Non-adiabatic Transitions on Metal Surfaces as a Mechanism of Dissociation of Adsorbed Molecules

Ronnie Kosloff* and Ofra Citri
Department of Physical Chemistry and the Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel

A non-adiabatic dynamical framework has been developed in which each identified chemical species on the surface is assigned a potential-energy function. Transitions between the various potentials are induced by non-adiabatic coupling terms. The numerical scheme based on this non-adiabatic framework is summarized and applied to the dissociation of N$_2$ on Fe and on Re and also to the O$_2$ on Ag system. The model for the N$_2$ dissociation on Fe and Re, is based on two non-adiabatic surfaces in three dimensions. The emphasis is on the recoil of the metal atom from the impinging nitrogen. This recoil is found to reduce the available energy required for the non-adiabatic transition. A large non-monotonic isotope effect as a function of the initial kinetic energy has been found. The O$_2$ Ag system is studied by employing three non-adiabatic surfaces. The scenario for dissociation starting from the gas phase encounters first the physisorption potential. From this potential a non-adiabatic transition leads to a chemisorbed molecular ion, from which another non-adiabatic transition leads to the dissociated state. The dissociation probability, as a function of kinetic energy, shows a qualitative resemblance to a molecular beam experiment where the dissociation probability first decreases and then increases. The implication of the non-adiabatic framework for multidimensional studies including coupling to surface motion, is outlined.

1. Introduction

The dissociation of molecules on catalytic metal surfaces has been the subject of intensive study for many years. The essence of the catalytic process is to replace strong molecular bonds with weaker atomic-metal bonds. The specific dissociated fragment is considered to be the intermediate chemical species responsible for such catalytic action. For many years experimental observations were rationalized by using a kinetic framework. In this picture intermediate species were postulated on which to construct a set of rate equations leading to dissociation. A common term for these intermediate species is a precursor state. In recent years, primarily due to the introduction of molecular beams and sensitive spectroscopic techniques, a dynamical picture has emerged in which the influence of dynamical variables such as the initial kinetic energy of the molecule, on the dissociation, has been studied. The main difference between the dynamical picture and the kinetic one is that in the latter a quasi-equilibrium of internal degrees of freedom is assumed for the intermediate species. In the dynamic picture, the process has memory of its initial internal and external state which then influences directly the dissociation rate. Owing to the improvement in experimental techniques dynamical information has
been obtained on many processes which were considered in the past to be of a kinetic character.

The theoretical framework presented here incorporates the intermediate species *en route* to dissociation into a dynamical picture. The picture is based on a non-adiabatic quantum-mechanical description which assigns a non-adiabatic potential-energy surface to each chemically distinct species on the metal surface. The dynamics leading to dissociation is then described by a series of non-adiabatic transitions.

It is important to obtain direct experimental evidence for the existence of a dynamical picture. The first clue for a dynamical picture is that the dissociation probability depends on the initial translation, vibrational or rotational energy of the gas-phase molecule. Further evidence comes from the orientation dependence of the process where both azimuthal and normal angles can play a role.

Although the description presented in this study is general, it is limited to diatomic molecules. Even so, the large number of degrees of freedom makes a full quantum-mechanical dynamical study difficult. This theoretical study is therefore based on a reduced-dimensionality model which concentrates on qualitative aspects of the process. The purpose is to gain insight into the role played by non-adiabatic multidimensional transitions on the dissociation dynamics, in particular to reveal the dynamical observables which carry the signature of the underlying dynamics.

2. Generic Potentials

Generally three major types of chemically and physically distinct species on a metal surface can be defined. The first is the physisorption state where the gas-phase molecule is only weakly bound to the surface by polarization forces. The characteristic of this species is that the molecule is only slightly perturbed from its gas-phase vibration and rotational properties. The second species is a molecular chemisorption where the molecular bond still exists but is significantly weakened in comparison with that in the gas phase owing to a charge transfer from the metal to the molecule. As a result the binding to the metal increases significantly. Molecular species lying flat on the surface are the favourable candidates for dissociation. The third chemical species are the dissociated atoms. Within this framework a set of universal functional forms for the different potentials for the three types of chemical species has been constructed and a limited number of adjustable parameters used to fit each potential to *ab initio*, spectroscopic and thermochemical data.

For the physisorption potential, the forces operating on the molecule are dispersion forces. On first approximation, these forces are considered universal since they are the result of the attraction between the polarization of the molecule and its image charge distribution in the metal. The physical picture of the physisorbed state is of a molecule whose internal degrees of freedom are very slightly perturbed *i.e.* the molecule is almost freely rotating and vibrating. This state can be characterized by a very low molecule-surface vibrational frequency. The potential of the internal molecular bond has a Morse function form, whose parameters depend on the distance from the surface. The interaction of the molecule with the surface is described by a combination of an exponential repulsion term at short range, and by a long-range electrostatic attraction. To eliminate the singularity of the electrostatic term at short distances where the Pauli repulsion takes over, an interpolation function is introduced which gradually turns off the electrostatic terms. This interpolation function is also used to interpolate the molecular parameters from their gas-phase value to the value they obtain on the surface.

The dependence of the physisorption potential for most collision energies, on the orientation angles θ and φ can be omitted. Only at very low temperatures does the anisotropic part of the polarization become important where it causes preferable perpen-
dicular orientation. The following functional form has been chosen to describe the physisorption potential:

\[ V_g(r, \theta, z) = A_g \exp(-b_g z) - \frac{C_g(\theta)}{z} \left[ 1 - \Gamma_4(z, 0, 2b_g) \right] \]

\[ + D_g(1 - \exp\{-x_{\theta \phi}(z)[r - r_c(z)]\})^2 \]

(2.1)

where \( z \) is the distance of the centre of mass of the molecule from the top atom of the metal. \( r \) is the internuclear distance in the molecule. \( \theta \) is the orientation angle, \( \theta = 0 \) represents a molecule perpendicular to the surface, and \( \phi \) is the azimuthal angle. The incomplete gamma function \( \Gamma^4 \) is used as an interpolation function from the gas-phase to the adsorbed values:

\[ \Gamma_m(z, z_0, a) = \sum_{k=0}^{k=m} \frac{a(z - z_0)}{k!} \exp[-a(z - z_0)] \]

(2.2)

The molecular parameters become \( z \) dependent:

\[ x_{\theta \phi}(z) = x_{\theta \phi}^d; \quad \text{for} \quad z < z_e \]

\[ x_{\theta \phi}(z) = x_{\theta \phi}^d - (x_{\theta \phi}^d - x_{\theta \phi}^a) \Gamma_4(z, z_e, b_g); \quad \text{for} \quad z > z_e \]

(2.3)

and:

\[ r_c(z) = r_c^d - (r_c^d - r_c^a) \Gamma_4(z, z_e, b_g) \]

(2.4)

This potential form has to be adjusted to the gas phase, to the adsorbate vibrational frequencies and to the gas-phase dissociation energy. Also, the potential should be fitted to the molecular-surface vibrational frequency and to the adsorption energy. In this potential form, the plane where \( z = 0 \) is somewhat arbitrary. Physically it represents the plane where the gradient in electron density is maximized when going from the bulk of the metal into the gas phase. Since the source of the physisorption potential is the dispersion forces, it has a universal character depending on the polarization properties of the molecule.\(^5\) As a result, scaling relations exist between the gas-phase polarization and the surface potential parameters. These scaling relations are used to check the consistency of the potential parameters used in the calculation.

The other extreme species, that of dissociated atoms, is characterized by a strong atom–surface bond resulting in a high vibrational frequency. This dissociative species is also characterized by a net negative charge on the molecule which results in a long-range dipole–dipole repulsion between the adsorbed toms. The potential of this atomic species can be described as:

\[ V_a(r, z) = A_a \exp(-b_a z) - \frac{C_a}{z} \left[ 1 - \Gamma_4(z, 0, 2b_a) \right] + \frac{F}{r^2} + E_a + S(r) \]

(2.5)

where \( S(r) \) is a short-range repulsion, \( S(r) \approx S_0 \exp(-\beta_r r) \).

The potential of the species most involved with the surface is the one which describes the molecular chemisorption. This potential has to describe specific ionic and covalent bonding between the molecule and the surface atoms. This means that the potential is site dependent and non-isotropic. To simplify the description the model is restricted to a flat molecular orientation which is preferential for dissociation. The following functional form is used:

\[ V_m(r, z) = A_m \exp(-b_m z) - \frac{C_m}{z} \left[ 1 - \Gamma_4(z, 0, 2b_m) \right] \]

\[ + D_m(1 - \exp\{-x_{\theta \phi}(z)[r - r_c(z)]\})^2 + E_m \]

(2.6)
where the functional dependence of the molecular parameters on the molecule surface distance is as in eqn. (2.3) and (2.4). The relative energetics determining the zero energy of each species are important in determining their accessibility in different experiments.

Finally, for all the non-adiabatic coupling terms a common functional form is used which vanishes asymptotically:

\[ V_{ij}(r, z) = G \exp(-\alpha_z z)\exp(-\alpha_r r) \]  

(2.7)

Once the functional forms of the potential of each species have been worked out, calculations can be made with various sets of potential parameters. Varying these parameters allows a systematic study of different dynamical scenarios. The functional forms described above can be amended to include the motion of the metal atoms at the adsorption site. The most important of these motions is the perpendicular vibration of the uppermost metal atom. A harmonic potential is used to describe this motion:

\[ V(x) = \frac{1}{2}M\omega^2(x - x_0)^2 \]  

(2.8)

where \( M \) is the metal mass, \( \omega \) the frequency, \( x \) the metal–metal distance and \( x_0 \) the equilibrium distance. Since the kinetic energy is not diagonal in this set of coordinates a transformation to a new coordinate \( z = z + x \) is used. The frequency \( \omega \) is adjusted to the adsorbed species. For the physisorption potential the metal–metal distance, \( x_0 \), is obtained from the crystal structure data. For the chemisorbed species this distance should be larger, reflecting the reconstruction taking place on the metal surface upon adsorption. The motion of the other metal atoms can be considered collectively as a phonon bath.

### 3. Dynamical Calculations

The dynamics of the system is simulated by solving the time-dependent Schrödinger equation on a set of coupled potential-energy surfaces. The system is treated as an initial value problem starting with the amplitude in the gas-phase molecular species. The state of the system is treated as a multi-component wavefunction corresponding to the labelling of the chemical species. For example for three distinct species the wavefunction has the form:

\[ \psi = \begin{pmatrix} \psi_g(z, r) \\ \psi_m(z, r) \\ \psi_a(z, r) \end{pmatrix} \]  

(3.1)

and the system evolves by the Schrödinger equation:

\[ i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \]  

(3.2)

where:

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

(3.3)

and \( H_i = \frac{P^2}{2\mu} + V_i \), where \( i \) is the index of the species, \( g \) the gas-phase species, \( m \) the molecular-adsorbate species and \( a \) the atomic-dissociated species. The reduced mass \( \mu \) can be estimated by the hard cube model. The framework of chemical species defines the stage on which the dynamical events are to take place. Where a set of three spatial grids is constructed in the \( z \) and \( r \) coordinates which cover the range of coordinates where the different species acquire a significant amplitude. The values of each species potential \( V_i \) are calculated on these grid points. The crucial step in solving the dynamics...
is to calculate the operation of the Hamiltonian equation (3.3) on the wavefunction $\psi$. The operation is divided into a kinetic part and a potential-energy part. The potential operation which is local in coordinate space, becomes a multiplication of the potential matrix at a specific grid point for each chemical species by the wavefunction at that grid point. The coupling between species is by the non-diagonal potential terms at each grid point. The kinetic-energy operator is worked out by transforming the wavefunction to momentum space where the operation is local via the fast Fourier transform (FFT) algorithm. Once it is in momentum space the wavefunction is multiplied by $\frac{P_2}{2\mu}$ and transformed back to coordinate space. The evolution in time is then carried out by a polynomial expansion of the evolution operator:

$$\psi(t) = \exp[-(i/n)Ht]\psi(0) = \sum_{n=0}^{N} a_n(\Delta E/2\hbar) T_n(H)\psi(0)$$

(3.4)

where $a_n$ are the expansion functions $a_n(x) = 2J_n(x)$, $a_0(x) = J_0(x)$. $T_n$ are the Chebychev polynomials where the functions $\phi_n$ are calculated by the recursion:

$$\phi_{n+1} = 2H'\phi_n + \phi_{n-1}$$

(3.5)

where the recursion is initiated by $\phi_0 = \psi$, $\phi_1 = H\psi$. $H'$ is the normalized Hamiltonian operator:

$$H' = \frac{2H - I \Delta E}{\Delta E}$$

(3.6)

where $\Delta E$ is the spectral range of the Hamiltonian. In order to eliminate the effects arising from the finite size of the grids, the wavepackets $\psi_g$ and $\psi_a$ are absorbed by an optical potential of the form $-iU/\cosh^2(ax)$ as they are approaching the grid edges. The dissociation probability is calculated by integrating the flux of $\psi_a$ passing through a dividing plane just before the absorbing potential starts. The flux is calculated by the expression:

$$F_a(z, t) = \frac{ih}{2m} \left[ \psi(z, r) \frac{\partial \psi^*(z, r)}{\partial r} - \psi^*(z, r) \frac{\partial \psi(z, r)}{\partial r} \right]$$

(3.7)

The derivatives are calculated using the Fourier method. The flux is integrated to give the total probability that has reached dissociation:

$$P_a(t) = \int_0^t \int_{z_{\text{min}}}^{z_{\text{max}}} F_a(z, t') \, dz \, dt'$$

(3.8)

To check the convergence of the calculation, a flux integration is performed also on the $\psi_g$ wavefunction calculating the non-reactive accumulated probability. The sum of the integrated fluxes and the wavepackets remaining on the grids is calculated after every time-step to check for normalization conservation.

The numerical procedure summarized in this section has exponential convergence both with respect to the spatial grid variables and the time propagation. As a result, within a specific dissociation model, the calculation is numerically converged. This is important since simulation of isotropic substitution experiments for very low dissociation probabilities requires extremely high absolute accuracy.

4. Dissociation of Nitrogen on Catalytic Metal Surfaces

The dissociation of nitrogen molecules on metal surfaces has been extensively investigated over the years because of its relevance to industrial ammonia synthesis. When using Fe catalysts, the process has been shown to be the rate-limiting step of the entire
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complex ammonia synthesis from \( \text{N}_2 \) and \( \text{H}_2 \) at high pressures.\(^9\)\(^{-11}\) Similar results have been obtained also over model Re single-crystal catalysts.\(^12\) The kinetics of adsorption and desorption of \( \text{N}_2 \) and its dissociative chemisorption on Fe\(^10\),\(^13\) and Re,\(^14\) have been studied extensively. The dynamics of the dissociation event itself however, has been treated only recently by the application of molecular beam–surface collision methods.\(^15\)\(^{-18}\) In this research the dissociation of \( \text{N}_2 \) on Fe(111) was studied experimentally.\(^15\),\(^16\) The striking result was that the dissociation probability increased by five orders of magnitude when the incident kinetic energy increased by only one order of magnitude.\(^15\)

The relative importance of the vibrational and translational energies was also studied in the above system,\(^16\) and it has been found that the vibrational degree of freedom was less efficacious than the translational one. Qualitatively, the \( \text{N}_2/\text{Re} \) system shows great similarity to the \( \text{N}_2/\text{Fe} \) system.\(^19\) The dissociation probability is greatly enhanced by the incident kinetic energy. The initial vibrational energy also has a similar effect on dissociation as in the \( \text{N}_2/\text{Fe} \) system.

The detailed dynamics of this system and that of \( \text{N}_2 \) on Re(0001) was modelled theoretically, by applying quantum-mechanical\(^17\)\(^{-19}\) and classical\(^20\) approaches to simulate the dissociation event over model potential-energy surfaces. From the quantum-mechanical study the suggestion was taken that the dissociation of \( \text{N}_2 \) over Fe(111) as well as on Re(0001) at low initial kinetic energy proceeds via a tunnelling mechanism through a relatively high non-adiabatic barrier for dissociation.\(^18\),\(^21\)

The potential-energy surface of \( \text{N}_2 \) on Re(0001) has only one molecular well, as is evidenced by temperature-programmed desorption\(^14\) and by an unsuccessful low-temperature attempt to find a weakly chemisorbed precursor state.\(^22\) From the viewpoint of Section 2 there is a direct route from the physisorption potential to the atomic dissociation channel. This is in contrast to the \( \text{N}_2/\text{Fe}(111) \) system, in which a second molecular adsorption state was identified and considered to have an important role as precursor for dissociation.\(^23\) A simulation of this system should therefore include three non-adiabatic surfaces.

Within the framework of potentials of Section 2, the numerical calculations concentrated on the different roles of initial kinetic and vibrational energy in promoting the dissociation. Comparison of the calculations with experiment leads to a potential topology in which the seam or crossing between the physisorption potential and the atomic potential is located mostly perpendicular to the \( z \) coordinate. This topology makes the translational energy more effective in promoting the reaction. Fig. 1 shows a 2D projection in a possible potential. The series of calculations\(^17\)\(^{-19}\) and also the multidimensional quantum-classical calculation by Billing and co-workers\(^24\) satisfactorily explain the rapid increase of the dissociation probability with the initial kinetic energy and the role played by the initial vibration. In these respects the Re and the Fe surfaces show a very similar behaviour.\(^19\)

Experimentally the two surfaces differ in the dependence of dissociation on crystal temperature. On Re a small increase in dissociation probability is observed upon raising the temperature. In Fe a negative effect is measured. These temperature dependences can be fitted to an activation energy of 0.1 eV for Re or a negative activation energy of \( -0.2 \) eV for Fe. The values obtained are much smaller than the measured high-pressure activation energy of the dissociation or than the comparable value of the lowest crossing point on the potential seam. This means that the surface motion does not couple very strongly to the reaction path.

It is therefore desirable to explain the qualitative difference in the temperature effect between the Re and Fe systems. In particular because they have almost the same phonon Debye frequency. A possible source at such behaviour is the large change in mass between the two metals. It is expected that in the Fe crystal the top layer atoms will recoil much more than the Re atoms thus reducing the available effective energy for
Fig. 1 Contour map of a 2D cut in the 3D non-adiabatic potentials of the $N_2$/metal system. The uppermost metal–bulk metal bond is frozen at its equilibrium value. The contour intervals are of 0.4 eV. The total distance in the $z$ direction is 4 Å and in the $x$ direction is 1.5 Å.

Fig. 2 Dissociation probability as a function of kinetic energy. $\bigcirc$, represents 2D results. $\triangle$, represents 3D results with the surface metal mass of Re. $\Box$, represents 3D results with the surface metal mass of Fe using the same potential.
dissociation. To test this hypothesis a series of 3D dissociation calculations were performed where the extra degree of freedom was modelled by an oscillator describing the motion of the topmost metal atom. The surface Debye frequency was used. The dissociation probability as a function of kinetic energy is displayed in Fig. 2 and compared with the 2D calculations. A comparison of the 2D and 3D results shows that the recoil degree of freedom does reduce the amount of available energy required to dissociate the nitrogen. Comparing the N$_2$/Fe system with the N$_2$/Re with the same potential parameters shows, as expected, that this effect is reduced in the heavier metal.

In the calculation performed it was found that the vibrational energy in the metal–metal mode promotes the dissociation for both the Fe and Re mass combination. Thus the mass difference is not enough to explain the negative temperature effect in the N$_2$/Fe system. A model of the dependence of the dissociation on the crystal temperature requires a solution of the time-dependent Liouville von Neumann equation. Progress in numerical procedures is under way. It is speculated that a large change in the surface vibrational frequency following the creation of the new metal nitrogen bond, is the source of the differing temperature dependence.

It is interesting to examine the effect of substituting $^{15}$N$_2$ for $^{14}$N$_2$ on the dissociation. The isotope effect is defined as the ratio of dissociation probability of $^{15}$N$_2$ to $^{14}$N$_2$. Fig. 3 shows the isotope effect as a function of initial kinetic energy. It is apparent that the lighter isotope enhancement is not monotonic and is very sensitive to the detailed dynamical features. The isotope effect is also enhanced by the recoil of the metal atom. The absolute value of the effect is much lighter than would be predicted by a 1D adiabatic tunnelling model or by a non-adiabatic curve-crossing model.

5. Dissociation of Oxygen on Silver Surfaces

The O$_2$/Ag system has been the subject of extensive study owing to its use in the catalytic ethene oxidation process. Much effort, using a variety of spectroscopic techniques
has been devoted to the identification of intermediates which may be candidates for the
catalytic oxidation.\textsuperscript{28} As a result four stable or metastable species of oxygen on silver
have been identified: (a) The physisorption molecular species identified on all Ag sur-
faces which is characterized by a small perturbation of the gas-phase vibrational fre-
quency. (b), (c) Two molecular chemisorption species peroxide and superoxide
characterized by an extended oxygen–oxygen bond due to a charge transfer from the
metal to the oxygen molecule. Their existence depends on the crystal plane. These
species differ by the amount of charge transfer and as a result by a different weakening
of the oxygen–oxygen bond which is reflected in a reduced $O\!-\!O$ frequency. The exact
relation between the crystal face and the geometry and frequency of the molecular che-
misorbed state are still under dispute.\textsuperscript{29} (d) A dissociated atomic oxygen species charac-
terized by a net negative charge on the oxygen atom.

Experiments to probe the dynamics of oxygen dissociation have been carried out
using molecular beams to control the impinging kinetic energy.\textsuperscript{30,31} It was found that
increasing the kinetic energy has a negative effect on the dissociation which reverses at
higher values where the dissociation is enhanced. In all cases the dissociation probability
is of the low order of $10^{-6}$–$10^{-5}$. The dissociation process has been shown to have a
substantial isotope effect.\textsuperscript{32}

A three potential-energy surface non-adiabatic picture is employed to model the
dynamics. The scenario leading to dissociation starts from the gas-phase molecule
which, upon approaching the surface, may go through a non-adiabatic transition to a
chemisorbed molecular state. From there it may pass via another non-adiabatic tran-
sition to the dissociated atomic state. It is assumed that the dissociation goes through

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Contour map of the non-adiabatic potentials of the $O_2$/Ag system. The contour intervals are 0.2 eV. The total distance in the $z$ direction is 4 Å and in the $x$ direction is 2 Å.}
\end{figure}
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Fig. 5 Dissociation probability as a function of initial total energy, i.e., kinetic + vibrational, for the O₂/Ag system. Initial vibration v = 0, 1, and 2. The insert compares the v = 0 calculation with the experimental results of Spruit and Kleyn.¹¹

only one of the molecular chemisorption species. Fig. 4 shows a possible projection of the three potential surfaces involved. With an appropriate set of potentials the dissociation dynamics can be modelled using the framework of Section 3 without the surface motion. The potentials used are slightly modified versions of the potentials of Spruit.³⁰ A more extensive study as well as the potential parameters used will be presented separately.³³

Fig. 5 shows the dissociation probability as a function of incident kinetic energy. The dissociation probability shows a weak total-energy dependence up to an energy of 0.5 eV. Above this energy it seems that kinetic energy is more effective in promoting the dissociation than vibrational energy. It is apparent that, qualitatively, the behaviour matches the experiment shown in the insert. Although the experiment has a more pronounced drop at 0.3 eV. Exciting the initial vibration energy results in a small effect. Considering that the potential parameters used in this study have only qualitative value one can ask if these results are generic. Numerous calculations based on the same dissociation scenario of two non-adiabatic crossings to dissociation, which used different potential parameters led to the same qualitative picture as in Fig. 5. It is important to notice that the potential parameters are such that the initial kinetic energy was almost always above the minimum of the non-adiabatic seam of both crossings but still the dissociation probability stayed low.

6. Discussion

The non-adiabatic framework presented here supplies a unified picture in which the static measurements on the physical properties of surface-adsorbed intermediates can be incorporated into a consistent dynamical picture. A detailed understanding of the dynamical picture allows a full reconstruction of the kinetic measurements.

The most extensively studied dissociative process is that of H₂ on Cu. This is a unique system in that extremely good state-to-state measurements of almost all dynami-
The system has also been the subject of extensive theoretical study including high-quality multidimensional quantum-mechanical calculations and mixed quantum-classical calculations of all degrees of freedom of the molecule. The quality of the investigation has brought about a detailed understanding of the ability of the different degrees of freedom to promote the dissociation. Since multidimensional calculations for heavier molecules are much harder than for hydrogen it is tempting to use this system as a prototype for dissociation. The main difference between the H$_2$/metal studies and the work presented here is that the hydrogen dissociation was modelled on one adiabatic potential-energy surface. For the H$_2$/Cu system this assumption is probably justified due to the large non-adiabatic coupling term found for hydrogen. It is postulated that heavier molecules are able to create directional bonds with transition metals. This can reduce significantly the non-adiabatic coupling term owing to lack of overlap between the different electronic wavefunctions. For the system studied the dynamics would be significantly altered if only the adiabatic potential-energy surface were considered. The striking example is the O$_2$/Ag system in which the energy of collision is above the adiabatic barriers and still the dissociation probability found is very low.

The two dissociation models the N$_2$/Fe, N$_2$/Re system and the O$_2$/Ag system differ in the incorporation of an intermediate molecular species en route to dissociation. As a result a very different dynamical picture emerges. It seems that the intermediate surface drastically reduces the direct effect of the initial kinetic energy on dissociation. Also the dissociation probability stays low even for energies above both the crossing seams. This comparison is a confirmation that the N$_2$/Fe, N$_2$/Re dissociation process does not proceed through a precursor state which would drastically reduce the effect of incident kinetic energy. Going beyond the calculation presented here, it can be speculated that if the oxygen spends a long time in the chemisorbed surface dissipative forces will first cause loss of phase and eventually will equilibrate the chemisorbed oxygen molecule with the surface temperature. Once equilibrium has been reached the energetics of the potentials are such that the route to dissociation can proceed only via a tunnelling mechanism. An equilibrated oxygen species could be considered as a precursor to dissociation, nevertheless it will not fit classical rate theory since the transition to dissociation is governed by a quantum-mechanical tunnelling process. Both theoretical and experimental verification is required to establish this mechanism.

The recoil effect has been studied previously in the framework of one adiabatic potential-energy surface. The conclusions in the non-adiabatic case were qualitatively the same i.e. the available energy required to perform the non-adiabatic transition is reduced owing to the recoil of the metal surface atom. As expected, the recoil effect is smaller for heavier metal atoms. If an effective mass of the cube of more than one metal atom is used the recoil effect is further reduced.

One of the important findings in these studies is that the simple 1D Landau Zener (LZ) theory including the more modern extension is not appropriate to describe the multidimensional non-adiabatic transitions taking place in the molecular dissociation. This is true for both the N$_2$/Fe, N$_2$/Re system and the O$_2$/Ag system. Since classical simulations are also inappropriate it seems that the only route to obtain insight into the dynamics of the process is by numerical modelling.

The drawback of the studies presented here is their limited dimensionality. A realistic treatment should include all the surface degrees of freedom. One suggestion has been to include these degrees of freedom in a time-dependent mean-field approach of a time-dependent self-consistent field (TDSCF). Application of such a method to dissociation dynamics has been presented by Billing and co-workers and Jackson and co-workers. Their theory allows a mixing of classical and quantum degrees of freedom which means that many degrees of freedom can be considered. The simple TDSCF theory fails in a non-adiabatic picture due to omission of correlations induced by the
motion on multiple surfaces. In order to extend the theory to the framework presented here a multi-configuration time-dependent self-consistent field should be used. A formulation suitable for such an application has been worked out and its implementation is in progress.

6. Conclusions

For most dissociation processes, on transition metals, of molecules whose atoms are heavier than hydrogen a non-adiabatic picture of multiple-crossing non-adiabatic potential-energy surfaces seems to be the correct framework.

The isotope effect as a function of dynamical variables such as the initial kinetic energy makes a very sensitive probe for the detailed dynamics of the non-adiabatic process.

The recoil of the upper layer of metal atoms has significant influence on the dissociation process and may be responsible for the crystal temperature effect.

Multidimensional quantum-mechanical studies have to be performed in order to advance from a qualitative picture to a quantitative one. A multi-configuration Hartree approximation seems appropriate for the task.

The introduction of an intermediate chemical species in the O₂/Ag system drastically changes the dependence on the initial kinetic energy compared to the N₂ metal systems and reduces the total dissociation probability significantly.

Finally there is accumulated evidence from other field of condensed-phase chemistry that supports the view of a non-adiabatic picture of chemical change.

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R. Kosloff and O. Citri


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