

O^- Escape during the Oxidation of Cesium

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(Received 23 November 1992)

Exposure of Cs surfaces to O_2 causes ejection of O^- ions with low yields ($\sim 10^{-8}$ per incident O_2 molecule) during the first stages of dissociative chemisorption (followed by exoelectron emission at higher exposures), although the work function of the surface exceeds the electron affinity of O and the energetics of the overall reaction is almost zero. A mechanism is proposed whereafter the release of O^- is a consequence of strong repulsion in O_2^{2-} species intermediately formed in front of the surface.

PACS numbers: 79.20.Nc, 68.35.-p

The energy released in the course of a reaction between gaseous particles and a solid surface is usually dissipated into the heat bath of the solid. In the case of an interaction between electronegative particles (such as halogens or oxygen) and low work function surfaces there exist, however, alternate nonadiabatic channels with finite probabilities leading to electronic excitations which may manifest themselves in the emission of photons (chemiluminescence) or electrons ("exoelectrons") [1]. Reports on the emission of negatively charged particles upon exposure of alkali metal surfaces to halogens can be found in the earlier literature [2]. These particles were found not only to be electrons but to consist to an appreciable extent also of halide ions [3,4]. This result is perhaps not so surprising if one takes into consideration that the electron affinity of, e.g., Cl (3.5 eV) exceeds the work functions of alkali metal surfaces so that "harpooning" over distances exceeding those needed for strong chemical interaction ($\geq 6 \text{ \AA}$) becomes feasible. In the present paper we report on the ejection of O^- ions from a Cs surface exposed to oxygen molecules. The electron affinity of O (1.46 eV) is definitely smaller than the work function of the surface used ($\phi = 2.0 \text{ eV}$). The energy necessary for this electronic excitation has to originate from the exothermicity of the overall reaction, and hence evidence for still another type of nonadiabatic surface reaction is presented whose probability is, however, admittedly very small ($\leq 10^{-8}$).

The experiments were performed in a UHV chamber at a base pressure below 10^{-8} Pa . Cs was evaporated from SAES getter sources on a clean Ru(0001) substrate. Cleanliness and thickness of the alkali films were checked by thermal desorption spectroscopy (TDS) and metastable He deexcitation spectroscopy (MDS). The work function was determined from the width of the He I excited photoemission spectra. The negatively charged particles were identified as ions with a Balzers QMG 421 mass spectrometer equipped with single count electronics and appropriate ion optics. The kinetic energy distributions were measured by means of an electrostatic electron energy analyzer.

Figure 1 shows the current of negative ions with mass 16 emanating from an initially clean monolayer of Cs

with $\theta_{Cs} = 0.33$ ($5.3 \times 10^{14} \text{ atoms/cm}^2$) on a Ru(0001) surface ($\phi = 2 \pm 0.1 \text{ eV}$) as a function of thermal oxygen exposure. The ion current is strongest at the beginning of oxidation and decays exponentially with progressing oxidation. It lost half its intensity after 0.5 L (1 L = 10^{-6} Torrs) of O_2 exposure. The observed kinetics follows a simple first-order behavior, similarly as reported by de Blasi Bourdon and Prince for the Cl⁻ emission with the Cl₂-Y system [4]. The initial probability for the ion escape is estimated to lie between 10^{-8} and 10^{-9} per impinging O_2 . This value is derived from the ion count rate, the sample surface area, the O_2 pressure, and the mass spectrometer transmission (10^{-3} - 10^{-4}). At the work function minimum, a weak peak in emission is observed and then it drops below the detection limit. The ion emis-

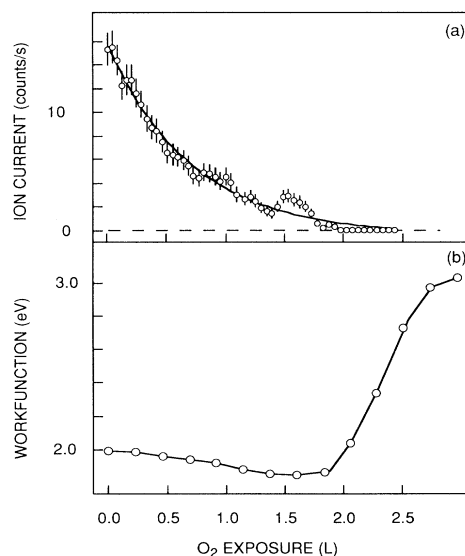


FIG. 1. O^- emission from a monolayer of Cs on Ru(0001) as a function of O_2 exposure (1 L = $1.3 \times 10^{-4} \text{ Pa s}$). The applied O_2 pressure was 10^{-6} Pa and the sample was kept at 200 K. (a) Ion current vs exposure. The solid line represents a fit of an exponential to the data. (b) Work function ϕ determined from the width of our ultraviolet photoemission spectroscopy spectra.

sion is therefore confined to the first oxidation stage of Cs where the oxygen molecule dissociates and atomic oxygen (O^-) is incorporated into the solid. In the case of one monolayer of Cs on Ru(0001), the dissociative O_2 chemisorption was verified by an extended low-energy electron diffraction study [5] and confirmed by high-resolution electron-energy-loss spectroscopy and ultraviolet photoemission spectroscopy [6]. This is also consistent with earlier findings [7]; particularly the work function displayed in Fig. 1(b) agrees qualitatively and reflects the typical shape observed during the oxidation of alkali films. Within the detection limits of our experiment we do not observe any O_2^- emission; the probability for such a process is $< 10^{-11}$. In the subsequent oxidation steps where oxygen builds up molecularly (peroxide Cs_2O_2 and superoxide CsO_2 type surface species) into the solid, no more ions are emitted, but exoelectron emission is observed [8-10].

Figure 2 shows the kinetic energy distribution of the emitted O^- ions. The distribution is peaked at the vacuum level, and its width is mainly determined by the limited energy resolution (250 meV). This indicates that the emitted ions (even if they would be accompanied by a small fraction of electrons) have close to zero kinetic energies. This is supported by thermodynamic considerations. While the reaction $4Cs + O_2 \rightarrow 2Cs_2O$ (+6.6 eV) is highly exothermic, the heat for formation of free O^- ions is very small: The energy for dissociation of O_2 amounts to 5.1 eV, and simple arithmetic yields that the reaction $2Cs + O_2 \rightarrow Cs_2O + O$ is exothermic by only 0.8 eV. This value has to be reduced by the energy cost $\Delta E = \phi - E_A$ for transferring an electron from the Fermi level ($\phi = 2.0$ eV), so that an excess energy of only about 0.2 eV is estimated to accompany the reaction $2Cs + O_2 \rightarrow Cs_2O + O^-$. The energetics for the reaction of O_2 with a chemisorbed Cs monolayer might differ somewhat from those for bulk Cs, but this will not affect the qualitative

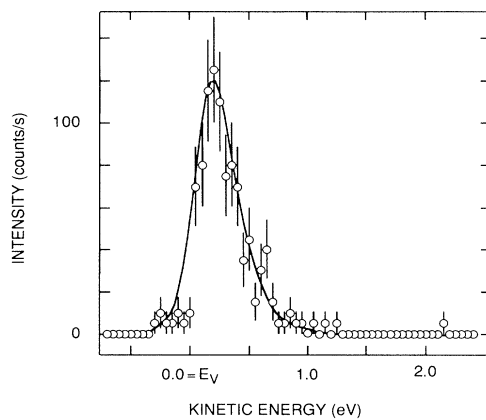


FIG. 2. Energy distribution of negatively charged particles, collected during the exposure of a clean monolayer of Cs to 0.2 L O_2 . The solid line is a guide to the eye.

conclusions. (It should be noted that the experimental observations with thick Cs films are quite similar.)

Interestingly, there appears to exist a continuous relation between the yield of ejected negative ions and the magnitude of the energy difference between work function and affinity level, $\Delta E = \phi - E_A$. An analysis of the data reported by Trowbridge and Herschbach [3] for the formation of halide (Cl^- , Br^-) ions on various alkali metal surfaces leads to a linear relation between the logarithm of the ion yield and ΔE , i.e., $Y \approx Y_0 e^{-\Delta E/\alpha}$, with $Y_0 \approx 2.3 \times 10^{-7}$ and $\alpha \approx 0.16$ eV. This trend may even be extended to the "uphill" reaction of the present system which is shown in Fig. 3 where the O^- yields for Cs and Na are compared with the halide yields. Such an exponential dependence was proposed by Nørskov and Lundqvist [11] to describe the secondary-ion emission probability in sputtering. In their description, α is determined by the velocity of the escaping ion as well as the (distance-dependent) overlap between the substrate wave functions and the affinity level. It is remarkable that the order of magnitude for α is correctly reproduced in the framework of their sputtering theory if one assumes that the ejected ions are not very hot, which is the case with the present system (see Fig. 2).

Further support for the crucial role of the work function is the weak bump in the ion yield of Fig. 1(a) which is found reproducibly in the region of the work function minimum. Furthermore, the yield decreases for Na ($\phi = 2.7$ eV) by 2 orders of magnitude and drops below

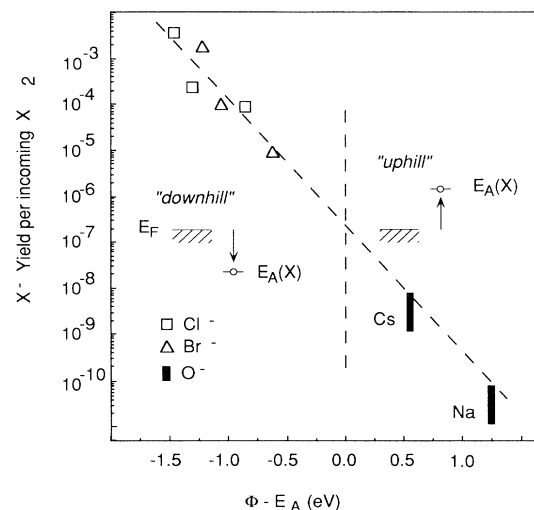


FIG. 3. Logarithmic plot of chemical ionization yields from surfaces vs the difference ΔE between the work function and the affinity level of the escaping atomic species. The open symbols are values taken from Ref. [3], and the dashed line is the exponential trend from these values. This trend, proportional to $\exp(-\Delta E/\alpha)$ ($\alpha = 0.16$ eV), continues for uphill reactions ($\phi > E_A$), as is indicated with the initial emission probabilities in the O_2 on Cs and O_2 on Na reactions.

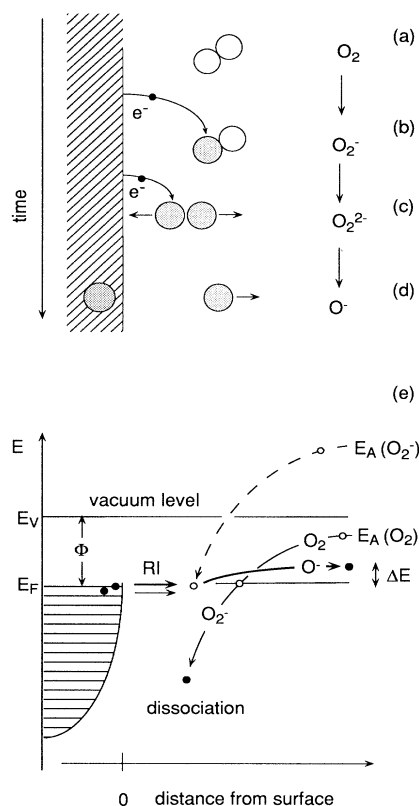


FIG. 4. Schematic diagram illustrating a mechanism for O^- ejection. Panels (a)–(d) mimic the steps yielding an O^- escape, and (e) is the energetic situation in this reaction. The approaching O_2 molecule gets resonantly ionized (RI) as its affinity level crosses the Fermi level. It accelerates to the surface and starts to dissociate. With a small probability (10^{-8} – 10^{-9}) an O^- ion may escape into the vacuum in gaining $\Delta E = \phi - E_A(O^-)$ of energy.

the detection limit ($< 10^{-11}$) for $\theta_{Cs} = 0.07$ ($\phi = 2.8$ eV).

Qualitatively, the mechanism of negative ion ejection is rationalized as illustrated by Fig. 4 in terms of a model proposed by Trowbridge and Herschbach [3] for halide ion formation in analogy to alkali-halogen reactions in the gas phase [12]: The affinity level of an O_2 molecule approaching the metallic surface (a) will be lowered in energy, first due to image force effects and closer to the surface by the onset of chemical interaction, until it crosses the Fermi level where harpooning leads to resonance ionization (b). (The latter process prevents the emission of exoelectrons [8] due to Auger deexcitation of the deeper lying hole state which might eventually form in front of the surface [13].) The O_2^- ion is further attracted and its affinity level crosses E_F even closer to the surface so that an O_2^{2-} ion might be formed (c). This species will be very unstable, not only because of the occupancy of antibonding orbitals but also because of the Coulomb repulsion between the negative charges. Because of the strong affinity of the surface to O atoms, the

preferred orientation of the molecular species will be with their axis parallel to the surface. (Such types of molecular precursors are fairly stable and readily identified, e.g., on palladium surfaces [14].) The energy release associated with dissociative chemisorption will then be “funneled” into motion parallel to the surface, and recent experiments with the system $O_2/Al(111)$ revealed that the “hot” adatoms formed may travel over distances > 100 Å across the surface before they become thermally equilibrated [15]. Far less favorable and hence very rare will be a situation for which the molecular axis is directed along the surface normal. Now the oxygen atom pointing into the vacuum “feels” the chemical interaction with the surface only weakly so that there is a finite chance for ejection of an O^- ion (d), whereby the overall energy balance outlined above has to be fulfilled.

It is noted in this context that NO is dissociatively chemisorbed on the Cs/Ru(0001) surface comparably readily as O_2 , but in this case no emission of O^- is detectable, presumably because of the less favorable overall energetics. (N is generally less tightly bound to metal surfaces than O and the NO bond is stronger than the O_2 bond.) Because of its weak interaction with the surface the ejected O^- will have a finite chance to survive reneutralization when its ionization level (equivalent to the affinity level of O) crosses the Fermi level on the path away from the surface, as described in Ref. [11].

In conclusion, the observation of O^- emission from Cs gives experimental evidence for a new nonadiabatic reaction branch during the dissociative chemisorption of O_2 on a low work function metal surface. It should contribute to a better understanding of the fundamental process of chemisorption.

For T.G. it is a pleasure to acknowledge financial support from the Schweizerischen Nationalfonds and the hospitality of the FHI. A.M. acknowledges financial support from the A. von Humboldt Foundation.

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- [1] B. Kasemo, Phys. Rev. Lett. **32**, 1114 (1974).
- [2] J. J. Thomson, Philos. Mag. **10**, 584 (1905); F. Haber and G. Just, Ann. Phys. (Lepizig) **36**, 308 (1911); A. K. Denisoff and O. W. Richardson, Proc. R. Soc. London A **150**, 495 (1935); W. Geiger, Z. Phys. **140**, 6008 (1935).
- [3] L. D. Trowbridge and D. R. Herschbach, J. Vac. Sci. Technol. **18**, 588 (1981).
- [4] E. B. de Blasi Bourdon and R. H. Prince, Surf. Sci. **144**, 591 (1984).
- [5] H. Over, H. Bludau, M. Skottke-Klein, and G. Ertl, Phys. Rev. B **45**, 8638 (1992).
- [6] H. Shi, K. Jacobi, and G. Ertl, Surf. Sci. **269/270**, 682 (1992).
- [7] M. Kiskinova, G. Rangelov, and L. Surnev, Surf. Sci. **172**, 57 (1986).
- [8] A. Böttcher, R. Imbeck, A. Morgante, and G. Ertl, Phys.

- Rev. Lett. **65**, 2035 (1990).
- [9] A. Böttcher, R. Grobecker, R. Imbeck, A. Morgante, and G. Ertl, *J. Chem. Phys.* **95**, 3756 (1991).
- [10] H. Brenten, H. Müller, W. Maus-Friedrichs, S. Dieckhoff, and V. Kempter, *Surf. Sci.* **262**, 151 (1992).
- [11] J. K. Nørskov and B. I. Lundqvist, *Phys. Rev. B* **19**, 5661 (1979).
- [12] E. G. Gislason and J. G. Sachs, *J. Chem. Phys.* **62**, 2678 (1975); G. P. Reck, B. P. Mathur, and E. W. Rothe, *J. Chem. Phys.* **66**, 3847 (1977).
- [13] B. Kasemo, E. Törnqvist, J. K. Nørskov, and B. Lundqvist, *Surf. Sci.* **89**, 554 (1979); J. K. Nørskov, D. M. Newns, and B. Lundqvist, *Surf. Sci.* **80**, 179 (1979).
- [14] R. Imbihl and J. E. Demuth, *Surf. Sci.* **173**, 395 (1986).
- [15] H. Brune, J. Wintterlin, R. Behm, and G. Ertl, *Phys. Rev. Lett.* **68**, 624 (1992).