Diffusion and reactivity of O and O2

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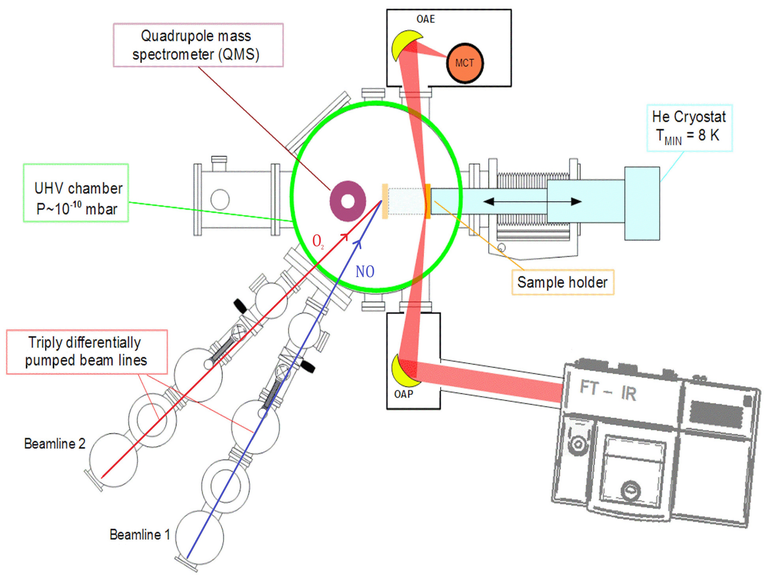
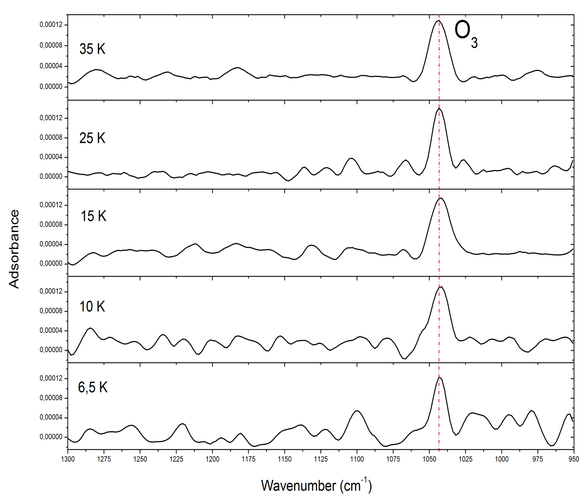
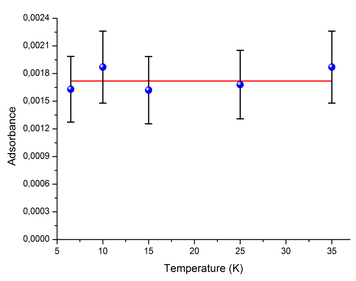
The products are probed using Temperature Programmed Desorption (TPD) and Reflexion Absorption Infrared Spectroscopy (RAIRS).



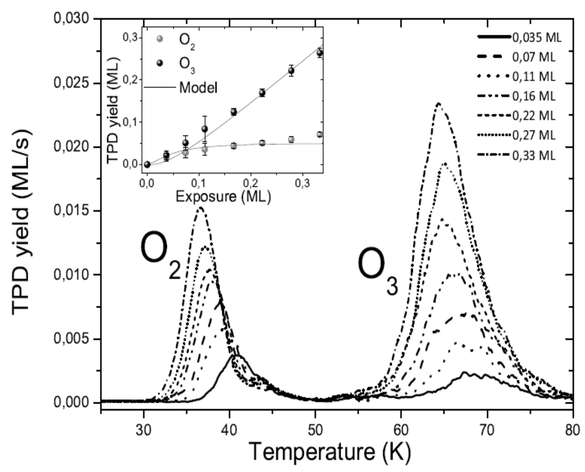
Reflection-Absorption Infrared Spectroscopy of ozone

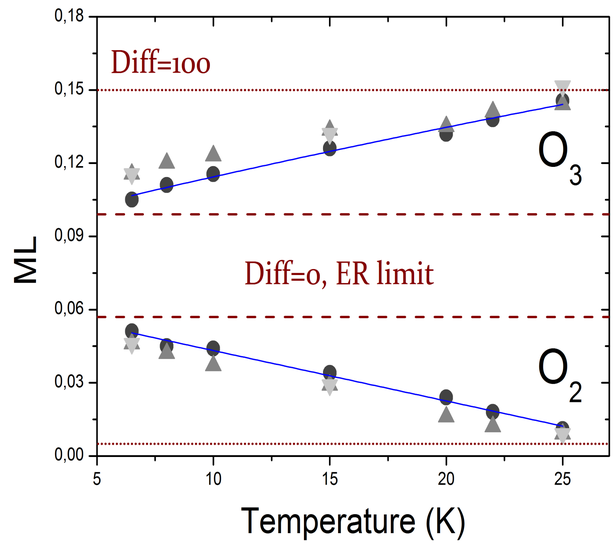


The O_3 infrared signature does not vary during the TPD, except during desorption. This finding confirms that the reactions occur at 6.3K and do not need any thermal activation.



The desorption peaks of O_2 as the surface is heated up (typical set of thermally programmed experiments, TPD). The O_2 desorption occurs between 35K and 50K, and the ozone desorption is observed between 55K and 75K (directly, or via the O_2^+ fragments). O desorption is never observed. The circles of the inset represent the area under the curves as a function of exposure doses.





O_2 and O_3 production for a fixed dose (0.15 ML, μ=71%) for various substrate temperatures during the deposition, and for the 3 substrates. The O_3/O_2 ratio increases with the temperature of the substrate, and depends on the substrate itself. For all the experiments, the total number of O atoms measured after a TPD is equal to the number of atoms sent, but partitioned differently between O_2 and O_3. The O_2/O_3 balance is due to the diffusion of atoms.

We have modeled our experiments adapting a classical set of differential equations.

Eley-Rideal

$$\frac{dO}{dt} = 2\mu\phi(1-2O-O_2)-(1-\mu)\phi O$$

$$\frac{dO_2}{dt} = (1-\mu)\phi(1-O)-2\mu O_2+2\mu\phi O$$

$$\frac{dO_3}{dt} = (1-\mu)\phi O+2\mu\phi O_2$$

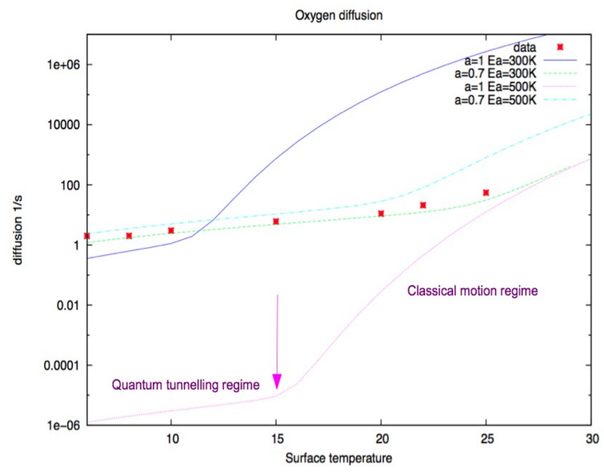
Langmuir-Hinshelwood

$$\frac{dO_3}{dt} = kOO_2$$

$$\frac{dO_2}{dt} = 2kOO-kOO_2$$

$$\frac{dO}{dt} = -4kOO-kOO_2$$

We assume a diffusion-limited reactivity, including the ER mechanism (same efficiency), and possible TPD adjustments due to thermally-induced diffusion. There is only one free physical parameter to adjust, *k*, which represents diffusion. We can reproduce all our data sets, and are able to propose a diffusion law for O as a function of the temperature.
The diffusion raises with T, but slowly. The high temperature points (T > 20 K) are overestimated, because at these temperatures O_2 can diffuse as well.



The diffusion can be simulated as in [4] . It includes two components, quantum-tunneling that dominates at low temperatures, and thermal diffusion predominant at higher temperatures.

REFERENCES
[1] Cuppen, H. M. & Herbst, E. *ApJ*, 2007
[2] Matar, E. et al, *A&A, 2008*
[3] Smoluchowski, R., *JPC*, 1983
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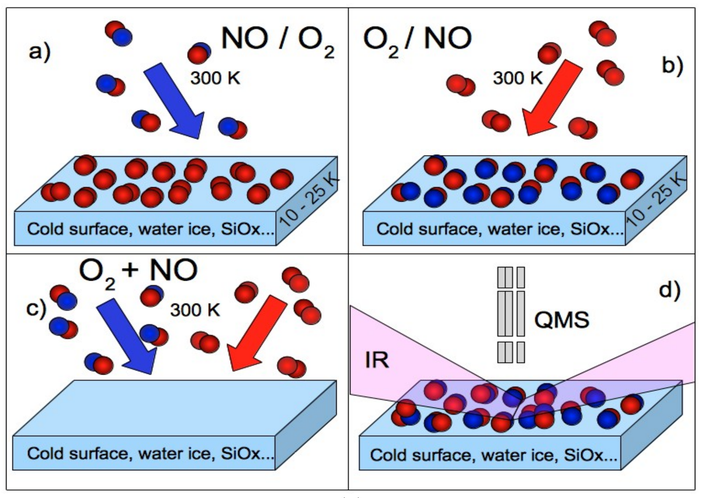
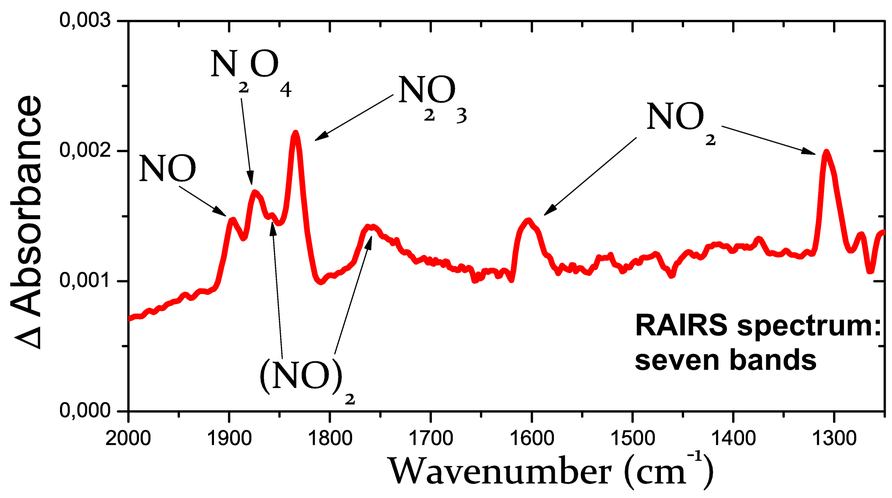
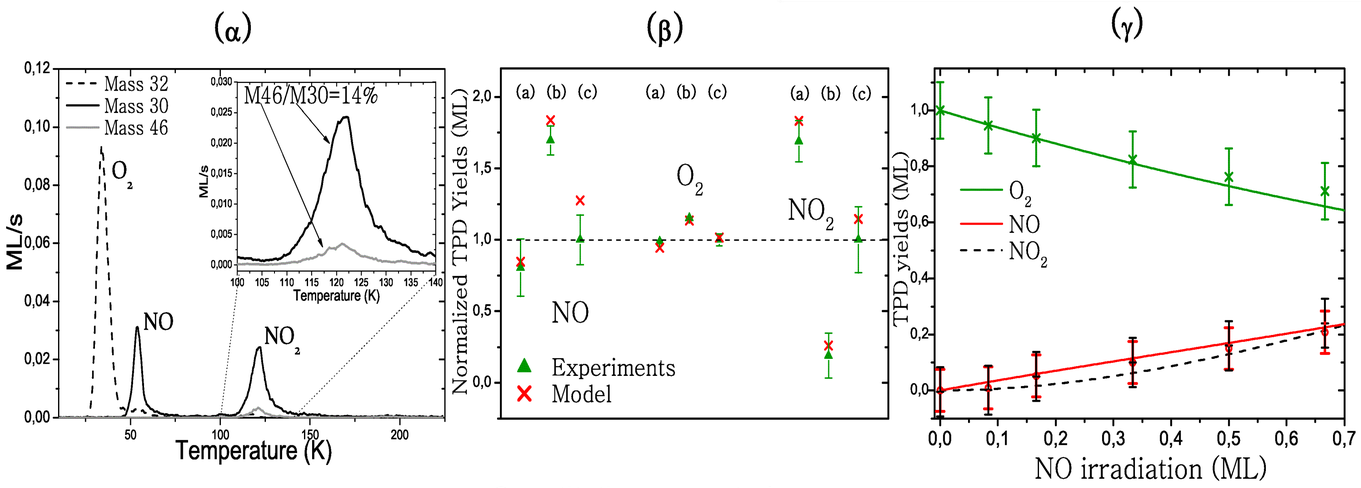
O_2 reactivity

We focus on the oxidation of NO molecules through O2 molecules.
All the experiments suggest formation of NO3 and NO2. It is formed with no dependence on the surface morphology and composition. The amount of NO2 formed, however, is dependent on the order of deposition. Of NO and O2 on the surface. In addition, experimental data are modelled using a set of rate equations. The model suggests that the NO+O2 reaction occurs mainly through the Eley Rideal mechanism (independently of the coverage), and that the intermediate species NO3 reacts with NO molecules to yield nitrogen dioxide.





(α) (β) (γ)



TPD curves of masses 30, 32 ane 46 u.m.a.

Quantitative amounts (green triangles) obtained for co-deposition (c method) or for the two sequential depositions (a and b methods).

Co-deposition experiments varying NO doses

Red cross in β and curves in γ are obtained by using a rate equations model, considering these reactions

$$NO + O_2 \rightarrow NO_3$$
$$NO + NO_3 \rightarrow 2NO_2$$

And the subsequent dimerization channels

$$NO + NO \rightarrow (NO)_2$$
$$NO_2 + NO_2 \rightarrow (NO2)_2$$
$$NO + NO_2 \rightarrow N_2O_3$$

REFERENCES
[1] Congiu, E. et al, ApJL, 2012
[2] Toon&Tolbert, Nature, 1995
[3] Honrath, R.E et al, GRL, 1999
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