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Chemical hole diving

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Abstract

The non-adiabatic reaction leading to the emission of exoelectrons during the adsorption of oxygen on lithium is exploited to estimate the time that elapses during the dissociation of the molecule. With a three-step model the exoemission probability is calculated. A comparison with experimentally observed probabilities predicts the reaction time to be 75 ± 25 O2p hole lifetimes at the final O2p binding energy. The width of the exoelectron energy distribution reflects this hole lifetime. The absence of visible light emission ($< 10^{-10}$ photons/O_2) is shown to be compatible with the model.

The observation of particle emission during a chemical reaction at a surface is attributed to non-adiabatic charge-transfer processes [1–5]. The phenomenon ranges from probabilities of 10^{-2} down to the detection limit of typically 10^{-12} particles per charge transfer where photons, electrons and ions are found. Since these particles get energy and momentum during the reaction, their probability is a direct consequence of the dynamics of the process. It is, therefore, a reverse problem to derive from these probabilities the reaction time.

The description of the excitation process in the reaction of oxygen with metallic lithium is based on the concept of the creation of a hole state below the Fermi level and the subsequent annihilation by an Auger transition or the production of a photon [2,3]. Here, absolute electron emission probabilities are calculated. From the comparison with experimentally observed probabilities and exoelectron energies it is possible to estimate the time scale and power dissipation $\Delta E/\Delta t$ for the charge transfer reaction from O^- to O^{2-}.

Li is a particularly clear-cut example for exoelectron emission because electrons are emitted in the first oxidation step i.e. from a metallic surface [6] and it allows the application of electron gas theory to the problem.

The experiments were performed in an UHV system (base pressure below 10^{-8} Pa) and are described elsewhere in detail [6,7]. The emission of exoelectrons from two monolayers of Li starts in the first oxidation step and drops before the surface reaches its work function minimum at about 2 L of O_2 exposure ($1\ \mathrm{L} = 1.3 \times 10^{-4}$ Pa s). The electron emission probability at the beginning of the oxidation is, however, fairly low (10^{-7} e^-/O_2) and the emission of light is even less probable ($< 10^{-10}$ photons/O_2). Parallel to the exoelectron emission a faint O^- emission between 10^{-10} and 10^{-11} O^-/O_2 is observed [7].

In the case of the $Cs + O_2$ system the O^- emission suggests a model that includes the intermediate formation of O_2^{2-} leading to the dissociation of the molecule [8]. For the reaction of O_2 with Li this picture was substantiated by total energy calculations [6]. From these experimental and theoretical findings the following model for dissociative adsorption of O_2 was derived (see Fig. 1).

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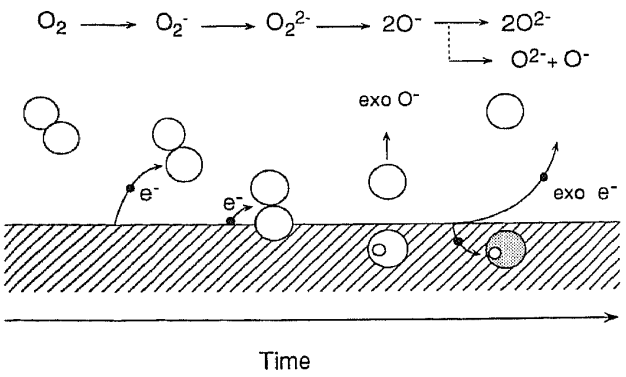

Fig. 1. Visualization of the dissociative O_2 adsorption on alkali metals leading to the emission of O^- ions and exoelectrons.

The adsorption starts with the approach of a thermal O_2 molecule to the metal surface. The image force lowers the affinity level of the O_2 molecule which resonantly ionizes as soon as it crosses the Fermi level. Now the O_2^- molecule is accelerated by its image charge to the surface and will pick up a second electron. This hot O_2^{2-} species is not stable and will burst into two O^- fragments. If the momentum of one of these fragments is large enough and directed away from the surface it may escape from the metal. The dissociation process will, on the other hand, leave an O^- ion close to the surface. This O^- state is a high excitation of the O^{2-} ground state that is reached after a complete reaction. In a one-electron picture the affinity level of the O^- that is degenerate with the Fermi-level at the beginning of the dissociation, will start to dive to its ground state position at the O2p binding energy (see Fig. 2a). The observation of electron emission suggests that this hole injection process, i.e. the O_2^{2-} dissociation, is so fast that some of the O2p holes may dive deeper than the work function and lead to the emission of Auger electrons. From such a situation, where the de-excitation happens at a site with high electron density, it is expected that the holes do not live long enough for the substantial production of light.

So far only qualitative arguments for the time scale have been given. A dynamical description has to take into account the evolution of total energy as a function of time. In the following it is shown that the survival probability of a hole that dives in the Fermi sea and the resulting Auger electron emission probability may yield a reaction time expressed in O2p hole lifetimes.

The model consists of three independent steps: (i) the chemical excitation, in this case expressed with the survival probability P_h of a chemically injected hole into an electron gas, (ii) the kinetic energy distribution of an Auger de-excitation leading to the emission of an electron inside the solid and (iii) the refraction of these Auger electrons at the potential that has to be overcome for an electron escape into the vacuum.

In Fig. 2b the hole injection process below the Fermi level is sketched. The insets show that emission is possible as soon as the hole dives deeper than the work function of the surface. In this picture the center of gravity of the hole may not be injected deeper than a maximum excitation energy ϵ_A. This is

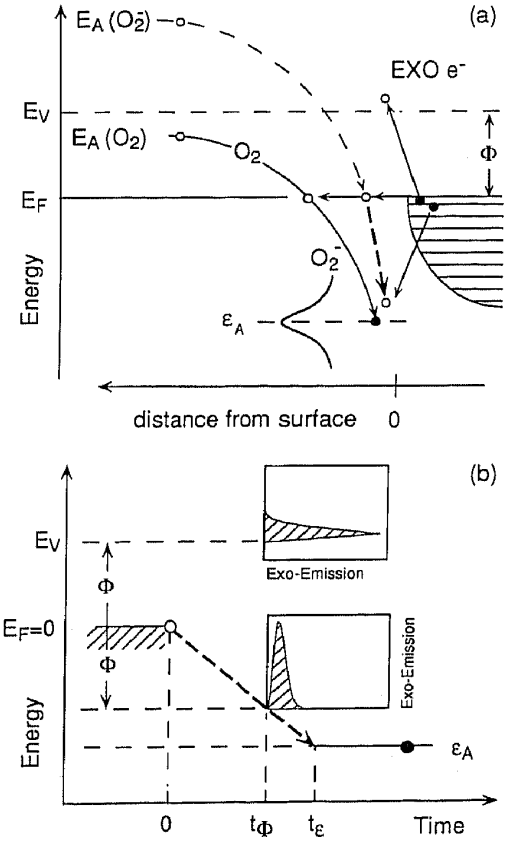

Fig. 2. (a) One-electron picture of the model in Fig. 1. As soon as the intermediate O_2^{2-} is formed via two resonant electron transfers, the molecule bursts and the holes on the O^- fragments start to dive below the Fermi level. The de-excitation of such a hole may lead to Auger emission of an exoelectron. (b) Model for the chemical hole diving process. The reaction starts at $t=0$ and ends at $t=t_\epsilon$, i.e. when the hole state has reached its maximum binding energy ϵ_A. As soon as the hole survives an injection deeper than the work function, exoelectron emission through an Auger de-excitation into the vacuum is possible. The insets show schematically the exoelectron distribution in energy and time, respectively.

suggested by the finite chemical energy that is released in the charge transfer process. The energy ϵ_A is expected to be smaller or equal to the Fermi energy, i.e. the bandwidth of the metal plus the atomic affinity [9]. This is supported by the fact that in the first reaction stage of oxygen with alkali metals the O2p shell pins to the lower level of the valence band [10]. The injection process is set to be linear with time $\epsilon_t = \alpha t$ where ϵ_t describes the center of gravity of the hole at time t and α is the power dissipation $\Delta E/\Delta t$. The hole lifetime is still to be implemented. Theory predicts for an electron gas a lifetime broadening proportional to $(E_F - \epsilon_t)^2$ [11]. This statement is based on density of states arguments and corresponds to an expansion of the integral of the Auger electron energy distribution $A_{\epsilon_t}(\epsilon)$ that results from the de-excitation of a hole at ϵ_t.

With this linear diving ($\varepsilon \propto t$) and the quadratic lifetime dependence ($\tau \propto \epsilon^{-2}$) the survival probability for the hole $P_h(t)$ becomes for $t < t_\epsilon$

$$P_h(t) = \exp(-t^3/3t_\epsilon^2\tau_\epsilon)\,, \tag{1}$$

while the parameter t_ϵ describes the diving time to ϵ_A, and τ_ϵ the lifetime of such a hole state at ϵ_A. The factor $\frac{1}{3}$ in Eq. (1) is a consequence of the integration of the decay rate dP_h/dt which is proportional to the square of the time.

Secondly, the energy distribution of the Auger electrons $A_{\epsilon_t}(\epsilon)$ inside the solid has to be described. For a constant density of states and a constant matrix element that implies e.g. no resonance in the final state of the emitted electron, $A_{\epsilon_t}(\epsilon)$ increases linearly with decreasing kinetic energy ($A_{\epsilon_t}(\epsilon) \propto \epsilon_t - \epsilon$).

Finally, the Auger electron has to overcome the inner potential to escape into vacuum. The simplest (classical) model for this refraction is an isotropic emission inside the solid and a step function describing the inner potential. The electron momentum parallel to the surface is conserved and the normal component pays for the overcoming of the inner potential. It turns out that the escape probability P_e is proportional to the electron momentum in the vacuum or, more precisely, that it is proportional to the solid angle of the total reflection cone [12].

Within the above approximations the integral $\int A_{\epsilon_t}(\epsilon) P_e(\epsilon)\, d\epsilon$ is for small excitation energies $(\epsilon_t - \Phi)/\epsilon_t \ll 1$ proportional to $(\epsilon_t - \Phi)^{5/2}$. Such a power law is expected in a sudden picture, i.e. describes the exoemission probability if the hole could not decay on its way to ϵ_t. The exponent in this power law is at some variance to another model that found a value of 3 [13] for the exponent which is a consequence of the different expansions for the integral $\int A_{\epsilon_t}(\epsilon) P_e(\epsilon)\, d\epsilon$.

To estimate the emission probabilities one has to make reasonable assumptions on the inner potential U and the Auger intensity distribution. For a constant density of states, a constant matrix element and a negligible number of radiative decays $A_{\epsilon_t}(\epsilon)$ becomes $2(\epsilon_t - \epsilon)/\epsilon_t^2$. The inner potential U corresponds to the bandwidth plus the work function [12]. With these assumptions the Auger electron yield $Y_s = \int A_{\epsilon_t}(\epsilon) P_e(\epsilon)\, d\epsilon$ of a suddenly created hole at energy ϵ_t (with respect to the Fermi level) becomes for $\epsilon_t/\Phi \approx 1$

$$Y_s = \frac{4}{15} \frac{(\epsilon_t - \Phi)^{5/2}}{\epsilon_t^2 \sqrt{U}}\,. \tag{2}$$

For typical values of ϵ_t, Φ and U Y_s is therefore less than 1%.

Now the exoemission probability for an excitation as described in Fig. 2 can be derived. The function $Y(t_\epsilon/\tau_\epsilon,\ \Phi/\epsilon_A)$ is the exoemission probability as a function of the hole lifetime τ_ϵ at ϵ_A, the diving time t_ϵ down to ϵ_A, and the work function Φ,

$$Y \propto \int P_h(t) \int_{\epsilon > \Phi} Y_s(\epsilon) f(\epsilon - \epsilon_t)\, d\epsilon\, dt\,, \tag{3}$$

where the broadening is implemented with a Gaussian $f(\epsilon - \epsilon_t) \propto \exp\{-[(\epsilon - \epsilon_t)/\gamma_t]^2\}$; $\gamma_t = \frac{1}{2}\hbar\sqrt{\ln 2}\,\tau(t)$. A Lorentzian tail decreases not steep enough to describe the kinetic energy distributions of the exoelectrons. Fig. 3 visualizes $Y(t_\epsilon/\tau_\epsilon,\ \Phi/\epsilon_A)$. It shows the exoemission probability (one oxygen atom may produce one exoelectron) as a function of the work function in units of ϵ_A. The reaction time and the energy broadening γ_ϵ are varied. The experimental input, i.e. the initial value of the work function ($\Phi_0 = 2.9 \pm 0.1$) as well as the position of the O2p level ($\epsilon_A = 5.2$ eV) are derived from the He I photoelectron spectra (UPS) [7] and the exoemission probability is estimated from the electron current, the sample surface and the oxygen flux on this surface. The comparison between experiment and theory allows an estimation of the reaction time to be between 50 and 100 hole lifetimes at ϵ_A.

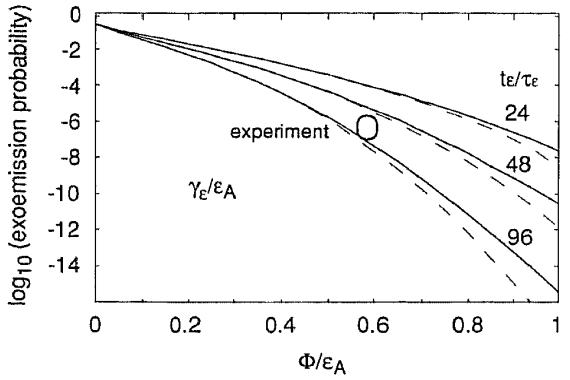

Fig. 3. Calculated exoelectron emission probabilities as a function of the ratio between the work function Φ and the final binding energy ϵ_A of the highest occupied oxygen level. The open dot indicates the experimentally observed probabilities (number of exoelectrons per oxygen molecule) at the beginning of the reactant of O_2 with 2 monolayers of Li. $\gamma_\epsilon/\epsilon_A$ is (——) 0.125, (– – –) 0.063.

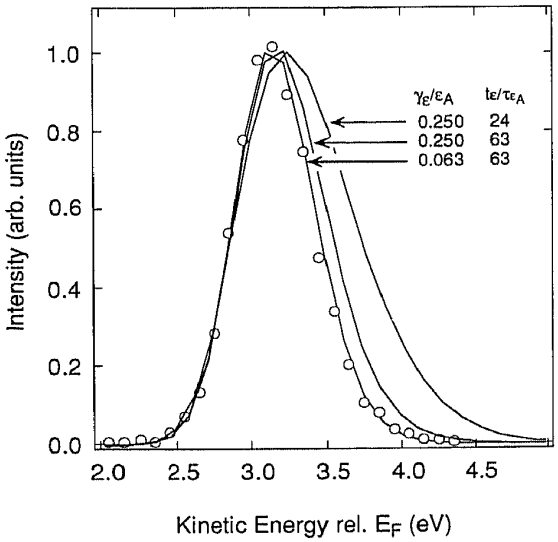

Fig. 4. Comparison between (——) theoretical and (O) experimental exoelectron energy distributions. The theoretical curves are folded with a 500 meV instrumental resolution function. Within the proposed model the hole lifetime at ϵ_A may be estimated.

So far no absolute time scale for τ_ϵ has been derived. The lifetime broadening γ_ϵ affects the energy distributions of the emitted electrons and, in principle, γ_ϵ and, therefore, τ_ϵ can be determined from the exoelectron energy distribution curves. Fig. 4 shows experimental and theoretical kinetic energy distributions. The theoretical spectra are derived from the above hole diving model and are convoluted with an instrumental resolution function. This indicates how the lifetime broadening affects the width of the energy distributions. In the framework of the proposed model the comparison with the experimental data provides an approximation of γ_ϵ and the time for the hole diving down to ϵ_A can be roughly estimated to be between 120 and 32 fs. Additionally, it is seen that the exoemission process takes place before the reaction is completed, i.e. before t_ϵ.

Further support for the consistency of the above model is given by a comparison of the calculated and measured limits for chemiluminescence cross sections. From relation (1) it is easy to calculate the expected light spectra as a function of the model parameters, if only a negligible portion of the de-excitations occur via the creation of spontaneous photons. Assuming a constant transition matrix element the emission probability for a photon $I(\omega)$ becomes with the ω^3 term for spontaneous emission [2],

$$I(\omega) \propto \omega^3 \int_{\hbar\omega}^{\infty} P_h(\epsilon)\, d\epsilon\,. \tag{4}$$

To some extent the spectra resemble those of Planck's black-body radiation where an ω^3 factor cuts the far infrared tail as well but the $\int P_h$ factor cuts the blue sharper than the occupation number in Planck's formula. It has to be noted that the emission maximum provides a direct measure of the hole injection time.

The total photon emission probability is low compared with the electron emission probability. Assuming at energy ϵ_A a branching between photon and electron de-excitation (note not electron emission) η of 10^{-6} (assuming optical lifetimes of 10 ns and electronic lifetimes of 10 fs) the photon emission probability is 0.010η, 0.005η and 0.002η for $t_\epsilon/\tau_\epsilon = 24$, 48 and 96, respectively.

These probabilities cannot be easily measured since the spectra have a large portion in the infrared. If, e.g. the sensitivity of our photo multiplier (EMI 9130B) is folded with the spectra from Eq. (4) the upper limit for light production indicates that reaction times between $48\tau_\epsilon$ where $6\times10^{-4}\eta$ photons/O_2 and $96\tau_\epsilon$ ($8\times10^{-5}\eta$) are expected. Within the proposed model the absence of chemiluminescence ($<10^{-10}$ 600 nm photons/O_2) is, therefore compatible with the observed electron emission probabilities.

In conclusion, a model is presented that deter-

mines the time scale for the charge transfer reaction during the dissociation of an O_2^{2-} species on alkali metal surfaces. It is shown that the width of the exoelectron energy distribution is affected by the lifetime broadening. As with the earlier model for the adsorption of halogens on alkali metal surfaces [2] this model is able to predict chemiluminescence spectra and rationalizes why the $Li+O_2$ reaction is dark. The presented model explains as well why the exoelectron emission probability in the first oxidation stage is so small for the heavy alkali metal Cs [5] for which the Φ_0/ϵ_A ratio is larger than that in the discussed case of Li.

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