfers energy to the metal surface phonons on impact. In fact, low dimensional calculations (including only \(r\) and \(Z\)) showed an increase in the classical reaction threshold of 0.5 eV upon inclusion of phonons. Although this result cannot be directly extrapolated to our 6D QCT calculations, it is likely that the inclusion of phonons will lower the reaction probability. Concerning (iii), in the case of e-h pair excitations the LAAD experiments13 and experiments on vibrationally inelastic scattering,13 as well as own our inelastic scattering study showing an overestimation of the energy transfer to molecular vibration (see Sec. III C), suggest that the remaining discrepancy between 6D adiabatic theory and experiment is, at least in part, due to nonadiabatic effects.

Taking into account that the inclusion of phonons should also reduce the reaction probability, we can establish the factor of 3 discrepancy observed between 6D adiabatic theory and experiment at the highest \(E_i\) (inset in Fig. 7) as a reasonable upper bound to the effect that e-h pair excitations might have on the reactivity, at high incidence energies (about 4 eV).

The experimental and theoretical probabilities increase considerably with \(T_n\) (Fig. 7). To study the effectiveness of initial vibrational excitation at increasing reaction, we have computed the vibrational efficacy, which is a measure of the relative importance of molecular vibration and translation for promoting reaction, and is given by

\[
\eta(S_0) = \left( \frac{\epsilon_{\text{vib}}(S_0) - \epsilon_{\text{vib}}(S_0)}{E_{\text{vib}}(v = 1) - E_{\text{vib}}(v = 0)} \right),
\]

where \(E_{\text{vib}}\) is the molecule’s vibrational energy in the gas phase and \(\epsilon(S_0)\) is the energy required to obtain a reaction probability \(S_0\) when the molecules are initially in a vibrational state \(v\). To evaluate \(\eta\) we have computed initial vibrational state resolved dissociation probabilities (Fig. 8). For an energy range of 3.3–5.5 eV and \(S_0\) between 2.5 \(\times 10^{-2}\) and 0.1, the average value we compute for \(\eta(S_0)\) is about 1.6 [as the value of \(\eta(S_0)\) depends slightly on the value of \(S_0\), we have computed \(\eta(S_0)\) for four different values of \(S_0\) obtaining values between 1.4 and 1.8]. Thus, in our 6D adiabatic model vibrational excitation promotes reaction more efficiently than normal translational energy \(E_i\). This result is in reasonable agreement with a previous estimated value of 1.3,5 where reaction probabilities were obtained from detailed balance. It is also in qualitative agreement with an analysis of the previous experiments.4 To calculate the value of \(\eta\) from the molecular-beam results, we suppose \(S_0(T_n = 700 \text{ K}) = S_0(v = 0)\) and \(S_0(T_n = 1850 \text{ K}) = (1 - c)S_0(v = 0) + cS_0(v = 1)\), \(c\) being the fraction of molecules in \(v = 1\) at 1850 K assuming that only \(v = 0\) and 1 are populated. Doing
Dashed line: 15N2. The inset shows the dissociation probability for energy can be more efficient than 114706-8 Díaz et al. vibrational state including and excluding the suggestion that excluding the to an overestimation of evidence energy.

In principle, a vibrationally excited molecule has a maximum that are compatible with the given energy are allowed, which means, from a statistical point of view, that the number of molecules approaching the surface with a geometry favorable to dissociation is very small (smaller than in the case of H2/Cu). On the other hand, if steering in the rotational and the translational motion parallel to the surface would be efficient enough to drive the molecule to the minimum energy reaction path, thereby avoiding the highest barriers when it approaches the surface, a strong corrugation and anisotropy would not be an impediment to reaction.

To study the efficiency of the dynamics to drive the molecule to the minimum energy reaction path, we have compared our 6D QCT results with that obtained using the hole model (HM). In the absence of complex dynamical behavior, this static model allows a good guess of the dissociation probability for a fixed 16, merely by looking at the fraction of molecular configurations leading to dissociation. From Fig. 9, there is a good agreement between the HM and QCT results for molecules in the vibrational ground state, for 16 < 5 eV, whereas for molecules with 16 = 1 the agreement is only good for 16 < 4 eV. These results can be taken as an indication of the inefficiency of the rotational and parallel translational motions to drive the molecule to the minimum

FIG. 8. (Color online) Computed dissociation probability vs incidence energy for several initial vibrational states 16, and 16 = 0. Continuous line: 14N2. Dashed line: 15N2. The inset shows the dissociation probability for 16 = 0 divided by the dissociation probability for 16 = 1 as a function of the incidence energy.

FIG. 9. The fraction of accessible 2D paths toward dissociation as a function of the translational energy. Solid lines and filled symbols: 6D QCT dissociative probabilities. Dashed lines and open symbols: hole model results.

this analysis we obtain 16 = 3.8. As we have neglected 16 = 2 (also present for 16 = 1850), we are overestimating the experimental value of 16. We have evaluated this possible overestimation by doing a similar analysis of our 16(16), both including and excluding the 16 = 2 contribution. Our analysis suggests that excluding the 16 = 2 contribution to 16(16) leads to an overestimation of 16(16) by about 0.5. The result of this analysis of the efficacy is in contrast with a previous statement 9 that the effect should be less than for H2/Cu (16 = 0.5). However, this statement was not backed up by an analysis in terms of the vibrational efficacy. Although quantitatively there are discrepancies between our adiabatic results and previous experiments, 4 both show that excitation of the N2 vibration promotes reaction much more efficiently than increasing the N2 translational energy normal to the surface. A similar finding was mentioned in Ref. 15.

This high vibrational efficacy contrasts with the relatively low 16 found in other N2/metal systems. 45,66 However, a similar high vibrational enhancement has been observed previously, for instance, for CH4/Ni(111). 67 It is worth noticing that in the case of N2/Ru(0001) the sticking curves for different 16 apparently saturate at about the same amplitude for 16 = 0 and 16 = 1 (see inset in Fig. 8); therefore, we can consider that all the 16 dependence is contained in 16 (see Ref. 68 for more details). Now the question is how the vibrational energy can be more efficient than 16 at promoting reaction. In principle, a vibrationally excited molecule has a maximum extra energy to overcome the barrier, 16,n = nhω, (n being the vibrational state), which means that, in principle, the vibrational excitation cannot reduce the 16 required to overcome the barrier by more than 16. One possible explanation to this phenomenon was proposed in Ref. 67: a vibrationally excited molecule surmounting a late barrier can in some cases access phase space regions where the transition state is lower than those accessed by molecules in 16 = 1 smaller (by Δ16) than for molecules in 16 = 0. Thus, the translation energy needed by a molecule in 16 = 1 to overcome the barrier is reduced by 16 + Δ16, which can explain how 16 can be bigger than 1.

In Fig. 8 we show the initial vibrational state resolved reaction probabilities for the heavier isotope 15N2. Taking into account the statistical errors intrinsic to the calculation, no isotope effect is observed. This result is in perfect agreement with the experimental findings, 6 according to which isotope effects are only observed for incidence energies below the minimum reaction barrier (the quantum regime).

We now address the following fundamental question: Why is the reactivity so small in the N2/Ru(0001) system? As we have shown in Sec. III A, the system shows a very high anisotropy and corrugation around the minimum reaction barrier (see Fig. 5), which means that the potential seen by a molecule approaching the surface depends strongly on its position and orientation over the surface. Of course, in a 6D scenario all values of (X, Y, θ, φ) that are compatible with the given energy are allowed, which means, from a statistical point of view, that the number of molecules approaching the surface with a geometry favorable to dissociation is very small (smaller than in the case of H2/Cu). On the other hand, if steering in the rotational and the translational motion parallel to the surface would be efficient enough to drive the molecule to the minimum energy reaction path, thereby avoiding the highest barriers when it approaches the surface, a strong corrugation and anisotropy would not be an impediment to reaction.

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energy reaction path. When \( E_i \) increases, the rotations become more efficient at steering the molecule towards the reaction path, because the high force zones of the PES start to play a predominant role.\(^ {70} \) This explains the difference between the HM probability and the 6D QCT results at high energies. In summary, the reaction probability is small at energies significantly above the minimum barrier height not only because of the presence of a narrow minimum reaction barrier but also because of the nature of the dynamics, which does not allow the molecule to get oriented or positioned in such a way as to be able to pass the barrier. In fact, most of the molecules do not even approach the barrier, they are scattered back to the vacuum far from the minimum reaction barrier, as we can see in Fig. 10, where we have plotted the probability of a molecule to reach an interatomic distance \( r_0 \) (see Sec. III A).

C. Scattering

As we have shown in Sec. III B reaction is the minority process for \( \text{N}_2 \) interacting with Ru(0001). Now we are going to focus on the majority process, scattering. Some extra information about the system can be extracted by looking at the molecules scattered back to the vacuum after the interaction with the surface. Experimentally it is not possible to study scattering under normal incidence conditions; therefore, most of the results we present in this section are for non-normal incidence. We defined the incidence angle \( \Theta_i \) as the angle between the incident velocity vector and the surface normal [see Fig. 1(c)].

In Fig. 11(a) we present the angular distribution of the scattered molecules, for an incidence angle \( \Theta_i = 40^\circ \). We can see that the maximum of the distribution increases and its fullwidth at half maximum (FWHM) decreases with incidence energy until \( E_i = 0.41 \) eV, and then the maximum decreases and the FWHM increases with \( E_i \). A similar behavior has been found experimentally.\(^ {12} \) In Fig. 11(b) we have plotted the FWHM as a function of the incidence energy for \( \Theta_i = 40^\circ \) and \( 50^\circ \). We see that for \( 50^\circ \) the increase of the FWHM with \( E_i \) is less pronounced and starts at a higher \( E_i \). It has been argued\(^ {12} \) that this behavior is related to the existence of two scattering regimes: thermal scattering should dominate at low incident energies, whereas structural scattering should dominate at high energies. The argument is that, in structural scattering, at higher normal energies (\( E_\perp \)) the molecule sees a more corrugated surface (higher penetration\(^ {11} \)), leading to a bigger momentum exchange and a broader distribution, consistent with the experimental and theoretical results. For the same incidence angle, \( E_\perp \) increases with \( E_i \), leading to an increase of FWHM with \( E_i \), and for the same incidence energy, \( E_\perp \) decreases with increasing \( \Theta_i \), leading to a smaller FWHM at \( \Theta_i = 50^\circ \). For low incidence energies, the argument of thermal scattering cannot be applied to our theoretical results (which nevertheless show a decrease of the FWHM with \( E_i \), like the experimental results), because we consider the surface atoms fixed in their equilibrium position (see Sec. II). The behavior of the FWHM at low \( E_i \) can, however, also be understood without invoking the effect of the phonons. For low \( E_i \) the molecules are reflected far from the surface, and for the energy range of 0.05–0.41 eV the corrugation seen by the molecules is more or less the same, which implies that the momentum exchange is similar for the smaller energies (see inset in Fig. 12). This implies that the relative momentum exchange, defined as \( |\Delta K|/K_\perp \), should decrease with increasing \( E_i \). The relative momentum exchange is directly related to the width of the angular distribution: the bigger the relative momentum exchange, the broader the angular distribution is expected to be and vice versa. From Fig. 12 we observe that the relative
momentum change indeed decreases with $E_i$ until $E_i = 0.41 \, \text{eV}$ and from this point on increases with $E_i$. Comparing Figs. 12 and 11(b) we see that the minimum of the FWHM of the angular distribution agrees with the minimum of the relative momentum exchange curve.

Other interesting features that we can extract from the scattered molecules, which contain information about the interaction between the molecule and the surface, are energy transfer to the molecule’s internal motion and to the parallel translational motion. The average energy transferred to translation parallel to the surface ($\langle \Delta E_p \rangle$) as a function of $E_i$ is shown in Fig. 13(a), along with the available experimental results. Both theory and experiment show a small excitation of the parallel motion via momentum exchange. In the theory, for the higher energies we observe a clear difference between the results for the initial conditions $\Theta_i = 19^\circ$ and $\Theta_i = 40^\circ$: $\langle \Delta E_p \rangle$ is twice as high as for the first condition. Two factors can explain this difference: (i) Penetration (and therefore corrugation) is expected to be increased when $\Theta_i$ decreases. \footnote{17} (ii) For $\Theta_i = 19^\circ$ there is a much bigger difference between the normal and the parallel energy, which favors the transfer of energy from normal to parallel motion. From the experimental data it is not possible to establish any kind of dependence of $\Delta E_x$ on $\Theta_i$, due to the magnitude of the errors and the small number of points for $\Theta_i = 40^\circ$.

Rotational excitation is overestimated in our theoretical calculations in comparison with the experimental findings,\footnote{13} as can be observed in Fig. 13(b), where we have plotted the average of the energy transferred to rotation ($\langle \Delta E_{rot} \rangle$) as a function of the incidence energy, for $J_i=0$. The disagreement between theory and experiment increases with $E_p$, and the theoretical value $\langle \Delta E_{rot} \rangle$ becomes twice the experimental one at $E_i \approx 2.8 \, \text{eV}$. The disagreement between theory and experiment is even worse for vibrational excitation [see Fig. 13(c)]. In this case, the theoretical average of the energy transferred to vibration $\langle \Delta E_{vib} \rangle$ is around seven times bigger than the experimental one at $E_i = 2.8 \, \text{eV}$ (the only available experimental data)\footnote{13}. Experimentally no measurable vibrational excitation was observed; the value given in Fig. 13(c) is merely an upper bound determined to $v = 1$ excitation. It is not clear whether an attempt was made to measure vibrational excitation to $v > 1$. The lack of vibrational excitation in this experiment was attributed in part to the spectral overlap associated with transitions of $v = 0, J > 49$ and the low $J$ transitions of $v = 1$. Taking into account that experiments did not consider transitions to $v > 1$ we have recalculated the $\langle \Delta E_{vib} \rangle$ as it would be measured in experiments only considering scattering to $v = 0$ and 1, i.e., we suppose that $P_{ref}(v_j = 0) + P_{ref}(v_f = 1) = 1$, where $P_{ref}(v_j)$ is the probability that a reflected molecule is scattered to the final state $v_f$. Figure 13(c) shows that when making this supposition our theoretical $\langle \Delta E_{vib} \rangle$ is lowered to a value that is only twice the experimental value (a difference similar to that found for rotational excitation).

Classical dynamics is not the best method to study energy transfer to molecule’s internal motions, because the selection rules limiting this transfer are not taken into account.

---

**FIG. 12.** The relative momentum exchange as a function of the incidence energy for $\Theta_i = 40^\circ$. The continuous lines through the data points are to guide the eye only.

**FIG. 13.** (a) The conversion of incidence energy $E_i$ into translational energy parallel to the surface, $\Delta E_x$, as a function of the incidence energy. The filled symbols are from experiment (Ref. 13). (b) The average of the energy transferred to rotation $\langle \Delta E_{rot} \rangle$ as a function of the translational energy. (c) The average of the energy transferred to vibration $\langle \Delta E_{vib} \rangle$ as a function of the translational energy. “Norm” means that we suppose $P_{ref}(v_j = 0) + P_{ref}(v_f = 1) = 1$. 
Quantum mechanically only transitions between internal energy states with \( \Delta \nu = n, \) \( n \) being 0,1,2,..., and \( \Delta J = 2n \) (because of the nuclear spin symmetry) are allowed for \( \text{N}_2 \), whereas classically the internal energy transfer presents a continuous distribution. Nevertheless, it has been shown previously that classical dynamics can account for some typical quantum features such as rotational excitation or even diffraction. The main problem classical dynamics face in this kind of studies is how to use “binning,” i.e., how to transform a continuous distribution into a discrete representation. In the case of rotational excitation we have checked our results using two different binning methods: (i) “Homogeneous binning,” in which we assign \( J \) to reflected molecules by evaluating the closest integer that satisfies \( J_{\text{cl}}=[-1+(1+4L^2/h^2)^{1/2}]/2 \) and \( \Delta J = 2n \), where \( L \) is the classical angular momentum, and we consider all trajectories to have the same weight in the final discrete distribution. (ii) “Non-homogeneous binning,” \(^74\) where each trajectory is weighted by a Gaussian-type coefficient such that the closer the \( J_{\text{cl}} \) values to integer values satisfying \( \Delta J = 2n \), the larger the coefficient. Both methods (i) and (ii) allow one to choose \( \Delta J = n \) or \( 2n \) \( (n=0,1,2,...) \). No significant differences in the results have been found using these two methods with the rule \( \Delta J = 2n \), which seems reasonable due to the small energy spacings between the rotational levels of \( \text{N}_2 \). This suggests that the disagreement between theory and experiment for the rotational energy transfer cannot be attributed to deficiencies of the QCT method.

The agreement between the scattering experiments and our 6D adiabatic calculations can also be affected by the use of the frozen surface approximation. Although the phonons seem to play a minor role for dissociative chemisorption, they could be important for rotational excitation, because the energy spacings between the rotational levels are small. As we do not include the phonons in our calculation we can only speculate about their effect using the previous experimental and theoretical results. Low dimensional calculations suggest that the inclusion of phonons in the dynamics increases the reaction threshold. This means that the molecule looses energy to the surface, thus less energy is available for rotational excitation and therefore the inclusion of phonons could lead to less rotational and vibrational excitations. Of course, once the phonons are taken into account the rotational excitation is expected to increase with \( T_s \), the larger \( T_s \) the smaller the transfer of energy from the molecule to the surface is expected, and then more energy is available for rotational excitation. The increase of rotational excitation with \( T_s \) has been observed experimentally. \(^13\)

It has been suggested \(^13\) that the absence of observable vibrational excitation in the experiment could be due to nonadiabatic coupling to e-h pair excitations. This conclusion is partly based on the previous observation of significant vibrational excitation and deexcitation for another “exit” channel system, \( \text{H}_2(\text{D}_2)/\text{Cu}(111) \), \(^20\) for which e-h pair excitations are expected to be unimportant, and also on the comparison between adiabatic and nonadiabatic low dimensional calculations (see above). But, as we have shown in Sec. III, \( \text{N}_2/\text{Ru}(0001) \) presents large differences with the other prototype exit channel system, \( \text{H}_2+\text{Cu}(111) \), and low dimensional calculations cannot be used to describe the dynamics of this system properly. On the other hand, our adiabatic 6D calculations do show more vibrational excitation than the experiments, and we cannot rule out that this is due to the absence of e-h pair excitations in our model. To obtain more insight in the role of phonons and e-h pair excitations, 6+2D calculations should be done in a fashion similar to that used in the 2+2D model of Diekhöner et al., \(^11\) using an appropriate coupling strength parameter describing the nonadiabatic coupling. \(^26\)

### IV. SUMMARY AND CONCLUSIONS

In this paper we have presented a six-dimensional (6D) quasiclassical dynamics study, within the adiabatic approximation, of \( \text{N}_2 \) reacting with and scattering from a \( \text{Ru}(0001) \) surface. The 6D potential energy surface (PES) has been constructed applying a modified Shepard method to a non-uniform set of electronic structure data, which are chosen using quasiclassical dynamics. The electronic structure data were obtained with density functional theory, using the RPBE generalized gradient approximation in a supercell approach.

The dissociative adsorption probabilities computed using 6D quasiclassical dynamics show good agreement with previous experimental results, with a very low reaction probability for incidence energies significantly above the minimum reaction barrier. A comparison with previous calculations using a 2+1D adiabatic model including phonons shows that the inclusion, in both a static description using the hole model (HM) and in the dynamics, of the four DOFs of the molecule associated with the rotation and translation parallel to the surface lowers the reaction probability by two orders of magnitude. Furthermore, the good agreement between the experimental and the HM probability shows that the low reactivity of the system can already be understood by looking only at the static properties of the PES. Our results show clearly that the previous experimental findings can be explained largely within an adiabatic framework, without invoking large nonadiabatic effects, if the six DOFs of the molecule are included in an accurate description of the PES. The low reactivity of the system reflects the high anisotropy and corrugation of the potential, making the barrier a very narrow bottleneck to reaction.

Theoretical angular scattering distributions show the same behavior as observed experimentally. In agreement with experiment, two scattering regimes can be distinguished: one operating at low energy and one at high energies. At high energies the decrease of the maximum of the distribution and the increase of its width with energy are due to the increase of the corrugation seen by the molecules (structure scattering). For low energies, the calculations suggest that the decrease of the width of the distribution with energy is not (entirely) due to the interaction with the surface phonons, because it is also observed in our static surface calculations. Instead, it reflects a decrease of the relative momentum exchange as the incidence energy is increased in a regime where structural scattering does not yet occur.

Finally, whereas our theoretical results show a small ex-
citation of the translation parallel to the surface increasing with $E_1$, in good agreement with the experiment, rotational and vibrational excitations are overestimated by our theoretical calculations. Additional work is needed in which motion in all six $N_2$ DOFs is considered alongside dissipation to phonons and electron-hole (e-h) pair excitations to explain these discrepancies.

Although our study by itself cannot be used to determine in an accurate way the influence of the e-h pair excitations on the interaction between $N_2$ and Ru(0001), it allows us, at least, to determine (assuming the experiments to be accurate and considering the factors that affect the accuracy in the theory) an upper bound to the influence that nonadiabatic effects have on the reactivity of this system. This influence is much smaller than previously suggested by low dimensional calculations: Our calculations suggest that at the highest in-duced reactivity by no more than a factor of 3, rather than by two orders of magnitude as suggested by the previous low dimensional calculations. On the other hand, it is essential to take into account the multidimensional effects (rotation and translation parallel to the surface) in the dynamics for an appropriate description of the system. This reduces the reactivity by two orders of magnitude. The minor role played by nonadiabatic effects in dissociative chemisorption of $N_2$ on Ru(0001) can be understood from recent theoretical work, which strongly suggests that a breakdown of the Born-Oppenheimer approximation should be expected for (i) molecules with high electron spin interacting with a metal surface with a low density of states at the Fermi level, due to spin quenching before the systems interact; and (ii) molecules with intermediate electronegativities, for which the time scale for the electron transfer process and the nuclear motion are comparable. $N_2$ has zero electronic spin, so that nonadiabatic spin quenching is not possible, and it also has a low electronegativity so that no nonadiabatic effects accompanying electron transfer from the surface to the molecule expected.

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