Surface chemical reactions induced by molecules electronically-excited in the gas phase

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ABSTRACT

We present a model suggesting high chemical activity of electronically-excited molecules colliding with an isolator surface. Initial photochemical event is accounted for as the result of molecular evolution on the electronically-excited potential energy surface (PES), where acceleration and alignment are taking place, guiding all the molecules towards the intersections with the ground state PES, where transitions to the ground state PES will occur with minimum energy dissipation. The accumulated kinetic energy may be used to overcome the chemical reaction barrier. While recombination chemical reactions in a gas phase require participation of a third body, this strong limitation on the reaction rates is removed upon interaction with a surface.

To observe the predicted phenomenon, we suggested a new experimental approach, Evanescent Wave Photocatalysis, based on application of total internal reflection on an insulator surface. Laser photoexcitation is localized in a narrow boundary gas layer just above the interface; majority of the excited molecules can reach the surface before the relaxation. The experiments are performed at high gas pressures, so that dense fluxes of the excited reagents can be readily produced. Products of chemical adsorption and/or chemical reactions induced within adsorbates are aggregated on the surface and observed by light scattering. We will demonstrate how pressure and spectral dependencies of the chemical outcomes, polarization of the light and interference of two laser beams inducing the reaction can be used to distinguish the new process we try to investigate from chemical reactions induced by photoexcitation within adsorbed molecules and/or gas phase photolysis.

Keywords: Laser chemistry, surface photochemistry, elementary chemical reactions, evanescent wave, aggregation, non-adiabatic, vibronic coupling, photocatalysis, adsorbates, nanoaggregates.

Recently the initiation of a chemical reaction was reported via collisions of electronically-excited, thermal velocity SO₂ molecules with an insulator surface leading to highly-efficient formation of photochemical products on the interface. The molecules were laser excited well below the dissociation limit. In this paper we present the theoretical arguments which...
stimulated us to undertake the original experiment and report new experimental observations made on other chemical systems and with application of further developed experimental methods.

1. THEORETICAL MODEL

Previously, the initiation of a chemical reaction via collisions of electronically-excited molecules with a surface was not considered to be more promising than the approach based on surface adsorbates excitation, which has been studied in great detail. So far, there exists no explicit theoretical prediction concerning the outcome of a chemical reaction based on surface-collision events, probably because the relaxation of the electronic excitation on a surface has been assumed to be a rapid process leading only to a low reaction probability.

The transfer of a chemical system from one (quasi-) stable state to another stable state is requiring displacement of the atomic nuclei, which starting at thermal equilibrium can be obtained by collisions, by infrared excitation of a specific vibration mode, or by photo-excitation of the initial system to an electronically-excited state potential energy surface (PES). The topology of the excited state PES differs from the topology of the ground state PES and thus the molecular system will start to evolve following the PES gradient until de-excitation will occur. Provided the displacement and the kinetic momentum of the molecular system, accumulated during the motion on the excited PES, are sufficient to overcome the reaction barrier a chemical transformation will take place. Fast de-excitation processes will, however, lead to a low quantum yield for the photochemical reaction. Vibronic coupling or conical intersections of the PES are known to be dominating decay mechanisms for excited states. The excitation of a specific vibrational mode by an infrared laser followed by UV excitation to the upper PES was already invented in 1973. This approach made it possible to control the displacements of the starting position on the upper PES for the nuclei coordinates and thus to control the outcome of the chemical reaction. However, it was very difficult to localize the vibrational excitation to one specific mode. With increasing excitation energy and size of the molecule the vibrational quasi-continuum will rapidly be reached and the motion along the excited normal coordinate will quickly be redistributed over all modes of the system.

There exists a close relationship between electronic photoexcitation of surface adsorbates and the description given above. Electronic excitation is known primarily to lead to nonradiative decay back to the ground state and will seldom result in desorption or fragmentation events. According to the Franck-Condon principle the nuclei will start their motion on the excited state PES with close to zero velocity and will require some time to be moved from the Franck-Condon region even if the gradient of the upper PES is rather large. On metallic surfaces the lifetime of the electronic excited state will be the limiting factor for the photodesorption yields, which can be obtained via the mechanisms described by Antoniewiez and Gadzuk. Furthermore electronic photoexcitation of adsorbates on isolator surfaces will not be able to provide sufficient energy for desorption within a single excitation event, which will be addressed in more detail later on in this paper. The interaction of an adsorbate with a surface will always result in broadening of the absorption lines and lead to a reduced photoexcitation cross section, which thus will make a direct laser excitation of the adsorbates less efficient. Indirect mechanisms for molecular desorption or fragmentation, initiated by substrate photoexcitation, have therefore been under intense study during the last decade.

Within the gas phase molecular electronic transitions are characterized by narrow spectral lines and large absorption cross-sections, thus providing a good basis for highly-selective and efficient photoexcitation. In addition, excited states belonging to small molecules can be very long-lived. The rate of any associative chemical reaction in the gas phase is known to be limited since the simultaneous fulfillment of the laws for energy and momentum conservation will demand the presence of a third body in the reaction event or the existence of an efficient internal decay channel, but small gas-phase molecular systems do not possess such properties.

To obtain efficient associative transformations one will need to deal with a system which is able to transform, at the proper inter-nuclear distances, all the excess energy of the kinetic motion along the reaction coordinate to other degrees of freedom. Thus, the molecular system has to be large, or at least become large. However, large molecular systems may not possess the long-lived states needed and will never obtain the rapid acceleration in its motion towards the collision partner. The following possibility remains, however, to be explored: The excitation of a small molecule in the gas phase, which subsequently collides with a large non-elastic system, a surface. The dynamics of such a system will now be considered in some detail.
Figure 1. A schematic one-dimensional diagram illustrating most general features in behaviour of a small molecular system AB that approaches an isolator surface M from gas phase (right side of the figure). Different states of the molecule are shown: the electronic ground state AB, the electronic excited states AB*, and the dissociated state A+B. Two different one-dimensional short-cuts of the corresponding PES will be discussed in the text: The shortcut G (upper figure) is taken following the reaction pass of the ground state molecule. The shortcut E is following the pass of an excited gas phase molecule. The arrows are indicating laser excitation to the excited electronic state in a gas phase molecule and in a molecular adsorbate (it is possible for G only).
The schematic Figure 1 illustrates the behaviour of a small molecular system AB with its different relevant states approaching an isolator surface M. The figure represents only a one dimensional representation of the behaviour of the corresponding PES in the multidimensional nuclei coordinate space. In this approach we are following the common Lennard-Jones model-like representation to show the evolution of the system along the primary reaction coordinate and along the minimum energy reaction pathway. In contrast to the Lennard-Jones model in which only two diabatic curves, AB ↔ AB + M and A + B ↔ A + B+ M and their avoided crossings are responsible for the reaction path, we also take into consideration the electronically-excited PES, which is connected to the excited state AB* of the molecule in the gas phase. Electronically-excited states can be strongly involved in the formation of the reaction path. For simplicity only one excited state is shown on the figure, but several excited states may have to be considered including those which can be dissociative for an isolated molecule, but will be stabilized close to a surface due to strong polarization interaction.

Figure 1 does not explicitly show the diabatic (i.e. isoelectronic) states, since it is assumed that phonon coupling will take place between all the diabatic states and lead to avoided crossing structures between them. The curves shown are the result of a one-dimensional cut through the adiabatic PES. The position of the original diabatic curves can, however, be traced throughout the figure. The most general features of the behaviour of the diabatic excited state AB* ↔ AB* + M are also included in the figure. The electron shell of the excited state AB* will be more flabby and polarizable compared with AB or A + B; thus a stronger polarizational binding is expected for AB* than for AB. At the same time, the repulsion interaction with the surface will start a bit later comparing with AB and will be characterized by a less steep slope.

The general arguments concerning the behaviour of the diabatic excited states PES are consistent with the results of the experimental studies performed so far with a number of different surface adsorbates in different isolators. For the various molecules investigated, photodesorption was observed at wavelengths much longer than the long wavelength absorption edge for these molecules in the gas phase. Since the physisorption binding to the surface for the studied species was only a fraction of an eV, the shift of the absorption suggests that the depth of the polarization well exceeds 1 eV for the excited states in the Franck-Condon region. For almost all the molecules studied the yield of the photodesorption has been observed to be proportional to the energy of the laser pulse in a high power, with n > 4-7. The authors assume that the vibrations of the adsorption bond are excited within a few cycles of photon adsorption followed by electronic-vibrational relaxation of the excitation energy. In the studies reported fragmentation of the molecules within the physisorbed monolayers has not been observed. This is consistent with localization of the Franck-Condon region close to the minimum of the excited PES along the reaction coordinate, as also shown on the figure. This minimum, however, is not expected to be a minimum along the other coordinates of the system; additional molecular orientations and/or displacements parallel to the surface will therefore most likely bring the excited state PES further down.

In the following sections we will use Figure 1 to discuss two different one-dimensional shortcuts through the multidimensional coordinate space of the system:

1) the shortcut G is made along the reaction path of the molecule in the Ground electronic state AB, while

2) the shortcut E will follow the reaction path of the molecule approaching the surface in the Electronically-excited state AB*.

Although the behaviour of the relevant potential curves is assumed to be rather similar for the two cases, the positions and particularly the energy gaps separating them in the regions of their avoided-crossing (and consequently the vibronic interaction between the corresponding PES) can be very different.

Case G: The lowest adiabatic curve shown on the figure can be used to trace the evolution of the ground state molecule on its way towards chemisorption. The figure shows that this curve experiences avoided crossings with the excited PES on the way towards the reaction barrier. The energy gap between the two curves can here be very large due to a stronger interaction (i.e. conical intersection) of the PES taking place somewhere else in the coordinate space, at the interaction points located on sides of the minimum reaction path. The AB molecules physisorbed on the surface can be photoexcited from the ground state minimum to the Franck-Condon region of the upper PES as shown on the figure.
Case E: The evolution of the electronically-excited molecules can be followed along the adiabatic curve representing \( AB^* \). Far from the interphase, the motion of the excited molecule will be strongly accelerated towards the surface following a trajectory determined by the landscape of the excited state PES. For a not too complicated topology the molecules will pass the minimum of the excited PES and continue their motion towards the surface following the minimum energy path on the upper PES. The points of intersections with the lower-lying PES are expected to appear near the energetically low-lying sections of the upper PES. The high velocity gained by the molecules may reduce the probability for an early decay of the electronic excitation. The decay rate induced by the surface phonons will be growing rapidly when the molecules are approaching the surface. Furthermore, at a given coupling strength (i.e. at a given distance) the rate of the vibronic decay is known to increase exponentially with the inverse excitation energy to be dissipated. Thus, the rate will increase considerably when the PES are close in energy, i.e. only a small energy gap separates them and can be bridged by phonons. Only a small fraction of the original excitation energy will be dissipated while the kinetic energy accumulated by the molecular nuclei still can be used to overcome the reaction barrier. Essentially the same conclusion could be obtained if a conical intersection of the PES or a diabatic passage of the avoided crossing took place. If the original electronic excitation energy of the gas phase molecule was larger than the sum of the energy needed to surpass the reaction barrier and the total energy dissipated to the phonons on the way towards the barrier, then the molecule will pass the reaction barrier and enter the region of the chemisorption valley \( M + A + B\), where the motion along the reaction coordinate will be strongly coupled to the vibrational quasi-continuum of the solid leading to relaxation of the system in the chemisorbed state.

It should be noted that the quasi-continuum nature of the kinetic energy transfer to the phonons in a large system involving a surface is significantly different from gas phase collisions between small atomic and molecular species. In the latter case diabatic or adiabatic crossings of energy levels are common and have been studied in great detail, for example in connection with excitation of discrete internal quantum states. For a recombination event, however, excitation of discrete levels in small atomic or molecular systems cannot resolve the issue of the energy and momentum conservations at arbitrary initial conditions.

In the model proposed above the motion of the molecular nuclei towards the reaction barrier is efficiently initiated as a result of acceleration of the excited molecules towards the minima of the upper PES. If the same chemical transformation obtained starting from the excited state PES should be possible starting from the ground state PES the molecules would need to have a much larger kinetic energy to be able to exceed the reaction barrier plus the transfer of energy to the phonons. Furthermore since the initial thermal kinetic energy of the molecules is small compared with the depth of the excited state physisorption well, the excited molecules will have a tendency to experience an alignment on their way towards the minima on the upper PES leading them further to the intersection points. Such natural alignment of the incoming molecules should have a strong effect on the outcome of the reaction.

The proposed model to account for chemical adsorption of electronically-excited molecules on an isolator surface is based on the evolution of the system along the excited state PES followed by a phonon-induced transition to the ground state PES at or near the (avoided) crossing points. In this model we have so far disregarded that at high pressures any surface will be covered by layer(s) of physisorbed molecules. Such homomolecular layer may, however, not change the chemical outcome very much, since a quasi-elastic collision will transfer both the kinetic and excitation energies from the incident gas phase molecule to the adsorbed one, which subsequently will be involved in the chemical transformation. It is very likely that high efficiency observed for the dissociative adsorption processes described in the following experimental section may result from such excitation and momentum transfer mechanism as well as benefit from the alignment of the physisorbed molecules in the layer(s).

The described mechanism of simultaneous electronic excitation and kinetic momentum transfer can be viewed as a formation of an exciton/polaron on the relaxation site. The phenomenon may open up new possibilities for laser control of associative chemical reactions within adsorbed molecular layer(s), including reactions that do not involve the photoexcited molecules and/or the bulk isolator surface themselves. Furthermore, it may become possible to develop a new approach for investigating chemical transformations, induced by excitation transfer, which are known to play an important role in photochemistry. Our observations, made with nitric oxide and briefly described in the next section, may indicate the first successful development in these directions.
2. EXPERIMENTAL METHODS AND OBSERVATIONS

Very little is known about the interaction of electronically excited molecules with surfaces, particularly, about possible chemical outcomes of such interactions. The lack of knowledge is due to the problem of producing sufficiently strong fluxes of excited species to make detailed measurements possible. Indeed, excitation of gas molecules has to take place very close to the surface, otherwise it will decay by one or another way within the gas volume. Gas-phase photolysis has been sorely investigated for very many systems with reasonable assumption that contribution from surface effects can be made negligible in a large gas vessel. With a pumped out vessel, photochemistry is known to proceed via photoexcitation of surface adsorbates or underlying substrate; these processes also have been studied in great detail.

With molecules excited in the gas phase, only reaction channels providing high detection efficiencies have been investigated experimentally. This was possible to achieve using detection of survived metastable states or ejection of an electron after the collision of excited molecule with the surface. Fragmentation of molecules, excited to just below the dissociation limit and collisionally induced at a surface, has been studied by Ferkel et al. Superelastic scattering of exited atoms upon their impact on the surface of wide-bandgap dielectrics was also reported; the conversion of the electronic excitation energy to kinetic energy of the scattered atoms agrees very well with the theoretical model described in the previous section. Associative chemical reaction channels have so far not been investigated. Non-reactive electronic relaxation of excited states on a surface is commonly assumed to be a very rapid process and consequently the reaction outcomes are believed to be hardly detectable.

Our approach is essentially different from the used previously methods and based on localization of the resonant laser field in a narrow boundary gas layer just above the gas-insulator interface. This is readily achieved by using total internal reflection phenomenon, in which an evanescent wave with penetration depth of about 50-100nm is formed above the fused silica surface of the cell window. Scheme of the experimental arrangement is shown on Fig.2.

![Figure 2](image-url)

**Figure 2.** Scheme of the experimental arrangement used to localize laser excitation in a narrow gas layer, within the volume of the evanescent wave field formed just above the fused silica window surface.

It should be noted that up to an atmospheric pressure, the mean free path of molecules in the gas remains larger than the thickness of the evanescent wave volume. It means that significant fraction of the excited molecules will reach the interface ballistically, while the rest will end on the surface after experiencing several collisions within gas phase.
In the case of experiments with \( \text{SO}_2 \), photochemical products accumulated on the illuminated interface undergo aggregation into nanodroplets, which give rise to light scattering. This scattering of light makes the spots visually observable. The apparent visibility is increasing with the time of illumination; this is used to compare spots produced at different illumination conditions.

An alternative online observation method using two intersecting each other parts of the same laser beam can be utilized also. Nonuniform distribution of the field intensity near the interface is resulting in production of a periodic structure, which starts to work as a diffraction grating (see Fig. 3). Time required to develop certain intensity in high order diffraction maxima can be recorded and used to compare rates of photoproduct formation at different conditions.

![Figure 3](image)

**Figure 3.** Microscopic image of fringes formed by photochemical products on the interface illuminated with two intersecting interfering beams (left). The corresponding diffraction pattern, which develops with time in the far field region around the two central spots coming from the laser beams.

Experiments done with NO/hydrocarbons mixtures as well as with illumination of a pumped out gas cell, have not been producing any immediately visible products on the surface. However, the chemical nature of the surface has been modified under the illuminations. The corresponding spots can be visualized on the interface when water vapours are condensed on it. This effect is likely due to change of hydrophobic/hydrophilic properties of the upper most layers of the molecules covering the surface. The shapes of the water droplets covering the illuminated area become than different from the rest of the substrate surface, resulting in difference in light scattering and making spots observable (see Fig. 4 and 5). In the case of evacuated cell the effect clearly must come from photoabsorption in the physisorbed molecules, since the rest gas density was very low (\(10^{-3}-10^{-5}\)Torr). The modifications of the surface induced these ways have been found very resistant to any mechanical cleaning. However, the spots can be fully removed by placing the substrates in concentrated \( \text{H}_2\text{SO}_4 \) acid over extended period of time, better at elevated above 80ºC temperature. Likely, heavy hydrocarbons present in the vacuum system have been modified under photoabsorption or bombardment with excited NO molecules towards more graphite/graphene like forms.

Both, \( \text{SO}_2 \) and NO have pronounced spectral variations in photoabsorption. With a loaded cell, very good correspondence between the observed reaction rates and the photoabsorption cross section of the gas was observed, indicating to photo processes starting in gas-phase molecules and not in their adsorbates, which would exhibit much more smoothed spectral behaviour.
In the following we will focus on the possibility of using polarization of light to distinguish between different mechanisms of photochemical processes on an interface. We will limit our discussion and experimental observations to fixed 45° angle of incidence of the laser beam on the interface.

In the case of s-polarized light, electrical field vector $F$ is tangential to the surface. The incident and reflected fields will be directed the same way, with a phase shift dependent on the refractive index of the glass $n$. Resulting intensity of the laser field ($\sim F^2$) will be thus close to 4 times intensity of the incident wave; it will be exactly the same for molecules situated just below and just above the interface, as well as for molecules adsorbed in a narrow layer on the surface.

For p-polarized light the situation becomes very different. Inside glass the incident and reflected field vectors are perpendicular to each other, resulting in a twice intensity of the incident beam. Electrical field vector component, which is normal to the interface, will be experiencing an increase by a factor of $n^2$ on the boundary between the glass (an insulator with dielectric constant $\varepsilon = n^2$) and the rare density media. The resulting change in the laser field intensity will be as large as $n^4$, making p-polarization effect within the gas media stronger than that of s-polarization. At the same time, for adsorbates with the same refractive index as the underlying substrate, effect of s-polarization is expected to be almost 2 times stronger than that of p-polarization.

![Figure 4. A photographic image of water condensates revealing chemical modifications induced on the inner surface of the fused silica substrate. Pumped out gas cell was illuminated using evanescent wave regime with s-polarized light for 210, 300, 480, 660 and 960s (spots 4 to 8, respectively) and with p-polarized light for 210, 300, 480, 660, 960 and 1320s (spots 9 to 14, respectively). The upper sequence reveals spots made with laser beam incident normally to the surface and propagating inside the cell volume (480, 660, 960, 1320 and 1920s illumination times for spots 15-19, respectively). 10mW single-mode He:Cd laser (325nm) was used.]

These conclusions are in a good agreement with our experimental observations. With pumped out gas cell (see Fig. 4), the spots made with p-polarized beam required about twice longer time to get the same visibility as spots produced by s-polarization. For cell containing NO (see Fig.5), the situation remains qualitatively the same for laser illuminations made off-resonance with gas-phase NO molecules; s-polarisation-made spots significantly exceed their p-polarization-made neighbors on the left. However, when the laser is on-resonance with NO absorption line, the p-polarised spots become the strongest in the pairs of two made for the same time but with different polarizations. Moreover, the rate of the chemical modification of the surface is increased by several times in comparison with a off-resonance case. That can be
easily concluded from the picture by comparing exposure times used to make spots of apparently equal visibility at different experimental conditions.

![Figure 5](image.png)

**Figure 5.** A photographic image of water condensates on the inner surface of fused silica window. The spots observed are results of evanescent wave illumination of the gas cell loaded with a mixture of NO and hydrocarbons (250 Torr of NO and 0.25 Torr of C₂H₄). The upper sequence is from on resonance illumination during 60, 40, 30, 20, 15, 10, 5, 10 and 120s, from left to right, starting from the marked by yellow spots (p-polarization is always on the left). The two lower sequences are from off resonance illuminations during 240, 120, 80, 60, 40, 30, 40 and 480s, with p-polarisation is always on the left side if the two spots made with the same time exposure. The laser light was produced via doubling followed by mixing with the fundamental from a dye laser pumped by second harmonics of Nd:YAG laser.

Thus, such polarization-based method can be applied to distinguish between processes induced by photoabsorption in the gas phase and those started by excitation within the aggregated media. That can be easily done and may become particularly valuable for substances which do not have characteristic spectral features, which can be used to recognize contributions from the evaporated and aggregated phases.

### 3. CONCLUSIONS

On two different chemical systems it was possible to realize conditions at which relaxation of electronically-excited in gas molecules on surface dominates photochemical transformations. Results of the experimental observations are sensitive to cleanness and preparation of the working interface. Exact knowledge of the sequences of chemical transformations, induced by relaxation of electronically excited molecules, as well as control of the final chemical products remains challenging.

**Acknowledgements**

We would like to acknowledge stimulating and fruitful discussions with Vladilen Letokhov, Torkild Andersen, Vladimir Bordo and Nikita Lukzen. The work has been performed with financial support from Lundbeckfonden and The Danish Council for Independent Research.

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**REFERENCES**


