Dissociative chemisorption of methane on Ni(111)

Krishna Mohan, G.P.

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Chapter 1

Introduction

1.1 Introduction

In most chemical reactions aimed at making specific chemicals, one needs to activate the stable reactants (like methane) to convert them into desired products using catalysts. Among the various types of catalysis, the heterogeneous version is attracting wide attention because of its immense industrial importance for the production of many commodity chemicals, e.g. hydrogen, ammonia, sulfuric acid [1]. In heterogeneous catalysis the catalyzed reaction occurs at the boundary between two phases. In this class of catalysis reacting molecules are adsorbed from a gas or liquid phase onto the surface of a solid catalyst (usually a metal). Thus, gas-surface interactions and reactions on metals play a crucial role in the science of heterogeneous catalysis reactions. A wide range of interesting gas-surface reaction systems can be observed, from the inside of a chemical reactor to the outside surface of a space ship. Many industrial processes benefit hugely from catalysis; these processes include the Haber-Bosch process for the production of ammonia, the hydrogenation of edible oils, and various processes within the petrochemical industry such as cracking of crude oil, to name a but a few. Indeed, the catalytic converters in automobiles are nothing but a small gas-surface reaction system which converts harmful exhausts into the less poisonous byproducts, thereby minimizing the environmental hazards.

Catalysis research has a long history. The alchemical era was dominated by the search for the 'philosophers stone' - a mystical catalyst - that could convert cheap metals into precious noble metals. The first successful use of a synthetic catalyst was reported by Valerius Cordus, who used sulfuric acid to catalyze the conversion of alcohol to ether [2]. Apparently, the first report of a gas-surface catalyst was authored by Prof. J. W. Doebereiner, who wrote *"... that finely divided platinum powder causes hydrogen gas to reaction with oxygen gas by mere contact to water whereby the platinum itself is not altered"* [3].

As for many other scientific fields, this area has been gradually strengthened by the development of various experimental techniques. Today, both scanning tunneling microscopy and modern spectroscopic measurements are regularly employed to observe details at the microscopic level of the system [4]. For example, the atomic positions of both the adsorbate and substrate are determined by scanning tunneling microscopes. Many spectroscopic methods, such as sum frequency generation and stimulated Raman pumping are used in conjunction with molecular beam experiments to study the details of 'state-specific' chemistry [5].

The investigation of details of reaction mechanisms in gas-surface systems is therefore now possible. Nevertheless, a full understanding of the reaction dynamics requires accurate theoretical calculations and modeling, and the comparison of theoretical results with experimental data. For instance, for a thorough understanding of a surface reaction, a dynamical simulation has to be performed to understand the femto-/pico-second atomistic level details of the reaction mechanism. With the use of state-of-the-art modeling codes and computers, it is now possible to accurately simulate several spectroscopic and molecular beam experiments of gas-surface systems [4]. Density functional theory (DFT) [6, 7] deserves a special mention here since without it many of the gas-surface theoretical calculations could not be performed, due to the large number of electronic and/or spatial degrees of freedom of the system that needed to be treated, and the demands this puts on the computational resources.

In this thesis we attempt to understand several aspects of the gas-surface physics/chemistry of (a) the dissociative chemisorption of CH_4 on the Ni(111) surface and (b) N_2 dissociation over the Ru(0001) surface. Apart from their industrial importance, these systems are regarded as prototypes for molecular beam and state-specific spectroscopic experiments. We performed both static DFT and dynamical calculations to understand better: (i) the role of the vibrational normal mode specificity and the collision energy dependence of the CH_4 reactivity, (ii) the possible reaction paths and dissociation dynamics of CH_4 and N_2, (iii) the role of different vibrational and rotational quantum states, (iv) the applicability of the Born-Oppenheimer approximation for N_2 dissociation and (v) the applicability of different DFT functionals for these systems.

1.2 Ruthenium and Nickel as industrial catalysts

From various experimental and theoretical studies, the role of Ruthenium catalysts in ammonia production is now reasonably well understood. By using a Ru catalyst, the reaction barrier of N_2 dissociation can be reduced to 1.4 eV from its gas phase dissociation value of 9.8 eV [8]. Since around 2% of the world's annual energy supply is used for making ammonia [9] it is natural to investigate this system in detail, in which the reaction

$$\mathrm{N}_2(gas) \rightarrow 2\mathrm{N}(adsorbed)$$

is the rate limiting step. Further studies of this reaction over the ruthenium surface are still necessary to understand how to avoid catalytic poisoning by steam [1] and to reduce the energy cost [10].

The need for sustainable energy has never been greater [11]. The quest for a green fuel – e.g. hydrogen - has been and remaining a serious global challenge. Although hydrogen could in principle be a 100% green fuel, more than 50% of its production still uses catalytic steam reforming, where methane is the major feedstock and nickel is the catalyst [12]. Unfortunately, this process leads to CO2 emission. In this endothermic process the rate limiting step is

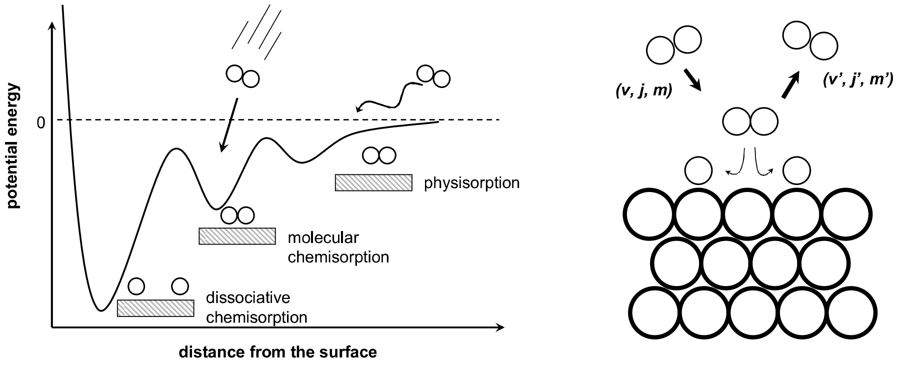
$$\mathrm{CH_4}(gas) \rightarrow \mathrm{CH_3}(adsorbed) + \mathrm{H}(adsorbed).$$

To enhance the rate of this reaction, vibrational excitation of CH_4 is found to be effective by many spectroscopic studies [13, 14, 15, 16, 17, 18] and chemical engineering works [19]. We also note that it has been observed that carbon deposition causes severe problems in the steam reforming process. Interestingly, Ni catalysts used in steam reforming are more resistant to deactivation by carbon deposition if the nickel surface contains a small amount of sulfur or gold [20].

1.3 Energetics and Dynamics at surfaces

1.3.1 Interactions at surfaces

The adsorption of a molecule on a surface - both chemisorption and physisorption - is a central concept in the field of surface science and heterogeneous catalysis. In chemisorption, the molecules stick to a surface by a strong chemical interaction, whereas in physisorption it is by weak interactions such as van der Waals forces (see Fig. 1.1(a)). In other words, physisorption does not involve electron transfer between the molecule and the substrate and hence it is highly non-directional, unlike chemisorption [4]. A typical energy range of chemisorption energies is 0.5 eV or more, while for physisorption it is less than 0.3 eV [21].



(a)

(b)

Figure 1.1: (a) Graphical representation of some gas-surface adsorption interactions, and (b) dissociative chemisorption and scattering events of a diatomic molecule.

The ability of a metal to act as a catalyst strongly depends upon the electronic structure of its surface atoms, with which the incoming gas molecule interacts. Since chemisorption creates new chemical bonds, the electronic structure of the adsorbate and substrate (generally metals) is strongly perturbed by their mutual interaction - the interaction leads to a significant hybridization of the electronic orbitals [22]. To explain how a catalyst works and what the trends are when going from one catalyst-surface/structure to another, one can use molecular orbital (MO) and band structure theory. MO theory provides a fair amount of detailed intuition about the energetics of chemical reactions based on the symmetry properties of MOs and atomic orbitals (AOs). On several transition metals the weakening of the molecular bond occurs through charge transfer from the metal to the empty or antibonding orbitals of the adsorbate molecule. For example, (transition) metals are able to catalyze many thermally assisted reactions (eg. production of cyclo-alkanes). In this case it is necessary to populate the antibonding π (or π^*) orbitals of alkenes to convert them into cyclo-alkanes. This can be done by using a transition metal as a catalyst. In the presence of a transition metal, the electrons from π-orbital of alkenes will pass to the AOs of the metal of the corresponding symmetry (the t_{2g} d-orbitals). This make the reaction thermally permitted.

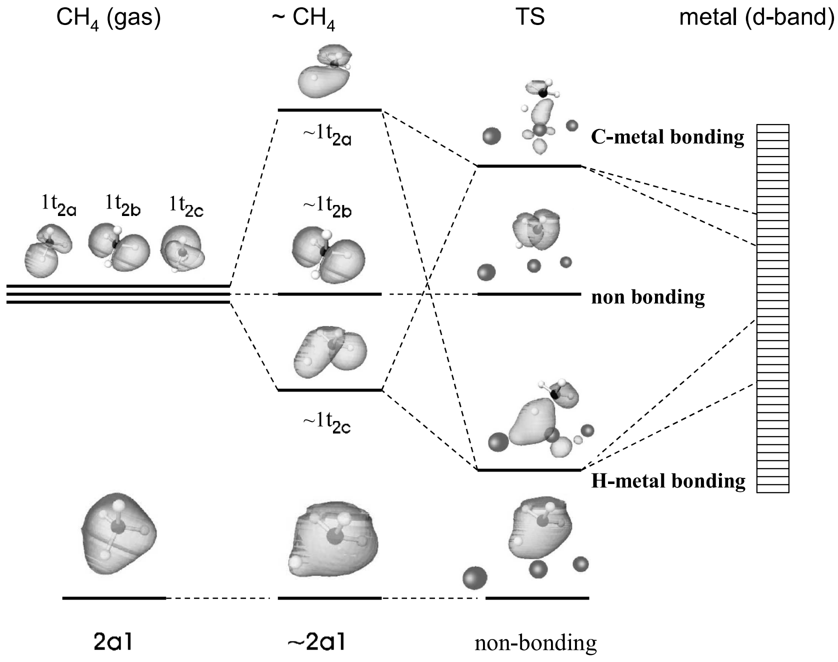


Figure 1.2: One electron Kohn-Sham real eigenstates of methane interacting with a d-band metal. Tildes indicate the distorted molecular orbitals and geometries. Reprinted with permission from A. T. Anghel et al., Phys. Rev. B, 71, 113410. © 2005 the American Physical Society.

In the context of extended MO systems, the local density of states at the Fermi level has been successfully correlated with the reactivity of metal surfaces [23]. To analyze and describe the nature of the chemical bonds, the local density of states or projected density of states are often used. Many models (e.g. Newns-Anderson) have been proposed to provide semi-quantitative results for chemisorption properties [24]. Nowadays many of these approximate methods are predominantly used for explanatory purposes, due to the ease of performing numerical self-consistent calculations based on the density functional theory (DFT) (See Chapter 2). Figure 1.2 depicts a DFT based MO description of the chemical interaction between methane and a transition-metal, in which the Kohn-Sham orbitals of CH_4 interact with delocalized metal orbitals, resulting in C-metal and H-metal bonds.

The adsorbate-surface interaction can be described my many models (using minimal DFT data), such as the *d*-band model developed by Hammer and Nørskov [25]. The model suggests that the degree of orbital overlap with the adsorbate (or the hybridization energy between the bonding and anti-bonding adsorbate states) and the degree of filling of the antibonding states on adsorption determine the reactivity of the transition metals [25].

1.3.2 Dynamic events at surfaces

To understand the detailed reaction mechanisms behind the various dynamics events, one needs to perform dynamics simulations. In this work we only consider ‘adiabatic’ dynamics, in which bond making as well as bond breaking events are described by motion of nuclei on a ground state potential energy surface (PES). Using adiabatic PESs, several surface chemical reactions can be described which occur on a pico-second timescale (e.g. dissociative chemisorption, associative desorption, etc.).

In experimental surface chemistry, much chemical dynamics is studied using molecular beam experiments. Some of the important gas-surface scattering events in the molecular beam experiments are elastic, inelastic and reactive scattering. In elastic scattering there will be no transfer of energy among different degrees of freedom in the reactant molecule and the surface. In the inelastic scattering process, the transfer of energy among degrees of freedom in the system is allowed, but no chemical reaction occurs. A special process that may occur in molecular-surface scattering is diffraction, which is due to the periodic nature of the surface.

Many molecular scattering events are accompanied by rotational or vibrational (de-) excitations (see Fig. 1.1(b)). For instance, in a scattering event the vibrational state of a molecule may change and the molecule may be vibrationally excited or de-excited. A vibrational excitation can only occur if there is sufficient energy available in the collision, since the total energy must always be conserved. The energy released from the vibrational de-excitation can flow to other degrees of freedoms, like rotation and translation. A rotational (de-) excitation can occur only when the molecule-surface potential is anisotropic. Energy that is released from a rotational de-excitation can also flow to other degrees of freedom, like translation and vibration.

Other important dynamics events that may occur on a surface are diffusion and desorption. Energy transfer from the surface lattice to the translational coordinates of the adsorbents may cause diffusion and desorption. These processes

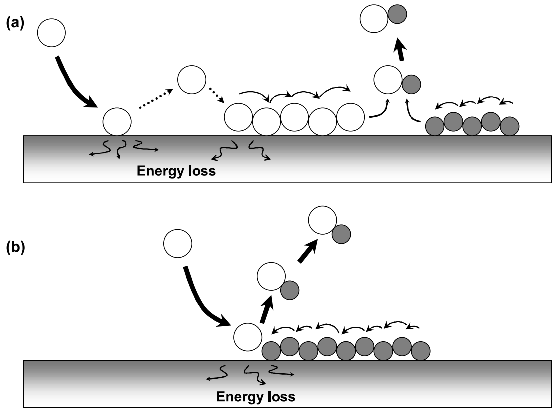


Figure 1.3: Schematic illustrations of (a) the Langmuir–Hinshelwood and (b) Eley–Rideal mechanisms in gas–surface dynamics.

involve bond breaking with the surface and have larger energy barriers than physisorption. Generally, diffusion energy barriers are found to be smaller (≈0.3 eV) on terraces, whereas barriers for diffusion across steps are much higher (≈1 eV) [26]. Desorption and adsorption are related to each other by time-reversal symmetry. The principle of detailed balance [27, 28] relates adsorption to desorption (at a particular coverage and temperature). It has been reported that thermally or photochemically produced electron-hole pairs can induce associative desorption [29] . DFT studies indicate a possible role of subsurface atoms in the desorption process, along with the importance of lattice relaxation [30].

To explain important reaction events at surfaces macroscopic reaction models are widely used. For example, a reaction would be considered to be of the 'Langmuir–Hinshelwood' type if both reactants first adsorbed onto the surface, and then reacted to form the products after equilibration with the surface. If one reactant first adsorbs, and the other then reacts with it directly from the gas phase, the reaction is of the 'Eley–Rideal' type. See Fig. 1.3 for a schematic illustration of these mechanisms. In the case of steam reforming reaction, the experimental data have a good fit with the 'Langmuir–Hinshelwood' model [31]. In general, the Eley–Rideal mechanism is more exothermic than the Langmuir–Hinshelwood mechanism [32]. In these two reaction-mechanisms at least one of the reactants, whether it is a molecule or a single atom, is already adsorbed on the metal. The process of adsorption of molecules or atoms on metals, which must precede these reactions, is one of the major steps in any gas-metal reactions.

To provide a detailed understanding of the origin of mode-specific disposal of energy and to understand the relative importance of kinetic energy versus internal energy (rotational or vibrational), a detailed understanding of the location of the transition state and motion of the nuclei over the PES is required. For instance, H_2 dissociation on nickel surfaces shows no vibrational enhancement [33]. On copper surfaces, however, vibrational enhancement of dissociation of H_2 has

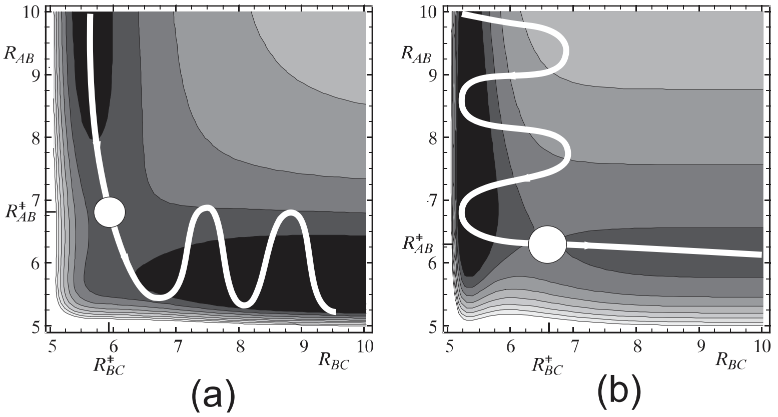


Figure 1.4: An illustration of the Polanyi's rule for an early barrier (a) and a late barrier system (b), for a collinear reaction, A + BC → AB + C, as a function of reaction coordinates, R_{AB} and R_{BC}. The transition state is indicated by the white dots with the trajectories (the white curves). Figure reprinted with written permission from L. Piela, Ideas of Quantum Chemistry, Elsevier, Amsterdam (2007). © L. Piela.

been demonstrated using molecular beam experiments [34]. This mode of energy utilization can be qualitatively predicted by Polanyi's rule. The rule suggests that reactions which possess '*early*' barriers will be promoted preferentially by initial translational excitation, while reactions with '*late*' barriers will be promoted preferentially by reactant vibrational excitation [35]. A schematic illustration of Polanyi's rule is shown in Fig. 1.4.

1.4 Major experimental results

In this section a summary of the major experimental results principal to the main work of this thesis is presented. The 'state-resolved' reactivity measurements of methane demand special attention because they provide many insights on vibrational mode-specific and bond-selective chemistry. In these experiments selective excitation of particular vibrational and rotational quantum states as well as local modes of CH_4 are possible. Although most of these experiments on CH_4 involve nickel surfaces, a variety of similar experimental results have been obtained for many other metal surfaces. For example, the molecular beam experiments of CH_4 dissociation on W(110) [36], Pt(111) [37] and Ru(0001) [38] surfaces all provide similar results to those on nickel surfaces, and show both translational and vibrational activation of the reaction.

The first state-resolved experiment on CH_4 + Ni was reported by Juurlink et al., using an infrared (IR) laser. They observed that on Ni(100) laser-excited CH_4 (excited to $v = 1$ of the ν_3 C-H stretching vibration) dissociates with up to 1600 times the probability of molecules that do not absorb IR light, i.e., CH_4 in its ground vibrational state [15]. A preference for vibrational over translational energy activation in this reaction was observed by Smith et al. [39] for the Ni(100) surface. They reported that CH_4 in its vibrational ground state requires 0.466 eV of translational energy to attain the same reactivity enhancement provided by

0.373 eV of ν_3 vibrational energy. Another study by Juurlink et al. [14] reported the efficiency of the ν_3 C-H stretch at promoting dissociative chemisorption on Ni(111) and Ni(100) surfaces with respect to the $3\nu_4$ bend vibrational state (see Fig. 1.5(a)). Even though $3\nu_4$ contains 30% more energy than the $1\nu_3$ state the results showed the $3\nu_4$ state to be at least 4 times less reactive than $1\nu_3$.

A recent work of Killelea et al. [16], which used CHD_3 molecules in a molecular beam with one quantum of C-H stretching vibration (ν_1), reconfirmed that the excitation of the C-H stretch in CHD_3 favors the dissociation. This work also suggests that the symmetric and antisymmetric stretches in methane or its isotopologues lead to very different reactivities. Indeed, molecules with the symmetric stretching vibration excited with one quant can be as much as 10 times more reactive than ones with the antisymmetric stretch excited with one quant at similar collision energies. [17]

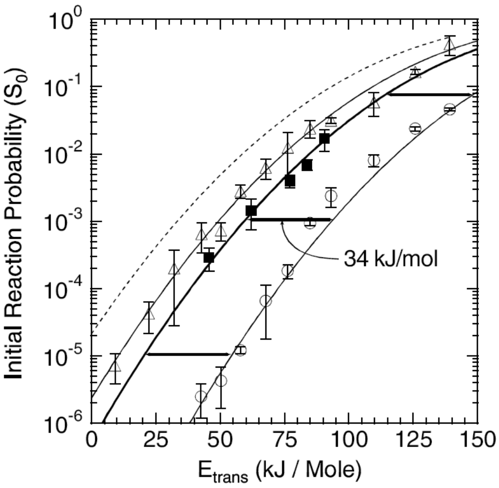
Laser experiments based on stimulated Raman pumping of CD_2H_2 excited to the |20> and |11> vibrational states, and incident on a Ni(100) surface, showed a higher reactivity (around 5 times) of the |20> state [18] (see Fig. 1.5(b) for a comparison). A stimulated Raman pumping experiment by Maroni et al. [17] showed that the reactivity of symmetric-stretch ($1\nu_1$) excited methane is about an order of magnitude higher than that of methane excited to ν_3 state. They also reported that the $1\nu_1$ and the $2\nu_3$ states have a similar reactivity.

All the discussed vibrational state-specific experiments indicate a failure of the statistical model [40, 41] used to calculate the reaction rate for the dissociative chemisorption. The statistical model treats the vibrational and translational energy on an equal footing, arguing that the reactivity is solely determined by the total energy of the molecule. This model therefore excludes the possibility of ‘mode-specificity’ in the reaction. Instead, the experiments demand full dimensional dynamical calculations to capture the necessary physics of the reactive CH_4[5].

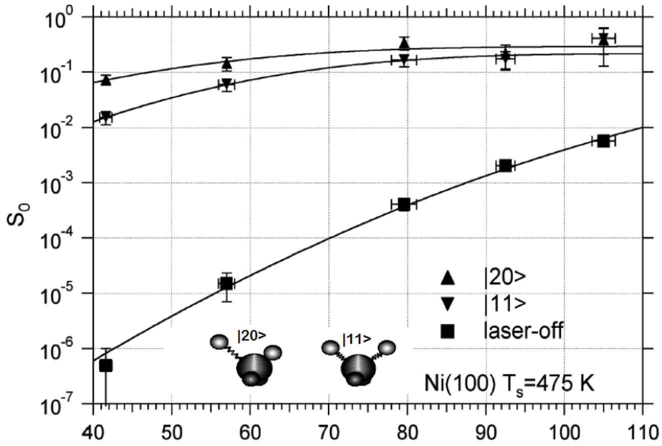
For the N_2+Ru(0001) system, the molecular beam experiments [42, 43, 44] showed a slow increase of the sticking coefficient (S_0) with incident kinetic energy (E_i), where $S_0 < 0.01$ at E_i up to 4.0 eV (see Fig. 1.6). From these experiments it can be noted that (1) S_0 is almost independent of the surface temperature, which suggest that phonons play a minor role in this system, (2) an increase of the nozzle temperature from 700 K to 1800 K increases S_0 by an order of magnitude, which gives evidence for vibrational as well as translational activation, and (3) a higher vibrational efficacy ($\approx$1.6) indicates that the vibrational excitation may promote reaction more efficiently than increasing E_i,- a consequence of the late barrier.

1.5 Theoretical approximations

In this section, we consider the two major approximations employed in the work. Since all the calculations were done using a static metal surface (Ni or Ru), the



(a) State-resolved initial reaction probability for CH_4 molecules incident on Ni(111) surface in ground state (circles), ν_3 (triangles), and $3\nu_4$ (squares). Etrans denotes incident kinetic energy normal to the surface. Reprinted with permission from L. B. F. Juurlink et al., Phys. Rev. Lett., 94, 208303. © 2005, the American Physical Society.



(b) The state resolved sticking coefficients for CH_2D_2 in the |20> |11> and ground vibrational states on Ni(100) surface as a function of incident kinetic energy normal to the surface. S_0 denotes initial reaction probability. Reprinted with permission from R. D. Beck and T. R. Rizzo, Chimia, 58, 306. © 2004, Swiss Chemical Society.

Figure 1.5: Results of two important state-resolved reaction probability measurements of CH_4 dissociation on nickel surface.

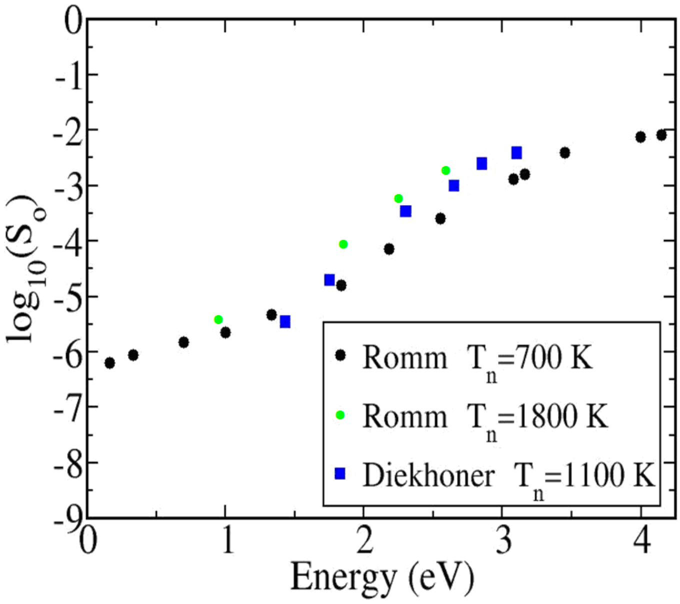


Figure 1.6: The experimental dissociation probability for N_2 on Ru(0001) plotted logarithmically vs. the incident normal energy for three different nozzle temperatures.

possibility of interaction between the molecule and the surface lattice vibrations is excluded. In other words, phonon interactions were neglected. In addition to this, we also neglected the possibility of electron-hole pair excitations in all our calculations.

The coupling of phonons to the motion of adsorbing species can often be neglected in the case of adsorbates with lower mass. For example, theoretical work by Dohle and Saalfrank [45] showed that the effects of including phonons in the calculation of reaction probabilities at 0 K is negligible in some diatomic molecule-surface systems such as dissociation of hydrogen isotopomers on copper. In their surface oscillator model calculations including phonon motions, they found a shift of the reaction probability curve of H_2 with 0.02 eV - which is within the error bars of the current supercell approaches of the DFT [46]. A recent experiment by Killelea et al. [47] on CH_4/Ni(111) revealed the surface temperature dependence of methane activation on Ni(111). In their vibrational state resolved measurements they observed an increase of the reactivity of CH_4 by up to 8 times, when the surface temperature was increased from 90 to 475 K. These results support the DFT calculations [48, 49] that predict an important role for lattice deformation in transition state access for CH_4/metal systems. The neglect of phonon interactions in this system is therefore not justified if quantitative accuracy is desired.

In the context of the N_2/Ru(0001) system, the exclusion of phonons can be considered as a reasonable approximation. Although N_2 is a heavy molecule and some energy exchange with phonons could be expected, experiments on Ru(0001) show the dissociation probability of nitrogen to be almost independent of surface temperature [42, 50].

Another major approximation in this work is the neglect of electron-hole (e-h) pair excitation. E-h pair excitation plays a crucial role in many systems such as photocatalysed dissociation of water [4]. Experiments show direct evidence for nonadiabatic effects in molecule-surface scattering in which e-h pair excitations accompany chemisorption of molecules [51]. The electron emission from low work function metal surfaces (e.g. Cs/Au(111)) accompanying scattering of highly vibrationally excited molecules (e.g. NO) with high electron affinity also points to considerable nonadiabatic coupling of nuclear motion to electronic excitations at metal surfaces [52]. In all of our dynamical simulations we assumed that the electrons stay in their electronic ground state. This intrinsically avoids the treatment of the electronic excitations in our study. In general, neglecting electron-hole pair excitations is a reasonable approximation in the case of adsorption on semiconductors and insulators [21], but its significance in gas-metal reactions is under ongoing debate [53]. This approximation is considered to be reasonable in the CH_4/Ni system [54, 55, 56], because of (1) the low electron affinity of the CH_4 precursor and (2) the absence of the chemisorption wells in front of the barrier to reaction[57].

In the N_2/Ru systems, the influence of nonadiabatic effects on molecule-surface reactions has become a hot topic. The experimental results for this system suggest the possibility of e-h pair excitations in the Ru surface [43, 44]. For example, (1) the system exhibits a very low reaction probability (10^{-2}) [42, 43] even when the incident energy of N_2 reaches a value of 4 eV - which is almost twice as high as the reaction barrier, (2) only a small degree of vibrational excitation is seen in molecular beam experiments on N_2 scattering from Ru(0001) [58]. The latter result is unexpected for a late barrier system, and to interpret these results it is assumed that incident energy dissipation to e-h pair excitations occurs. Furthermore, laser assisted associative desorption (LAAD) experiments [43] suggested that 2/3 of the energy used by N_2 to overcome the barrier was lost to the surface, which was also attributed to e-h pair excitation.

1.6 Outline and major results of this thesis

This thesis deals with two different dissociative chemisorption reaction systems viz., (1) CH_4/Ni(111) and (2) N_2/Ru(0001). In this section, we summarize the main results obtained and discussed in this thesis. The theoretical methods used to perform the calculations, such as DFT, potential energy surface (PES) fitting, and classical and quantum dynamics, are discussed in **Chapter 2**.

In **Chapter 3**, we investigated the vibrational mode specificity for dissociative chemisorption of CH_4 on Ni(111). It should be noted that in our calculations in some cases we made a comparison between theoretical data for the Ni(111) surface and experimental data for the Ni(100) surface regarding the effect of vibrational pre-excitation. Although the Ni(100) surface is more reactive than the Ni(111) surface, for qualitative purpose this comparison can be justified. For example, the $3\nu_4$ state is less reactive than $1\nu_3$ on both Ni(100) and Ni(111) [14].

This work is the first full-dimensional (with respect to the degrees of freedom of the molecule) study for analyzing the various normal modes along a minimum energy path for a dissociative chemisorption reaction of a polyatomic molecule. In the plane-wave DFT calculations we used the PW91 functional [59], and we made sure that the point-group symmetry of the dissociating molecule-surface system is preserved throughout the reaction path. We used nudged elastic band and steepest descent algorithms to obtain a dense reaction path.

Previous DFT calculations for the reaction barrier and transition state geometry [54, 20] are in good agreement with our results. The minimum energy path (MEP) displays a late barrier of 1.09 eV, which is reduced to 0.95 eV after zero-point energy corrections, and a considerable CH bond elongation was found at the transition state [54, 20] . A substantial "motion" along the different vibrational coordinates was observed on the way to the transition state. A vibrational analysis was performed along the MEP and it revealed a number of avoided crossing regions. We studied the nature (adiabatic/diabatic) of these different crossing regions in detail by calculating the Massey parameter and velocity. We found that pre-exciting the symmetric stretch vibration should be approximately 3 times as efficient at promoting reaction as pre-exciting the asymmetric stretch vibration. We also found indications as to why the vibrational bend modes are less efficient at promoting reaction than the stretch vibrations. Some of our results are similar to those from a previous study [60] in which the authors used a semi-empirical PES and a vibrationally adiabatic model. An important finding is the 'quarantining' of the vibrational energy in the methyl group in the case of the asymmetric excitation of the ν_3 mode. In the supplementary section of the chapter, we discussed the equivalence of vibrational eigenfunction and Cartesian normal mode eigenvectors, and a procedure to fit the Hessian matrix elements.

Chapter 4 describes a quantum dynamics study of methane on Ni(111) using a multiconfiguration time-dependent Hartree (MCTDH) method [61, 62] employing a full-dimensional (with respect to the CH_4 degrees of freedom) PES. The PES was created using DFT with the RPBE (revised Perdew-Burke-Ernzerhof) functional [63]. The RPBE functional gave a barrier of 1.38 eV. The modified Shepard interpolation scheme [64] was used to fit the 15D PES. In contrast to many other works in which the CH_4 was generally treated as a pseudo-diatomic [65, 66, 67], we modeled CH_4 as a polyatomic molecule. A 15D kinetic energy operator was derived that does not contain singularities in the operator and includes rotational and Coriolis couplings.

In our reduced dimensionality dynamics calculations we modeled the dissociative chemisorption of CH_4/Ni(111) at the atop site. Using some rigid constraints we derived two dimensional (2D), 3D and 4D Hamiltonians to perform the MCTDH calculations. We found that only four degrees of freedom evolve strongly along the 15D minimum energy path, viz. (1) the distance of the center of mass of the molecule to the surface, (2) the dissociative C-H bond distance, (3) the polar angle of orientation of the molecule and, (4) the bending angle between the dissociative C-H bond and the CH_3 umbrella. The comparison of our results with those of Xiang et al. [68, 69] is generally good. The helicopter motion of the CH_3 symmetry axis is found to be less efficient than its cartwheel motion at promoting the reaction. By comparing the vibrational efficacies from the 2D, 3D and 4D models, it can be seen that the efficacies of the 2D model are too small compared to the experimental results, even though the results are improved by the inclusion of a bending mode. In the 3D model, the dissociation probability appears to be an increasing function of the initial vibrational energy whatever the vibrational mode excited. The effect of the bending vibrations was correctly described in the 4D model at intermediate collision energies (1.1-1.4 eV), where the polar orientation of the molecule is explicitly described. In addition to this, for small energies, the reactivity is almost independent of the total angular momentum J in the 4D model. Finally, our results indicate the necessity of including additional rotational and translational degrees of freedom in our model to obtain better agreement with experiments.

Chapter 5 presents six-dimensional quasi-classical dynamics calculations of nitrogen dissociative adsorption on Ru(0001). The main goal of this work was to check the applicability of the Born-Oppenheimer approximation in a prototype activated dissociation reaction. All the DFT calculations were carried out by applying the RPBE functional. The PES was fitted by applying a modified Shepard interpolation method [64]. We performed quasi-classical trajectory calculations [70], to describe the vibrational motion of the N_2 molecule.

We found that the reaction barrier is located far in the exit channel. The value of the intramolecular distance at the minimum barrier geometry (rb) is greater than the equilibrium bond distance by 1.3a0 for N_2/Ru(0001) (rb≈3.4a0). The DFT barrier is found to be very high ($\approx$ 2 eV). According to our calculations the low reactivity of the N_2/Ru(0001) system is a result of the large corrugation and anisotropy of the PES near the minimum barrier. The theoretical and experimental angular scattering distributions show a similar behavior. In addition to this, our results show a small excitation of the translation parallel to the surface increasing with incidence energy of the molecule. However, rotational and vibrational excitation are overestimated by our theoretical calculations. Our calculations suggest that at the highest incidence energies considered, e-h pair excitations diminish the reactivity by no more than a factor of 3, in contrast to the two orders of magnitude suggested by the previous low-dimensional calculations of Diekhoner et al [43, 58]. Comparison to these low-dimensional calculations shows the importance of taking into account the multidimensional effects of N_2 rotation and translation parallel to the surface.

1.7 Outlook

In Chapter 3, we discussed the role of the fundamental vibrations of methane to promote the dissociative chemisorption of CH_4 on the Ni(111) surface employing the PW91 functional. Comparing these results to those of plane wave DFT calculations [71] using the RPBE functional, we found that the PW91 and RPBE functionals give similar frequencies and crossing regions. However, the PW91 functional seems slightly more suitable since it does not overestimate the reaction barrier, which is related to the theoretical molecular velocity along the reaction coordinate. The major challenge we faced in this project was the presence of numerical noise in the Hessian matrix elements, due to inaccuracies in the DFT gradients arising from the grid-representation to calculate exchange-correlation energies [72]. Although the noise in the forces can be reduced by using fitting methods, the DFT codes that calculate Hessians analytically by the linear response formalism give more accurate Hessians [71]. From this work we learned the importance of using the point-group symmetry of the reacting molecule-surface system to analyze the characters of the different vibrational modes, which are very sensitive to the molecule-surface geometry. Since our vibrational analysis was based on the harmonic approximation, the role of the vibrationally overtone states [60] could not be addressed properly. One approach to solve this issue would be to find a method to obtain the vibrational wavefunction of CH_4 for the overtones or combination vibrations without the knowledge of a full-dimensional PES.

A similar approach to study the effect of vibrational modes and its coupling to the reaction coordinates for gas-phase systems is reported elsewhere [73]. This method is based on Coriolis and curvature coupling constants, which were obtained from similar numerical data as used in our work (i.e., MEP geometries, energies, forces and Hessian matrices). These quantities can also be used to construct a 'reaction path Hamiltonian' (RPH) [74], which eventually can be used to calculate the rate of the reaction as a function of temperature. Since statistical models are based on the wrong assumptions, the RPH approach would be an alternative to calculate the rate constant. Interestingly the RPH approach is now well established for handling multidimensional systems [75]. Trying one or several of these approaches for molecules interacting with surfaces would be an important step forward for understanding the role of vibrational excitations on the reactivity [76].

It would also be interesting to study the changes in the molecular orbitals during reaction. For example, the reaction path calculations showed that the hydrogen atom moved to the hcp site earlier than the CH_3 fragment to the fcc site. A charge density difference plot could possibly add to the understanding of this finding based on the concept of charge redistribution [4] of the molecular fragments. Furthermore, it would be interesting to seek an explanation of why the Ni atom moves out of the surface (in the CH_4–Ni transition state geometry) in terms of the charge densities.

In Chapter 4 we presented some quantum dynamics results for the CH_4/Ni(111) system. Although we used a full-dimensional PES (with respect to the CH_4 degrees of freedom), we treated only up to four degrees of freedom in the dynamics. A major approximation we made was that we used a frozen nickel surface. Several studies from the Jackson group indicate the involvement of the Ni atoms during the dissociation process [77, 49]. Likewise, recent quantum dynamical calculations using the surface oscillator model to include phonons clearly showed that phonons affect the barrier height [49]. Thus, a natural step to extend our efforts would be to go beyond the static surface model in the description of the dissociation dynamics. Another natural step would, of course, be to increase the number of degrees of freedom of CH_4 treated in the dynamics. The necessity of high-dimensional studies has already been pointed out by the early works of Luntz and Harris [65] and Carré and Jackson [67].

Another step would be to improve our PES by e.g. adding more points, especially near the transition state and in the exit channel. An 'n-mode' representation [78] of the PES could be necessary for future MCTDH calculations, because a non-separable PES with more than 6 degrees of freedom cannot be used in MCTDH in its most efficient form. In this work we treated methane as a polyatomic molecule. By including even more degrees of freedom one opens up the possibility for studying many different properties. For example it could be possible to study the effect of combined excitation of stretch and bend states of CH_4 on reactivity.

In Chapter 5 we described the result of quasi-classical trajectory calculations on the dissociative chemisorption of N_2 on Ru(0001) based on a DFT PES and treating all six molecular degrees of freedom. The multidimensional effects of N_2 rotations and translations parallel to the surface dramatically lowered the reactivity of N_2 on Ru(0001) compared to earlier low-dimensional calculations. This lead to good agreement between electronically adiabatic theory and experiment, suggesting a much smaller role for nonadiabatic effects than previously assumed. This also suggests that the RPBE functional performs well in this system. Our result is in agreement with the recent findings by J. I. Juaristi et al. [79] on the 6D reactive dynamics of H_2 on Cu(110) and N_2 on W(110). Their calculations suggested that the contribution of electronic excitations is marginal and, therefore electronic adiabatic calculations are still meaningful.

It is reasonable to say that the theoretical description of nonadiabatic phenomena has not yet reached the same level of maturity as the treatment of electronic ground-state properties in the field of gas-surface chemistry. One could also aim to verify our quasi-classical dynamics results by applying quantum dynamics using the MCTDH method. Finally, in this work we used a PES based on the orthogonalized plane wave DFT [63]. However, a PES based on the projector augmented-wave DFT might be faster to calculate and prove more accurate [80].

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