Vibrations and Rotations of Diatomic Molecules at Surfaces

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Cover:
A snapshot picture of the calculated two-dimensional wavefunction for
D$_2$ scattering from a Cu surface. The horizontal coordinate is the angle,
$0 < \theta < 2\pi$, between the molecular axis and the surface, and the vertical
coordinate is the distance, $z$, between the molecule and the surface, with
$z = 0$ at the bottom and $z = 10$ Å at the top.

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ABSTRACT

The dynamics of atoms and molecules at surfaces is a topic of much scientific and technological interest, with application in, for instance, heterogeneous catalysis and epitaxial growth. The dynamics is governed by a multidimensional potential energy surface (PES), which is often characterized by the bound vibrational and rotational properties of the adsorbate. Comparisons between calculated and measured vibrational and rotational properties can yield a detailed description of the PES and the interaction behind the adsorption.

This thesis presents theoretical studies of the vibrational and rotational character of diatomic molecules at surfaces. Two and three-dimensional PESs have been constructed for non-dissociative adsorption of H$_2$ and N$_2$ on Cu(111) and for H$_2$ on Cu(510), using density functional theory (DFT). The adsorbate dynamics for these systems, and for H$_2$ on Cu(100), has been investigated using time-dependent wavepacket calculations, which are described in detail. For CO chemisorbed in the c(4 × 2) structure on Pt(111), the bound vibrational modes have been studied within the harmonic approximation, using DFT.

For H$_2$ on flat Cu surfaces, calculated dipole activity for vibrational motion in the physisorption well, shows non-negligible intensities for transitions to continuum levels, indicating the possibility of direct photodesorption. Calculated rates for such a process agree well with measured rates of desorption, induced by infrared radiation from the walls of a UHV chamber. For H$_2$ at the step edge of Cu(510), calculations reveal the existence of states, in which the molecule is confined to perform two-dimensional quantum rotation. Rotational and vibrational transition energies of these states agree well with results from EELS measurements. Scattering calculations show that an observed large difference in the probability for rotational inelastic scattering of D$_2$ and N$_2$ from Cu(111), is due to the difference in the rotational constant of the molecules. The calculated vibrational modes of c(4 × 2) CO-Pt(111) show small energy splittings among lateral modes that have previously been assumed to degenerate, based on the local adsorption symmetry, and a reassignment of previously measured vibrational energies to low-energy modes is suggested. Two modes which have previously been assumed to be dipole forbidden are found to be weakly dipole active.

Keywords: physisorption, chemisorption, photodesorption, surface scattering, potential energy surfaces, wavepacket calculations
LIST OF PUBLICATIONS

This thesis consists of an introductory text and the following papers:

I. Direct infrared photodesorption of physisorbed $H_2$
   M. Hassel, K. Svensson, M. Persson, and S. Andersson,

II. Infrared radiation-induced desorption of physisorbed hydrogen molecules
    M. Hassel and M. Persson,

III. Two-dimensional quantum rotation of adsorbed $H_2$
     K. Svensson, L. Bengtsson, J. Bellman, M. Hassel, M. Persson, and
     S. Andersson,

IV. $H_2$ adsorbed in a 2D quantum rotor state on a stepped copper surface
    L. Bengtsson, K. Svensson, M. Hassel, J. Bellman, M. Persson, and
    S. Andersson,

V. Coherent elastic and rotationally inelastic scattering of $N_2$, $O_2$ and $CH_4$ from a 10 K Cu(111) surface
   T. Andersson, F. Althoff, P. Linde, M. Hassel, M. Persson, and
   S. Andersson,

VI. Vibrational modes of $c(4\times2)$ CO-Pt(111) from first principles calculations
    M. Hassel,
Specification of my contributions to the included papers:

I. I performed the calculations. The paper was written jointly.

II. I performed the calculations. The paper was written jointly.

III. I contributed to the correct interpretation of experimental data by performing model calculations for constrained 3D rotor states.

IV. I performed the 1D and 3D wavepacket calculations of bound state energies and wavefunctions. The paper was written jointly.

V. I performed the calculations and wrote the corresponding theory text.

VI. I formulated the problem, performed the calculations and wrote the text.
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Chapter 1

Introduction

One of the goals in surface science is to understand the nature of the forces that act on, and among, atoms and molecules (adsorbates) at surfaces. For instance, the pathways of surface dynamical processes, including technologically important processes such as heterogeneous catalysis, oxidation and epitaxial growth, are governed by these forces. An understanding of the interatomic forces and the associated dynamics, can help to comprehend, predict and, ultimately, control dynamical processes at surfaces.

To understand the dynamics of a surface process, it is in general necessary to systematically study the elementary steps of the process in terms of simple model systems. A surface process is often quite complex, but can be decomposed into a number of elementary processes, such as adsorption, vibration, diffusion, rotation, reaction and desorption. In practice, these elementary processes are studied by identifying and considering simple model systems. For instance, the vibrational dynamics of CO on Pt surfaces has been investigated in detail with CO molecules adsorbed in ordered structures on well-characterized single crystal surfaces.

The forces among atoms can be described in terms of a potential energy surface (PES), when neglecting electron excitations. For many important elementary processes, PESs can nowadays be calculated without experimental input, using the celebrated density functional theory (DFT), for which Walter Kohn was awarded the 1998 Nobel Prize in Chemistry. For instance, the energy barrier for dissociation of $\text{H}_2$ on Cu has been calculated using DFT [1,2], and found to be in good agreement with experiments.

Investigations of the vibrational and, in the case of molecules, rotational dynamics of adsorbates, which are the subjects of this thesis, provide an important interplay between a theoretical description of a PES and experiments. For instance, because PESs cannot be calculated completely for the physisorption regime of the adsorbate–surface interactions, comparisons be-
tween calculated and measured vibrational and rotational energies of adsorbates have provided valuable input for constructing physisorption PESs. Similarly, interpretations of results from vibrational and rotational spectroscopic experiments, can be greatly facilitated by calculations of the vibrational and rotational dynamics of adsorbates, based on calculated PESs. Within the work presented in this thesis, PESs have been constructed for H\textsubscript{2} and N\textsubscript{2} on Cu surfaces, and quantum dynamical calculations have been performed on the PESs. The results, in terms of vibrational and rotational dynamics, have been used for interpretation of results from spectroscopic experiments and scattering experiments. A calculation of the vibrational modes of CO chemisorbed on a Pt surface has been performed, initiated by several issues that were left unresolved from available vibrational spectroscopic experimental data.

Investigations of the forces that act on an adsorbate irradiated by light, have become a field of intense research due to the development of laser technology [3,4]. The laser provides a high-intensity beam of photons with high energy resolution. These properties of the laser suggests the possibility of inducing surface processes by selective excitation, or breaking of specific bonds. However, in many cases the energy of the initial excitation is thermally equilibrated with the surrounding of the adsorbate, before the onset of the desired reaction.

Of high technological and scientific interest are the processes that are of a non-thermal nature. These processes occur on a time-scale ($\sim 10^{-15}$ s) that is much shorter than for the thermal equilibrium process. Non-thermal surface processes are now readily observable in real time, due to the recent development of femto-second lasers, for which Ahmed H. Zewail was awarded the 1999 Nobel Prize in chemistry. The ability to open new reaction pathways using femto second lasers has also recently been demonstrated [5]. In the work presented in this thesis, an investigation, based on both theory and experiments, of non-thermal photodesorption, has been performed for H\textsubscript{2} physisorbed on Cu.

The thesis is organized as follows: In Section 2.1, adsorbate–surface interactions in the physisorption regime is discussed, with particular emphasis on the vibrational and rotational properties of physisorbed diatomic molecules. Studies of surface scattering, dipole activity, and direct photodesorption of physisorbed molecules, are presented. In Section 2.2, adsorbate–surface interactions in the chemisorption regime are presented, and properties of the vibrational and rotational dynamics of chemisorbed diatomic molecules are discussed. Studies of the vibrational modes of CO on Pt, and the rotational and vibrational dynamics of H\textsubscript{2} adsorbed at a stepped Cu surface, are presented. Section 3.1 describes the theories behind the quantum dynam-
ics calculations. The numerical method of one set of these calculations—the time dependent wavepacket calculations—is described in Section 3.2. Finally, in Section 3.3, the theory and method of the DFT calculations are briefly described.
Chapter 2

Adsorption interaction

2.1 Physisorption

2.1.1 Origin and nature of physisorption interaction

The weakest form of interaction between an adsorbate and a surface is the physical adsorption (physisorption) interaction. This interaction originates from attractive van der Waals forces that act between the surface and the adsorbate at large separations. At present, there exists no complete theoretical method for treating the physisorption interaction. The exchange and correlation energy functionals that are used within density functional theory (DFT) today, cannot correctly describe the van der Waals interaction, although work is in progress to develop new energy functionals that include this interaction [6]. It has been found, however, that the generalized gradient approximation (GGA), which introduces some non-local effects in the exchange and correlation functionals, can give reasonable descriptions of adsorption energies and bond lengths typical for physisorption [7]. The commonly accepted praxis for describing the physisorption interaction is based on a superposition of two branches of the interaction—the asymptotic part of the long-range van der Waals attraction and the short-range Pauli repulsion—which are treated by separate theories.

The attractive van der Waals force is a quantum effect that appears between two charge neutral and non-polar species, as a result of quantum fluctuations in their charge distributions. A fluctuation in the charge distribution of one of the species results in a dipole field, which polarizes the other species, and these correlated charge fluctuations result in an attractive Coulomb interaction between the two species. For two particles, separated by a distance, $R$, that is large compared to the size of the particles, the interaction energy $V_{vdw}$ varies as $V_{vdw} \propto -1/R^6$ [8,9]. For a particle far outside a flat surface
of a metallic or dielectric material, the variation of the van der Waals energy with the distance, $z$, between the particle and the surface, is given by

$$V_{vdW} = -\frac{C_{vdW}}{(z - z_{vdW})^3}. \quad (2.1)$$

Here, $C_{vdW}$ characterizes the strength of the van der Waals attraction and $z_{vdW}$ defines a reference plane that depends on the electronic response properties of the surface region [10]. $C_{vdW}$ can be calculated from the substrate dielectric function and the dynamical polarizability of the adsorbate, and tabulations of $C_{vdW}$ are available for various adsorbates and substrates [11]. The expression in Eq. (2.1) is only valid asymptotically far outside the surface and, in particular, it diverges at $z = z_{vdW}$. In reality, the attraction saturates close to the surface, due to the finite size of the adsorbate. To introduce this saturation and obtain a description of the attractive interaction that is valid also in the vicinity of the equilibrium distance between the adsorbate and the surface, the expression in Eq. (2.1) is commonly weighted by a damping function $f_2$:

$$V_{vdW}(z) = -C_{vdW} f_2(\frac{2k_c(z - z_{vdW})}{(z - z_{vdW})^3}). \quad (2.2)$$

Here $k_c$ is related to the inverse size of the adsorbate, and the damping function is defined by

$$f_N(x) = 1 - e^{-x} \sum_{n=0}^{N} \frac{x^n}{n!}. \quad (2.3)$$

The damping function vanishes as $x^{N+1}$ for small $x$, and it tends to unity for large $x$. This kind of damping function was first used by Tang and Toennies [12] for atomic pair potentials. The damping function was introduced for the physisorption interaction between helium atoms and metal surfaces by Nordlander and co-workers [13], who also used this function in describing physisorption of $H_2$ on various metal surfaces [14,15].

As noted, the van der Waals treatment is not valid at short distances between the adsorbate and the surface, but instead new interactions become important, as the electron states of the adsorbate and the substrate start to overlap. A chemically inert adsorbate will then experience a repulsive force from the surface, leading to the formation of a physisorption well at the surface. This repulsive force originates from the Pauli principle, which states that the electron states of the adsorbate and the substrate must be orthogonal. The orthogonalization costs energy, because the electrons acquire a higher kinetic energy, resulting in a net repulsion between the adsorbate and the substrate.
The repulsive part of the physisorption interaction has been calculated for a number of physisorption systems, using various approximations [16]. In their pioneering studies of He at metal surfaces, Zaremba and Kohn [17] used the Hartree-Fock approximation and a jellium model for the surface. Assuming small overlaps between the atom and metal wavefunctions, they obtained a repulsive energy that is given by the energy shifts of the single particle metal wavefunctions. Esbjerg and Nørskov [18] treated the same system, using the effective medium theory, and obtained a repulsive energy basically proportional to the substrate electron density at the position of the He atom. Nordlander and co-workers have successfully applied the approach of Zaremba and Kohn, in calculations for physisorption of H$_2$ on metal surfaces.

The results from theoretical studies of the repulsive part of the physisorption interaction, have shown that the laterally averaged, and, for adsorbed molecules, rotationally averaged repulsive potential energy can be well described with the simple function

$$V_R = C_R \exp(-\alpha z). \quad (2.4)$$

Here $C_R$ and $\alpha$ characterize the strength and inverse range of the repulsive interaction, respectively, and $z$ is the distance between the adsorbate and the surface. A physical argument for this form of $V_R$ can be based on the observation that the repulsive potential energy is approximately proportional to the substrate electron density, $\rho(r)$, at the position, $r$, of the adsorbate. This substrate electron density varies only weakly with the lateral position of the adsorbate and decreases exponentially outside the surface, ($\rho(r) \approx \rho(z) \propto \exp(-z)$).

The one-dimensional description of the physisorption potential energy, $V_0(z)$, is based on a superposition of the contributions from the van der Waals attractive and the Pauli repulsive branches of the interactions,

$$V_0(z) = V_R(z) + V_{vdW}(z). \quad (2.5)$$

The potential energy curve and the well depth of $V_0$ are generally very sensitive to the parameters in Eqs. (2.2) and (2.4). This sensitivity is due to the fact that the description of the potential energy in Eq. (2.5), in terms of a superposition of the attractive and repulsive terms, involves a strong cancellation between these terms. For physisorption of H$_2$ on flat Cu surfaces, the current models for $V_0(z)$ are based on the description given in Eq. (2.5). In Fig. 2.1, the model for the H$_2$-Cu(100) physisorption potential [19] is shown. For this potential, the parameters in Eqs. (2.2) and (2.4) have been calculated by Nordlander and co-workers [15]. The parameters have later
Figure 2.1: The current model for the laterally and rotationally averaged physisorption potential, $V_0(z)$, for H$_2$ at a Cu(100) surface. The dashed and dashed-dotted lines show the contributions from the repulsive and attractive branches, respectively. $z$ is the distance between the bond centre of the molecule and the jellium edge of the surface.

been adjusted in order to reproduce experimental data [19], as described in Section 2.1.2.

That DFT-GGA cannot correctly describe the complete physisorption well, is illustrated in Fig. 2.2. This Figure displays the results from DFT-GGA calculations of the laterally and rotationally averaged potential energies for H$_2$ at Cu(111) ($V_{\text{DFT}}$), and the current model for the H$_2$-Cu(111) physisorption potential ($V_0$) [20]. As indicated in the Figure, $V_{\text{DFT}}$ is too shallow, by about 10 meV, and has a minimum that is located about 0.5 Å outside the minimum of $V_0$. That DFT-GGA fails to describe the asymptotic tail of the long-range van der Waals attraction, is illustrated by the difference between the two curves at large separations between the surface and the molecule.

2.1.2 Vibrational motion in the physisorption well

The physisorption potential well may support several bound states, in which the adsorbate performs vibrational motion relative to the surface. Through-
Figure 2.2: Laterally and rotationally averaged potential energy curves for H$_2$ at Cu(111). The interpolated curve, labeled $V_{\text{DFT}}$, is based on results from DFT-GGA calculations and the curve labeled $V_0$ is the current model for the H$_2$-Cu(111) physisorption potential. $z$ is the distance between the bond centre of the molecule and the jellium edge of the surface.
out this thesis, these bound vibrational states are labeled by quantum numbers \( n \), where \( n = 0 \) denotes the groundstate. The energies of the bound states are defined by \( E_n < 0 \) and the binding energy is given by \( D = -E_0 \). The potential also supports a continuum of scattering states, with energies \( E \geq 0 \). Because the shape of the potential energy curve and the well depth are so sensitive to the parameters in Eqs. (2.2) and (2.4), as discussed in Section 2.1.1, experimental values for the vibrational energies \( E_n \) provide a valuable opportunity to scrutinize proposed theories of the physisorption interaction.

Accurate values for the bound state vibrational energies can be obtained from scattering experiments, by measuring, for instance, the energies of corrugation-mediated selective adsorption (CMSA) resonances. A CMSA resonance occurs when an incident adsorbate is temporarily trapped in a bound state of \( V_0(z) \), by a diffractive event in which translational energy is transferred from the motion normal to the surface to motion along the surface. Note that, since the process involves diffraction, CMSA resonances are difficult to observe for other than very light adsorbates. Because the diffraction can only involve lateral momentum changes that are given by the surface reciprocal lattice vectors, there will be a kinematical connection between the initial translational energy of the adsorbate, the angle of incidence, the bound state vibrational energy and the reciprocal lattice vector involved in the scattering event. This connection gives dispersion relations for the selective adsorption resonances, by which experimental data can be analyzed in order to obtain the bound state vibrational energies and their dispersion with lateral momentum (See, e.g., Ref [19]).

The energies for vibrational motion in the potential \( V_0 \) in Eq. (2.5) can be calculated using, for instance, the semi-classical Wentzel-Kramers-Brillouin (WKB) approximation, as described by Le Roy [21]. By comparing the calculated and measured vibrational energies, the accuracy of the theoretical description of \( V_0(z) \) can be examined. The calculated parameters of \( V_0(z) \) can be tuned in order to get a good agreement between the calculated and measured vibrational energies, resulting in a very well-characterized potential. The current model for the \( \text{H}_2-\text{Cu}(100) \) physisorption potential, shown in Fig. 2.1, has been derived from CMSA measurements, using a Le Roy-analysis of the bound state vibrational energies [19].

### 2.1.3 Orientational anisotropy

For adsorbed molecules, the physisorption interaction depends not only on the molecule–surface distance, but also on the orientation of the molecule relative to the surface. This orientational anisotropy of the interaction is,
however, generally weak and the molecule is almost free to rotate in the physisorption well. For instance, electron energy-loss spectroscopy (EELS) experiments for $\text{H}_2$, $\text{D}_2$ and HD physisorbed on Cu(100) [22] and for $\text{H}_2$ physisorbed on graphite [23] have revealed resonant states with transition energies that are close to those of the free rotational states of the gas-phase molecules. Because of the weakness of the anisotropy, it is generally described by the lowest order, non-vanishing term in an expansion of the potential energy in Legendre polynomials, $P_n(\cos \theta)$, where $\theta$ is the angle between the molecular axis and the surface normal. For a homonuclear diatomic molecule, this description results in a potential energy given by

$$V(z, \theta) = V_0(z) + V_2(z)P_2(\cos \theta). \quad (2.6)$$

Here $z$ is the distance between the bond centre of the molecule and the surface. The anisotropic term, $V_2(z)$, is generally written as a linear combination of the contributions from the Pauli repulsive and the van der Waals attractive branches as

$$V_2(z) = \beta_R V_R(z) + \beta_{vdW} V_{vdW}(z). \quad (2.7)$$

The contribution to the anisotropy from the van der Waals forces derives from the different polarizabilities of the molecule along the molecular axis and transverse to the molecular axis. Because of this difference in polarizability, the response of the molecular dipole moment to dipole moment fluctuations in the substrate will depend on the orientation of the molecular axis. The relative strength of the anisotropy, $\beta_{vdW}$, is given approximately by [24]

$$\beta_{vdW} = \frac{\alpha_L - \alpha_T}{2(\alpha_L + 2\alpha_T)}, \quad (2.8)$$

where $\alpha_L$ and $\alpha_T$ are the static polarizabilities of the molecule, along and transverse to the molecular axis, respectively. Because $\alpha_L$ is larger than $\alpha_T$ [25], the van der Waals interaction favours an orientation of the molecular axis normal to the surface, that is, $\beta_{vdW} > 0$.

The relative anisotropy of the Pauli repulsive interaction, $\beta_R$, has been calculated for $\text{H}_2$ on various surfaces [14, 15]. The results have yielded repulsive anisotropies favouring an alignment of the molecular axis along the surface, that is, $\beta_R > 0$. This behaviour of the repulsive anisotropy is not unexpected, since the overlap between the substrate and molecular orbitals is larger for a molecule that is positioned with its axis normal to the surface than parallel to the surface. We have found a similar behaviour of the repulsive interaction for $\text{N}_2$ on Cu(111), from DFT total energy calculations.
that were performed in relation to molecule-surface scattering calculations, presented in Paper V.

However, later studies of H$_2$ physisorbed on flat Cu surfaces, have shown that the anisotropy of the repulsive interaction seems to promote a configuration with the molecular axis normal to the surface, that is, $\beta_R < 0$. This observation was first made from an analysis of the rotational splitting of resonant state energy levels on Cu(100), as observed from CMSA resonances in molecular beam scattering experiments [26]. The origin and nature of these splittings are described briefly in Section 2.1.4. The conclusion regarding the repulsive anisotropy of H$_2$ on Cu is supported by our results from DFT total energy calculations for H$_2$ on Cu(111), described in Paper V. As displayed in Fig. 2.3, these results show that in the physisorption region, ($z > 2.2$ Å, $V_0 < 200$ meV), the anisotropy favours an upright position of the molecule. At distances closer to the surface than 2.2 Å, where $V_0 > 200$ meV, we find that the anisotropy is shifted and the molecule prefers to be oriented parallel the surface. The latter result is in agreement with the results from previous DFT calculations for H$_2$-Cu(111) [1].

For the heteronuclear HD molecule, the asymmetric mass distribution leads to an anisotropy that is effectively larger than for the homonuclear H$_2$ and D$_2$ molecules. The difference in position of the centre of mass and the bond centre of this molecule implies that rotational motion around the centre of mass results in a motion of the bond centre and a fluctuation of $z$. Therefore, the appropriate interaction potential for HD, as a function of the distance, $z_{cm}$, between the centre of mass of the molecule and the surface, is given by $V(z, \theta)$ in Eq. (2.6) with

$$z = z_{cm} - d \cos \theta$$

where $d$ is the distance between the centre of mass and the charge symmetry centre. The resulting PES, for the motion of HD in the $z_{cm}$- and $\theta$-coordinates, has an orientational anisotropy that is stronger than the anisotropy of the PES for the homonuclear molecules. Note also that for HD, the variation of the PES in the $\theta$-coordinate has a period of $2\pi$, whereas for H$_2$ and D$_2$, it has a period of $\pi$.

### 2.1.4 Rotational motion in the physisorption well

The anisotropy of the physisorption interaction affects the rotational motion of adsorbed molecules, and introduces a coupling between the vibrational and rotational motion. In the absence of anisotropy, the rotational states, in the internal vibrational groundstate, are the three-dimensional free rotor states,
Figure 2.3: The laterally averaged potential energy for H\textsubscript{2} at a Cu(111) surface, from DFT total energy calculations. The crosses are calculated values and the solid and dashed curves show the interpolated potential energies for the molecule oriented with its axis perpendicular and parallel to the surface, respectively. \(z\) is the distance between the bond centre of the molecule and the jellium edge of the surface.
with energies \([27]\), 

\[ E_{3D}(j) = Bj(j+1) \quad (j = 0, 1, 2, \ldots), \]

where \(B = \hbar^2/2I\) is the rotational constant, \(I\) is the moment of inertia of the molecule and \(\hbar j = J\) is the total angular momentum of the molecule. Note that this expression for the 3D rotor energies is based on the rigid rotor approximation, in which the internal bond length is assumed to be independent of the rotational state of the molecule. The energies, \(E_{3D}(j)\), of the three-dimensional free rotor states are degenerate with respect to the \(z\)-component of the angular momentum, \(\hbar m\). This degeneracy is \((2j+1)\)-fold, because the allowed values of \(m\) are given by \(|m| = 0, \ldots, j\). In the presence of a weak anisotropy, this degeneracy is lifted, with the magnitude of the \(m\)-dependent sublevel splittings determined by the strength of the anisotropy. The shift in energy of a homonuclear molecule in a bound vibrational state \(n\) and a rotational state \((j, m)\) is given by first order perturbation theory as \([24]\)

\[ \Delta E_n(j, m) = \frac{3\langle n|V_2|n \rangle}{2j+3} \left( \frac{j^2 - m^2}{2j-1} - \frac{j}{3} \right). \quad (2.10) \]

The signs of the splittings depend on whether the anisotropy favour an alignment of the molecular axis normal to the surface (\(\langle n|V_2|n \rangle < 0\)) or parallel to the surface (\(\langle n|V_2|n \rangle > 0\)).

The dependence of the magnitude and sign of the rotational energy splittings on the anisotropy, enables us to test the calculated anisotropy from measurements of the rotational energy levels. The splittings of these levels have been measured for various adsorption systems, from CMSA resonance energies observed in molecular beam scattering experiments. The calculated relative anisotropies \(\beta_R\) have been found to be compatible with the observed magnitudes, but not the signs, of observed splittings for \(\text{H}_2\) on \(\text{Cu}(100)\) and \(\text{Ag}(110)\) \([28]\). It has been shown that the observed magnitudes \textit{and} signs of the splittings, for \(\text{H}_2\)-\(\text{Cu}(100)\), are compatible only with a small negative value of \(\beta_R\) \([26]\).

### 2.1.5 Rotationally inelastic scattering of \(\text{D}_2\) and \(\text{N}_2\)

The coupling between translational and rotational motion of the molecule in the physisorption well, gives rise to the possibility of rotational transitions of a molecule that is scattered from a surface. In particular, by transfer of energy from translational motion normal to the surface to rotational energy, the molecule may get temporarily trapped in a resonant state of the adsorption well. Such an event is called rotation-mediated selective adsorption (RMSA) \([29]\). The energies of the RMSA resonances can be determined from molecular beam scattering experiments, and the results can be com-
pared with calculated resonance energies, providing further opportunities to scrutinize the theoretical description of the potential well [30].

The probabilities for rotational transitions of a molecule that is scattered from a surface, depend on several factors. For instance, for a given anisotropy of the PES, the initial translational energy normal to the surface, the potential well depth and the rotational constant of the molecule have a large influence on this probability. That these quantities are important, is most easily understood by noting that for a rotational excitation to occur, enough total kinetic energy must be available. Within the rigid lattice approximation and the rigid rotor approximation, a necessary condition for a rotational excitation to occur is that the sum of the initial translational energy and the potential well depth is larger than the smallest rotational energy difference, which is governed by the rotational constant, $B$.

We have investigated the influence of the initial translational energy, the potential well depth and the rotational constant, on the probability for rotationally inelastic scattering, by studying N$_2$ and D$_2$, scattering from a Cu(111) surface, as described in Paper V. The probabilities for rotational transitions of the D$_2$ and N$_2$ molecules, were calculated using numerical wavepacket propagations, described in Section 3.2, in the $z$- and $\theta$-coordinates. The initial wavefunction in the propagation was given in the $z$-coordinate by a Gaussian function and in the $\theta$-coordinate by a free 3D rotor state with a definite rotational quantum number $j$. The probability for rotational transitions were determined by following the time-evolution of the projection of the wave-packet onto the 3D free rotor states.

The propagations were performed on two-dimensional model PESs for the physisorption interaction. For D$_2$-Cu(111), the laterally averaged potential, $V_0(z)$, was given by the current model for the H$_2$-Cu(100) potential, since $V_0(z)$ varies only marginally between the two surfaces Cu(100) and Cu(111) [31]. For N$_2$-Cu(111), we have used parameters of $V_0(z)$ that have been derived for Ar-Cu(111) [32]. Our choice of the latter potential is based on the results from thermal desorption experiments, which suggest similar binding energies of about 60 meV for N$_2$ and Ar on Cu(111). Some further support for using the Ar-Cu(111) potential is given by the similar polarizabilities for Ar [33] and N$_2$ [34], which yield similar values for the van der Waals coefficient, $C_{vdW}$. The relative anisotropy of the repulsive interaction, $\beta_R$, was derived from DFT calculations. The parameter $\beta_R$ was chosen for the best fit of the anisotropy of $V(z,\theta)$ to the calculated anisotropy at the classical turning point of the incident particle. For the H$_2$-Cu(111) potential, we obtained a slightly larger absolute value of $\beta_R$ than has previously been inferred from observed sublevel splittings of rotational resonances [26]. Calculated rotational sublevel splittings for the H$_2$-Cu(111) potential are ac-
Accordingly slightly larger (by about 25 – 50 %) than the observed splittings for H$_2$-Cu(100). The relative anisotropy of the attractive interaction, $\beta_{vdW}$, was determined in the conventional manner from the static polarizabilities of the D$_2$ and N$_2$ molecules [25], using Eq. (2.8). The magnitude of the anisotropy is found to be similar for the two H$_2$-Cu(111) and N$_2$-Cu(111) potentials.

Molecular beam scattering experiments, presented in Paper V, have been performed for various values of the incident translational energy normal to the surface, and with various rotational temperatures of the beams. The translational energy, normal to the surface, was varied via the angle of incidence of the beam, the pressure of the molecular beam source and the nozzle temperature. The amount of rotational transitions from a rigid surface was derived from Debye-Waller plots of the elastic intensity, by extrapolating to zero substrate temperature.

The theoretical and experimental results show that, at low incident normal translational energies of 4.2 meV and 9.0 meV, the probabilities for rotational transitions of N$_2$ are large, about 80–95 %. For D$_2$ at normal translational energy 4.2 meV, the probabilities for rotational transitions are, in contrast, negligible, whereas at normal translational energy 56 meV, the probability is small but distinct, about 20–30 %. The large difference in probability for rotational transitions of D$_2$ and N$_2$, under similar conditions, is mainly due to the large difference between the rotational constants for these two molecules. The rotational constant is 0.248 and 3.70 meV for N$_2$ and D$_2$, respectively. The associated much smaller differences between the rotational energy levels of N$_2$ than of D$_2$, results in a much larger probability for rotational transitions.

### 2.1.6 Polarization and dipole moment

The physisorption interaction is associated with a weak induced dipole moment of the adsorbate-surface complex. At large distances, where the van der Waals interaction dominates, the dipole moment normal to the surface is given by [35,36]

$$\mu(z) \propto \frac{1}{(z - z_{ref})^4},$$  \hspace{1cm} \text{(2.11)}

where $z_{ref}$ defines a reference plane [36]. As discussed in Section 2.1.1, the van der Waals treatment is not strictly valid in the region of the physisorption well. In particular, the expression for the dipole moment in Eq. (2.11) is singular at $z_{ref}$. Furthermore, the contribution to polarization from the repulsive Pauli forces should be substantial in the vicinity of the equilibrium position of the molecule.
The variation of the dipole moment with $z$ leads to the possibility of dipole active transitions among the vibrational states of the physisorption well. The first observations of such dipole active transitions were made in EELS experiments by Svensson and Andersson [37], for hydrogen molecules on a Cu(100) surface. They observed dipole activity of the $n : 0 \rightarrow 1$ and $n : 0 \rightarrow 2$ vibrational transitions for $\text{H}_2$, $\text{D}_2$ and $\text{HD}$, and the $n, j : 0, 0 \rightarrow 0, 1$ resonant transition for HD. In later EELS measurements, presented in Paper I, they observed similar dipole activities of vibrational transitions for $\text{H}_2$ and $\text{D}_2$ adsorbed on the terraces of the stepped Cu(510) surface.

The dipole activity of rotational transitions for HD in the physisorption well has the same origin as the effectively large anisotropy of the physisorption potential energy for HD, discussed in Section 2.1.3. Rotational motion around the centre of mass is associated with a fluctuation of the distance between the surface and the molecule bond centre, $z$, resulting in a fluctuation of the dipole moment, $\mu(z)$.

From the EELS measurements, Svensson and Andersson were able to extract absolute values of dipole moment matrix elements for vibrational transitions, as shown in Table 2.1 and Table 2.2 for molecules on Cu(100) and the terraces of Cu(510), respectively. Note also in Table 2.2, that the measured vibrational transition energies for terrace-adsorbed $\text{H}_2$, are in close agreement with the transition energies for $\text{H}_2$ on Cu(100). This agreement indicates that the terrace-adsorbed molecules experience a physisorption potential that is similar to the $\text{H}_2$-Cu(100) potential. Table 2.1 also displays the results from a calculation, performed by Svensson and Andersson, of the dipole moment matrix elements for $\text{H}_2$ on Cu(100). This calculation was based on a Taylor expansion of the dipole moment function of Eq. (2.11) around the equilibrium position of the molecule and a harmonic oscillator model for the vibrational motion in the physisorption well. As shown in Table 2.1, the calculated matrix elements were of the right order of magnitude, but, as noted previously, the expression for the dipole moment in Eq. (2.11) is not strictly valid in the region of the physisorption well and, in particular, a calculation with the full dipole moment function would diverge due to the strong singularity in $z_{ref}$.

We have found that the measured dipole moment matrix elements for hydrogen molecules on Cu(100) and on the terraces of Cu(510), can be better reproduced with a simple phenomenological model for the variation of the dipole moment with $z$,

$$
\mu(z) = \mu_0 \exp(-\beta(z - z_{\text{min}})).
$$

(2.12)

Here $\mu_0$ and $\beta$ are parameters and $z_{\text{min}}$ is the position of the potential minimum. A simple argument for the functional form of this model is that it
Table 2.1: Measured and calculated dipole moment matrix elements, $|\langle n, j|\mu|0, 0 \rangle|$, for hydrogen molecules physisorbed on Cu(100). Our values were calculated with a dipole moment function $\mu = \mu_0 \exp(-\beta(z - z_{\text{min}}))$, where $\mu_0 = 0.051$ D, $\beta = 0.9a_0^{-1}$, $z$ is the distance between the surface and the bond centre of the molecule, and $z_{\text{min}}$ is the position of the potential minimum. $n$ and $j$ denote vibrational and rotational quantum numbers, respectively. The unit is Debye.

<table>
<thead>
<tr>
<th>$n, j$</th>
<th>$H_2$</th>
<th>$HD$</th>
<th>$D_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp. $^a$</td>
<td>Calc.$^a$</td>
<td>Calc.$^b$</td>
</tr>
<tr>
<td>0, 0</td>
<td>0.045</td>
<td>0.026</td>
<td>0.045</td>
</tr>
<tr>
<td>1, 0</td>
<td>0.020</td>
<td>0.016</td>
<td>0.020</td>
</tr>
<tr>
<td>2, 0</td>
<td>0.009</td>
<td>0.006</td>
<td>0.010</td>
</tr>
<tr>
<td>0, 1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference [37]
$^b$Our work.

mirrors the overlap between the molecular and metal electron states. Dipole moment matrix elements for this model were determined, as described in Section 3.1.2, using a time-dependent wavepacket calculation. The method of wavepacket propagation is described in Section 3.2 and the propagation was performed using the current model for the $H_2$-Cu(100) physisorption potential [26], since, as noted, the molecules on Cu(100) and the terraces of Cu(510) experience similar physisorption potentials. By adjusting the parameters $\mu_0$ and $\beta$, we are able to get a good agreement between calculated and measured dipole moment matrix elements, as shown in Tables 2.1 and 2.2 for molecules on Cu(100) and on the terraces of Cu(510), respectively. Note that the dipole activity of the rotational transitions of HD are also well described with this dipole moment model. That the model gives a reasonable description of the Pauli contribution to the dipole moment, is supported by results from DFT calculations of the dipole moment normal to the surface. This is demonstrated in Fig. 2.4, which shows a good agreement between the model function for $H_2$-Cu(100) and results from a DFT calculation for $H_2$-Cu(111).
Figure 2.4: The dipole moment normal to the surface for $\text{H}_2$ physisorbed on Cu, as a function of the distance between the molecule and the surface. The crosses show the results from DFT calculations for $\text{H}_2$-Cu(111) and the solid line shows the model dipole moment function, $\mu(z) = \mu_0 \exp(-\beta(z - z_{\text{min}}))$. $z$ is the distance between the bond centre of the molecule and the jellium edge of the surface, and $z_{\text{min}}$ is the position of the potential minimum. The parameters $\mu_0$ and $\beta$ were chosen in order to reproduce measured dipole moment intensities for transitions among the bound states of $\text{H}_2$ on Cu(100), as shown in Table 2.1.
Table 2.2: Measured and calculated dipole moment matrix elements $\mu_n = |\langle n | \mu | 0 \rangle|$ and measured energies, $E_n - E_0$, for vibrational transitions of $H_2$ adsorbed on the terraces of Cu(510). The values in the parentheses are the deviations of the transition energies from the values for $H_2$ on Cu(100). The matrix elements were calculated with a dipole moment function $\mu = \mu_0 \exp(-\beta(z - z_{min}))$, where $\mu_0 = 0.0342$ D, $\beta = 1.5$ $a_0^{-1}$, $z$ is the distance between the bond centre of the molecule and the surface, and $z_{min}$ is the position of the potential minimum.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\mu_n$ (D)</th>
<th>$E_n - E_0$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.021</td>
<td>0.021</td>
</tr>
<tr>
<td>2</td>
<td>0.015</td>
<td>0.014</td>
</tr>
<tr>
<td>3</td>
<td>0.009</td>
<td>0.009</td>
</tr>
</tbody>
</table>

2.1.7 Direct photodesorption of $H_2$, HD and $D_2$

The dipole activity of the vibrational motion of hydrogen molecules in the physisorption well, discussed in Section 2.1.6, makes a direct photodesorption process conceivable for these molecules. In the direct photodesorption process, the molecule makes a transition from the groundstate to a continuum state of the physisorption potential, by absorption of a single photon. The possibility for such a process was first discussed by Pearlstine and McClelland [38]. They derived an expression for the rate of direct photodesorption, using a Morse potential to describe the adsorbate–surface bond and a model function for the variation of the dipole moment with the vibrational coordinate in the potential well. They applied the model in a calculation of direct photodesorption rates for $D_2$ physisorbed on LiF(001), with the dipole moment determined from the electric field at the surface and the polarizability of the free $H_2$ molecule. Their results suggested that thermal blackbody radiation can induce direct desorption at a rate large enough for the desorption to be observable in experiments. However, there was no experimental support for their dipole moment model, and observed infrared radiation-induced desorption of physisorbed molecules has instead been attributed to an indirect process, involving excitation of substrate phonons [39, 40].

We have calculated rates of direct photodesorption of hydrogen molecules on Cu(100) and the terraces of Cu(510), using the dipole moment models in Tables 2.1 and 2.2, respectively. The calculations are detailed in Paper II.
The rate, $W$, of direct desorption induced by an electric field oscillating at a frequency $\omega$, is given by Fermi’s golden rule as

$$W = \frac{\pi}{2\hbar} C_{\mu}(\omega) E_z^2(\omega),$$

where $E_z$ is the amplitude of the electric field in the $z$-direction and $C_{\mu}(\omega)$ is the dipole spectral function, given by

$$C_{\mu}(\omega) = \sum_f |\langle f | \mu | 0 \rangle|^2 \delta(\omega - (\omega_f - \omega_0)).$$

Here $|f\rangle$ are final continuum states of the potential and $\hbar \omega$ is the photon energy, which must satisfy $\hbar \omega > D$. Note that for physisorbed species, the energy $D$ corresponds to photons in the infrared spectral range. For the direct photodesorption process to occur, it is thus necessary that transitions from the groundstate to continuum states of the physisorption potential are dipole active, that is, $C_{\mu}(\omega)$ is non-zero for $\hbar \omega > D$. We have performed calculations of $C_{\mu}(\omega)$, with the phenomenological model in Eq. (2.12) for the dipole moment function, using the parameters given in Tables 2.1 and 2.2. These calculations were performed using a time-dependent wavepacket calculation, as described in Section 3.1.2. The method of wavepacket propagation is described in Section 3.2 and the propagations were performed using the current model for the $\text{H}_2$-$\text{Cu}(100)$ physisorption potential [26]. The results, displayed in Fig. 2.5 for $\text{H}_2$-$\text{Cu}(100)$, show a tiny dipole intensity for transitions to continuum levels, indicating the possibility of direct photodesorption.

Our results also show that the dipole activity of rotational transitions for HD, discussed in Section 2.1.6, makes it conceivable to induce resonant photodesorption of this molecule. Overtone rotational transitions of HD have transition energies that are larger than the binding energy $D$. The dipole intensities of these transitions are superimposed on the continuum of intensities for transitions to unbound translational states. The resulting dipole intensity spectrum has a strongly oscillating structure, as shown in Fig. 2.6. By tuning an infrared laser beam to the energy of a resonant state, it should be possible to induce resonant photodesorption of HD.

In Paper I, we present the first proof for observation of direct photodesorption. Our conclusion is based on the good agreement between measured rates of desorption and calculated rates of direct photodesorption, induced by infrared radiation from the walls of a UHV chamber. Experimental rates of photodesorption of $\text{H}_2$ and $\text{D}_2$ from the terraces of $\text{Cu}(510)$ were determined both by measuring the background pressure that was required to maintain a constant coverage and by observing the decay of the $n : 0 \rightarrow 1$ EEL peak.
Figure 2.5: The calculated dipole spectral function, $C_{\mu}(\omega)$, for H$_2$ physisorbed on Cu(100). The magnified curve shows the intensity for transition energies larger than $D = 25.5$ meV, corresponding to transitions to continuum levels. The spectral function was calculated using the dipole moment model specified in Table 2.1.
Figure 2.6: The calculated dipole spectral function, $C_\mu(\omega)$, for HD physisorbed on Cu(100). The magnified curve shows the intensity for transition energies larger than $D = 26.4$ meV, corresponding to transitions to continuum levels. The spectral function was calculated using the dipole moment model specified in Table 2.1.
Table 2.3: Measured desorption rates and calculated direct photodesorption rates for H\textsubscript{2} physisorbed on the terraces of Cu(510). The calculations were performed using the dipole moment model specified in Table 2.2. \(T\) is the temperature of the UHV chamber.

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>Measured rate (s(^{-1}))</th>
<th>Calculated direct rate (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>210</td>
<td>(5\times10^{-4})</td>
<td>(4\times10^{-4})</td>
</tr>
<tr>
<td>296</td>
<td>(8\times10^{-4})</td>
<td>(8\times10^{-4})</td>
</tr>
<tr>
<td>370</td>
<td>(15\times10^{-4})</td>
<td>(12\times10^{-4})</td>
</tr>
</tbody>
</table>

The rates were found to be independent on the substrate temperature, below 14 K, but sensitively dependent on the temperature of the UHV chamber, indicating that the desorption has a non-thermal nature, and is induced by infrared radiation from the UHV chamber walls. Our theoretical values for the direct rates of photodesorption, induced by this radiation, were obtained from the calculated dipole spectral function and the expression in Eq. (2.13), by integrating over energy and direction of propagation, and summing over polarization, for blackbody radiation incident on a surface. Since the Cu surface is almost perfectly reflecting in the infrared spectral range, the normal component of the incident electric field at the surface is enhanced by a factor of two. As shown in Table 2.3, there is an excellent agreement between the measured desorption rates and the calculated direct photodesorption rate, for a substantial range of UHV chamber temperatures.

In Paper II, we also demonstrate that an indirect process, which previously observed photodesorption has been attributed to [39, 40], cannot account for the observed infrared radiation-induced desorption of H\textsubscript{2} from the terraces of Cu(510). The proposed indirect process involves excitation of substrate phonons, which decay by transferring energy to the vibrational coordinate of the adsorbed molecule, leading to desorption. We have calculated the rate of desorption for this indirect process, based on previous studies of the dipole activity of phonons in the surface region of Cu [41], and we obtain a rate that is several orders of magnitude smaller that the direct rate.
2.2 Chemisorption

2.2.1 Origin and nature of chemisorption interaction

In contrast to physisorption, chemisorption of an atom or a molecule on a surface involves the formation of a chemical bond. Chemisorption typically occurs as an adsorbate that has an open shell structure (i.e., partially filled electronic levels) approaches a metal surface. The orbitals of adsorbate and the surface can then hybridize, forming a low-lying bonding level and a high-lying antibonding level. While the bonding level is filled, by charge transfer from the surface, the antibonding level is unfilled, resulting in a net binding between the adsorbate and the surface. Similarly, a molecule may be chemisorbed if it has a lowest unoccupied molecular orbital (LUMO) that is close in energy to the highest occupied molecular orbital (HOMO). Because the LUMO is an intra-molecularly antibonding orbital, the charge transfer from the surface to the LUMO weakens the internal molecular bond. In particular, the bond may break upon adsorption, leading to dissociative chemisorption.

Although there is a tradition of associating chemisorption with large charge rearrangements and large binding energies, there exists no unambiguous formal distinction between the physisorption and chemisorption regimes. One typical example of an adsorption system that can be attributed to the chemisorption regime is atomic hydrogen, which has an open valence shell, on a Cu surface. The amount of charge rearrangement involved in adsorption of H on Cu is substantial and the binding energy for this system is large, $\sim 2.5$ eV [42]. In contrast, H$_2$ on a flat Cu surface, discussed in Section 2.1, is a typical example of a physisorption system. H$_2$ has a closed shell structure, with a large energy gap between the HOMO and the LUMO. In this case, both the bonding and antibonding orbitals, involving the metal states and the HOMO, will be filled, resulting in a net repulsion between the H$_2$ molecule and the Cu surface. As described in Section 2.1.1, this repulsion and the long-range van der Waals attraction results in a small ($\sim 30$ meV) physisorption well. An adsorption system that falls in between the two extreme limits of H and H$_2$ on a flat Cu surface, but is still referred to as a chemisorption system, is CO on Pt, which is the subject of Section 2.2.3. The gap between the HOMO and the LUMO is smaller for CO than for H$_2$. The adsorption of CO on Pt involves a substantial amount of charge rearrangements [43] and the binding energy is about 1.5 eV [44]. The orientation of the CO molecule, with the C atom closest to the surface, can be understood from the concentration of the LUMO (the antibonding $2\pi^*$ orbital) at the C atom [45]. An adsorption state that shows characteristic features of both physisorption
and chemisorption, has been found for H$_2$ adsorbed at the step of a Cu(510) surface, as will be discussed in Section 2.2.4. This adsorption state involves interaction between the metal states and the LUMO of the H$_2$ molecule.

PESs for the dynamics of chemisorbates can be determined, with useful accuracy, from DFT calculations. For instance, accurate barriers for dissociative adsorption [1,2] and diffusion [46] of chemisorbates have been calculated, and PESs for dissociative adsorption dynamics in up to six dimensions have been constructed [47,48] using DFT-GGA.

2.2.2 Vibrational and rotational character of chemisorbates

Because of the complex interactions that are involved in chemisorption, the dynamics of chemisorbates is often more involved than that of physisorbates. For instance, the site preference and, for molecules, orientational preference is much stronger for chemisorption than for physisorption. Associated with these preferences, is a hindering for lateral translational and rotational motion that is often strong, and the molecule may be constrained to perform vibrational motion in the lateral and rotational coordinates. These kinds of vibrational modes are denoted frustrated translational and rotational modes.

Experimental investigations of the vibrational modes of chemisorbates can be of great value in characterizing the adsorption system. Because the vibrational spectrum is a characteristic feature of a specific adsorbate, the adsorbates on a surface may be identified from vibrational spectroscopic measurements. Furthermore, the nature of adsorption of a molecule can be investigated from the internal vibrational energy, since chemisorption weakens the internal bond, whereas physisorption leaves the internal bond practically unaffected.

For chemisorption on metal surfaces, vibrational and rotational modes may be characterized from measurements of the dipole activity of these modes. In practice, only modes that produce a dipole moment normal to the metal surface will be observed in dipole scattering experiments. This selectivity is a consequence of the good screening properties of the metal in the infrared spectral range of the vibrations. The screening results in a cancellation of the tangential component of the incident electric field, and an enhancement of the normal component. The dipole selection rules, within the harmonic approximation, can be determined from symmetry considerations.

Present day vibrational spectroscopic techniques can provide a wealth of data with very high resolution, but to correctly interpret these data often requires comparisons with results from theoretical models. For instance,
as argued in the previous paragraph, information can be obtained from vibrational spectroscopic results, using symmetry considerations. For many cases, it is sufficient to consider the local symmetries of the adsorption sites. However, as the energy resolution of the vibrational spectroscopic methods increases, the interpretation becomes increasingly dependent on comparisons with theoretical models that include the full symmetry of the adsorption system.

2.2.3 Vibrational modes of CO on Pt(111)

CO on a Pt surface is an adsorption system that is of high technological interest due to important applications in, for instance, car catalysts. CO on the Pt(111) surface is also interesting from a scientific point of view, due to the ordered adsorption structures that may be formed at substrate temperatures of about 100 K [44]. At low coverages (less than 0.17 of a monolayer) only top sites are occupied. Above this coverage, bridge sites become occupied and at 0.5 of a monolayer it is possible to obtain a highly ordered c(4 × 2) adsorption structure, shown in Fig. 2.7. The variation of site-preference with coverage enables investigations of the dynamics of the molecules at the different sites, without changing the adsorbate or the substrate.

There is a long history of experimental and theoretical studies of the vibrational modes of c(4 × 2) CO-Pt(111). For the two molecules in the surface unit cell, there are 12 associated vibrational modes. However, based on the local symmetries of the adsorption sites, the frustrated rotational modes (ν₃) and the frustrated lateral translational modes (ν₄) of the top-adsorbed molecules have, in previous work, been assumed to be doubly degenerate. Several spectroscopic methods have been applied in order to determine the 10 remaining fundamental vibrational energies and the results are summarized in Table 2.4. The fundamental energies of the dipole active internal vibrations, υ₁, and vibrations relative to the surface, υ₂, have been determined from EELS [44] and infrared spectroscopy (IRS) experiments [49–51]. From the EELS experiments, the fundamental energies of the two frustrated rotational modes, υ₃ and υ₄, were also determined. Three low-energy loss peaks, observed in helium atom scattering (HAS) experiments [52], have been attributed to the supposedly degenerate frustrated lateral translation of top-bonded CO (υ₅), the frustrated translation of bridge-bonded CO towards the hollow site (υ₆) and the frustrated translation of bridge-bonded CO towards the top site (υ₇). The remaining mode, frustrated rotation of bridge-bonded CO towards the top site (υ₈), has never been observed experimentally. In IRS experiments, a double peak structure has been observed.
Figure 2.7: Top view of CO adsorbed on Pt(111) in the c(4 × 2) structure. The coverage is 1/2 of a monolayer with the molecules evenly distributed among top and bridge sites. The parallelogram indicates the (4 × 2) surface unit cell.

at the energy of the $\nu_2^b$ mode. Based on the observed disappearance of the double peak at low substrate temperatures, it has been suggested that the double peak derives from a Fermi resonance [53] between the $\nu_2^b$ mode and a combination of the unobserved $\nu_4^b$ mode and a low-energy frustrated lateral translational mode [54].

Prompted by the uncertainty regarding the energy of the $\nu_4^b$ mode, the question regarding the validity of local symmetry analyses and the uncertainty about the nature of the IRS-observed double peak structure, a theoretical study of the vibrational modes of c(4 × 2) CO-Pt(111) has been performed, as described in detail in Paper VI. The normal mode polarization vectors and frequencies were determined within the harmonic approximation, by a diagonalization of the dynamical matrix, as described in Section 3.1.1. The matrix elements of the force constant matrix, $\mathbf{K}$, defined in Eq. (3.2), were determined from first principles DFT calculations, by making small symmetric displacements around the equilibrium configuration and calculating the ionic forces from the converged electron density, using the Hellman-Feynman theorem [55]. The force derivatives were evaluated using the central force approximation. The dipole activities of the vibrational modes were also calculated within the harmonic approximation, as described in Section 3.1.1.
Table 2.4: Measured fundamental vibrational energies and assignments of the energies to modes, for CO in the bridge and top sites of a Pt(111) surface. The arrows indicate the displacements of the atoms. Horizontal arrows correspond to motion towards top sites. The energies are in meV.

<table>
<thead>
<tr>
<th>Energy Assignment</th>
<th>Mode</th>
<th>Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h\nu_1^b$</td>
<td>(\uparrow\downarrow)</td>
<td>230.0$^{a,b,c}$</td>
</tr>
<tr>
<td>$h\nu_2^b$</td>
<td>(\uparrow)</td>
<td>47.0$^{a,d}$</td>
</tr>
<tr>
<td>$h\nu_3^b$</td>
<td>(\Rightarrow)</td>
<td>10$^e$</td>
</tr>
<tr>
<td>$h\nu_4^b$</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>$h\nu_5^b$</td>
<td>(\oslash\oslash)</td>
<td>45$^a$</td>
</tr>
<tr>
<td>$h\nu_6^b$</td>
<td>(\oslash\oslash)</td>
<td>8$^e$</td>
</tr>
</tbody>
</table>

$^a$Ref [44], $^b$Ref [49], $^c$Ref [50], $^d$Ref [51], $^e$Ref [52]
Table 2.5: Measured and calculated fundamental vibrational energies for CO on the top (t) and bridge (b) sites of the c(4 × 2) overlayer structure on Pt(111). The previous assignments of measured energies to vibrational modes and the suggested reassignments are shown.

<table>
<thead>
<tr>
<th>Energy (meV)</th>
<th>Mode</th>
<th>Exp.</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>old assignment</td>
<td>reassignment</td>
<td></td>
</tr>
<tr>
<td>260.9</td>
<td>(\nu_1^t)</td>
<td>270.2</td>
<td>(\nu_1^b)</td>
</tr>
<tr>
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<td>(\nu_2^t)</td>
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<td>(\nu_2^b)</td>
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<td>57.9</td>
<td>(\nu_3^t)</td>
<td>58.6</td>
<td>(\nu_3^b)</td>
</tr>
<tr>
<td>52.5</td>
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<td>(\nu_4^b)</td>
</tr>
<tr>
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<td>(\nu_4^b)</td>
<td>48.3</td>
<td>(\nu_4^t)</td>
</tr>
<tr>
<td>51</td>
<td>(\nu_5^t)</td>
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<td>(\nu_5^b)</td>
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<td>47.7</td>
<td>(\nu_5^b)</td>
<td>46.9</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>(\nu_6^b)</td>
<td>45.3</td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>-</td>
<td>26.0</td>
<td>(\nu_6^t)</td>
</tr>
<tr>
<td>10</td>
<td>(\nu_3^b)</td>
<td>12.3</td>
<td>(\nu_3^t)</td>
</tr>
<tr>
<td>8</td>
<td>(\nu_4^b)</td>
<td>10.4</td>
<td>(\nu_4^t)</td>
</tr>
<tr>
<td>7</td>
<td>(\nu_4^t)</td>
<td>6.9</td>
<td>(\nu_6^b)</td>
</tr>
</tbody>
</table>

The dipole moment normal to the surface, \(\mu\), associated with displacements in various directions \(x_i\) from the equilibrium configuration, were obtained from the DFT calculated charge densities. The effective charges, \(Q_i^* = (d\mu/dx_i)_0\), were determined using the central difference approximation.

The results from the calculations reveal the importance of considering the full symmetry of the adsorption system, when characterizing the vibrational modes. The symmetry-breaking that is imposed by taking the full adsorbate layer into account, results in a small 2 meV splitting between the fundamental energies the frustrated lateral translational modes of bridge-bonded CO. This energy splitting suggests a reassignment of the observed low energy vibrational modes, as shown in Table 2.4, which displays the calculated and measured fundamental vibrational energies and the assignments of these energies to modes, based on the results from the calculations. With the new assignments, there is a good agreement between measured and calculated vibrational energies. The results also show dipole activity of modes that are dipole forbidden within previous local symmetry analyses. For instance, the symmetry breaking that is imposed by the subsurface Pt layers, results in dipole activity of the \(\nu_5^b\) mode.

The results give some support to the interpretation of the double peak
structure, observed in IRS experiments, in terms of a Fermi resonance between the $\nu_2^b$ mode and a combination of the $\nu_4^b$ mode and a low energy mode. Combining the modes $\nu_4^b$ and $\nu_6^b$, it is possible to obtain an energy $h\nu_4^b - h\nu_6^b = 45.6$ meV, which is close to the energy 46.9 meV of the $\nu_2^b$ mode. It is interesting to note, however, that the dipole active $\nu_5^b$ mode, which is dipole forbidden within previous local symmetry analyses, has an energy (45.3 meV) that is also close to that of the $\nu_2^b$ mode.

### 2.2.4 Two-dimensional quantum rotation of H$_2$ and D$_2$

Although hydrogen physisorbs molecularly and chemisorbs dissociatively on a flat Cu surface, we have identified a molecular state with chemisorption-like features at the step edge of a Cu(510) surface. As described in Papers III and IV, the state has been identified from a combination of EELS experiments, total energy calculations and quantum dynamics calculations. That steps can have a significant influence on adsorption properties, is known from previous work. For instance, from DFT calculations and adsorption experiments, it has been shown that lower barriers for dissociation of N$_2$ at the steps than at the terraces of a Ru(0001) surface, leads to a reactivity that is almost an order of magnitude larger at the steps than at the terraces [56].

The work presented in Papers III and IV was initiated by results from EELS experiments, performed for this system, which revealed molecular adsorption states with transition energies close to those of an ideal two-dimensional quantum rotor. From the spectroscopic measurements, it was also found that for this molecular adsorption state, the energies for internal vibrational excitation of the molecules were significantly lower than for the free molecules. This indication of a weakened internal molecular bond suggests that the molecule is chemically adsorbed.

The adsorption site and nature of adsorption for the molecule in this 2D rotor state, were determined from DFT calculations. A 90 meV deep potential energy minimum was identified at about 1.8 Å above the step atom, in the configuration shown in Fig. 2.8. An analysis of the electron charge densities shows that the adsorption at this site involves charge transfer from the step Cu atom to the antibonding LUMO of the hydrogen molecule. The small binding distance and the charge transfer give further support for the interpretation of the molecule–surface bond as being of a chemical nature.

An initial characterization of the motion of the molecules adsorbed at this site was obtained using the harmonic approximation for the PES. The results suggested that translational motion in the $x$- and the $y$-directions are approximately decoupled from the other degrees of freedom. Furthermore, azimuthal rotation of the molecule around the $z$-axis was found to be almost
free, whereas rotation in the polar angle, $\theta$, is strongly hindered.

A more detailed description of the dynamics of a molecule adsorbed at this site, was obtained from a reduced 3D PES, depending on the $z$-, $r$-, and $\theta$-coordinates. From DFT calculations of the total energies and ionic forces for different configurations of the molecule, the potential energy and its directional derivatives were obtained in discrete points in the configurational space. A continuous PES was then constructed using a cubic spline interpolation in each coordinate. The states and energies for the motion of the molecule on this PES were derived from a time-dependent wavepacket calculation, as described in Section 3.1.2. The method of wavepacket propagation is detailed in Section 3.2. The results reveal 2D rotor-like states, in which the molecule is confined to rotate around the $z$-axis, in the plane indicated in Fig. 2.8. The rotational and vibrational transition energies of these states agree well with experiments. Although the adsorption interaction shows characteristic features of chemisorption, the potential well is found to be narrow, with a large-zero point energy that results in a small, physisorption-like, binding energy of about 46 meV for $\text{H}_2$. 

Figure 2.8: Adsorption site and geometry of $\text{H}_2$ adsorbed in the 2D rotor state at the step of a Cu(510) surface. The configuration of the molecule is described by the position of the centre of mass, $(x, y, z)$, the internal bond length, $r$, the polar angle, $\theta$, and the azimuthal angle, $\varphi$. 

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Chapter 3

Theory and methods

3.1 Quantum dynamics theory

3.1.1 Harmonic approximation

The quantum dynamics of the low lying vibrational states in the adsorption well, can in many cases be well described within the harmonic approximation for the potential energy surface. An important advantage of the harmonic approximation is that it enables a treatment of the dynamics for systems of many degrees of freedom. The main drawback of the approximation is that it fails to describe highly excited vibrational states, with large displacements from the equilibrium configuration.

The harmonic approximation, which is valid if the vibrational amplitudes are small, is based on a Taylor expansion of the potential energy around the equilibrium position of the molecule. Keeping only the lowest order non-vanishing term in this expansion results in a potential energy given by

\[ V(x_1, \ldots, x_{3N}) \approx V_0 + \frac{1}{2} \sum_{ij} \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 u_i u_j \]  

(3.1)

Here \( N \) is the number of dynamic atoms, \( x_i \) are coordinates that describe the positions of the dynamic atoms, \( i \) and \( j \) are composite indices that specify both atom and cartesian coordinate, \( V_0 \) is the potential energy in the equilibrium position and \( u_i \) are the displacements from the equilibrium positions. The expansion of the potential energy can be expressed in terms of the force constant matrix, \( K \), which is defined by

\[ K_{ij} = \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 = - \left( \frac{\partial F_j}{\partial x_i} \right)_0, \]  

(3.2)
where $F_j$ is the force component in the direction of the coordinate $x_j$. Note that $K$ is by definition a symmetric matrix. The Lagrangian for the vibrational motion, in the harmonic approximation, can be written in terms of the mass-weighted generalized coordinates, $q_i \equiv \sqrt{m_i}u_i$, as

$$L = \frac{1}{2} \sum_i \dot{q}_i^2 - \frac{1}{2} \sum_{ij} D_{ij} q_i q_j$$ (3.3) where $D$ is the dynamical matrix, which is defined by $D_{ij} = K_{ij} / \sqrt{m_i m_j}$, and the energy scale has been set so that $V_0 = 0$.

The normal modes and frequencies for the vibrational motion in the harmonic approximation are obtained from a diagonalization of $D$. The diagonalization is performed by making a transformation of the generalized coordinates to a set of normal mode coordinates $\xi_\lambda$,

$$q_i = \sum_\lambda C_{i\lambda} \xi_\lambda. $$ (3.4)

Here $C$ is the orthogonal transformation matrix, which consists of column vectors that are the eigenvectors of $D$. The Lagrangian is given in the normal mode coordinates by

$$L = \frac{1}{2} \sum_\lambda (\dot{\xi}_\lambda^2 - \omega_\lambda^2 \xi_\lambda^2), $$ (3.5)

where $\omega_\lambda^2$ are the $3N$ eigenvalues of $D$. This expression for the Lagrangian is exactly that of $3N$ harmonic oscillators in the generalized coordinates $\xi_\lambda$, with frequencies $\omega_\lambda$.

The quantization of the vibrational states of the normal modes can be introduced in a conventional manner, by defining the annihilation and creation operators,

$$a_\lambda = \sqrt{\frac{\omega_\lambda}{2\hbar}} \left( \xi_\lambda + \frac{i}{\omega_\lambda} \dot{\xi}_\lambda \right), $$ (3.6)

$$a_\lambda^\dagger = \sqrt{\frac{\omega_\lambda}{2\hbar}} \left( \xi_\lambda - \frac{i}{\omega_\lambda} \dot{\xi}_\lambda \right). $$ (3.7)

The Hamiltonian is given, in terms of these operators, by the familiar result for $3N$ quantum mechanical harmonic oscillators,

$$H = \sum_\lambda \hbar \omega_\lambda \left( a_\lambda^\dagger a_\lambda + \frac{1}{2} \right), $$ (3.8)

each with the set of eigenenergies

$$E_{n_\lambda} = \hbar \omega_\lambda \left( n_\lambda + \frac{1}{2} \right), \quad n_\lambda = 0, 1, 2, \ldots, $$ (3.9)
where \( n_\lambda \) is the number operator, \( n_\lambda = a_\lambda^\dagger a_\lambda \).

It is also straightforward to calculate the dipole activity of the vibrational modes in the harmonic approximation. The evaluation of this dipole activity, is based on a Taylor expansion of the dipole moment around the equilibrium configuration of the molecule,

\[
\mu \approx \mu_0 + \sum_i \left( \frac{d\mu}{dx_i} \right)_0 u_i = \mu_0 + \sum_i Q_i^* u_i. \tag{3.10}
\]

Here \( \mu_0 \) is the static dipole moment of the equilibrium configuration and \( Q_i^* \equiv (d\mu/dx_i)_0 \) is the effective charge of a displacement in the direction \( x_i \).

The fundamental dipole moment matrix element of a normal mode \( \lambda \) is then given by

\[
\langle 1_\lambda | \mu | 0 \rangle = \langle 1_\lambda | \xi_\lambda | 0 \rangle \sum_i Q_i^* \frac{C_{\lambda i}}{\sqrt{m_i}} = \sqrt{\frac{\hbar}{2\omega_{\lambda}}} \sum_i Q_i^* \frac{C_{\lambda i}}{\sqrt{m_i}}. \tag{3.11}
\]

Note that non-zero overtone matrix elements derive from anharmonic terms in the potential energy expansion (so-called mechanical anharmonicity) or non-linear terms in the dipole moment expansion (electrical anharmonicity).

### 3.1.2 Time-dependent wavepacket calculations

For many of the most interesting problems that concern the dynamics of adsorbates at surfaces, the harmonic approximation is not sufficient. If the dynamics involves highly excited states in the adsorption well, the harmonic approximation is likely to break down due to large vibrational amplitudes of these states. In particular, for many important dynamical surface processes, such as surface scattering, surface reactions, adsorption and desorption, in which the continuum levels of the adsorption potential are involved, the harmonic approximation is, of course, invalid.

Time-dependent wavepacket methods have proven powerful for calculating the quantum dynamics for many reactive and non-reactive surface processes [57]. The purpose of these methods is to solve the time-dependent Schrödinger equation,

\[
\frac{i\hbar}{\partial t} \frac{\partial \psi}{\partial t} = \hat{H}(t)\psi \tag{3.12}
\]

for the wavefunction \( \psi(t) \). This equation is solved by propagating an initial wavefunction, \( \psi(0) \), in time. One attractive property of the time-dependent wavepacket methods, is that they can handle time-dependent Hamiltonians, allowing treatment of externally driven systems. Perhaps the most rewarding
feature of the time-dependent wavepacket methods is that they provide a description of the time evolution of a process. The computational results from these methods are therefore comparatively easy to visualize and can provide a good physical insight into a process. This quality of time-dependent wavepacket methods can be very valuable in studies of molecule–surface dynamical processes, which can have quite complicated pathways. The main drawback of the time-dependent wavepacket methods is that only problems that include quite a limited number of degrees of freedom can be treated. At present, the largest quantum dynamical problems that have been treated using wavepacket calculations, have included dynamics in six degrees of freedom [48].

The eigenenergies and wavefunctions of a time-independent Hamiltonian can be obtained in a straightforward way from a quantum mechanical propagation of a wavefunction [58]. The eigenenergies, $E_m$, are obtained from the Fourier transform, $C(\omega)$, of the wavefunction autocorrelation function, $C(t) = \langle \psi(0) | \psi(t) \rangle$, weighted by a window function, $W(t)$:

$$C(\omega) = \frac{1}{2\pi} \text{Re} \int_0^T W(t) C(t)e^{i\omega t} dt = \sum_m |c_m|^2 \text{Re} W(\omega - \omega_m).$$ (3.13)

Here, $E_m = \hbar \omega_m$, and $c_m$ are the coefficients for an expansion of the initial wavefunction in the energy eigenfunctions, $\psi_m$: $\psi(0) = \sum_m c_m \psi_m$. The window function is introduced in order to reduce high order Fourier terms, which derive from the finite time, $T$, for which the time evolution of the wavefunction is calculated [59]. The characteristic features of the window function are that the real part of the Fourier transform, $\text{Re} W(\omega)$, is peaked at $\omega = 0$, has a width that is proportional to $1/T$ and has an integrated strength of unity. The spectrum $C(\omega)$ is thus peaked at the eigenenergies, $E_m$, and the coefficients $c_m$ determine the intensities of the peaks. Once the eigenenergies are known, the corresponding eigenfunctions, $\psi_m$, can be derived by performing a new wavefunction propagation. The eigenfunctions are obtained from a weighted Fourier transform, for each energy $E_m$, of the time evolving wavefunction,

$$\psi_m \propto \int_0^T W(t) \psi(t)e^{i\omega_m t} dt.$$ (3.14)

Note that this method can have complications if there is energy degeneracy between states of the potential. The calculated wavefunction $\psi_m$ may then have contributions from the different degenerate states with energy $E_m$. However, by a proper choice of the initial wavefunction, $\psi(0)$, it is possible to enhance the contribution of a specific eigenfunction to the calculated wavefunction $\psi_m$. 

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It is also straightforward to calculate intensities for transitions among the eigenstates of a time-independent Hamiltonian, using a method that is similar to the one described for the eigenenergy calculations. The intensity of, for example, a dipole transition from an initial state $|i\rangle$, is obtained from a propagation of an initial wavefunction given by $|\psi_\mu(0)\rangle = \mu|i\rangle$, where $\mu$ is the dipole moment operator. The wavefunction autocorrelation function $C_\mu(t) = \langle \psi_\mu(0)|\psi_\mu(t)\rangle$ is then given by

$$C_\mu(t) = \langle i|\mu e^{-i\hat{H}t/\hbar}\mu|i\rangle = \sum_m |\langle m|\mu|i\rangle|^2 e^{-i\omega_m t}$$

and the transition intensities are obtained from the weighted Fourier transform of $C_\mu(t)$:

$$C_\mu(\omega) = \sum_m |\langle m|\mu|i\rangle|^2 \text{Re} W(\omega - \omega_m).$$

The dipole intensity for a specific transition, $|i\rangle \rightarrow |f\rangle$ is obtained by integrating $C_\mu(\omega)$ over the corresponding peak, at $\omega = \omega_f$. This method of calculating transition intensities is particularly useful in summations of transition intensities for a continuum of states. In analogy to the discussion in relation to the eigenfunction calculations, it is not possible to distinguish intensities for different degenerate transitions.

### 3.2 Method of wavepacket propagation

#### 3.2.1 Short time evolution operators

The general solution to the time-dependent Schrödinger equation in Eq. (3.12) can be expressed in terms of the time evolution operator, $\hat{U}$ [9], as

$$\psi(t) = \hat{U}(t, 0)\psi(0).$$ \hspace{1cm} (3.17)

Various approaches are possible for evaluating the effect of $\hat{U}(t, 0)$ on $\psi(0)$, depending on whether the Hamiltonian is time-dependent or not. A method that is generally applicable is to decompose $\hat{U}$ into a product of short time evolution operators, using the Trotter formula,

$$\hat{U}(t, 0) = \prod_{n=0}^{N-1} \hat{U}([n+1]\Delta t, n\Delta t),$$

where $t = N\Delta t$. By choosing the time increment $\Delta t$ sufficiently small, the Hamiltonian is approximately constant during each time step. The short time evolution operator is then given by the simple expression

$$\hat{U}(t + \Delta t, t) = \exp\left(-\frac{i}{\hbar}\hat{H}(t)\Delta t\right).$$

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Note that if the Hamiltonian is time-independent, which is the case in the calculations presented in this thesis, this decomposition of the total time evolution operator does not involve any approximation.

In the time-dependent wavepacket calculations that are presented in this thesis, the symmetric Split Operator approximation [58] has been used for the short time evolution operator. In this approximation, \( \hat{U}(t+\Delta t, t) \) is given by

\[
\hat{U}(t+\Delta t, t) = \exp \left( -\frac{i}{2\hbar} \hat{V} \Delta t \right) \exp \left( -\frac{i}{\hbar} \hat{T} \Delta t \right) \exp \left( -\frac{i}{2\hbar} \hat{V} \Delta t \right), \quad (3.20)
\]

where \( \hat{V} \) and \( \hat{T} \) are the potential energy operator and the kinetic energy operator, respectively. Because the split operators are each unitary, this method of propagation conserves the norm. The error that is introduced by splitting the time evolution operator is due to the non-commutivity of \( \hat{T} \) and \( \hat{V} \). This error accumulates in the phase and the energy of the wavepacket and the size of the error is \( O(\Delta t^3) \). Note that an absolute upper boundary for the time increment in any short-time evolution propagation method is determined by the maximum spectral bandwidth, \( \Delta E_{\text{max}} \), of the wavepacket, by \( \Delta t < \hbar / \Delta E_{\text{max}} \). If this criterion is not satisfied, the effects of different frequency components in the time evolution will be mixed (Aliasing errors).

### 3.2.2 Approximate Hamiltonians

The time evolution of the wavefunction that describes the adsorbate-substrate system is determined by the Hamiltonian for the system. In the rigid substrate approximation, which is valid if the mass of the adsorbate is much smaller than the mass of the substrate atoms, the Hamiltonian for a single diatomic molecule adsorbed at the surface depends on six coordinates. In this thesis, the coordinates are chosen to be the position of the center of mass of the molecule, \((x, y, z)\), the distance between the ions, \(r\), and the polar and azimuthal angles, \(\theta\), and \(\varphi\), that describe the orientation of the molecular axis (see Fig. 3.1).

Although, for some systems, it is possible to perform six-dimensional time-dependent wavepacket calculations [48], it has only been necessary to treat up to three dimensions in the wavepacket calculations presented in this thesis. For the systems presented in this thesis, the lateral motion of the molecule has been found to be approximately decoupled from the other degrees of freedom, so that the dynamics for the \(x\)- and \(y\)-coordinates may be solved separately. For instance, for the case of molecular hydrogen physisorbed on Cu(100) and Cu(111), the lateral motion is essentially free. Furthermore, the potential energy has been found to vary only marginally with
Figure 3.1: A six-dimensional coordinate system describing the configuration of a diatomic molecule at a rigid surface. The Cartesian coordinates, $(x, y, z)$, describe the position of the centre of mass and $r$ is the internal bond length. The polar angle, $\theta$ and the azimuthal angle, $\varphi$, describe the orientation of the molecule relative to the surface.
the azimuthal angle, \( \varphi \). The variation of the energy eigenfunctions with \( \varphi \), is then to a good approximation given by \( e^{im\varphi} \), where \( \hbar m \) is the \( z \)-component of the angular momentum. The wavefunction may therefore be separated, 
\[
\psi(x, y, z, r, \theta, \varphi) = X(x)Y(y)\sum_m \psi_m(z, r, \theta)e^{im\varphi},
\]
and the main problem is reduced to solving the time-dependent Schrödinger equation for \( \psi_m(z, r, \theta) \) in a three-dimensional potential energy \( V(z, r, \theta) \). The Hamiltonian for the effective wavefunction, defined by 
\[
\psi_{\text{eff}}^m(z, r, \theta) \equiv \psi_m(z, r, \theta)/r,
\]
is given by
\[
H_{\text{eff}} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2} \hat{L}^2 + V(z, r, \theta),
\] (3.21)
where \( M \) and \( \mu \) are the total and reduced masses of the molecule, respectively, \( \hat{L} \) is the angular momentum operator,
\[
\hat{L}^2 = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta}
\] (3.22)
and \( \hat{I} = \mu r^2 \) is the moment of inertia of the molecule.

In some of the adsorbate dynamics studies presented in this thesis, the number of dimensions in the wavepacket calculation has been further reduced by decoupling the motion in the \( r \)-coordinate from the motion in the \( z \) and \( \theta \)-coordinates. This adiabatic approximation is valid in these studies because the energy for internal vibration is much larger than the translational and rotational energies. For instance, in the molecular scattering calculations for \( \text{D}_2 \) and \( \text{N}_2 \), presented in Paper V, the total kinetic energy (< 100 meV) is substantially smaller than the energy for excitation of an internal vibration (about 300 meV for \( \text{N}_2 \) and about 400 meV for \( \text{D}_2 \)).

### 3.2.3 Pseudo spectral representation of the wavefunction

In the numerical computation, the wavefunction must be represented on a discrete grid. This representation may be viewed as a sampling of the true continuous wavefunction, with the functional values between the gridpoints given by an interpolating function. The specific choice of the interpolating function is intimately connected to the representation of quantum mechanical operators. For instance, using a finite difference approximation for the derivative operator, is equivalent to an expansion of the wavefunction in local polynomials [60].

The pseudo spectral methods are based on a representation of the wavefunction on both a real space grid and a spectral grid [61]. The representation on the spectral grid is based on an expansion of the wavefunction in a set of
global basis functions. In a one-dimensional example, the value of a wavefunction $\psi$ at a grid point $x_q$ is expanded as

$$\psi(x_q) = \sum_n a_n g_n(x_q),$$

(3.23)

where $a_n$ are expansion coefficients and $g_n(x)$ are the basis functions. The evaluation of the expansion coefficients can be made in a straightforward way, if the basis functions obey the discrete orthogonality relation,

$$\sum_q g_n(x_q) g_{n'}(x_q) = \delta_{nn'}.$$  
(3.24)

Eq. (3.23) can then be directly inverted to obtain the expansion coefficients,

$$a_n = \sum_q \psi(x_q) g_n(x_q).$$  
(3.25)

The requirement of discrete orthogonality introduces a relation between the choice of basis functions and the choice of sampling points. Note that a wavefunction that is band limited, that is, the wavefunction can be described by a finite expansion in the discretely orthogonal basis functions, is specified exactly by its values in the sampling points.

The convergence with respect to grid size is generally more rapid for the pseudo spectral methods than for finite difference methods. For instance, using the pseudo spectral Fourier method [62] for a Gaussian type wavefunction, the convergence is exponential with grid size [57]. The reason for the better convergence for the pseudo spectral methods than for the finite difference methods, is that the expansion of the wavefunction in global basis functions allows for a more accurate representation of non-local operators, such as the kinetic energy operator, than is obtained by an expansion in local basis functions.

The choice of basis functions and, hence, sampling points, is guided by the form of the Hamiltonian operators. For the effective Hamiltonian in Eq. (3.21), a convenient choice for the spectral basis consists of a product of plane waves, $\exp(ik_z z)$ and $\exp(ik_r r)$, and associated Legendre functions, $P_j^m(\cos \theta)$ for the $z$-, $r$- and $\theta$-coordinates, respectively. The effective kinetic energy operator of Eq. (3.21) then has the following simple form in the spectral space:

$$\hat{T}_{\text{eff}} = \frac{\hbar^2 k_z^2}{2M} + \frac{\hbar^2 k_r^2}{2\mu} + \frac{\hbar^2}{2I} (j + 1).$$  
(3.26)

Thus, the potential energy operator and the kinetic energy operator are local operators in the real and spectral spaces, respectively. Using the split time
evolution operator [Eq. (3.20)], the time evolution for the effective wavefunction, $\psi_{\text{eff}}$, over one time step is therefore conveniently performed by the following steps: (i) The operator $\exp(-i\hat{V}\Delta t/2\hbar)$ is applied to the initial wavefunction. (ii) The resulting wavefunction is transformed to the spectral basis and the operator $\exp(-i\hat{T}_{\text{eff}}\Delta t/\hbar)$ is applied. (iii) The resulting wavefunction is transformed back to the real space and $\exp(-i\hat{V}\Delta t/2\hbar)$ is applied.

The representation of the effective wavefunction in the spectral $\exp(ik_zz)$ and $\exp(ik_rr)$ spaces, is based on discrete Fourier transforms of the wavefunction. The real space grids in $z$ and $r$ are uniform, given in an arbitrary coordinate $x$ by $x_q = x_0 + q\Delta x$, $q = 0, \ldots, N - 1$, where $N$ is the number of sampling points. The expansion in the basis functions is given by

$$\psi(x_q) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} a_n e^{ik_n x_q}$$

(3.27)

where $k_n = (n - N/2)\Delta k$ and $\Delta k = 2\pi/N\Delta x$. Note that the exponential functions obey the discrete orthogonality condition over the uniformly distributed discrete points in the real and momentum spaces [63]. Therefore, a wavefunction that is band limited, that is, has a finite maximum wavevector, $k_{\text{max}}$, is specified exactly by its values in the sampling points, provided that $2|k_{\text{max}}| < N\Delta k$, that is, the grid spacing satisfies $\Delta x < \pi/|k_{\text{max}}|$. In the work presented in this thesis, the discrete transformations of the wavefunction between the real and spectral spaces were efficiently performed using fast Fourier transforms (FFT) [59]. Note that the discrete Fourier transforms implicitly introduce periodic boundary conditions. Therefore, to prevent the continuum states of the potential in the $z$-direction from scattering against the backside of the repulsive wall, an imaginary absorbing potential [64] has been introduced at the grid boundary. This potential absorbs an incident wavefunction, with a minimum of reflection, before it reaches the grid boundary.

The representation in the spectral basis of the variation of the effective wavefunction with $\theta$, is based on an expansion in the associated Legendre functions. In a one dimensional example, the value of the wavefunction at a gridpoint $\theta_i$, is expanded as

$$\psi_m(\cos \theta_i) = \sum_j a_j c_{jm} P_j^m(\cos \theta_i),$$

(3.28)

where $c_{jm}$ are normalization constants, given by

$$c_{jm} = \sqrt{\frac{(j + 1/2)(j - m)!}{(j + m)!}}.$$  

(3.29)
The real and spectral grids are determined by the maximum rotational quantum number, $j_{\text{max}}$, that needs to be represented. The associated Legendre functions, $P_{ji}^m(\cos \theta)$, of degrees $j \leq j_{\text{max}}$, satisfy the discrete orthogonality condition in Eq. (3.24), provided that the sampling points $\theta_i$ are chosen to be the roots of the Legendre polynomial $P_{j_{\text{max}}+1}(\cos \theta)$. The discrete orthogonality can be demonstrated by first noting that the associated Legendre functions can be written as

$$P_{ji}^m(\cos \theta) = (1 - \cos^2 \theta)^{m/2}Q_{j-m}(\cos \theta),$$

where $Q_i(x)$ denotes a polynomial in $x$ of order $i$. The sum over the discrete sampling points in Eq. (3.24) can then be written

$$\sum_i c_{ji}c_{j'i}P_{ji}^m(\cos \theta_i)P_{j'i}^m(\cos \theta_i) = \sum_i Q_{j+j'}(\cos \theta_i)$$

where $Q_{j+j'}(\cos \theta)$ is a polynomial in $\cos \theta$ of maximum degree $2j_{\text{max}}$. The theory of Gaussian quadrature [63] states that the sum in Eq. (3.31) over this choice of sampling points is exactly equal to the definite integral,

$$c_{ji}c_{j'i}\int_{-1}^{1} P_{ji}^m(\cos \theta)P_{j'i}^m(\cos \theta)d(\cos \theta) = \delta_{jj'}.$$  

Thus, from Eqs. (3.31) and (3.32), it has been shown that the associated Legendre functions satisfy the discrete orthogonality condition in Eq. (3.24) over the sampling points $\theta_i$ and, accordingly, that the wavefunction, with maximum rotational quantum number $j_{\text{max}}$, can be exactly represented on the real and spectral grids.

As has been shown in the previous two paragraphs, the wavefunction can be represented exactly on the discrete grids if it is localized both in the real and the spectral space. In real problems, this condition is generally not satisfied. For instance, the wavefunction of a free particle is localized in momentum space, but stretches over all real space. In the numerical computation, the true wavefunction is therefore approximated by a confined wavepacket, which has an amplitude that is negligible outside the real and spectral spaces of the calculational cell. The wavefunction that is most well confined, in a linear coordinate, is the well-known Gaussian wavepacket.

### 3.3 Density functional calculations

#### 3.3.1 Density functional theory

The development of density functional theory (DFT) has had a tremendous impact on the ability to theoretically investigate and predict the bonding
between atoms in molecules and solids. DFT calculations of the charge density and total energy can, at present, be performed with useful accuracy for systems including hundreds of atoms. The impact that DFT has had in the field of quantum chemistry, is illustrated by the awarding of the 1998 Nobel Prize in Chemistry to Walter Kohn for his development of the theory.

The power of DFT is that it reduces the extremely difficult problem of treating the many-body wavefunction of interacting electrons, into the problem of treating single-electron wavefunctions and the electron density. The foundation of the density functional theory is based on the Hohenberg-Kohn theorem [65], which states that for a system of interacting electrons in an external potential, \( v_{\text{ext}}(\mathbf{r}) \), the groundstate electron density, \( n(\mathbf{r}) \), uniquely determines the potential \( v_{\text{ext}}(\mathbf{r}) \). Hence, the electron density determines the Hamiltonian of the system, and accordingly all properties that are governed by the Hamiltonian. Specifically, the total energy of the groundstate, \( E[n(\mathbf{r})] \), is a unique functional of the groundstate electron density. Thus, the groundstate electron density and energy can, in principle, be obtained by minimizing the total energy functional with respect to the electron density. However, a straightforward minimization technique to derive the groundstate properties is not possible, since the exact form of the universal energy functional is not known. Only the energy of the electron-ion interaction and, trivially, the ion-ion interaction is known exactly in terms of the electron density.

The expression for the total energy can, however, be formulated in terms of a set of self-consistent one-particle Schrödinger-like equations, as was first shown by Kohn and Sham [66]. These equations are identical to the Schrödinger equations for a set of non-interacting electrons in a potential \( v(\mathbf{r}) \), which includes \( v_{\text{ext}}(\mathbf{r}) \), the average electrostatic potential and an exchange-correlation potential term. This exchange-correlation potential, which is the functional derivative of the total exchange-correlation energy with respect to the electron density, contains all many-particle effects. The Kohn-Sham equations are self-consistent in the respect that the Hartree energy and the exchange-correlation energy of the Hamiltonian are generated by the eigenfunctions of the Hamiltonian, through the electron density. The equations are solved by an iterative process, in which an initial set of one-particle eigenfunctions are used to construct the Kohn-Sham Hamiltonian. This Hamiltonian is then diagonalized and a new set of one-particle eigenfunctions are obtained. The iteration is performed until selfconsistency is obtained.

The form of the exchange-correlation energy functional is not known exactly, but various approximations are available. The simplest choice for this approximation is the local density approximation (LDA). In this approximation, the exchange-correlation potential at each point, \( \mathbf{r} \), is given by
the potential for a homogeneous electron gas of density $n(r)$. Non local exchange-correlation effects have been successfully introduced by constructing functionals that depend also on the gradient of the electron density. Such approximations of the exchange-correlation energy are denoted generalized gradient approximations (GGA). Although LDA works surprisingly well for bulk systems, which have a slowly varying electron density, GGA generally gives more accurate results for systems of low coordination, such as atoms, molecules and surfaces [67].

Several groundstate quantities, other than total energy and electron density, can also be obtained from DFT calculations. For instance, the forces on the atomic ions can be directly obtained from the calculated one-electron wavefunctions, using the Hellman-Feynman theorem [55].

### 3.3.2 Plane wave, pseudopotential method

Several approaches exist for implementing the iterative process by which the Kohn-Sham equations are solved. The major difference between the approaches is the representation of the one-electron wavefunctions. For example, in the so-called tight-binding method, the wavefunctions are expanded in local atomic orbitals. In the DFT calculations presented in this thesis, a global plane wave expansion has been used. A thorough description of this plane wave method is provided in Ref. [68]. Some properties of plane wave expansions of wavefunctions are discussed briefly in Section 3.2.3.

The plane wave expansion is particularly suitable for treating bulk and surface systems, which exhibit spatial periodicity. As stated by the Bloch theorem [69], the wavefunction, $\psi_k(r)$, of a single electron in a periodic potential, can be written as a sum of plane waves, $\psi_k(r) = \sum G a_{k+G} \exp(i(k + G) \cdot r)$, where $\exp(i G \cdot r)$ are plane waves that are periodic with the potential. Although, in principle, the sum is infinite, plane waves with energies above a certain value are expected to contribute only minor to the description of the wave function, and the sum may be truncated. Still, the implicit periodicity means that an infinite number of electron wavefunctions, each associated with a $k$-point, must be represented in the calculation. However, because wavefunctions for $k$-points that are close will be almost identical, a discrete $k$-point sampling will give a good description of the system of electrons. The plane wave description of the electron wavefunctions can be made arbitrarily accurate by increasing the $k$-point sampling and the energy cutoff. As noted in Section 3.2.3, a plane wave expansion also simplifies the evaluation of the kinetic energy operator in the Hamiltonian. One major problem with plane wave methods is that the representation of core electrons, which have very high kinetic energies, requires a large number of basis functions.
The problem of representing core electrons can be overcome by replacing the effect of the nuclei and the core electrons with pseudopotentials. The physical argument for this treatment of the core electrons is that the valence electrons give the major contributions to the interaction between atoms, while the low-lying core electron states are practically inert. The pseudopotentials are constructed so that, outside a certain radius from the nuclei, the valence orbitals of the pseudopotential are similar to those of the true ion.

Although the Bloch theorem, relying on periodicity of the potential, is formally invalid for describing the variation of a wavefunction in the direction normal to a surface, plane wave methods can still be used for surface systems. The surface system is modeled by a supercell that contains a slab and a vacuum region. By increasing the vacuum region, the interactions between the periodicly repeated slabs can be made arbitrarily small.
Conclusions and outlook

Theoretical studies of the vibrational and rotational motion of diatomic molecules at surfaces have been performed. Two and three-dimensional PESs have been constructed for non-dissociative adsorption of H$_2$ and N$_2$ on Cu(111) and for H$_2$ on Cu(510), using density functional theory (DFT). The adsorbate dynamics for these systems, and for H$_2$ on Cu(100), has been investigated using time-dependent wavepacket calculations. For CO chemisorbed in the c(4×2) structure on Pt(111), the bound vibrational modes have been studied within the harmonic approximation, using DFT.

Proof for the observation of a non-thermal direct photodesorption process has been presented, based on a good agreement between measured rates of desorption and calculated rates of direct photodesorption, induced by infrared radiation from the walls of a UHV chamber. From scattering calculations it has been shown that an observed large difference in the probability for rotational inelastic scattering of D$_2$ and N$_2$ from Cu(111), is mainly due to the difference in the rotational constant of the molecules. Exotic adsorption states have been identified for H$_2$ at the step of a Cu(510) surface. In these states, which show characteristic features of both chemisorption and physisorption, the molecule is confined to perform two-dimensional quantum rotation. From a calculation of the vibrational modes of CO adsorbed in a c(4×2) structure on Pt(111), reassignments of previously measured vibrational energies to low-energy modes have been suggested and two vibrational modes, which are dipole forbidden from the local adsorption site symmetry, have been found to be weakly dipole active.

The results presented in this thesis point to several interesting paths of future work. For instance, all the quantum dynamics calculations have been based on the rigid substrate approximation. An interesting route to follow in the future, would be to try to take the coupling to the substrate into account, by incorporating dissipation into the calculations. This route is particularly interesting in view of the available experimental data from the scattering experiments presented in Paper V.
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