Computer Simulations of State-Specific Laser-Induced Desorption of NO from NiO

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We have performed classical trajectory calculations to simulate the processes accompanying laser-induced desorption of NO from NiO(100) and NiO(111) surfaces. Within an Antoniewicz-like desorption model we have used model potentials characterized by two parameters: the center of gravity distance of the molecule from the surface, and the angle between the surface normal and the molecular axis. The transition probabilities of excitation and relaxation were calculated quantum mechanically. The calculated momentum distributions show two maxima in accordance with the experimental results, if the lifetime of the excited state is chosen to be of the order of some 10^{-14} s. Other experimental data as for example the rotational temperature were reproduced also.

1. Introduction

Compared to gas-phase photodissociation processes our understanding of the analogous processes at surfaces, i.e., photoinduced desorption, is rather limited. One problem in connection with experiments at metal surfaces is the short lifetime of the excited states¹⁻³ which leads to very low yields unless femtosecond laser experiments are carried out.⁴ Further problems arise because only a few experimental data are found in the literature which were measured after carefully characterizing the state of the system at the surface.⁵⁻¹² From a theoretical point of view it is considerably more difficult to calculate properties of an adsorbed molecule than to calculate properties of a molecule in the gas phase.

In contrast to metal surfaces, adsorbates on oxide surfaces exhibit much larger photodesorption yields. Over the past few years, experiments at NiO surfaces of different crystallographic orientation, i.e., the (100) and (111) surfaces,¹³⁻²² have been performed, where desorption of NO and CO has been detected state specifically. For example, NO adsorption on NiO(100) has been studied via a variety of surface analytical techniques.¹⁶⁻²¹ The following results have been obtained: (a) There is only one NO species at the surface at T = 100 K. (b) Adsorption takes place above a Ni ion. (c) The adsorption energy is 0.52 eV as determined by thermal desorption spectroscopy. (d) According to NEXAFS measurement the tilt angle between molecular axis and the surface normal is 45°. (e) The vibrational frequencies of the NO stretch are 1800 cm⁻¹ for NiO(100) and 1830 cm⁻¹ for NiO(111)).

After desorption we have determined the following: (a) velocity flux distributions of the desorbing molecules resolved for rotational and vibrational quantum numbers; two maxima were observed; (b) the rotational temperatures of the desorbing molecules vary between 250 and 450 K; (c) the vibrational temperatures of the desorbing molecules are 1900 K for NiO-(100) and 1700 K for NiO(111); (d) coupling of the rotational and translational degrees of freedom has been observed after desorption from NiO(100); (e) the photon energy dependence of the velocity flux distributions has been studied and a threshold at about 3.5 eV has been observed; (f) the angular distributions of desorbing molecules have been measured for some velocities of the desorbing molecules.

We have tried to model the desorption process with regard

to the large amount of data by using classical trajectory calculations. In this paper we present the results of such computer simulations.

2. The Desorption Model

As the experimental data have shown, the desorption is not thermally induced.¹⁸ Nonthermal desorption processes are usually explained by assuming an electronic excitation of the adsorbate-substrate complex. In the literature a variety of desorption models have been discussed (MGR,^{23,24} Antoniewicz,²⁵ Gortel²⁶) which consider different shapes and relative positions of the potential minima in ground and excited states. In our calculations we have used potentials similar to those chosen by Antoniewicz²⁵ as shown in Figure 1: The minimum of the excited-state potential is deeper and closer to the surface as compared with the ground-state potential. Within the framework of the Antoniewicz model, the initial step of the desorption process is an excitation onto the electronically excited state. Under the influence of the attractive potential the molecule moves toward the surface until it relaxes into the ground state. Because of momentum conservation during the relaxation the molecule will be scattered at the surface before it desorbs. Desorption is only possible if the gained kinetic energy exceeds the depth of the ground-state potential energy at the relaxation position.

It is clear that the lifetime on the excited state determines whether or not a molecule desorbs: After short lifetimes a molecule relaxes close to the minimum of the ground-state potential and the gain in kinetic energy is negligible. Therefore, the molecule has not enough energy to leave the surface. However, if the lifetime is longer, propagation on the excited state leads to changes in the position where relaxation occurs and thus possibly to a larger gain in kinetic energy.

From a quantum mechanical point of view there exists a certain relaxation probability at any given time on the excited state. Therefore, we have introduced in our calculations a relaxation probability which is evaluated after every short time step on the excited state. The results presented in this paper were obtained using relaxation probabilities not dependent on the distance between molecule and surface. Some results assuming distance-dependent relaxation probabilities for excitation and relaxation into a distinct final state were calculated by the equations in section 4.

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Figure 1. Schematical drawing to illustrate the desorption model proposed by Antoniewicz.

3. The Potentials

In principle, a potential to describe the dynamics of an NO molecule bound to a metal oxide surface should include all degrees of freedom, i.e., vibronic and rotational motion. However, this renders the problem intractable. We have therefore decoupled certain degrees of freedom if there were experimental hints that this would be a reasonable approximation.

We have only implicitly treated the internal NO vibration because the experiments¹⁸ suggested a decoupling between vibrational and translational/rotational motion. The implicit treatment follows Gadzuk²⁷ by assuming two harmonic oscillator potentials for ground and excited states. The parameters of the ground-state potential were those of a gas-phase NO molecule in its electronic ground state; the parameters of the excitedstate potential were taken from data of gas-phase NO⁻, NO⁺, and the first electronically excited state of NO.

The calculation starts by assuming that only the vibrational ground state of NO is populated at a surface temperature of 100 K. The corresponding wave function is projected onto the vibrational states of the excited-state potential using numerical integration to determine the overlap integrals. It is then possible to evaluate the wave function after a given lifetime of the excited state by calculating analytically the phase shifts for every vibrational state. The final step is the projection of the wave function back onto the electronic ground-state vibrational wave functions which leads to values for the relative populations of the vibrational system.

Mull et al.^{18,20} have shown that the relative populations of the vibrational states depend strongly on lifetime. If we choose a potential simulating NO⁻ as the excited state, the lifetime was determined to be about 2×10^{-14} s or integer multiples of this value because due to the harmonic potentials the motion in the excited state is periodic. (The vibrational-state populations can also be reproduced by using a lifetime of about 2×10^{-15} s. As we will show below, the trajectory calculations do not produce a desorption signal above 1500 m/s if the mean lifetime is below about 1×10^{-14} s; we have therefore excluded this possibility.) It can be shown that the different force constants of the ground and excited states have only minor influence on the degree of vibrational excitation. The main source of the vibrational excitation is the difference in the positions of the potential energy minima.

Figure 2 presents a schematic drawing of the involved potentials with respect to two coordinates, i.e., to the internal N-O distance and the distance of the molecule from the surface. The potential energy minimum of the excited-state internal N-O



Figure 2. Potentials involved in our model of the desorption process with respect to the internal N-O distance and the distance of the molecule from the surface.

coordinate is placed at larger distances which is the situation if the excited state is taken to approximate NO⁻.

There exists no experimental proof up to now that the excited state is connected with the formation of NO⁻; but Menges et al.^{21,28} have found out that the cross section after laser-induced desorption shows the same photon energy dependence as the charge carrier creation in NiO. Including energetic arguments, they proposed an NO⁻ like excited state. Additionally, first results of ab initio cluster calculations²⁹ support this proposal because the calculated excitation probabilities of charge-transfer states are relatively high. The calculated potential energy curves of the charge-transfer states possess shapes which are well reproduced by a sum of a Morse potential and an attractive Coulomb term. Therefore, we have modeled the excited-state potential by using a Morse potential which represents a cut through the ground-state potential at 45°; an attractive Coulomb term and a constant were then added. Because the minimum of the potential constructed by this procedure is placed closer to the surface and is deeper than that of the ground-state potential, the situation is similar to the one used in the Antoniewicz model; however, NO is not physisorbed on NiO but rather weakly chemisorbed.

After the excitation from the ground to the excited state has taken place, the molecule moves toward the surface and starts vibrating around the potential energy minimum of the excited state. Therefore, most of the time in the excited state the internal N-O distance is longer than the equilibrium value of the ground state. As a consequence the relaxation normally takes place far away from the equilibrium position which results in highly vibrational excited molecules in line with the experimental observations.

In our discussion so far we have neglected the orientation of the molecule with respect to the surface normal. In spherical coordinates, the polar angle θ represents the tilt angle i.e., the angle between the molecular axis and the surface normal. The behavior of the potential with respect to the azimuthal angle ϕ is governed by the symmetry of the surface (Figure 3).

The experimentally observed coupling of rotational and translational motion demands the use of potentials with at least two coordinates: the distance of the molecule to the surface and the angle between the surface normal and the molecular axis. Including only these coordinates neglects the atomic corrugation of the surface (with respect to ϕ) as well as the dynamical properties of the surface and treats the NO molecule as a rigid rotor.



Figure 3. Schematic drawing of the angular dependencies (spherical coordinates) of the ground state potential. The distance from the midpoint of the front line represents the angle θ ; the ϕ coordinate is given by the angle to the front line of the figure. Because of clearness, only half the range of the ϕ coordinate is shown. The potential shows minima in the region of $\theta = 45^{\circ}$; the adsorption is stronger in the case of $\theta = 0^{\circ}$ than at $\theta = 180^{\circ}$. Outside of the circle with $\theta = 180^{\circ}$ the potential value has been set to a constant value.



Figure 4. Ground-state potential (drawn for three orientations of the molecular axis) and the excited-state potential used in the calculations.

The ground-state potential was constructed with respect to the available experimental data. Our ground-state potential was built by modifying a potential proposed by Smedley et al.³⁰ describing a flat and rigid surface. Three cuts of the groundstate potential at different tilt angles are given in Figure 4 (together with the excited-state potential).

4. Transition Probabilities

Transition rates are given by using Fermi's golden rule, a result of first-order perturbation theory³¹

$$W_{i,f} = \hbar^{-1} |\langle \Psi_f | \hat{H} | \Psi_i \rangle|^2 \varrho \tag{1}$$

where \hat{H} is the perturbation operator and ϱ is the density of state of the initial state. Applying some further assumptions, namely (a) replacement of the perturbation operator by the dipole operator, (b) Born-Oppenheimer approximation: separation of electronic and nuclear motion, (c) assumption of an electronic transition, and (d) replacement of the density of states by a Boltzmann distribution, one arrives at the often used formula for the relative transition probabilities:

$$P_{i,f} \propto |\langle \psi_{f} | \psi_{i} \rangle|^{2} \exp\left(\frac{-E_{i}}{kT}\right)$$
 (2)

Equation 2 involves only the nuclear wave function of the final and initial state. The overlap integrals are known as

Franck-Condon factors in the case of vibrational wave functions. As we are interested in rotational and translational distributions, we have to look for nuclear wave functions including two degrees of freedom.

Because of the assumption of vanishing angular dependence in the excited state and the assumption of a rigid rotor it is possible to describe the final state wave function by a product of a spherical harmonic and a plane wave (this assumption is probably a poor approximation since ab initio calculations suggest similar angular dependences²⁹ in the excited state as compared with the ground state):

$$\psi_{\rm f}(\vec{r},\vec{k}) = Y_{\rm lm}(\theta,\phi) \exp(i\vec{k}\cdot\vec{r}) \tag{3}$$

where \vec{k} is the momentum vector and \vec{r} is the center of gravity vector with the spherical coordinates r, θ , and ϕ .

We model the ground state by taking the N atom as being fixed above a Ni atom of the surface; the O atom can move at a given distance (rigid rotor) around the N atom. The motion of the O atom is restricted to a certain range of the angular coordinate θ because of the angular dependence of the groundstate potential. In an earlier work we approximated the groundstate wave function by using a potential with infinite high walls along the angular coordinate which allows an analytical solution of the Schrödinger equation (as was shown by Landman³²). In our present calculations the initial-state wave function was determined by solving a one-dimensional Schrödinger equation (with respect to θ) numerically with respect to the given angular dependence of the ground-state potential.

As a consequence of the flat surface assumption the groundstate potential does not depend on ϕ with the result that the ground-state wave functions are characterized by a magnetic quantum number *m* analogous to that used to characterize spherical harmonics. Therefore, the ground-state wave functions are expanded in a sum of spherical harmonics where the summation runs only over the quantum number *l*. Note that the overlap integrals characterized by different quantum numbers *m* of the wave function and the spherical harmonics are zero:

$$\psi^{i}_{\nu,m_{\nu}}(\theta,\phi) = \sum_{l_{\nu}=0}^{\infty} \langle Y_{l_{\nu},m_{\nu}} | \psi^{i}_{\nu,m_{\nu}} \rangle Y_{l_{\nu},m_{\nu}}(\theta,\phi) \delta(r)$$
(4)

 ν is simply an index to distinguish the wave functions; the delta function represents the rigid rotor assumption.

The next steps follow a route explored by Landman³² in connection with a special angular dependence of the groundstate potential, i.e., like a particle in a box. Both wave functions in eq 2 are replaced by the given expressions and then the plane wave is expanded into spherical harmonics and spherical Bessel functions $j_1(x)$. The integration with respect to θ and ϕ can be carried out analytically by using a formula including Wigner 3j symbols. The overlap integrals of eq 2 are finally given by

$$\langle \psi_{\mathbf{f}} | \psi_{\mathbf{i}} \rangle = (-1)^{m_{\nu}} (4\pi)^{1/2} (2\mathbf{l}+1)^{1/2} \times$$

$$\sum_{\mathbf{l}' = |m_{\nu} - m|}^{\infty} (-\mathbf{i})^{\mathbf{l}'} j_{\mathbf{l}'}(\mathbf{kr}) Y_{\mathbf{l}', m_{\nu} - m}(\theta_{\mathbf{k}}, \phi_{\mathbf{k}}) (2\mathbf{l}'+1)^{1/2} \times$$

$$\sum_{\mathbf{l}_{\nu} = |m_{\nu}|}^{\infty} \langle Y_{\mathbf{l}_{\nu}, m_{\nu}} | \psi_{\nu, m_{\nu}}^{\mathbf{i}} \rangle (2\mathbf{l}_{\nu}+1)^{1/2} \begin{pmatrix} \mathbf{l}' & \mathbf{l} & \mathbf{l}_{\nu} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \mathbf{l}' & \mathbf{l} & \mathbf{l}_{\nu} \\ \mathbf{m} - \mathbf{m}_{\nu} & -\mathbf{m} & \mathbf{m}_{\nu} \end{pmatrix}$$

(5)

5. Results and Discussion

As there exist no experimental data about the lifetime of the excited state we have performed calculations with relaxation probabilities covering a range of more than one order of



velocity [m/s]

Figure 5. Momentum distributions calculated by using different relaxation probabilities. The curve at t = 0.0 represents the momentum distribution in the excited state just after the excitation. Please note that this curve is determined only by the excitation probabilities; therefore the curve has been scaled to fit into the figure.

magnitude. Some calculated momentum distributions summed over all rotational states are presented in Figure 5 where each distribution is characterized by the mean value of the lifetime.

Lower mean lifetimes than about 1×10^{-14} s do not produce desorption at higher velocities than 1500 m/s (which was experimentally observed).

In two panels of the figure, we have also plotted experimental data representing the rotational quantum state j = 5.5 of the desorbing molecules (crosses) for both NiO(100) and NiO(111) surfaces. In contrast to the calculated data the experimental values were gained within a certain detection angle around the surface normal (about $\pm 20^{\circ}$). Therefore, the calculations may overestimate the slow desorption channel. Reducing the sampling angle would most probably produce improved agreement between experiment and theory. Some further remarks concerning angle distributions are given at the end of this section.

Comparison of the calculated momentum distributions with the measured velocity flux distributions shows that the desorption in the system NO/NiO(111) is well represented by a mean lifetime of 1.8×10^{-14} s; the best correspondence with the NO/ NiO(100) system is given by the calculated distribution according to a mean lifetime of 4.4×10^{-14} s. The shape of the distributions can be explained as follows:

After very short lifetimes the relaxation occurs nearly at the position where the excitation has taken place. Therefore, the molecules are in the region of the ground-state potential energy minimum, and the kinetic energy gained during the excitedstate lifetime is small. As a consequence only some molecules have enough energy to desorb and their momenta are small. With increasing lifetime of the excited state the relaxation takes place at positions closer to the surface, i.e., in the region of the repulsive branch of the ground-state potential. Likewise the gained kinetic energy increases and the calculated momentum distributions show increasing ranges of momenta.

The highest possible momenta are observed if the relaxation occurs near the position of the innermost classical turning point. The exact position depends on the slopes of both the excitedand the ground-state potential: As a molecule reaches the repulsive branch of the excited state, longer lifetimes result in a loss of kinetic energy which may be compensated for by a gain in potential energy with respect to the ground state.

Regarding the low momenta of molecules around the turning point it is clear that the time spent in this region is relatively long compared to the time spent around the minimum of the excited-state potential. Because the total relaxation probability according to a given distance involves an integral over the time spent at that distance, one observes a maximum in the momentum distribution if the relaxation probability is low enough to allow the molecules to reach the innermost turning point.

In Figure 5 we have plotted for comparison the distribution of momenta immediately after the transition from the lower to the higher potential energy curve has taken place. This distribution is not bimodal, thus corroborating the idea that the bimodality is induced via propagation on the excited state.

In our earlier work using a purely repulsive potential energy curve and a fixed lifetime of the excited state, it could be shown that the direction of the momentum just after the excitation determines to which maximum the desorbing molecules contribute. Molecules carrying a momentum directed away from the surface constitute the part of the distribution with its maximum at higher velocities; the other maximum is built up by the molecules with momenta directed toward the surface. The use of lifetime distributions (relaxation probabilities) in the present work broadens the range of possible momenta connected with a certain initial direction so much that the unique assignment of one initial direction of momenta to one maximum is softened, but a major contribution of a particular direction of momentum to the maxima is recovered.²²

The above discussion of the momenta distributions was mainly carried out with respect to the distance of the molecule from the surface. Very long lifetimes show only one broad momentum distribution; in this case most of the molecules have spent more than one vibrational period (vibration of the whole molecule against the surface) in the excited state. After long lifetimes the rotation of the molecule is not negligible: Because of the angular dependence of the ground-state potential the relaxation may now occur at positions where the shape of the ground-state potential along the distance coordinate is significantly altered compared to relaxation after short lifetimes. In effect, nearly all energetically accessible positions in momentum space are possible and the structures observed for shorter lifetimes are completely washed out.

Let us consider next the rotational temperatures of the desorbing molecules. Equilibrated rotational-state distributions follow a straight line if the relative populations are plotted according to Boltzmann. The slope of the line is then connected with the temperature of the system. In Figure 6 we present a calculated rotational-state distribution (mean lifetime: 4.4×10^{-14} s) together with experimental data. Although the complete set of data cannot be described by a straight line, especially if values at very low quantum numbers are considered, a large



Figure 6. Measured and calculated rotational-state distributions (Boltzmann plots). The calculated data points are connected by straight lines.

portion does follow a straight line. In this region we have characterized the distributions by rotational temperatures to allow an easy comparison of theory and experiment. The calculated rotational temperatures range from about 350 K (mean lifetime 1.8×10^{-14} s) to about 500 K (mean lifetime 4.4×10^{-14} s) and are therefore comparable to the experimental data. The important point here is not the exact value of the temperature but the observation of clearly higher temperatures than a thermal desorption process would imply.

The mechanism of the rotational excitation is similar to that proposed for the vibrational excitation: During the lifetime in the excited state the molecule leaves the region of the groundstate potential minimum. Therefore, relaxation transfers the molecule onto a high-lying part of the ground-state potential with respect to the angular coordinate which results in rotationally excited molecules.

In the last part of this chapter we want to analyze the calculated data with respect to the experimentally observed coupling of rotation and translation (in the system NO/NiO-(100)). We have split the momentum distribution with a mean lifetime of 4.4×10^{-14} s (comparable to NO/NiO(100)) into several parts according to different ranges of the rotational quantum number as presented in Figure 7. The straight line in the figure indicates a shift of the second maximum at higher momenta with increasing rotational quantum number. This shift is not found if the data corresponding to the mean lifetime of 1.8×10^{-14} s (comparable to NO/NiO(111)) are plotted in the same manner. In other words the simulation reproduces the coupling between rotational and translational motion.

Our simple model allows a clear identification of the origin of the coupling: Because we have built the excited-state potential without an angular dependence, the coupling is a consequence of the ground-state angular dependence. After short lifetimes the relaxation occurs near the minimum of the ground-state potential energy with respect to both the distance and the angular coordinate. If the molecule can desorb at all, momentum and angular momentum will be small. Long lifetimes result in relaxation at positions, where the groundstate potential is steep according to both coordinates. A coupling of rotation and translation will be observed, because in this case the degree of excitation of rotation and translation depend in the same manner on the lifetime: longer lifetimes result in higher excitation (higher momenta and higher angular momenta).

In general, not only one of the potential energy surfaces involved in the process will show an angular dependence; in this more general case a rotational excitation has to be explained by taking the differences of the angular dependences of the two potential energy surfaces into account.



Figure 7. Momentum distribution characterized by a lifetime of 4.4 $\times 10^{-14}$ s (Figure 5) split up with respect to several ranges of the angular momenta of the desorbing molecules. The coupling of the rotation and the translation is shown by the line connecting the maxima of the "fast desorption channel".

We have also tried to model changes in the velocity flux distributions upon changing the excitation energy²² but we shall not discuss the results in the present paper.

In addition to state specificity, our experiments allow for spatial resolution which in turn opens the possibility to determine angular distributions.³³ Our desorption model may be not a very good one to calculate angular distributions, because the use of potentials describing flat and rigid surfaces are severe limitations.^{34–36} These limitations may have strong influence on angular distributions. Nevertheless, we have analyzed our data with respect to angular distributions and have found an interesting result which is presented in the following.

Our trajectory calculations include only two degrees of freedom: the distance of the center of gravity to the surface and angle between the molecular axis and the surface normal. Therefore, a momentum component parallel to the surface will not be changed during the calculation. Just after the excitation has taken place the momentum vector \vec{k} is decomposed in two components parallel and perpendicular to the surface. The component perpendicular to the surface is used in the trajectory calculation and the parallel component remains unchanged until the molecule is desorbed.

In Figure 8 we present measured angular distributions (points) obtained at different velocities of the desorbing molecules; the symbols connected by straight lines represent the results of a calculation split in two parts belonging to different ranges of momenta. As the velocity increases, the experimental data show smaller angular distributions which is confirmed by further data



Figure 8. Angular distributions of the desorbing molecules. The small data points were measured for velocities of 250 m/s and 1200 m/s.²⁸ The connected points were calculated using momentum ranges of 0-20 and 20-40 atomic units.



Figure 9. Desorption angle of a molecule defined by the momentum components parallel and perpendicular to the surface. For a given momentum parallel to the surface the detection angle is smaller for molecules with a larger perpendicular momentum component.

not shown here. In principle the same trend is observed in our calculation: the distribution connected with relatively low momenta is significantly broader than that at high momenta.

Within our model the trend can be explained in a straightforward manner: If the momentum component parallel to the surface is fixed, a simple geometrical consideration shows that lower momenta perpendicular to the surface must result in broader angular distributions (Figure 9).

It is clear that a more accurate simulation of the angular distributions has to use potentials which are modeled including surface corrugation and possibly motion of the surface atoms, but the simple effects discussed here have to be considered.

6. Summary

We have presented a model which simulates laser-induced desorption of NO from NiO surfaces. Assuming that the excited state is NO⁻ like we have used model potentials describing a

situation which is similar but not identical to the Antoniewicz desorption model: The minimum of the excited-state potential is positioned closer to the surface and its depth exceeds that of the ground-state potential. An angular dependence is explicitly included only for the ground state. In future studies we will also include angular dependences in the excited state.²⁹ The transition probabilities between the two states were found by calculating overlap integrals of nuclear wave functions. The ground-state nuclear wave functions were obtained by numerically solving a Schrödinger equation with respect to the angular coordinate; the excited-state nuclear wave functions were modeled by products of spherical harmonics and plane waves. The results of our classical trajectory calculations are as follows: (1) The calculated momentum distributions show two maxima. (2) Depending on the excited-state lifetime it is possible to simulate the relative intensities observed experimentally¹⁶⁻²¹ for NiO(100) or NiO(111). (3) The calculated rotational temperatures are well above the surface temperature in accordance with experimental results. (4) The trend that faster desorbing molecules show more narrow angular distributions can be reproduced in the calculations.

In effect, most of the experimental data can be reproduced qualitatively. Vibrational excitation is only treated implicitly. Furthermore, the observed trends can be explained within simple classical pictures.

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