Dynamics of charge transfer states on metal surfaces: The competition between reactivity and quenching

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The dynamics of excited states of adsorbates on surfaces caused by charge transfer is studied. Both negative and positive charge transfer processes are possible. In particular we are interested in positive charge transfer from a metal surface to molecular or atomic oxygen adsorbed on the surface. Once the negatively charged oxygen on the surface loses an electron it becomes chemically activated. The ability of this species to react depends on the quenching time or back transfer. The analysis of these processes is based on a set of diabatic potential energy surfaces each representing a different charged oxygen species. The dynamics is followed by solving the multichannel time-dependent Schrödinger equation or Liouville von Neumann equation. Due to the nonadiabatic character of these reactions large isotope effects are predicted.

I. Introduction

Charged molecular and atomic species adsorbed on a metal surface are well documented phenomena. In transition metals it is energetically cheap to move electrons in and out of the d orbitals creating a partially charged molecular or atomic adsorbate. For oxygen for example, two stable adsorbed molecular species, peroxide and superoxide, have been observed, differing by the amount of negative charge transferred from the metal.[1–8] The extra charge weakens the molecular bond and increases the bond distance. In addition, the binding of the molecule to the surface is strengthened due to the Coulombic attraction between the molecular charge and its image in the metal. Adsorbed atomic oxygen on a metal surface is also partially charged due to the large negative affinity of the oxygen atoms (-1.4 eV).

Adsorption of N_2 is quite different since it has a high ionization energy and negative electron affinity. Only positively charged molecular excited states of nitrogen can be stabilized. The low energy adsorbed states are the ones that bind through the π orbitals resembling the binding of CO. Atomic nitrogen creates a very strong bond with transition metals where the net charge transfer is small.

In the adsorption of CO the charge transfer to or from the metal is small. The binding energy of CO to metals is weak and is similar to the binding energy of metal carbonyl compounds. In the gas phase CO is quite an inert material. The triple bond between the carbon and oxygen is almost immune to chemical attack. The adsorption of CO on a metal surface only slightly reduces the bond energy.

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These examples illustrate that molecules adsorbed on transition metal surfaces possess a variety of electronic configurations. A key question is the role of these electronic configurations in elementary catalytic processes. Insight into this question requires methods to calculate the electronic configurations, and to follow the transitions from one electronic configuration to another.

One approach is to follow the dictum of the Born–Oppenheimer approximation and to consider adiabatic dynamics on a single ground electronic state. The assumption is that the electronic structure of a dynamical encounter changes continuously from one configuration to another. The advantage of this approach is that the powerful methods of quantum chemistry, in particular density functional theory (DFT), are most effective in calculating the ground state potential surfaces.[9,10]

The other approach is a non-adiabatic one in which the nuclear dynamics is followed on more than one potential energy surface simultaneously. The topology of crossings and conical intersections between potentials determines the outcome of the chemical event. The difficulty of this approach is due to the lack of effective methods to calculate the various potentials and non-adiabatic coupling terms for extended systems on metals. There are only a few exceptions,[11–13] based on embedding a cluster of primary atoms into a continuous description of the bulk. For non-metallic surfaces, such as metal oxides, the excitation process is more localized, therefore cluster calculations are more justified and give reasonable results for excited electronic surfaces.[14,15]

Obtaining the potential surfaces and nonadiabatic coupling terms is only the first step in the task of modeling nonadiabatic chemical encounters on surfaces. The next step is to simulate the nuclear dynamics on these surfaces. The difficulty is that the cost of a full quantum representation scales exponentially with the number of degrees of freedom. For this reason current time-dependent methods for solving the Schrödinger equation are capable of representing problems with up to 6 degrees of freedom for the effective mass of hydrogen[16,17] and up to 3–4 degrees of freedom for the effective masses of nitrogen or oxygen.[18,19] This limits the application of direct quantum simulation to model problems. There is the option of employing approximate semiclassical methods for describing nuclear nonadiabatic dynamics.[20] In a careful comparison between the best semiclassical methods and full quantum calculation for multidimensional nonadiabatic transitions we found qualitative discrepancies between the two approaches.[21]

The dynamics of molecules adsorbed on metal surfaces are complicated due to the simultaneous encounter with dissipative forces from two origins: electronic and phononic. Electronic dissipative forces are caused by the interaction of the free metal electrons, or more precisely electron–hole pairs with the adsorbate. These electron–hole pairs are able to exchange a continuous amount of energy. The other source of dissipative forces is the lattice vibrations or phonons, which again form a band of energy levels. Dissipation has a strong influence on the nonadiabatic dynamics.[22] We have shown a general turnover behavior as a function of the dissipative parameters describing electronic dephasing and vibrational relaxation. For small values of these parameters the non-adiabatic rate is enhanced. Above a critical value the nonadiabatic rate decreases. In any event dissipation does not justify a reduction of the dynamical description to motion on a single adiabatic electronic surface. In this study, different quantum theories are considered to describe the short-time dissipative dynamics of an adsorbate interacting with a metal surface. The alternatives range from solving the Liouville von Neumann equation using an empirical description of the dissipation to the use of a surrogate Hamiltonian formulation cast into a wavepacket description.

II. The non-adiabatic model

In the generic non-adiabatic model the dynamics of the system is simulated by solving the time-dependent Schrödinger equation on coupled potential energy surfaces. As an example the dynamics on three potential energy surfaces and three effective coordinates is examined. The wavefunction has the form:

$$\psi = \begin{pmatrix} \psi_g(z, r, \theta) \\ \psi_m(z, r, \theta) \\ \psi_a(z, r, \theta) \end{pmatrix} \qquad (2.1)$$

where z is the molecular distance from the surface, r the internuclear distance and θ the orientation angle (see Fig. 1).

Once an initial state is described, The evolution in time is generated according to the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \tag{2.2}$$

where the Hamiltonian is described as:

$$\hat{H} = \begin{pmatrix} H_g & V_{gm} & V_{ga} \\ V_{mg} & H_m & V_{ma} \\ V_{ag} & V_{am} & H_a \end{pmatrix} \tag{2.3}$$

and $H_1 = P^2/2\mu + V_l$ where l indicates the species: g, gas phase species, m, molecular surface species and a atomic dissociated species. Within this general framework one can study the basic encounters on surfaces. Fig. 2 shows a typical topology of the charge transfer states of oxygen on a metal surface. It is clear that due to different coulombic stabilization, spin states and atomic surface bonding, the different charge transfer states cross each other.

A nonadiabatic dynamical encounter is determined first by the charged state of its initial wavefunction. Following the event in time, the system will cross from one potential to another. The topology of the crossing seams has a profound influence on the outcome, leading to propensity rules.[23] Enhancement by incident translational energy of nonadiabatic transition requires a crossing seam perpendicular to the z direction. A parallel seam will cause enhancement by vibrational excitation of the incoming molecule.

A signature of nonadiabatic dynamics is a large isotope effect. The crossing seams and conical intersections represent a breakdown of the Born–Oppenheimer approximation. As a propensity rule, when the collision energy is below the crossing seam nonadiabatic tunneling takes place and the light isotope has a larger propensity for transition. Above the crossing seam the heavy isotope which is more adiabatic has a larger propensity for nonadiabatic transition.[21,24–26]

A hidden assumption in the reduced dynamical description is that the other coordinates are frozen. The time-scale of the encounter determines if this assumption is valid. For extremely short reactions only a few degrees of freedom participate. For longer times the influence of the other

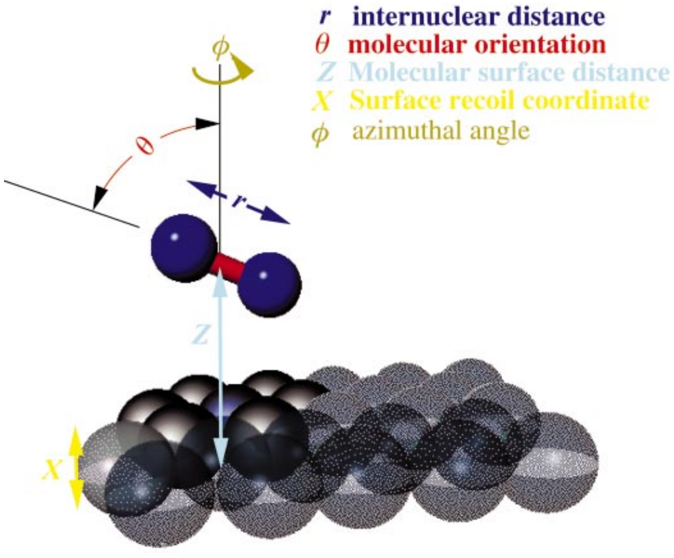

Fig. 1 The coordinate system of a molecule–surface encounter. A reduced description treats only part of the coordinates explicitly.

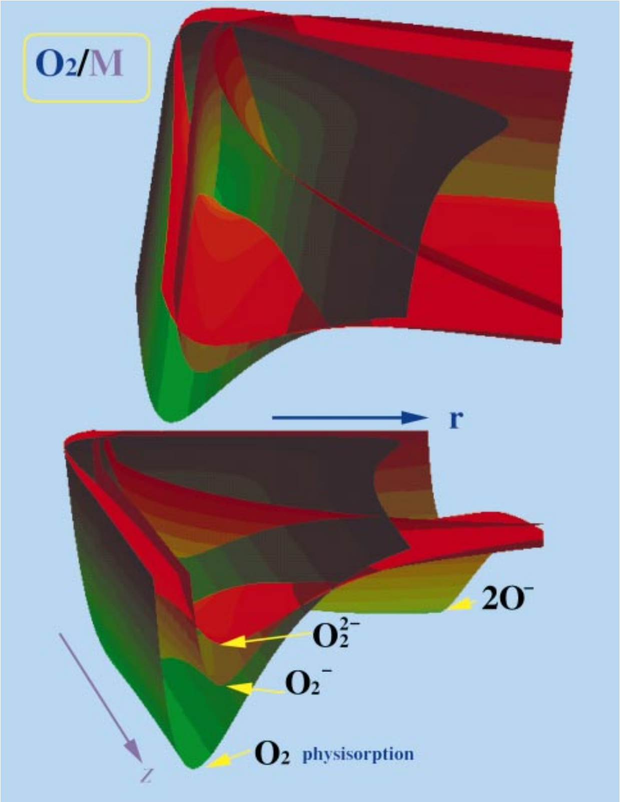

Fig. 2 Potential energy surfaces of oxygen on a metal surface showing the different charge transfer states.

degrees of freedom has to be accounted for. Due to the exponential growth of quantum computation with dimensionality one wants to avoid explicit inclusion of these degrees of freedom. The aim of a theoretical description is therefore to find an implicit description of the influence of the extra degrees of freedom.

III. Reduced dynamics

The basic idea is to distinguish between the dynamics of the primary system, the adsorbate, and that of the bulk, which consists of the electronic and lattice degrees of freedom. The focus of the study is the dynamics of the primary system which therefore requires a detailed description. The treatment of the bulk, or the bath modes, includes the minimum details required to specify their influence on the primary system. The system–bath representation is developed through the study of the total Hamiltonian. This Hamiltonian is partitioned into the primary system's bare Hamiltonian $\hat{H}_s$ the bath Hamiltonian $\hat{H}_B$ and an interaction term $\hat{H}_{int}$ leading to:

$$\hat{H} = \hat{H}_s + \hat{H}_B + \hat{H}_{int}. \tag{3.1}$$

The primary system Hamiltonian has the form:

$$\hat{H}_s = \hat{T} + V_s(\hat{R}) \tag{3.2}$$

where $\hat{T} = \hat{P}^2/2M$ is the kinetic energy of the primary system and V_s is an external potential which is a function of the system coordinates $\hat{R}$.

The idea of partitioning the system into primary and bath modes has been the key element in the quantum theory of dissipative dynamics. Starting from the work of Bloch,[27–29] reduced equations of motion for the primary system have been derived. The reduction is obtained by performing a partial trace over the bath degrees of freedom resulting in a Liouville description of the primary mode. The most well studied derivation is based on the assumption of weak coupling between the system and bath leading to a differential equation describing the system's dynamics.[30–33] In this derivation, commonly called Redfield dynamics, the influence of the bath is described by its correlation functions. This basic derivation has been supplemented by the requirement that the reduced equations of motion have the semi-group form, meaning that they preserve the complete positivity of the density operator.[34–36]

A complementary approach to dissipative dynamics is to axiomatically require a semi-group form. This leads to a general form for the reduced evolution equations.[37–39]

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\rho}] + \mathscr{L}_{\mathrm{D}}(\hat{\rho}), \tag{3.3}$$

The generator of the dissipative dynamics, $\mathscr{L}_{\mathrm{D}}$, embodies the effect of dissipation. The form of $\mathscr{L}_{\mathrm{D}}$ in eqn. (3.3) describes Markovian evolution and may be cast into the Lindblad semi-group form:

$$\mathscr{L}_{\mathrm{D}}(\hat{\rho}) = \hat{F}\hat{\rho}\hat{F}^{\dagger} - \tfrac{1}{2}\{\hat{F}^{\dagger}\hat{F}, \hat{\rho}\} \tag{3.4}$$

where $\hat{F}$ is an operator defined on the Hilbert space of the primary system. These equations allow a consistent study of different dissipative models,[40,41] but require an empirical treatment when a particular system is studied.

The practical disadvantage of both the semi-group and the Redfield theories is that they are formulated in Liouville space where the state of the system is represented by a density operator. This fact squares the number of required representation points in comparison to a wavefunction description. Although powerful numerical techniques have been developed to solve the dynamics in Liouville space[32,42–46] it still is extremely taxing to treat these problems, limiting the scope of systems that can be studied.

An alternative approach, is based on constructing a surrogate finite system bath Hamiltonian.[47,48] In the limit of an infinite number of bath modes the true system's dynamics is reconstructed. The procedure constructs a surrogate Hamiltonian in which the system–bath interaction term is renormalized. To reduce further the computational effort, the bath modes are represented by the elementary two-level system (TLS). The primary system is represented by the Fourier method,[49–52] allowing a very general description. The dynamics generated by the finite surrogate Hamiltonian are able to reproduce, for a specified period of time, the true system–bath dynamics. This construction is not Markovian and therefore differs from the Redfield or semi-group treatments. The use of a finite number of degrees of freedom to represent the bath limits the length of time in which the dynamics is consistent with that of an infinite bath. The finite nature of the bath usually shows up as recurrences which eventually appear. Increasing the number of bath modes postpones the recurrence to a later time, thus the number of modes needed is determined by the time-scale of the dynamics.

The surrogate Hamiltonian approach is close in spirit to real time path integral techniques,[53,54] where a large many-body propagator is constructed and approximated. These approximations represent the bath modes as harmonic oscillators,[55–58] for which the path integration can be carried out analytically.[59]

The model of the harmonic bath has been used almost exclusively in modeling dissipative dynamics. The bath Hamiltonian $\hat{H}_{\mathrm{B}}$ is then decomposed to an infinite sum of normal modes:

$$\hat{H}_{\mathrm{B}} = \sum_{j} \varepsilon_j \hat{b}_j^{\dagger} \hat{b}_j. \tag{3.5}$$

The index j is a multidimensional index describing a complex bath of Bosonic modes with energies ε_j.

Further simplification is obtained if the interaction term is a multiplication of a dimensionless geometric function $f(\hat{R})$ with a Boson mode $\hat{b}_j^{\dagger}$ of potential coupling strength V_j:

$$\hat{H}_{\mathrm{int}} = f(\hat{R}) \sum_{j} V_j(\hat{b}_j^{\dagger} + \hat{b}_j). \tag{3.6}$$

The operators $\hat{b}_j^{\dagger}$ and $\hat{b}_j$ are Boson type creation and annihilation operators, obeying the commutation rules: $[\hat{b}_j, \hat{b}_{j'}^{\dagger}] = \delta_{j,j'}\hat{I}$. This system–bath Hamiltonian already represents a drastic reduction in complexity compared to the generic system–bath entity, mainly due to the simple linear (in the bath coordinate) interaction term. The advantage of the model is that it enables an *ab initio* computational procedure. Due to the harmonic assumption classical molecular dynamics can be employed to calculate the bath correlation functions which determine the bath parameters V_j.[48]

The harmonic bath model has fundamental flaws. An important one is that rare Poisson type processes are not described properly. We speculate that Poisson processes are responsible for electronic dephasing on surfaces.[60] Their origin is elastic binary collision of electron–hole pairs with the charge distribution induced by the adsorbate. In a semi-group description the dissipative generator has the form:

$$\mathscr{L}_{\mathrm{D}}(\hat{\rho}) = \gamma(\mathrm{e}^{-(\mathrm{i}/\hbar)\hat{H}_{\mathrm{s}}\phi}\hat{\rho}\mathrm{e}^{+(\mathrm{i}/\hbar)\hat{H}_{\mathrm{s}}\phi} - \hat{\rho}) \tag{3.7}$$

where γ is the collision rate and ϕ determines the phase shift per collision. Another more subtle effect is that in the harmonic bath quantum entanglement between the system and bath is truncated.

Electronic quenching is a typical example of dissipative nonadiabatic event. On metallic surfaces the process is known as the MGR model.[61–63] The process has been simulated by solving the Liouville von Neumann equation using semi-group dynamics[64–66] or by using stochastic wavepacket methods. In both descriptions the crucial parameter is the residence time on the excited electronic surface. The surrogate Hamiltonian method allows an alternative to these empirical approaches. The bath can be described as a collection of two-level systems each representing a localized electron–hole pair. The system bath coupling can be calculated directly and is the result of dipole–dipole coupling.

The influence of the surface induced dissipation can be classified into the following categories: (i) Direct quenching and excitation which is caused by free charge carriers in the metal. (ii) Electronic dephasing *i.e.* loss of phase coherence between the ground and excited surfaces. (iii) Nuclear dephasing *i.e.* loss of vibrational coherence. (iv) Nuclear relaxation decay of vibrational excitation to equilibrium. Typical time-scales of the electronic processes are in the few femtosecond range thus they are of direct relevance to the nonadiabatic encounters considered.

IV. Oxidation by hole induced processes

Oxygen negative ions are inert which is in contrast to atomic oxygen which is a very stong oxidizing agent. Molecular oxygen is a much less potent oxidizer, nevertheless the low-lying excited states of oxygen are strong oxidizers. On metallic surfaces the stable form of oxygen is negatively charged. To activate the oxygen as an oxidizing agent the amount of charge has to be reduced *i.e.* an oxygen to metal charge transfer has to take place.

Charge transfer from the oxygen to the metal can be promoted chemically. Bombarding a surface with energetic particles or with atoms which have a stong attraction to the surface will excite free charge carriers. Nienhaus *et al.*[67] have shown direct evidence for the creation of electron–hole pairs in collision of hydrogen atoms with a Cu and Ag surfaces. Lee and Rettner and Rettner and Auerbach[68,69] have suggested that these free charge carriers will promote dissociation and desorption of other adsorbed molecules.

A. Oxygen dissociation

Oxygen molecules adsorb on metals in two stable charged states peroxide and superoxide. These two states differ in the amount of negative charge, the peroxide being more negatively charged than the superoxide. The amount of excess charge on the adsorbate is located in an anti-bonding orbital, therefore the O–O bond is weakened and extended. The species is partially stabilized on the surface by an image potential, therefore the peroxide has a stronger binding and shorter equilibrium distance in the oxygen–metal coordinate compared with the superoxide. To complete the description of the O_2–metal interaction, these charged molecular states must be coupled to two additional states: one describes interaction of a neutral molecule with the substrate (physisorption) and the other leads to dissociative adsorption.

Within certain limits, the magnitude of the substrate work function can be manipulated experimentally by co-adsorption of small amounts of electron donors or acceptors.[70–72] Hence, the relative location of the potential wells in the two molecular states can be controlled.

A hole-induced process starts with the initial state of the process corresponding to an adsorbed oxygen in the most stable state, the peroxide state. The hole promotes the initial state into either the superoxide or into the physisorption states. This transition is a vertical electronic transition with no nuclear geometry change.

Starting initially in the peroxide state of the adsorbed O_2, the two possible hole-induced excitations are: Franck–Condon transitions to the physisorption state or to the superoxide state. This is described by a vertical shift of the initial nuclear wavefunction from the peroxide well to the physisorption or superoxide potentials. A third possibility is that the molecular oxygen is initially in the superoxide state. The charge transfer to the hole at the surface leads to excitation of the molecule into the physisorption state. The difference in equilibrium geometry of the peroxide and superoxide states means that the vertical transition to the physisorption potential will be to a different region and the subsequent dynamics is expected to exhibit new features. After the vertical excitation step, the dynamics is followed to final states by solving the multi-channel time dependent Schrödinger equation.[23]

The relaxation dynamics of the excited adsorbate is expected to depend on the initial state and on the amount of energy available by the hole. The maximum vertical transition that can be induced by the hole is limited by the adsorption energy of the impinging atom. Starting at the peroxide potential well the hole can induce a transition either to the physisorption state or to the superoxide state, provided that the required energy for such transitions is available. The lifetime of the hole has to be considered with respect to the dissipative processes taking place. Strong dephasing processes will increase the lifetime. Electronic quenching processes will destroy the "hole". Work in this direction is in progress.

The hole-induced desorption and dissociation play an important role in a variety of systems. Some photo-induced processes on solid surfaces exhibit similarities to the system described above. For example, the dissociation of oxygen molecules following the irradiation of the O_2/Ni(110) system can be interpreted as a hole-induced desorption.[73] In this case the irradiation leads to the dissociation of adsorbed oxygen molecules. The dissociation fragments, oxygen atoms, migrate along the substrate. Eventually the excess translational energy is dissipated. The quenching rate determines the distance the fragment can move.

B. CO oxidation

Oxidation of CO in the gas phase is a slow process. In combustion conditions the reaction is carried out by free radicals for example $O(^3P)$.[74–76] This reaction is also spin forbidden. Metal surfaces can catalyze this reaction. One may ask what is the role of the metal in the mechanism of CO oxidation. In general this is quite a complex question.[77–80] It has structural aspects due to the different forms of oxygen which can reside on the surface.[81] In this study we are only interested in dynamical aspects. In the nonadiabatic framework the reactivity of oxygen either as a molecule or as an atom is related to the small gap between the ground and low-lying excited electronic states.[82,83] Preliminary electronic structure calculations we have carried out on small metal clusters show a small HOME–LUMO gap of approximately 2 eV. On the ground electronic surface the charge transfer is always from the metal to the oxygen atom.[1–4,72] The excited state in the calculation showed a back charge transfer from the oxygen to the metal. DFT calculations of spin-restricted oxygen on Pt show a small energy gap in the range 1–2 eV between the ground and excited spin-restricted oxygen forms.[71]

These excited states suggest a possible explanation for the promotion of CO oxidation on a Ru surface by producing free charge carriers by an ultrashort laser pulse.[84] Two mechanisms have been proposed to explain these observations. The first mechanism termed *electron-induced* is thought to be the result of free photo-induced electrons which occupy an anti-bonding orbital on the oxygen atom. As a result the oxygen–metal binding is weakened allowing the oxygen atom to attack the CO molecule and create CO_2. The second mechanism termed *hole-induced* is thought to be the result of a charge transfer from the oxygen atom to fill a positive hole in the metal. As a result the negatively charged oxygen becomes almost neutral, increasing its chemical reactivity substantially. This reactive oxygen will eventually lead to CO_2 formation. The reactivity of the excited oxygen is limited by the finite lifetime of this state. Quenching times are estimated to be in the femtosecond range. Increasing the lifetime will increase the oxygen oxidation power. Co-adsorption of electron acceptors may cause such an effect. A large isotope effect has been observed in the reaction[84] when the adsorbed ^{16}O is replaced with ^{18}O. A possible explanation is that, to a large extent, the excited oxygen is quenched before reacting; the lighter isotope will move further during this period, thus enhancing its chance of reacting. Other nonadiabatic explanations are possible.

C. Orientation effect in the dissociation of N_2

The favorable orientation for an activated dissociation process on a surface is parallel. The reason is that in this orientation the two new atom metal bonds are formed simultaneously. This orientation is the surface analogue of a four-center reaction.

The nonadiabatic framework is a source of a new orientation effect which is due to the different favorable orientation of the different molecular species on the surface. As an example we consider the N_2/Ru system. In the physisorption potential the molecular surface forces due to polarization of the molecule for N_2 are almost isotropic. As a result there is no preferred orientation for the physisorption state, as can be seen in Fig. 3. The well depth for this state is approximately -0.1 eV. Nitrogen, which is isoelectronic to CO, has a low-lying molecular chemisorption state where the nitrogen is perpendicular to the surface (see Fig. 3). There is experimental evidence for this state[85,86] with a well depth of -0.25 eV. The third surface is the dissociative chemisorption surface where the preferred orientation is flat.

Non-adiabatic dynamical 3-D calculations were performed on these potentials with three degrees of freedom, Z the distance from the surface, r the internuclear distance and θ the molecular orientation. The initial state was chosen to mimic a scattering encounter starting from the physisorption potential in the gas phase. At high incident kinetic energies, the direct dissociation

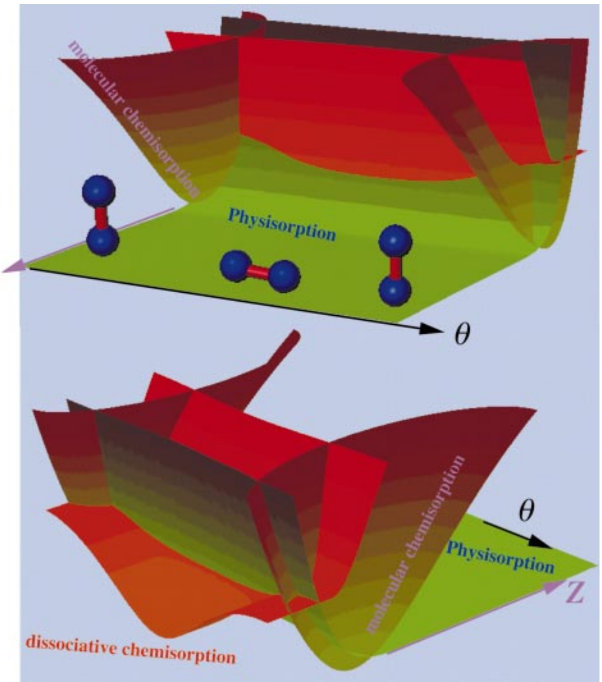

Fig. 3 Three diabatic potential energy surfaces for N_2 on Ru, representing the physisorption state, the dissociative chemisorption state and a molecular chemisorption state. The coordinates are Z, the distance of the molecule from the surface and θ, the orientation. Top: front view from the gas phase, bottom: back view.

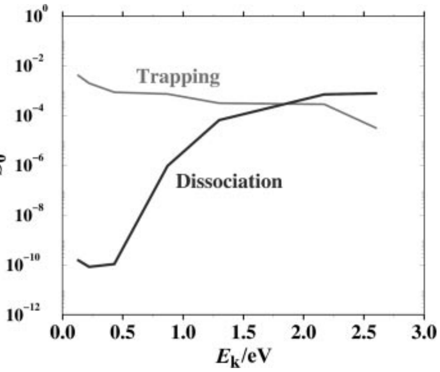

Fig. 4 Competition between dissociation and trapping for a model of N_2 on Ru.

channel was not influenced by the existence of the molecular chemisorption state, *i.e.* the dynamics was diabatic. At low incident kinetic energy an adiabatic steering force took over leading away from the favorable dissociation orientation. The competition between dissociation and trapping is shown in Fig. 4.

The overall effect of the nonreactive molecular chemisorption state on the dissociation probability is quite complex. At first one would expect that this state would always suppress the dissociation channel by diverting flux into the trapped state. But at particular energies there is a possibility of trapping in an upper adiabatic potential with favorable orientation for dissociation. The large trapping time can enhance the dissociation channel.

The orientation effect may explain the large discrepancy between the dissociation probability of the N_2/Ru system in a molecular beam experiment and a thermal experiment with comparable incident energy. The initial state of the molecular beam experiment is dominated by $j = 0$ projectiles. The thermal experiments are dominated by $j = 6$–8. For a low-energy collision the lower j states can be steered more easily than the high j states, thus they are more reactive.

V. Conclusions

Charge transfer states play important roles in surface reactions. The most relevant states are those which are easily excited *i.e.* are low in energy. The structure of the surface can alter considerably the location, charge and energetics of these excited states. For example, co-adsorption of an electron donor and oxygen will increase the charge on the oxygen and reduce its chemical reactivity. Charge transfer reactions can be promoted either chemically, by light or by a beam of electrons. On metals the indirect promotion of the reaction through free charge carriers is the dominant mechanism. The theory of these reactions lacks a reliable method to calculate excited states of adsorbates on metals. The development of such methods is a crucial step for obtaining quantitative nonadiabatic descriptions.

Reduced quantum dynamical descriptions have progressed considerably in recent years. Many new approaches have been developed that can simulate dissipative encounters. Due to the difficulty of the subject more than one approach should be compared. The theoretical challenge is to find first principle methods to calculate quenching times and dephasing times on metal surfaces.

For charge transfer reactions the quenching rate which determines the excited state lifetime is a crucial parameter. Direct measurements should be compared to first principle calculations. A more subtle issue is the role of electronic dephasing. The phenomenon can either enhance or suppress nonadiabatic transfer. The actual role in charge transfer processes on surfaces is not known. A fingerprint of these nonadiabatic reactions is a large isotope effect.

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