

# Interaction of CO and O<sub>2</sub> with Pt Studied by Field Ion Appearance Energy Spectroscopy

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Using field ion appearance energy spectroscopy we have examined the interaction of CO and O<sub>2</sub> with stepped platinum surfaces in the presence of electrostatic fields ranging between 10 and 20 V/nm. Mass-to-charge resolved retarding potential analyses have been carried out for single sites of [001] and [111]-oriented Pt field emitter exposed to a continuous flow of CO and O<sub>2</sub>. Applying a thermionic cycle, binding energies of molecularly adsorbed CO and O<sub>2</sub> were derived from the appearance energies of field desorbed CO<sup>+</sup> and O<sub>2</sub><sup>+</sup>. The data reveal an effect of the high field on the molecule-surface interaction, which is most pronounced for CO/Pt(111) steps. Implications for FIM studies of catalytic CO and H<sub>2</sub> oxidation reactions are discussed.

## 1. Introduction

In a recent pioneering approach the field ion microscope (FIM) has been employed for the nanoscale imaging of heterogeneously catalyzed reactions, such as the oxidation of carbon monoxide and hydrogen at small crystal facets of a highly stepped platinum surface [1, 2]. The new observations have provided direct insights into steady state and oscillatory modes of surface catalyzed reactions at the molecular level. Several questions have been raised which concern for example the origin of contrast, image formation and chemical identity of product ions [3]. Combined FIM and field electron microscopic studies strongly suggested that O<sub>2</sub> is preferentially field ionized above oxygen-covered regions whereas the CO and H-covered areas remain essentially dark. Further detailed FIM investigations have re-

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vealed a field influence on the kinetic phase diagram of the CO oxidation reaction [4]. The observed differences between the field-free and field-modified phase diagrams of this reaction cannot be traced back to the field-enhanced kinetic gas flux (field-compression effect [5]). The observed phenomena can hardly be explained within the framework of the traditional view of field ionization processes occurring in the FIM [6]. Therefore, the ions emitted during the imaging of a catalytically active surface are particularly interesting for a dedicated analysis such as field ion appearance energy spectroscopy [7]. This method has already been proven to give information on field-modified gas-surface interactions for selected, single sites of catalytically relevant surfaces. Through recent improvements of the experimental technique, *absolute* measurements have become routinely accessible [8]. This has made possible quantitative studies of the field-dependent contributions to the field ion appearance energy of noble and reactive gases [8, 9], as well as of field-desorbed and field-evaporated metals [10, 11].

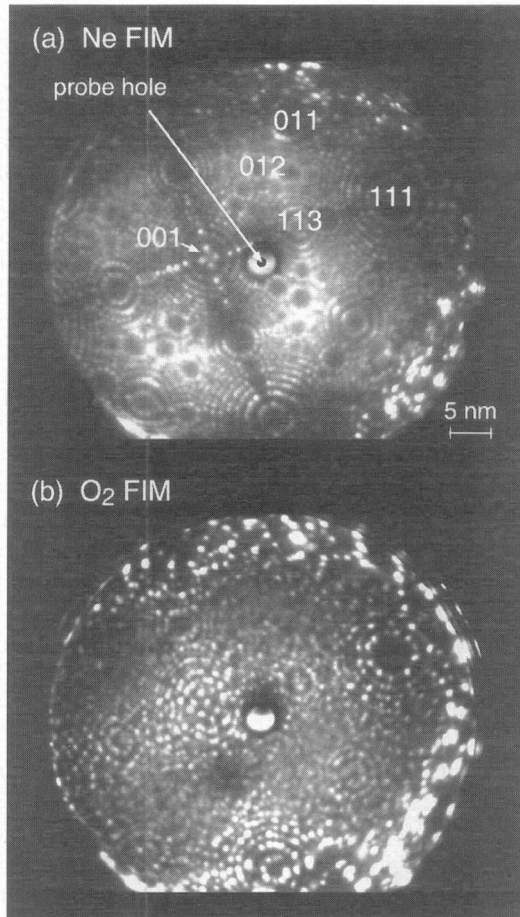
To characterize field-induced contributions to catalytic surface reactions, such as the CO and H<sub>2</sub> oxidation, we have applied the improved field ion appearance energy technique for studies of the field-modified interaction of reactive gases, like CO and O<sub>2</sub> with platinum. This approach promises to give valuable energetic data for kinetic modeling of surface reactions, as reported for H<sub>2</sub>/H<sub>2</sub>O/Pt [12]. In this contribution we would like to present new results of mass-to-charge resolved retarding potential analyses of CO<sup>+</sup> and O<sub>2</sub><sup>+</sup> ions originating from a few surface sites of [001]- and [111]-oriented Pt field emitter tips.

## 2. Experimental

Early experiments by Müller and Bahadur [13] showed that retarding potential analyses of field ions provide information on the energetics of field ionization processes occurring at the surface. The concept of field ion appearance energy spectroscopy grew on the basis of further experimental developments [14]. Especially for the field ionization of molecules, Goldenfeld *et al.* [15] introduced an empirical value for the appearance energy of singly charged species

$$A = \phi_{\text{ret}} - e\delta^{\text{on}}. \quad (1)$$

In Eq. (1),  $\phi_{\text{ret}}$  is the work function of the retarder electrode,  $e$  is the positive elementary charge of the ion and  $\delta^{\text{on}}$  is the (negative) onset voltage, applied between emitter and retarder, at which the ions are just collected. A related concept was proposed by Heinen *et al.* [16] and applied on protonation reactions of small, inorganic and organic molecules, such as H<sub>2</sub>O/Pt and CH<sub>3</sub>OH. The first appearance energy spectroscopic activities in the Berlin



**Fig. 1.** Probe-hole FIM of a [001]-oriented Pt field emitter tip. The Ne<sup>+</sup> ion-image (a) was obtained at 79 K and 11.2 kV. The ion-pattern in (b) shows the same surface but imaged with O<sub>2</sub><sup>+</sup> ions at 79 K and 5.0 kV. The projected area of the illuminated probe-hole is marked in the center.

completing the determination of *absolute*  $A(\text{O}_2^+)$  values according to Eq. (2a). The same procedure was applied in the other set-up [9, 10] for the appearance energy spectroscopy of O<sub>2</sub><sup>+</sup> and CO<sup>+</sup> emitted from Pt(111) step sites. In this case, however, Ar<sup>+</sup>, field-ionized at  $T_{\text{F}} = 160$  K, was used for calibration of the energy analyzer. The kinetic energies of ions, which originated from a few surface sites of the apex plane of a [111]-oriented Pt tip, were measured in the same way as described above.

Field penetration through the retarder meshes causes slight shifts of the onset values of retardation curves [8], which are equal for different ions

group were devoted to surface phenomena occurring at activated (organic) multi-tip emitter and single platinum and rhodium tips [17]. These early investigations revealed already field effects on the appearance energy of molecular species such as protonated ammonia and hydrazine field ions. Applying the field desorption model of Gomer and Swanson [18] preliminary values of the binding energy of N<sub>2</sub>H<sub>4</sub>/Rh have been derived [17].

Recently, progress has been made in solving problems with the determination of absolute  $A$  values involving the *in situ* measurements of  $\phi_{\text{ret}}$  by field electron energy spectroscopy [8]. This has made possible a quantitatively more refined comparison between experimentally obtained  $A$  data and *standard* field ion appearance energies introduced by Forbes [19] for theoretical discussions. The physical origin of field-dependent terms, contributing to the appearance energy of atomic and molecular species can now be identified in a more reliable manner. The capabilities of the improved experimental approach have been demonstrated through high precision measurements of the neon appearance energy which allowed the determination of the local field enhancement above individual surface atoms [20]. Further studies were again devoted to field desorption and field evaporation processes providing binding energy data of alkali and transition metal atoms for selected, single surface sites [10, 11].

In the present work, we have used two similarly designed UHV set-ups containing FIM sections which had been combined with mass-to-charge-resolved retarding potential analysis. Each set-up allowed cleaning, shaping by field evaporation and visualization of the specimen surface using different imaging gases. Fig. 1a shows the surface of a [001]-oriented Pt tip imaged with Ne<sup>+</sup> ions at 79 K. For a selected (001) step site, the imaging ions were first mass and then energy analyzed using a probe-hole technique [7]. After replacing the neon gas by oxygen, the same surface was imaged with O<sub>2</sub><sup>+</sup> at 79 K (Fig. 1b). Simultaneously, O<sub>2</sub><sup>+</sup> ions, emitted from the selected surface site were energy analyzed with a five-electrode electrostatic retarding potential analyzer [17].

Appearance energies of O<sub>2</sub><sup>+</sup> ions,  $A(\text{O}_2^+)$  are determined from the equation

$$A(\text{O}_2^+) = \phi_{\text{ret}} - e\delta^{\text{on}}(\text{O}_2^+), \quad (2a)$$

where the  $\delta^{\text{on}}(\text{O}_2^+)$  value is read from the onset of O<sub>2</sub><sup>+</sup> retardation curves, such as shown in Section 3.2. The  $\phi_{\text{ret}}$  value is obtained from the onset voltages of retardation curves for rare gas ions emitted at elevated temperatures [17], i.e. for krypton,  $\delta^{\text{on}}(\text{Kr}^+)$  at  $T_{\text{Pt}} = 298$  K. Such a curve is shown in Fig. 5 further below. In this case the field ion appearance energy of Kr<sup>+</sup> is equal to the ionization energy of the free Kr atom,  $I(\text{Kr})$  [8]. Thus, the actual value of  $\phi_{\text{ret}}$  is obtained from the equation

$$\phi_{\text{ret}} = I(\text{Kr}) + e\delta^{\text{on}}(\text{Kr}^+), \quad (2b)$$

at the same ion beam energy (2 keV). Thus absolute values of the appearance energies have been unambiguously determined within error limits of  $\pm 60$  meV. The calibration of the applied external field,  $F_0$  was based on the evaporation field strength of platinum and the best image field for Ne [21]. A detailed description of the experimental set-ups, the entire experimental procedure and a discussion of the physical significance of the appearance energy of field ions can be found elsewhere [7–9, 19–22].

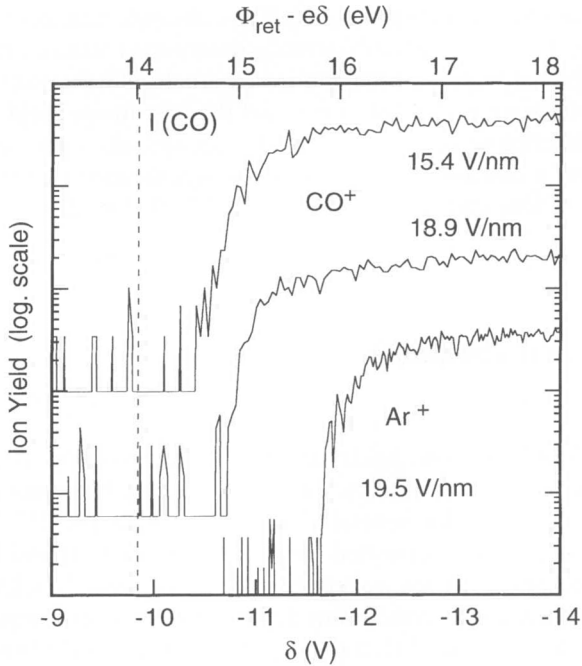
### 3. Results and discussion

#### 3.1 CO/Pt

The capability of field ion appearance energy spectroscopy to unravel field ionization mechanisms of reactive gases has recently been proven in detailed studies carried out for several CO/metal systems [9, 23]. The studies have shown that CO<sup>+</sup> ions emitted from Rh(111), Au(111) and W(111) step sites originate mainly from weakly bound, highly mobile CO layers [23] via a field desorption process. From these data and from comparisons with “field-free” experiments [24], a distinct field effect on the binding energy of CO at elevated coverage was established for all the systems mentioned above. We have extended the same type of experimental approach to platinum, aiming to contribute to an improved characterization of field effects on the binding energy of relatively weakly adsorbed molecular species. Such weakly bound (field-chemisorbed) molecules can be expected to play an important role for the kinetics of the CO oxidation reaction on Pt at high-field (FIM) conditions.

Field-dependent terms in the appearance energy of field ions, such as CO<sup>+</sup> can provide energetic information on the molecule-surface interactions at judiciously chosen conditions [9, 23]. Therefore, we have measured CO<sup>+</sup> retardation curves in the field range 15 to 19 V/nm for Pt(111) step-sites at a constant surface temperature of 79 K (Fig. 2). The upper scale in the figure was calibrated using a value of  $\phi_{\text{ret}}$ , which has been determined *in situ* from onsets of the retardation curves for Ar<sup>+</sup> emitted from the same surface sites (see also section 2).

Three main features have been observed: (i) The CO<sup>+</sup> curves have steep onsets indicating small widths of the intrinsic ion-energy distributions (which is a consequence of a high degree of spatial localization of the ionization process); (ii) The onsets of the retardation curves are shifted well above the ionization energy threshold (dashed line) of the free CO molecule; (iii) As the field strength increases the onsets shift to the right, i.e. increasing appearance energy. These findings agree with the features earlier observed for other metals and are in accord with the *field desorption* model

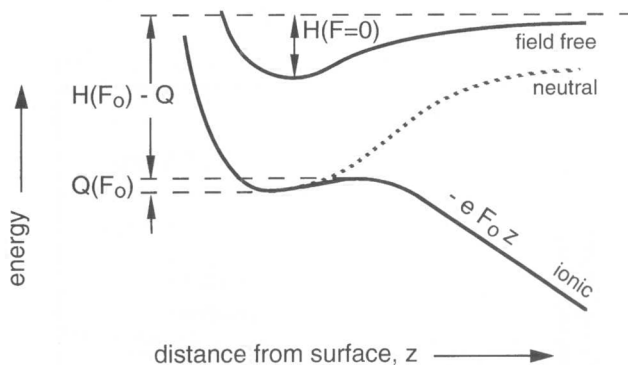


**Fig. 2.** Retarding potential analysis of  $\text{CO}^+$  emitted at 15.4 V/nm and 18.9 V/nm from a few, CO-covered Pt(111)-step sites at 79 K. The dashed line indicates the ionization energy for a free CO molecule. The  $\text{Ar}^+$  retardation curve measured at 160 K and 19.5 V/nm for the same surface sites serves for the *in situ* determination of a  $\Phi_{\text{ret}}$  value. This value is used for calibration of the upper energy scale.

of  $\text{CO}^+$  ion formation [9]. Following arguments based on a thermionic cycle [19], the appearance energy of singly charged field-desorbed ions is given by

$$A = I + H(F_0) - Q(F_0), \quad (3)$$

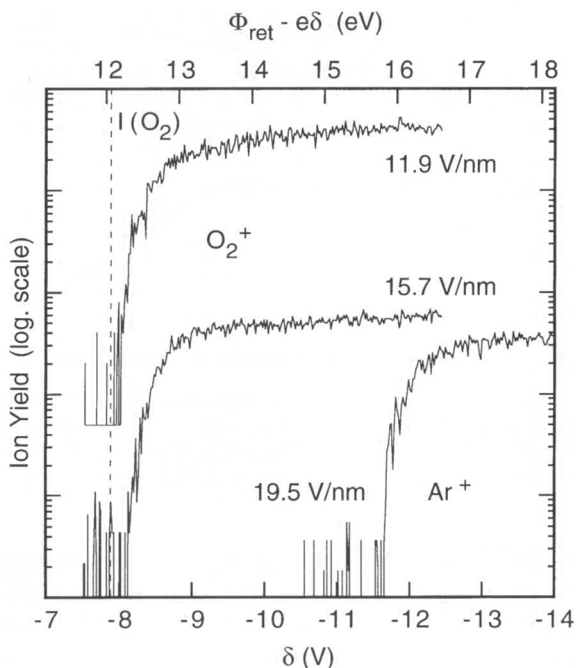
if (relatively small) contributions of temperature dependent terms are neglected [7]. In Eq. (3),  $H(F_0)$  is a binding energy, defined by the difference between the minimum of the total energy (ground state) of a field-adsorbed and the energy of a free molecule (removed to a field-free space).  $Q(F_0)$  is the activation energy of field desorption (Fig. 3), which can be obtained from ion-rate measurements [10, 22]. Since in the present case the diffusional supply of CO to the probed sites is prevailing [24], the ion-rate measurements provide activation energy values which are affected by the peculiarities of the field-assisted surface diffusion of CO. Nevertheless, these *effective* values should be close to the real  $Q(F_0)$  values as follows from the detailed analysis in Ref. [10]. In present case, the value for  $Q$



**Fig. 3.** Energy scheme illustrating effects of a high external field strength, ( $F_0 = 10\text{--}20$  V/nm), on molecule/surface interactions. Presently measured values for the quantity,  $A(F_0) - I \approx H(F_0) - Q$  range between 0.7 and 0.9 eV (0.1 and 0.2 eV) for CO<sup>+</sup> (O<sub>2</sub><sup>+</sup>) field desorbed from stepped Pt-surfaces covered with CO<sub>ad</sub> (O<sub>ad</sub>).

estimated from the measured temperature dependence of the CO<sup>+</sup> rates does not exceed 0.1 eV. Thus, data of the field dependent contribution to the CO<sup>+</sup> appearance energy,  $H(F_0) - Q(F_0) = A(F_0) - I$ , give approximate binding energy values of CO molecules,  $H(F_0)$ . Presently measured values for this contribution range between 0.7 and 0.9 eV (see Fig. 6 further below) for field strengths, 15 to 19 V/nm, being close to that measured for CO<sup>+</sup>/Rh [9]. The latter results strongly suggested a CO<sup>+</sup> field desorption mechanism involving a second mobile CO adlayer [23, 24]. For such a layer the substrate-specific peculiarities of the electron density distribution [20] are effectively screened by the tightly bound chemisorbed CO. The nature of the (field-stabilized) chemisorption bond of the weakly bound CO molecules to the CO-precovered metal surface is presumably similar to that of field-adsorbed noble gas atoms [25] characterized by a significant field-induced charge transfer to the substrate. Recent density functional calculations of the field effect on the charge distribution in the CO/metal system [9] are in accord with present modeling.

Weakly bound CO molecules on different, CO-precovered Rh and Pt surfaces with a binding energy of about 0.3 eV have very recently been detected at field-free conditions at high CO coverage ( $n > 1.0 \times 10^{15}$  cm<sup>-2</sup>) using the reverse flash method [25]. In a field above 15 V/nm, these protruding CO molecules are easily field desorbed from the apex of the tip. New measurements of the CO<sup>+</sup> field-ion current fluctuations [24] suggest a CO supply to the probed sites, which is dominated by the field-assisted surface diffusion from peripheral regions to the apex. Thus, the FIM visualization of the Pt surface using CO as imaging gas is governed by field desorbed CO<sup>+</sup> being actually analyzed in our retarding potential experiments.



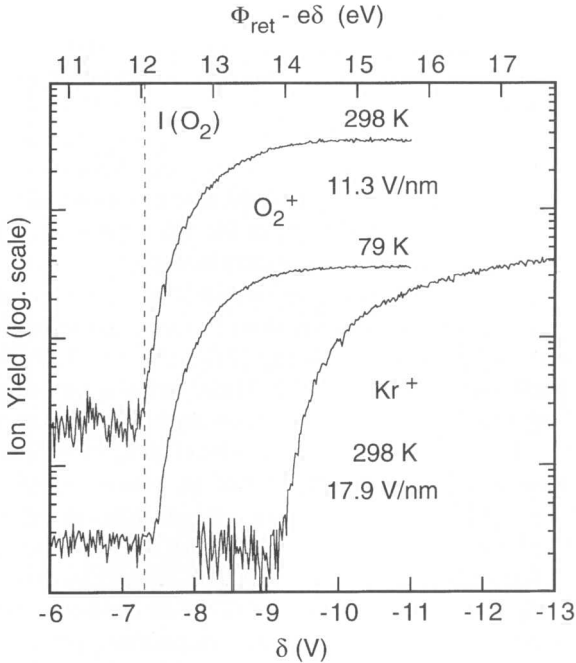
**Fig. 4.**  $\text{O}_2^+$  retardation curves measured at 11.9 V/nm and 15.7 V/nm for O-covered Pt(111) step sites at 79 K. The dashed line indicates the ionization energy for a free  $\text{O}_2$  molecule. The  $\text{Ar}^+$  retardation curve used for calibration of  $\Phi_{\text{ret}}$  is also shown.

Concerning implications for FIM studies of the CO oxidation reaction, one has to be aware that these measurements are usually performed at somewhat lower applied fields (11–14.5 V/nm), i.e. at relatively low CO ionization rates ( $\text{O}_2$  is used as imaging gas) [1, 2]. At such conditions, however, the field-induced chemisorption of very mobile CO in a second layer still provides a strongly enhanced supply of CO molecules towards the reaction zone even at elevated temperatures. This must affect the reaction kinetics of the CO oxidation as observed by FIM. To understand experimentally observed trends in the CO-oxidation reaction dynamics, the field-modified behavior of the other reactant (oxygen) has to be studied.

### 3.2 $\text{O}_2/\text{Pt}$

In order to characterize a possible field dependent contribution to the  $\text{O}_2^+$  appearance energy, that can be used to quantify the effect of the applied field on the  $\text{O}_2$  binding energy, we have applied the same approach for the  $\text{O}_2/\text{Pt}$  system. Fig. 4 shows two  $\text{O}_2^+$  retardation curves measured for Pt(111)





**Fig. 5.** Retarding potential analysis of O<sub>2</sub><sup>+</sup> for two different emitter temperatures, 298 K and 79 K at 11.3 V/nm. A single step site close to the apex plane of a [001]-oriented Pt tip has been examined. At 298 K, one finds  $A(\text{O}_2^+) = I(\text{O}_2)$  indicated by the dashed line. The Kr<sup>+</sup> retardation curve used for  $\Phi_{\text{ret}}$  calibration is shown as well.

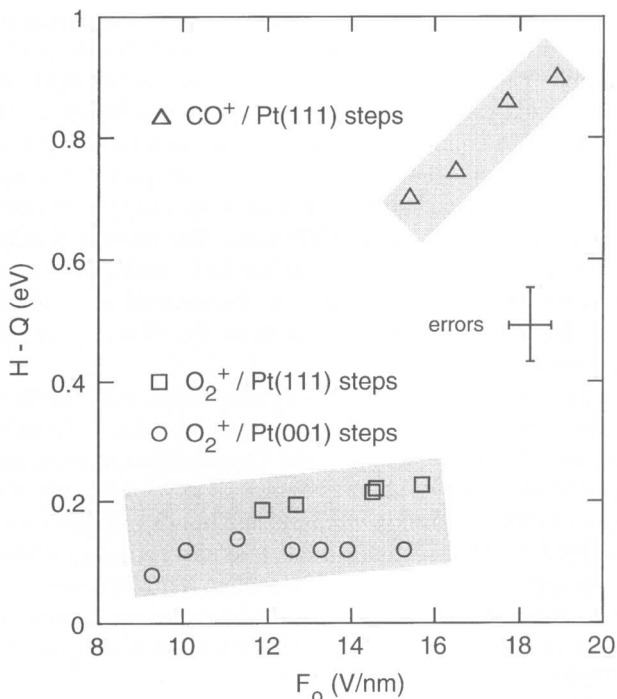
step-sites at a surface temperature of 79 K. For comparison we have also drawn a curve for Ar<sup>+</sup> ions emitted from the same surface sites at a surface temperature of 160 K. The O<sub>2</sub><sup>+</sup> curves measured in the field range 12 to 16 V/nm show essentially the same features as discussed above for CO<sup>+</sup>. The retardation curves have steep onsets, which shift to the right, i.e. to higher appearance energies as the field strength increases. The maximum value of the O<sub>2</sub><sup>+</sup> appearance energy exceeds the ionization energy of a free oxygen molecule by 0.22 eV, which is distinctly below the result for CO<sup>+</sup> (0.9 eV).

To analyze the effect of surface structure on the (field-modified) oxygen-platinum interaction, we would like to present O<sub>2</sub><sup>+</sup> retardation curves for Pt(001) step sites measured at 79 K and 298 K (Fig. 5). In addition, we show a calibration curve using Kr<sup>+</sup> ions emitted from the same surface sites at 298 K. Compared to the Pt(111) step site, one measures a smaller, but still significant shift of the O<sub>2</sub><sup>+</sup> appearance energies to values higher than the ionization energy of a free O<sub>2</sub> molecule, when the surface temperature is lowered from 298 K to 79 K. Thereby, the width of the retardation curve gets smaller in line with the behavior observed for CO<sup>+</sup> curves.

The differences between the appearance energy of  $O_2^+$  ions (at 79 K) and the ionization energy of  $O_2$  molecules range around 0.2 eV, which is close to the polarization energy of the oxygen molecule in the presence of a (locally-enhanced [8, 20]) field of about 19 V/nm. Thus we have to distinguish between two alternative possibilities of the interpretation of the physical meaning of the measured field-dependent term of the  $O_2^+$  appearance energy: as a polarization energy of the free gas molecule as in the case of the noble gases, such as  $Ne^+/Rh$  [8] or  $He^+/W$  [26], or as a term involving a binding energy as in the above mentioned case of  $CO^+$ .

To distinguish between these two possibilities and to gain further insights into the details of the  $O_2$  ionization process, we refer to new calculations performed by Kreuzer and Wang [27] for the  $O_2/O/Pd$  system using the *cluster embedded in jellium* model. These calculations suggest the resonant field ionization of  $O_2$  above  $O_{ad}$  involving a field-induced strengthening of the  $O_{2ad}-O_{ad}$  interaction; the calculated field-modified binding energy of  $O_2$  molecules ranges near 210 mV at a field of 10 V/nm. If we interpret our  $A-I$  data for  $O_2^+$  as binding energy data (in the same way as done for  $CO^+$ ) the Kreuzer-Wang result is very close to the results of the present work. The existence of a *physisorbed* molecular oxygen layer on Pt(111) involving a binding energy of 0.12 eV at field-free conditions has earlier been reported [28, 29]. Since the thermodesorption peak for this layer was measured at 45 K [28], the question arises whether a field in a FIM (10 to 18 V/nm) can strengthen the bonding of physisorbed  $O_2$  molecules such that they will still cover the surface even at higher temperature (79 K). Our results on the shift of the  $O_2^+$  appearance energy, as well as functional dependences of the width of the energy distribution on temperature and field, suggest a field desorption process. We therefore favor the presence of a field-stabilized, but still highly mobile  $O_2$  layer on the Pt surface at present FIM conditions ( $T_p = 79$  K,  $F_0 \approx 12$  V/nm). Adopting the field desorption model we arrive again at Eq. (3), which allows us to obtain the  $H(F_0) - Q(F_0)$  term from our  $O_2^+$  appearance energy data. In our present view, the quantity  $Q(F_0)$  again characterizes the field desorption activation energy for  $O_2^+$  involving a continuous supply of  $O_2$  molecules to the probed surface sites at the apex. From our  $O_2^+$  rate measurements, we conclude that  $Q$  is smaller than 0.1 eV for field strengths ranging between 10 and 18 V/nm. Consequently, the values measured for  $A-I$  give information on the binding energy of  $O_2$  molecules to the O-precovered Pt(111) surface (see Fig. 3) as in the case of  $CO^+$ .

Results, summarized in Fig. 6, suggest quantitatively different effects of the applied field and the surface structure on the energetics of the molecular adsorption of  $O_2$  and CO on Pt. This must lead to the markedly different field effects on the adsorption/desorption equilibrium of  $O_2$  and CO, which is especially relevant for the CO oxidation reaction. Because of the relatively small (field-enhanced) binding energy of  $O_2$  molecules, one expects



**Fig. 6.** Data for  $H-Q$  as a function of applied field strength,  $F_0$ . The upper (lower) results have been obtained from  $\text{CO}^+$  ( $\text{O}_2^+$ ) field ion appearance energies measured at 79 K for stepped Pt-surfaces covered with  $\text{CO}_{\text{ad}}$  ( $\text{O}_{\text{ad}}$ ).

a significantly lower effect of the field on the supply-rate of  $\text{O}_2$  into the reaction zone, at least in comparison with CO as discussed above. This difference in the  $\text{O}_2$  and CO field-adsorption has therefore to be considered as one of the main reason for the *decrease* of critical CO pressures (for  $\text{O}_{\text{ad}} \leftrightarrow \text{CO}_{\text{ad}}$  transitions) observed recently during detailed FIM characterizations of the kinetic phase diagram [4]. In our present modeling we expect decreasing supply-rates of CO at increasing temperatures mainly due to increasing desorption rates for highly mobile CO. As a consequence, the high-field phase diagram should approach the zero-field one at higher temperatures in full agreement with the recent experimental results.

## Summary

In 1974 the late Professor Jochen Block initiated the development and application of field ion appearance energy spectroscopy for surface reaction studies in his Berlin group [14]. We have attempted to point out that this

technique has not only matured in age but also in the capability to yield valuable data for gas-surface interactions at catalytically active surfaces such as platinum. Stimulated by recent fascinating *in situ* FIM observations of surface catalyzed reactions, we have focused our report on new results obtained for the CO/Pt and O<sub>2</sub>/Pt interactions at high field (FIM) conditions.

Our analyses of CO<sup>+</sup> and O<sub>2</sub><sup>+</sup> appearance energies for stepped Pt surfaces revealed field-induced shifts reaching values of 0.9 eV above the free space ionization energy for the CO<sup>+</sup>/Pt case. The present results for CO<sup>+</sup>/Pt agree with earlier spectroscopic data for CO<sup>+</sup> emitted from other metal surfaces (Au, Rh, W) and are in line with the theoretically supported interpretation that the data provide information on the effect of the applied field on the molecule-surface interaction.

Conclusively, weak molecular adsorption bonds with the Pt surface are markedly modified for CO and O<sub>2</sub> molecules by a high electrostatic field. The binding energy of the CO and the O<sub>2</sub> admolecule increases with increasing field by an amount which is comparable with the initial (field-free) value. Because of the differently strengthened bonds of CO/Pt and O<sub>2</sub>/Pt, the effect of the field on the (precursor-mediated) adsorption/desorption kinetics becomes different for CO and O<sub>2</sub> molecules. This difference contributes essentially to the shift of critical pressures as recently observed during measurements of the kinetic phase diagram for the CO/O<sub>2</sub>/Pt reaction system using FIM.

In view of the present and earlier results [30] we also conclude that an applied electrostatic field changes the energetics of adsorption for both, O<sub>2</sub> and H<sub>2</sub> molecules to a similar (relatively small) extent. Consequently, the adsorption/desorption kinetics for O<sub>2</sub> and H<sub>2</sub> and thus the catalytic H<sub>2</sub> oxidation on Pt should only slightly be modified by the presence of the high electrostatic field, if other field-induced phenomena such as the formation of H<sub>3</sub>O<sup>+</sup> ions are discarded [31].

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