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# Orientation dependent CO<sub>2</sub> production by exposing a CO precovered Pt(100) surface to gas phase oriented NO

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## Abstract

Using a hexapole technique, a beam of gas phase oriented and state selected NO molecules is directed onto a CO precovered Pt(100) surface. Two quadrupole mass analyzers behind the platinum target record the yield of NO and CO<sub>2</sub> molecules leaving the surface. The platinum single crystal acts like a catalyst and the CO<sub>2</sub> reaction signal strongly depends on the initial NO orientation, that is to say preferential N- or O-end collisions perpendicular to the surface. At first the orientation asymmetry of the CO<sub>2</sub> signal, defined positive for a higher N-end collision signal, has a positive initial value of 0.30, 0.16 and 0.07 for substrate temperatures of  $T_s = 120$ ,  $T_s = 130$  and  $T_s = 140^\circ\text{C}$ , respectively. The dependence of the reaction and of the sticking on the initial NO orientation leads to a transition from Eley–Rideal/Harris–Kasemo to Langmuir–Hinshelwood reaction.

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## 1. Introduction

The conversion of NO and CO into the less toxic gases N<sub>2</sub> and CO<sub>2</sub> is catalyzed by platinum (see for instance Refs. [1,2]). Yet the exact kinetics of the NO–CO reaction on platinum is not understood. It is not even known, whether both reaction partners have to be chemisorbed before the reaction can proceed. Usually, surface reactions are classified as either Eley–Rideal (ER) or Langmuir–Hinshelwood (LH) type. Unfortunately, their exact definition is not given in a textbook. Neither Atkins [3] nor Zangwill [4] distinguish between reactions from chemisorption or precursor states concerning the ER- or LH-type. For instance, the ER-type is interpreted both

ways by different authors [5,6]. A detailed discussion of this definition problem is given in Ref. [7]: The Langmuir–Hinshelwood reaction process takes place between two chemisorbed reactants, which are in thermal equilibrium with the surface. The Eley–Rideal reaction describes the case, in which a direct impact of a molecule or an atom on a chemisorbed reactant leads to a formation of the reaction product desorbing from the surface. These clear definitions only represent extreme situations, which can have intermediates, especially, since the existence of precursor states has become more and more established. The precursor-mediated surface reaction mechanism described by Harris and Kasemo [7] will be abbreviated by HK. With the intention of distinguishing between these three processes, we carried out investigations with gas phase oriented NO molecules colliding with a CO precovered Pt(100) single crystal. If the yield of the reaction products

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depended on the initial NO orientation, the process would be assigned to the ER category, unless the sticking probability was orientation dependent. In that case orientation asymmetries (N-end and O-end collisions) could be expected as a superposition of sticking and possibly reaction asymmetries.

Investigations of adsorption systems including oriented molecules have already been carried out successfully with symmetric top molecules [8,9] and NO [10–13]. The coadsorption of NO and CO on a Pt(100) crystal has been investigated by a variety of surface techniques [14–18]. At  $T_s \leq 80^\circ\text{C}$  the reaction yield is negligible. Both reactants do not even displace the other partner at surface temperatures below  $-50^\circ\text{C}$ . They simply fill up the entire surface until saturation coverage is reached [15,17]. At room temperature there is evidence that CO is able to penetrate an NO layer and eventually remove it, but a saturated CO layer cannot be penetrated by NO [18]. When increasing the substrate temperature two main phenomena have been observed: Firstly, in temperature-programmed reaction (TPR) studies the so-called surface explosion can be obtained which is an intense reaction within a small temperature region [17,19,20]. Secondly, under steady flow conditions the kinetic oscillations occur in which the reaction rate oscillates as a function of time [21–23]. For the experiments reported here, the surface is precovered with CO and is exposed to the beam of oriented NO molecules, while the temperature is kept constant. Consequently, the initial system will be CO/Pt(100) and the final system NO/Pt(100), if the surface temperature is high enough ( $T_s \geq 100^\circ\text{C}$ ). Previous investigations for these two adsorbate systems, which also took into account the lifting of the hexagonal superstructure ( $5 \times 25$ ) of clean Pt(100) [24,25] by the adsorbates, can be found in Refs. [26–28] for NO and in Refs. [29–31] for CO.

## 2. Experimental

A general overview of the experimental set-up with the oriented NO molecular beam is already given in Refs. [12,13,32]. The vacuum chamber

consists of two main parts: Firstly, the high vacuum beam line side includes the pulsed nozzle, the skimmer and the hexapole. Secondly, the ultra-high vacuum side starting with the guiding field contains the subsequent orientation aperture, the platinum single crystal and the two quadrupole mass analyzers. The NO beam is seeded in 35% He and 45% Ne at a nozzle temperature of  $90^\circ\text{C}$  resulting in a translational energy of 150 meV. In contrast to earlier studies [12], the rotational temperature is below  $T_{\text{rot}} = 5$  K using now a pulsed nozzle leading to a mean degree of NO orientation of  $\langle \overline{\cos \Phi} \rangle = \frac{1}{3}$ .

The surface preparation procedure is carried out as follows: Firstly, to clean the platinum crystal, it is treated with  $\text{Ar}^+/\text{Ne}^+$  sputtering, heating in  $\text{O}_2$  ( $5 \times 10^{-8}$  mbar, 5 min,  $350^\circ\text{C}$ ) and flashing ( $700^\circ\text{C}$ ). The hex-superstructure of clean Pt(100) [24,25] is observed by LEED. Secondly, the crystal is cooled down and kept at a constant temperature of  $-80^\circ\text{C}$ . Thirdly, the target is exposed to  $10^{-6}$  mbar of CO for 3 min corresponding to about 135 L. This exposure leads to the CO saturation coverage, the  $(4 \times 2)$  superstructure [33]. Finally, the crystal is heated again to the desired surface temperature, which is kept constant within 1 K by a computer PID technique [34]. Two quadrupole mass analyzers (operated at mass numbers 30 and 44 for NO and  $\text{CO}_2$ ) are mounted behind the target and therefore shielded from the direct beam, which is directed to the surface at normal incidence. Both partial pressures are recorded as a function of time. By opening a beam shutter the surface is exposed to the pulsed NO molecular beam until all the CO adsorbate molecules have reacted with the NO molecules, forming  $\text{CO}_2$ . This takes several minutes depending on the surface temperature.

## 3. Results and discussion

The CO precovered platinum(100) surface ( $T_s = 130^\circ\text{C}$ ) was first exposed to the NO beam without any preferential NO orientation. Both partial pressures (NO and  $\text{CO}_2$ , background corrected) are shown as a function of time in Fig. 1: The NO partial pressure (measured behind the crystal

representing all NO molecules leaving the surface) starts at a point which only depends on the initial trapping probability of NO on CO precovered Pt(100). Of great importance is the fact that both CO [29] and NO [27] form a  $c(4 \times 2)$  saturation superstructure on Pt(100), corresponding to relative coverages of  $\theta_{\text{CO}} = 0.75$  and  $\theta_{\text{NO}} = 0.5$ , respectively. This leads to the assumption that there are no free sites on the surface for NO chemisorption after exposing the crystal to 135 L CO as carried out in our case. After this initial value, three main processes influence the further course. Firstly, the NO starts to react with the chemisorbed CO, and both  $\text{CO}_2$  and  $\text{N}_2$  desorb, leaving free sites for the NO to adsorb, which results in the minimum value at 25 s. Secondly, the NO partial pressure increases afterwards, because the NO coverage of the crystal becomes higher, causing the adsorption probability to decrease and more NO molecules scattered at the surface to be detected. Thirdly, at  $T_s = 130^\circ\text{C}$  the surface diffusion reduces this increase, because NO molecules move from the spot which is hit by the focused incident NO beam. Simultaneously, at surface temperatures above  $100^\circ\text{C}$ , NO on Pt(100) dissociates partially and  $\text{N}_2$  desorbs [35]. The  $\text{CO}_2$  partial pressure graph almost describes a solution of the reaction differential equation  $\theta_{\text{CO}} \approx \theta_{\text{CO}} \cdot \theta_{\text{NO}}$  [36]. The maximum at 20 s occurs earlier than the minimum of the NO curve and

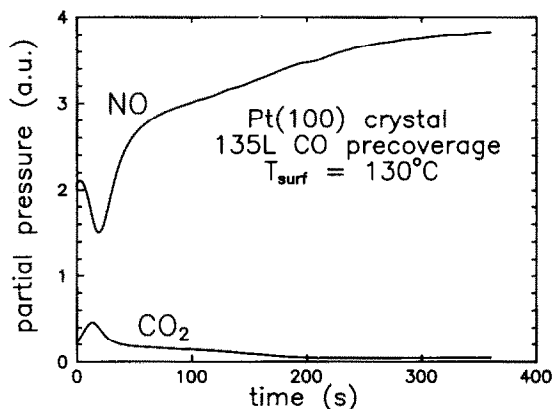


Fig. 1. NO and  $\text{CO}_2$  partial pressures for focused and unoriented NO molecules incident on a CO saturation precovered Pt(100) as a function of time. The surface temperature is kept at  $130^\circ\text{C}$ .

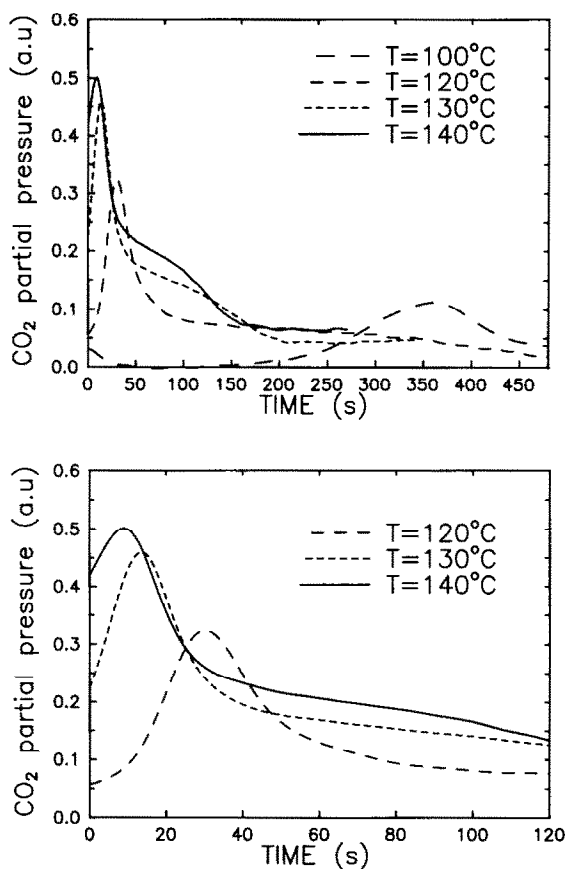


Fig. 2. Temperature dependence of the  $\text{CO}_2$  production of CO precovered Pt(100) exposed to focused and unoriented NO molecules. The lower graph represents a detail of the upper graph.

even after 300 s the reaction is detectable due to diffusing NO molecules reacting with CO molecules near the edge of the crystal.

Fig. 2 shows the  $\text{CO}_2$  signal as a function of time and surface temperature. It has been found that the higher the temperature, the earlier and the more intense the reaction peak occurs. Within our time resolution of about two seconds the  $\text{CO}_2$  signal seems to jump to a high reaction rate after admission of the NO beam to the surface. For  $T_s = 100^\circ\text{C}$  the maximum of the background corrected  $\text{CO}_2$  signal does not appear until 350 s. The only deviation from the solution of the differential equation mentioned above occurs at the more or less distinct shoulder in the decay of the

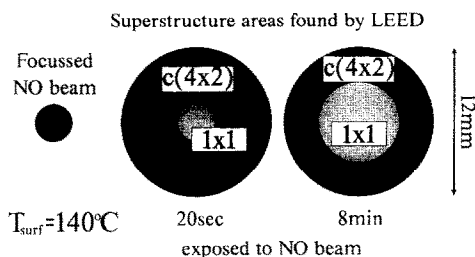


Fig. 3. Lateral distribution of superstructure areas of CO precovered Pt(100) exposed to focused and unoriented NO molecules at  $T_s = 140^\circ\text{C}$  after 20 s and 8 min found by LEED. The focus dimension of the NO beam is indicated on the left.

reaction peak, which can be assigned to a special superstructure phase developed from the previous reaction. The strong dependence of the initial  $\text{CO}_2$  production on the surface temperature most likely results from the narrow explosive reaction region [17,19,20], in which the chemisorbed CO molecules transfer the energy from the surface to incoming NO molecules.

The quadrupole mass analyzer detection measurements were accompanied by LEED investigations (Fig. 3). In the starting phase of the experiment the CO precovered surface is observed to be a  $c(4 \times 2)$  CO superstructure with a relative coverage of 0.75 [29]. By exposing the surface to the focused NO beam with a diameter of 3 mm (indicated on the very left-hand side of Fig. 3), the adsorbate superstructure is lifted locally.

Therefore, only the  $(1 \times 1)$  spots of the substrate are detectable. When exposing the crystal for just 20 s, only the NO beam covered area of the crystal is affected. The results are obtained by stopping the admission of the NO beam and fast cooling down of the crystal to  $T_s = -100^\circ\text{C}$ . The relevant adsorption system is frozen and can be investigated by LEED afterwards. When the system is exposed to NO for 8 min, the area on which the initial CO  $c(4 \times 2)$  superstructure is removed by NO increases beyond the diameter of the incident beam since the surface diffusion becomes effective. The NO molecules move further out until the inner edge of the remaining CO is reached, where the reaction can occur.

In order to obtain the orientation asymmetry of the reaction, these experiments were carried out for both orientations, i.e. for preferential N-end and preferential O-end collisions. The orientation asymmetry of the  $\text{CO}_2$  production, which is defined as the difference of both signals divided by the sum ( $A_{\text{reac}} = (p_{\text{CO}_2}^{\text{N}} - p_{\text{CO}_2}^{\text{O}}) / (p_{\text{CO}_2}^{\text{N}} + p_{\text{CO}_2}^{\text{O}})$ ), is shown in Fig. 4 as a function of surface temperature and time. There are three main arguments why the NO molecules do not have to be chemisorbed before reacting with the already adsorbed CO molecules. Firstly, although the crystal is completely precovered and the saturation coverage for CO/Pt(100) ( $\theta_{\text{CO}} = 0.75$ ) is higher than for NO/Pt(100) ( $\theta_{\text{CO}} = 0.5$ ), a reac-

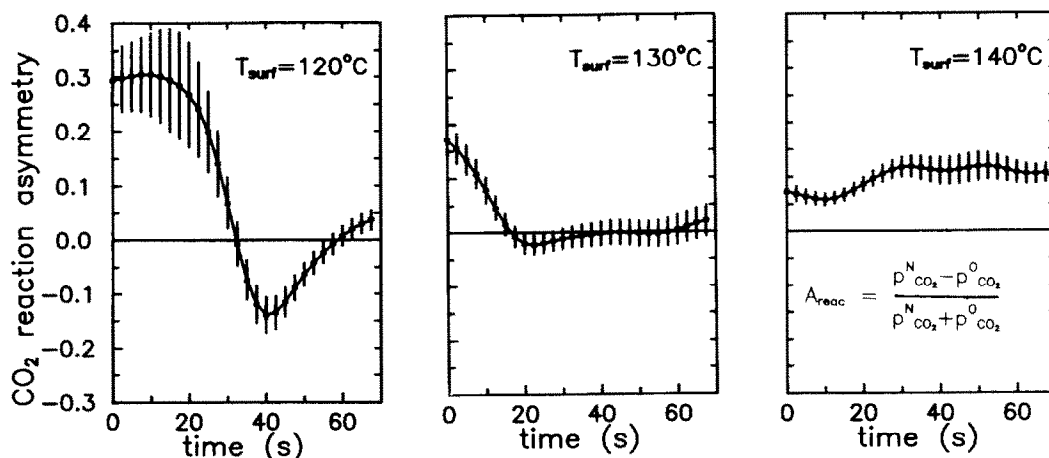


Fig. 4. Orientation asymmetry of the  $\text{CO}_2$  production of CO precovered Pt(100) exposed to oriented NO molecules as a function of temperature and time ( $A_{\text{reac}} = (p_{\text{CO}_2}^{\text{N}} - p_{\text{CO}_2}^{\text{O}}) / (p_{\text{CO}_2}^{\text{N}} + p_{\text{CO}_2}^{\text{O}})$ ,  $p^{\text{N,O}}$  being the  $\text{CO}_2$  signal for preferential N-end and preferential O-end collisions).

tion yield has been found. The probability for NO to adsorb between the CO molecules must be low considering the lack of adsorption sites available. Secondly, as already mentioned in the introduction, the displacement of CO by NO is negligible [15,18]. Therefore, NO cannot generate free chemisorption sites necessary for the LH reaction type. Thirdly, the initial asymmetry values are found to be 0.30, 0.16 and 0.07 (without taking the degree of orientation  $\langle \cos \Phi \rangle = \frac{1}{3}$  into account) for surface temperatures of  $T_s = 120^\circ\text{C}$ ,  $T_s = 130^\circ\text{C}$  and  $T_s = 140^\circ\text{C}$ , respectively. Three considerably different values occurring within a very small temperature region do not point to an effect of an orientation dependent direct chemisorption probability, which should not change much within 20 K. On the other hand, an orientational asymmetry for a reaction could change strongly within a narrow temperature range. These three arguments lead to the conclusion that at the beginning the reaction can be assigned either to an Eley–Rideal-type or, most likely, to a precursor-mediated process as described in the introduction (Harris–Kasemo), constituting an intermediate between a Langmuir–Hinshelwood process and a direct impact reaction. Consequently, the NO molecules do not have to be chemisorbed and fully accommodated to the surface. In similar investigations with un-oriented CO molecules directed onto a NO pre-covered Pt(111) surface, an ER reaction has not been found [37]. After a certain time (at  $T_s = 140^\circ\text{C} \rightarrow t \approx 20$  s) the CO in the focusing area of the NO beam has already reacted and subsequent  $\text{CO}_2$  production can only be accounted for by the mobility of chemisorbed NO. Consequently, the  $\text{CO}_2$  yield has to be independent of the orientation of the incoming NO molecules and a measured asymmetry can only result from a sticking asymmetry of NO, since the NO molecules lose their initial orientational information after chemisorption and before their migration. This implies a typical LH reaction (shown experimentally with reflection electron microscopy [16] and photoemission electron microscopy PEEM, a technique described in Ref. [38], and theoretically in Refs. [20,39]). As a result, in the course of time a transition between different reaction processes

has occurred. At times between those two processes, a superposition of both has to take place. Comparing the reaction spectra of the two configurations, for all three cases of Fig. 4, the  $\text{CO}_2$  peak occurs earlier and is more intense for preferential N-end collisions than for preferential O-end collisions. These two peaks are shifted against each other, which results in an at first positive followed by a negative value for the reaction asymmetry  $A_{\text{reac}}$ .

#### 4. Conclusion

Orientation dependent NO–CO reaction experiments have been carried out with gas phase oriented NO molecules. The orientation asymmetry of the reaction was found to be high, especially at the beginning of the reaction. The behavior is explained by a transition of the type of reaction, namely from Eley–Rideal or Harris–Kasemo to Langmuir–Hinshelwood.

#### 5. Acknowledgements

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#### 6. References

- [1] R.M. Lambert and C.M. Comrie, *Surf. Sci.* 46 (1974) 61.
- [2] T.E. Fischer and S.R. Kelemen, *J. Catal.* 53 (1978) 24.
- [3] P.W. Atkins, *Physical Chemistry* (Oxford University Press, New York, 1990).
- [4] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).
- [5] E.W. Kuipers, A. Vardi, A. Danon and A. Amirav, *Phys. Rev. Lett.* 66 (1991) 116.
- [6] C.T. Campbell, G. Ertl, H. Kuipers and J. Segner, *J. Chem. Phys.* 73 (1980) 5862.
- [7] J. Harris and B. Kasemo, *Surf. Sci. Lett.* 105 (1981) L281.
- [8] R.S. Scott, T.J. Curtiss and R.B. Bernstein, *Chem. Phys. Lett.* 164 (1989) 341.
- [9] T.J. Curtiss and R.B. Bernstein, *Chem. Phys. Lett.* 161 (1989) 212.
- [10] E.W. Kuipers, M.G. Tenner and A.W. Kleyn, *Chem. Phys.* 138 (1989) 451.
- [11] E.W. Kuipers, M.G. Tenner and A.W. Kleyn, *Phys. Rev. Lett.* 62 (1989) 2152.

- [12] G.H. Fecher, N. Böwering, M. Volkmer, B. Pawlitzky and U. Heinzmann, *Surf. Sci. Lett.* 230 (1990) L169.
- [13] H. Müller, B. Dierks, F. Hamza, G. Zagatta, G.H. Fecher, N. Böwering and U. Heinzmann, *Surf. Sci.* 269/270 (1992) 207.
- [14] W.F. Banholzer and R.I. Masel, *Surf. Sci.* 137 (1984) 339.
- [15] M.W. Lesley and L.D. Schmidt, *Surf. Sci.* 155 (1985) 215.
- [16] Y. Uchida, R. Imbihl and G. Lehmppfuhl, *Surf. Sci.* 275 (1992) 253.
- [17] G. Zagatta, Diploma Thesis, Universität Bielefeld, 1992.
- [18] P. Gardner, R. Martin, M. Tüshaus and A.M. Bradshaw, *Surf. Sci.* 269/270 (1992) 405.
- [19] Th. Fink, J.-P. Dath, M.R. Basset, R. Imbihl and G. Ertl, *Vacuum* 41 (1990) 301.
- [20] Th. Fink, J.-P. Dath, M.R. Basset, R. Imbihl and G. Ertl, *Surf. Sci.* 245 (1991) 96.
- [21] S.B. Schwartz and L.D. Schmidt, *Surf. Sci.* 206 (1988) 169.
- [22] Th. Fink, J.-P. Dath, R. Imbihl and G. Ertl, *Surf. Sci.* 251/252 (1991) 985.
- [23] J.-P. Dath, Th. Fink, R. Imbihl and G. Ertl, *J. Chem. Phys.* 96 (1992) 1582.
- [24] P. Heilmann, K. Heinz and K. Müller, *Surf. Sci.* 83 (1979) 487.
- [25] E. Lang, PhD Thesis, Friedrich-Alexander-Universität, Erlangen-Nürnberg, 1982.
- [26] P. Gardner, M. Tüshaus, R. Martin and A.M. Bradshaw, *Vacuum* 41 (1990) 304.
- [27] H.P. Bonzel, G. Brodén and G. Pirug, *J. Catal.* 53 (1978) 96.
- [28] K. Mase and Y. Murata, *Surf. Sci.* 277 (1992) 97.
- [29] R.J. Behm, P.A. Thiel, P.R. Norton and G. Ertl, *J. Chem. Phys.* 78 (1983) 7437.
- [30] P.A. Thiel, R.J. Behm, P.R. Norton and G. Ertl, *J. Chem. Phys.* 78 (1983) 7448.
- [31] P. Gardner, R. Martin, M. Tüshaus and A.M. Bradshaw, *J. Electron Spectrosc. Relat. Phenom.* 54/55 (1990) 619.
- [32] G.H. Fecher, M. Volkmer, B. Pawlitzky, N. Böwering and U. Heinzmann, *Vacuum* 41 (1990) 265.
- [33] G. Brodén, G. Pirug and P.P. Bonzel, *Surf. Sci.* 72 (1978) 45.
- [34] U. Tietze and Ch. Schenk, *Halbleiter-Schaltungstechnik* (Springer, Berlin, 1986).
- [35] R.J. Gorte and L.D. Schmidt, *Surf. Sci.* 109 (1981) 367.
- [36] U.P. Zhdanov, *Elementary Physicochemical Processes on Solid Surfaces* (Plenum, New York, 1991).
- [37] J. Hall, I. Zorić and B. Kasemo, *Surf. Sci.* 269/270 (1992) 460.
- [38] H.H. Rotermund, S. Nettesheim, A. von Oertzen and G. Ertl, *Surf. Sci. Lett.* 275 (1992) L645.
- [39] J.W. Evans, H.H. Madden and R. Imbihl, *J. Chem. Phys.* 96 (1992) 4805.