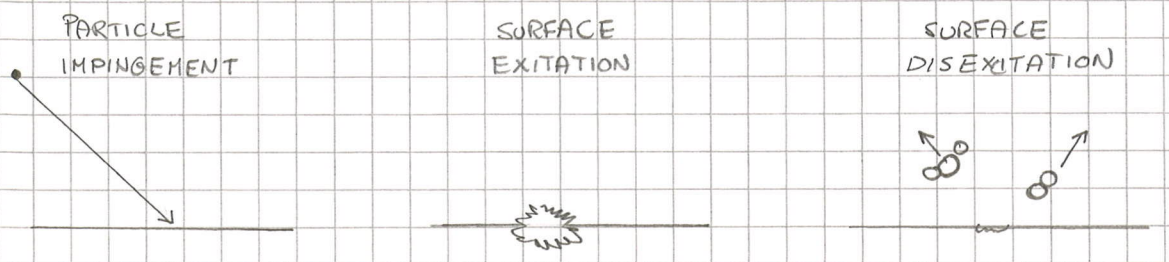
7. DEGASSING INDUCED BY PARTICLE BEAMS.

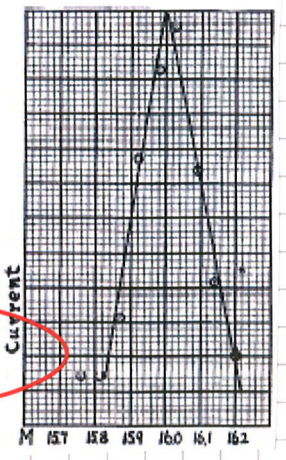


The impingement of particles (electrons, ions, photons) of energy higher than a few eV results in gas molecules desorption from solid surfaces.
The first observations of particle induced desorption were underlined at the beginning of the XX century in parallel with the first growth of vacuum technology.

In 1918, Dempster observed ion desorption from electron bombarded salts (Phys. Rev. 11, 323).

POSITIVE IONS FROM ELECTRON BOMBARDMENT.

It was thought that the bombardment of salts by electrons might break up the chemical compounds and give rise to many positive ions. At first a Wehnelt cathode was used; the ions formed passed beside the cathode (Fig. 1) and were then accelerated by a large potential difference. Aluminium phosphate on a piece of platinum foil was first bombarded. The intensity of the rays increased very rapidly with a slight increase in the amount or energy of the bombarding electrons, indicating that the salt needs to be heated to a certain degree before the ions are separated. Although the aluminium phosphate was chemically pure, the rays obtained under the bombardment of 128 volt electrons were very complex; the following ions were observed besides a couple of unresolved groups; H_1, H_2, Li (weak), O_1 (strong), Na (strong), O_3 (?) (weak), $M = 62$ (weak, possibly Na_2O), $M = 67$ (strong, possibly $H_3PO_2 = 66$), $M = 76$ (strong), $M = 86$ (weak, possibly Rb = 85.5), $M = 112$ (strong, possibly $P_2O_3 = 110$).



The experiments indicated the convenience of the method of obtaining positive rays and opened up an interesting field for investigation.

The experiments were however first directed

Millikan reported the first evidence of photon induced desorption in 1909, during the measurement of the photoelectric current of metallic surfaces exposed to ultraviolet radiation. The first interpretation of the phenomenon is attributed to Winch in 1930 (Phys. Rev. 36, 601). He was the first to understand the implication of photoelectrons in the photon induced desorption.

specimen to ultraviolet fatigue curves, taken by leaving the specimen in a vacuum of 10^{-7} mm of Hg unexposed, showed during the first stages a rapid decrease in photo-current with time of standing, but, after 360 hours of exposure for the film and 160 hours for the solid gold, the photo-current from the former held constant for 3 hours, and from the latter 1½ hours. This seemed to indicate that a fairly stable equilibrium had been reached, and the subsequent fatigue was consistent with the idea that it was due to return of gas to the surface.

The experiment was repeated, using a silver filament approximately 0.025 mm thick, and an increase in emission comparable to that for the gold film was obtained.

The probable explanation is that photo-electrons, both when ejected and returned to the surface by a reverse field, remove adsorbed gas from the surface.

Millikan[1] noted an increase in photoelectric emission on exposure of certain metals to ultraviolet, but did not note the corresponding change in long wave-length limit or that the photoelectrons themselves apparently play an important part in the outgassing.

Work is being carried forward testing this explanation and obtaining more data on photoelectric properties of thin films.

RALPH P. WINCH
Laboratory of Physics,
University of Wisconsin,
Madison, Wisconsin,
July 15, 1930.

Millikan, Phys. Rev. 29, 85 (1909).

In modern accelerators, most of the gas source is ascribed to particle induced desorption. The thermal outgassing is still the main gas source for low energy proton accelerators, LINACs and antimater facilities.

7.1 ELECTRON STIMULATED DESORPTION (ESD)

7.1.1 General experimental observations

The most relevant parameter in ESD is the desorption yield η:

$$\eta = \frac{\text{number of molecules desorbed}}{\text{number of electrons bombarding the surface}}$$

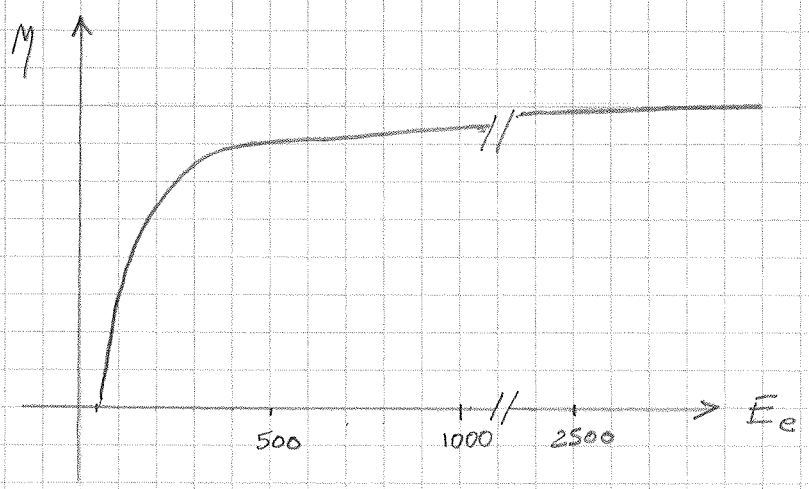
(1) η is a function of the electron energy and depends on the nature of the gas molecule and of the metallic surface.
For typical metals of vacuum technology:

$$\eta_{H_2} > \eta_{CO} > \eta_{CO_2} > \eta_{CH_4}$$

For electron energies of about 500 eV, typical values for η are

$$\eta_{H_2} \approx 10^{-1} \qquad \eta_{CH_4} \approx 10^{-3}$$

η depends strongly on electron energy in the range $0 \div 500$ eV; for energy in the $2 \div 15$ keV, η can be considered as constant.



Most of the desorbed molecules are neutral, but ions are also present to a much lower extent (100 times less).

(2) The molecules desorbed by electrons acquire a kinetic energy of a few eV, up to 10 eV.

(3) η depends on dose of electrons that have bombarded the unit surface

$$D \left[\frac{\text{electrons}}{\text{cm}^2} \right]$$

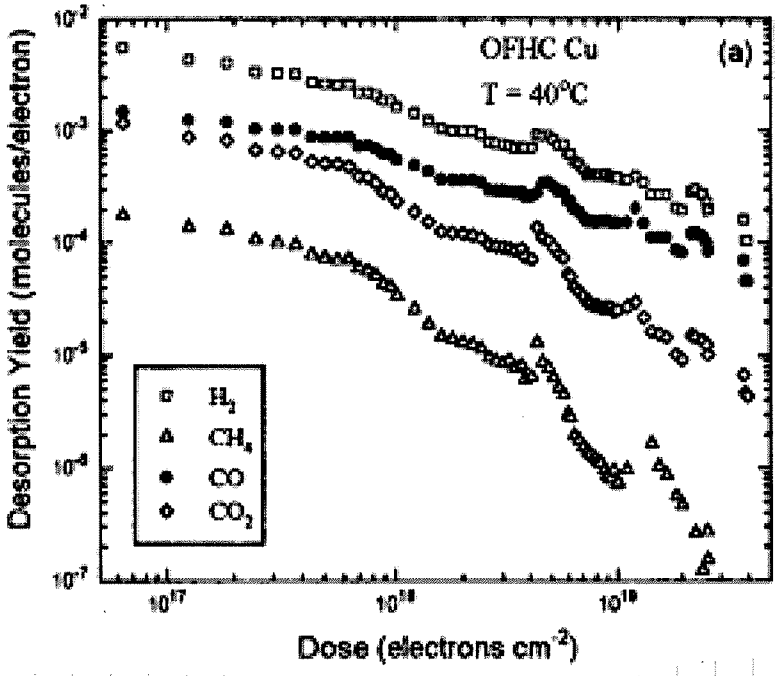
This is easily understood; the previous electrons have removed gas from the surface → the surface is cleaner.

Except for H_2O, the measured η has a power law dependance on the dose D:

$$\eta = \eta_0 D^{-\alpha}$$

where $0,6 < \alpha < 1$.

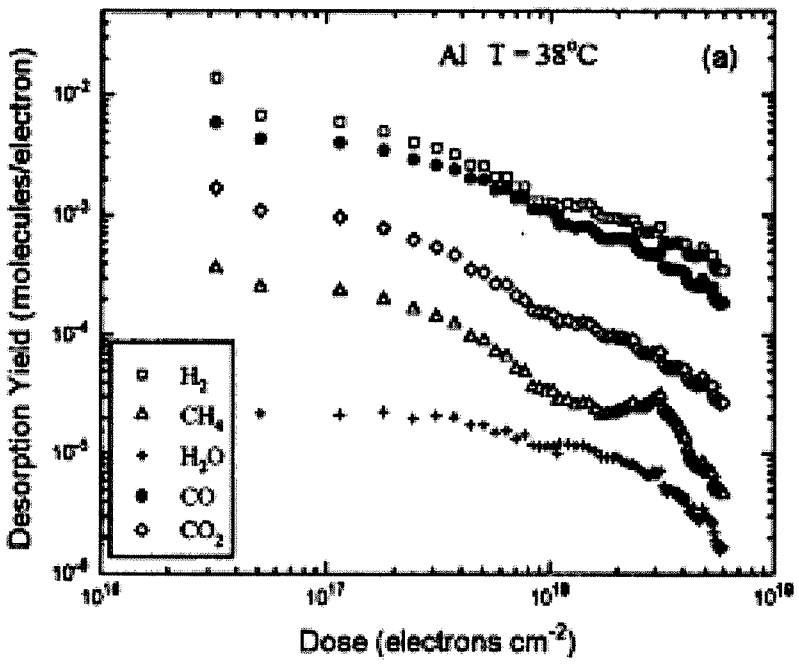
α=0.62



E_e = 300 eV

Samples baked at 150°C for 24 h and 300°C for 2 h

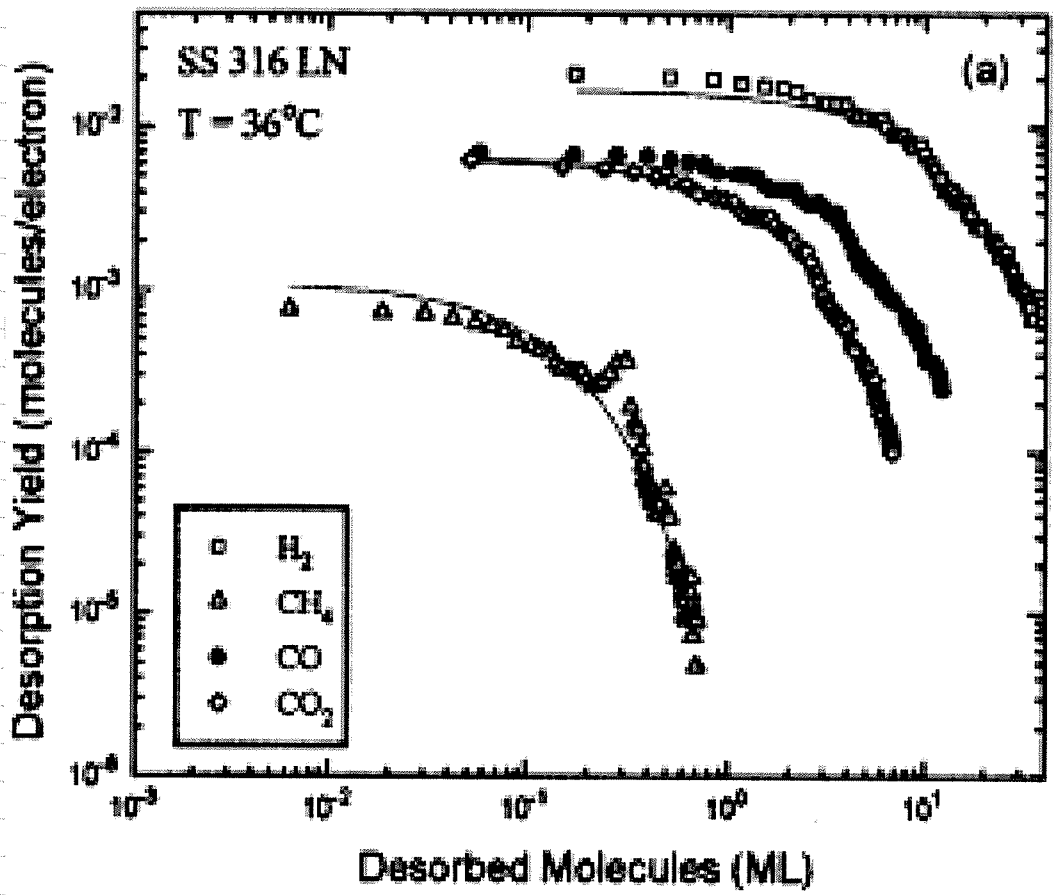
α=0.68



E_e = 300 eV

The positive effect of the accumulate dose on η is mostly lost when the bombarded surface is vented to air. A residual effect can be measured (memory effect) for a short stay in air.

④ The total quantity of desorbed gas molecules exceeds one monolayer. Some authors explain these results assuming a stimulated diffusion of C, O, H atoms from the bulk of the oxide layer.



$1ML = 2 \times 10^{15}$ molecules/ cm^2

The samples were baked at 150 C for 24 h and at 300 C for 2 h

7.1.2 The physical models of electron stimulated desorption

References
- T.E. Madey, D.E. Ramaker and R. Stockbauer, Ann. Rev. Phys. Chem. (1984), 35, p. 215-40
- R.D. Ramsier and J.T. Yates Jr., Surface Science Report (1991), 12, p. 243-378

The desorption mechanism can be described as a sequence of 3 steps:

1) a fast initial electronic excitation (10^{-16} s)
2) a decay of the exited state by displacement of atomic position in competition with other decay channels ($10^{-15} - 10^{-14}$ s)
3) a modification of the desorbing species as they get farther from the surface ($10^{-14} - 10^{-13}$ s).

$1\,\text{Å} = 10^{-10}$ m $E \cong 1$ eV $\rightarrow$ $E = \frac{1}{2} m v^2 \rightarrow \sqrt{\frac{1.6\times10^{-19}\ \text{J} \times 2}{9.1\times10^{-31}}} \simeq 6\times10^{5}\ \frac{m}{s}$ (↑ electron mass)

$\Delta t(1\,\text{Å}) = \frac{\Delta s}{v} = \frac{10^{-10}}{6\times10^{5}} = 1.6\times10^{-16}$ s (↑ electron movement involved)

$\sqrt{\frac{1.6\times10^{-19}\ \text{J} \times 2}{2\times10^{-26}}} = 4000\ \frac{m}{s}$ (↑ carbon atom) $\Delta t(1\,\text{Å}) = 2.5\times10^{-14}$ s (↑ atom movement involved)

In the range of electron current recorded in particle accelerators, namely less than 10^{13} electrons $cm^{-2} s^{-1}$, the probability for an interaction among one molecule and more than one electron is negligible. Therefore the ESD is an isolate electron-adsorbate interaction.

When considering collisions between an incident low-energy particle ($E \sim 500$ eV) of mass m_e and a free particle of mass M, one can estimate the

order of magnitude of the maximun energy transferred (ΔE) during the process with classical kinematics.

For hard-sphere scattering the result is:

$$\frac{\Delta E}{E_e} = \frac{2 m_e M (1 - \cos\Theta)}{(m_e + M)^2}$$

Θ is the scattering angle in the centre of mass reference frame.

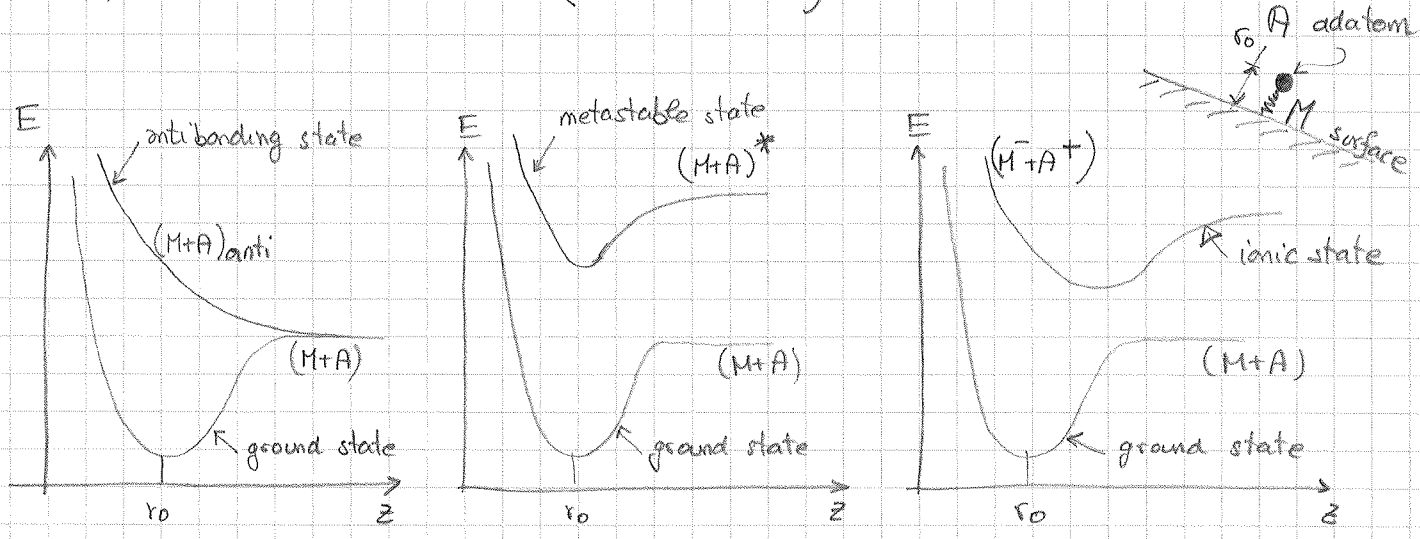
For $m_e \ll M$, which is always the case in ESD,

$$\frac{\Delta E}{E_e} \approx \frac{2 m_e}{M}$$

So the fraction of energy transfer is of the order of $2/1840 \approx 10^{-3}$ for electron - H collision. For typical energy of $E_e \approx 500\ eV \Rightarrow \Delta E \approx 0.5\ eV$ which is much less than the observed 2-10 eV for heavier molecules.

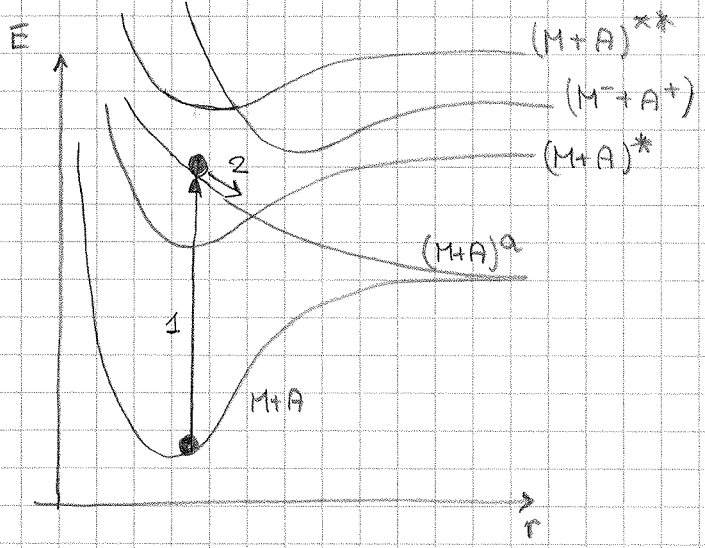
$\Rightarrow$ The direct momentum transfer is not dominant in ESD $\Rightarrow$ electronic energy tranfer must be considered.

One of the earliest model to explain ESD was introduced in 1964 by Menzel, Gomer and Readhead (MGR model).



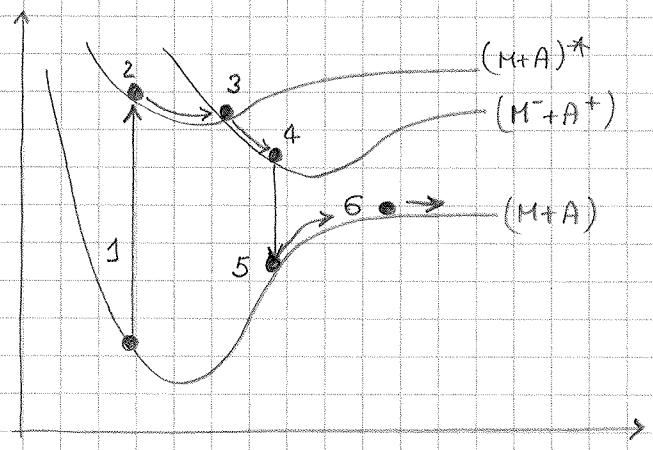
The MGR model assume that the M+A system is initially in its ground state (M+A). The interaction with the incident electron provokes an adiabatic transition (Franck-Condon principle) to exited states,

antibonding, metastable or ionic. The Franck-Condon principle implies that the transition is vertical with respect to z, namely the electronic rearrangement is much faster than the nuclear movement.



Adiabatic transition following electron collision.

After excitation, nuclear motion may occur over a time scale of $\approx 10^{-13} \div 10^{-14}$ s converting potential energy into traslational kinetic energy.
Potential curve crossing is possible resulting in different de-exitation pathways.

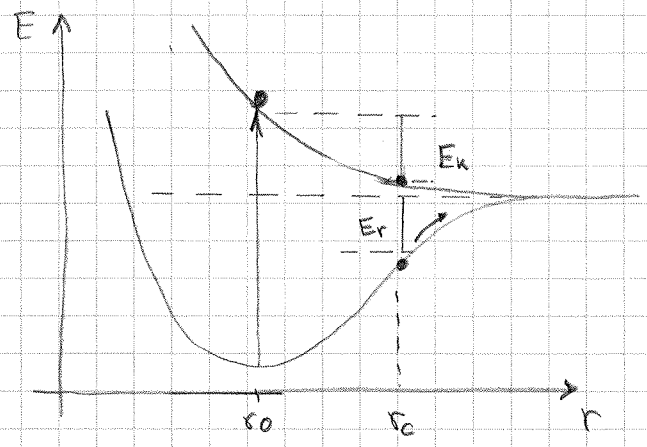


The ESD cross section can be written as

$$\sigma = \sigma_0 \cdot P_e \leftarrow \text{escape probability}$$

σ_0: primary electron excitation

The escape probability is higher when the adatom move faster beyond a critical distance r_c.



At the critical distance r_c, in case of de-exitation, the adatom has enough translational kinetic energy to escape.

The time needed to reach r_c is roughly:

$$t_c \approx \frac{r_c}{v} \approx \sqrt{M_a}$$

Because $P_e \propto e^{-t/\tau} \rightarrow P_e \propto e^{-\sqrt{M_a}}$

$\Rightarrow$ The MGR model predict an isotope effect $\rightarrow$ experimentally verified.

7.2 PHOTON STIMULATED DESORPTION

Particle beams produce photons whenever they are accelerated, i.e. whenever their velocity vectors are changed, for example by bending magnets.
The emitted photons are adsorbed by the walls of the vacuum system and, as a result, gas molecules are desorbed.
There are experimental evidence that the desorption mechanism evolves in two steps:

1) the hitting photons extract photoelectrons with probability $\eta_e(\varepsilon)$ (ε = photon energy)
2) the emission and subsequent readsorption of the photoelectron provoke the desorption of gas molecules by ESD with probability η_d.

The total desorption flux is calculate by considering the number of photons emitted per second in a small interval of energy ε

$$\frac{dN(\varepsilon)}{dt} d\varepsilon$$

multiplying by the photoelectron yield at photon energy ε

$$\eta_e(\varepsilon) \cdot \frac{dN(\varepsilon)}{dt} d\varepsilon$$

and integrating photon energies:

$$\frac{dN_{e^-}}{dt} = \int_{\varepsilon_{min}}^{\infty} \eta_e(\varepsilon) \frac{dN(\varepsilon)}{dt} d\varepsilon$$

ε_{min} is the threshold for photoelectron extraction.

Finally multiplying by the electron desorption yield η_d:

$$\Rightarrow \quad Q = 2\eta_d \cdot \frac{dN_{e^-}}{dt} \Rightarrow \text{gas flux}$$

SOME ISSUES !

The number of photoelectrons extracted per photon is not well known for technological materials and it depends strongly on the surface cleanness. In addition the ESD yield of photoelectrons is not well defined because it depends on the photoelectron energy which is a priori not known.

For this reason the double step process is neglected and a global photodesorption yield η_{ph} is introduced.
In general η_{ph} is shown as a function of a typical synchrotron light parameter: the photon critical energy.

7.2.1 Photon power and energy spectrum

A particle moving on circular orbit radiate electromagnetic radiation with the following power:

$$P_{rad} = \frac{e^2 c}{6\pi\varepsilon_0 (m_0 c^2)^4} \cdot \frac{E^4}{\rho^2}$$

ρ = bending radius
E = beam energy
m_0 = rest mass
ε_0 = vacuum permittivity

Important consequence ⇒ the power emitted by electrons or positrons is much higher than that by protons:

$$\frac{P_{rad,e}}{P_{rad,p}} = \left(\frac{m_p c^2}{m_e c^2}\right)^4 = 1{,}13 \times 10^{13}$$

for the same bending radius and beam energy.

In practical units for electrons:

$$P[W] = 1{,}59 \times 10^{-14} \cdot B^2[T] \cdot (\beta\gamma)^2 = 88{,}6 \frac{E^4[GeV] \cdot I[mA]}{\rho[m]}$$

(B: bending magnet field)

- The synchrotron radiation power is a very important parameter for vacuum engineers in the phase of the vacuum system design. The power has to be collected, adsorbed or transmitted. This defines shapes and materials of the vacuum chambers.

The energy loss per turn is:

$$U_0 = \oint P_{rad}\, dt = P_{rad} \cdot t_b = P_{rad} \cdot \frac{2\pi\rho}{c} = \frac{e^2}{3\varepsilon_0 (m_0 c^2)^4} \cdot \frac{E^4}{\rho}$$

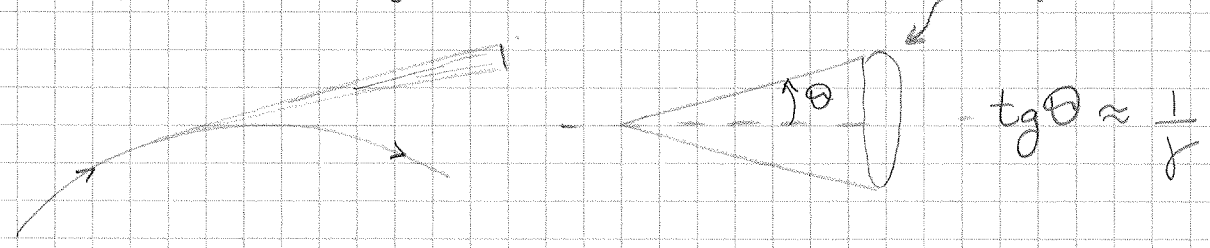
t_b = travelling time in the bending magnets.

In practical units for electrons:

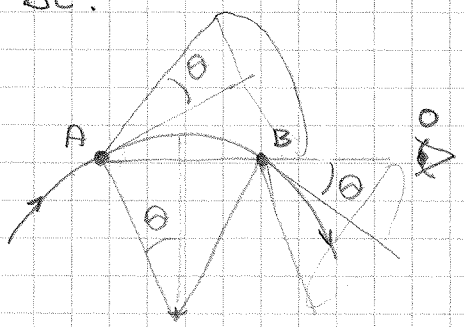
$$U_0\,[keV] = 88{,}5\, \frac{E^4\,[GeV]}{\rho\,[m]}$$

IMPORTANT: The power emitted depends strongly on the beam energy.

- The synchrotron light at relativistic beam energy is emitted from the bending magnets in a very narrow cone:



This means that an observer receives the radiation for a very short time Δt.



The observer receives the first light from A after:

$$t_1 = \frac{\overline{AB}}{c} + \frac{\overline{BO}}{c}$$

and the last:

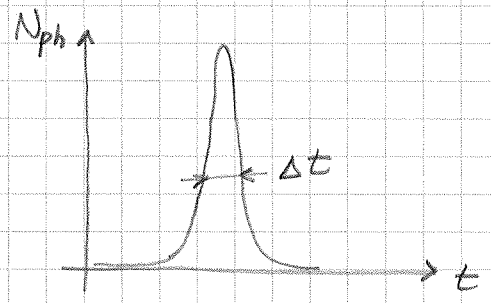
$$t_2 = \frac{\widehat{AB}}{v} + \frac{\overline{BO}}{c}$$

Therefore the pulse lasts $\Delta t = \frac{\widehat{AB}}{v} - \frac{\overline{AB}}{c}$

$$\Delta t = \frac{2\rho\theta}{c\beta} - \frac{2\rho\sin\theta}{c} = \frac{2\rho}{c}\left(\frac{\theta}{\beta} - \theta + \frac{\theta^3}{3!} - \frac{\theta^5}{5!} + \dots\right)$$

$\theta \approx \frac{1}{\gamma}$ $\Rightarrow$ it can be shown that

$$\Delta t = \frac{4\rho}{3c\gamma^3} \rightarrow \text{very small number}$$



The Fourier transform of this short signal gives a very wide broad spectrum. The typical frequency is

$$\omega_{typ} = \frac{2\pi}{\Delta t} = \frac{3\pi c\cdot\gamma^3}{2\rho}$$

The critical frequency is defined as: $\omega_{CR} = \frac{\omega_{typ}}{\pi} = \frac{3c\gamma^3}{2\rho}$

As a consequence the critical energy is:

$$\boxed{\mathcal{E}_c = \hbar\omega_c = \frac{3}{2}\frac{\hbar c}{\rho}\gamma^3}$$

In practical unit:

$$\mathcal{E}_c\,[keV] = 2{,}218\,\frac{E^3[GeV]}{\rho} = 0{,}665\,E^2[GeV]\cdot B\,[T]$$

The critical energy divides the photon spectrum in two parts of equal power.

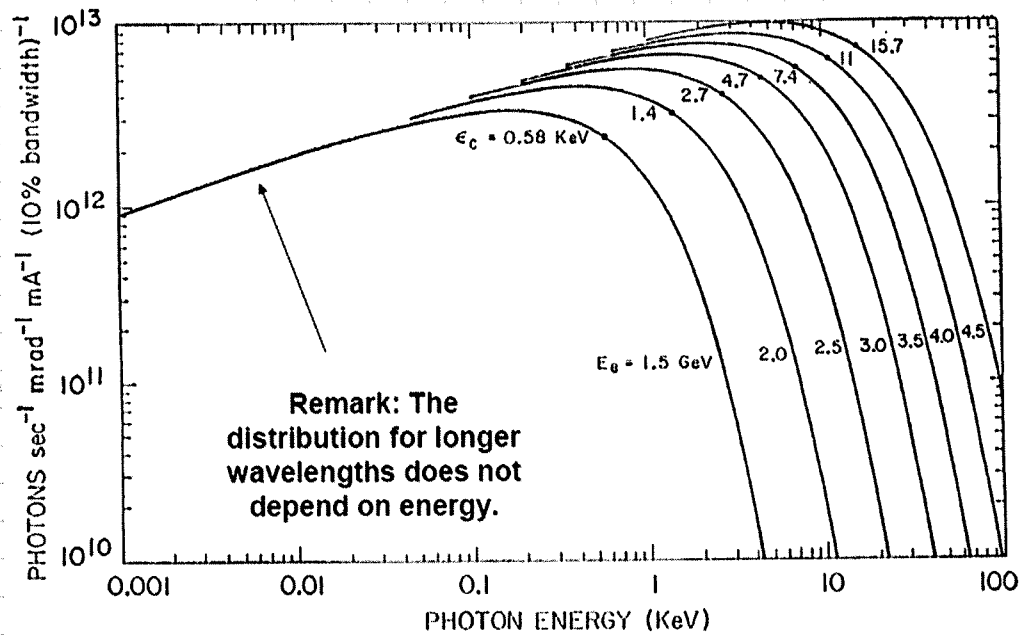
– The spectral photon density is given by:

$$\frac{d\dot{N}_{Ph}}{d\left(\frac{\varepsilon}{\varepsilon_c}\right)} = \frac{P_{TOT}}{\hbar\omega_c} \cdot S\left(\frac{\omega}{\omega_c}\right) \qquad \int_0^\infty S(\xi)d\xi = 1$$

$$\int_0^1 S(\xi)d\xi = \frac{1}{2}$$

The spectrum for a storage ring is fully determined by the three parameters:

$$I_b, \; E, \; \rho$$



It can be shown that the number of emitted photon per second is

$$\dot{N} = \frac{15\sqrt{3}}{8} \cdot \frac{P}{\varepsilon_c}$$

and the mean photon energy is:

$$\langle\varepsilon\rangle = \frac{P}{\dot{N}} = \frac{8}{15\sqrt{3}}\varepsilon_c$$

In practical unit

$$\dot{N} = 8{,}08 \times 10^{17}\, I[mA] \cdot E[GeV]$$

and the linear flux (photons $m^{-1} s^{-1}$)

$$\frac{d\dot{N}}{ds} = 1{,}28 \times 10^{17}\, \frac{I[mA] \cdot E[GeV]}{\rho[m]}$$

The degassing rate is written as

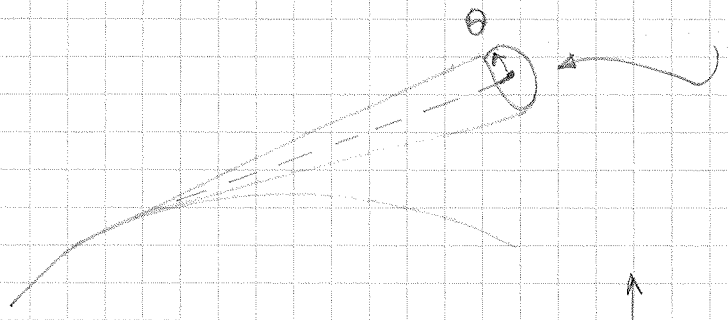
$$Q = \eta_{ph} \cdot \dot{N}$$

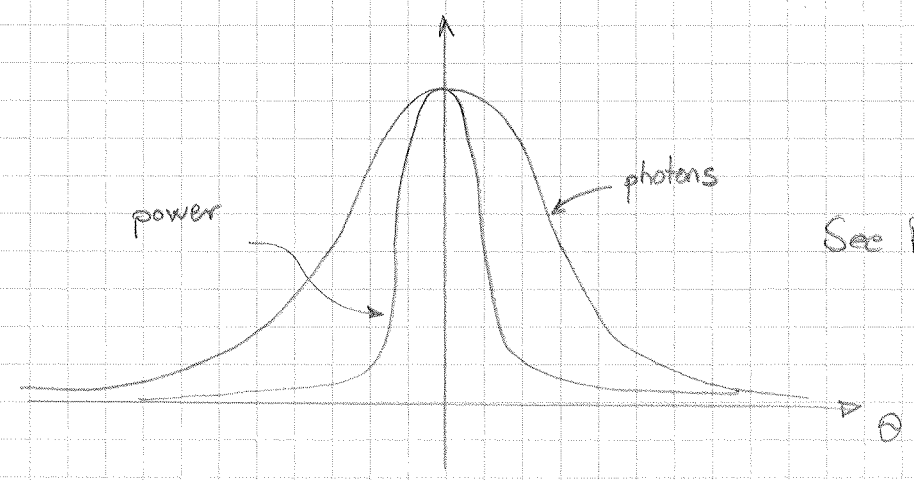
where η_{ph} is the synchrotron ligth desorption yield. It is a measured value that averages the contribution of a large spectrum of photon energy.

WARNING: Do not confuse "power" and "number of photons"

50% power $\leftarrow \varepsilon_c \rightarrow$ 50% power

$\approx$ 90% of photons $\leftarrow \varepsilon_c \rightarrow \approx$ 10% of photons





See Roberto's tutorial

7.2.2 The photon desorption yield of technological materials

The photon induced desorption yields have been measured by means of synchrotron radiation sources and dedicated setups. The results are in general plotted as a function of the dose of bombarding photons (p.ex. photons/metre).

- The desorption yields do not depend significantly on the photon dose up to about 5×10^{20} photons per metre of vacuum chamber. For higher doses, η_{ph} varies as a power law function of D:

$$\eta_{ph} \propto D^{-\alpha}$$

α has values similar to those of electron stimulated desorption.

- η_{PH} varies roughly linearly with the critical energy for $E_c < 280$ eV.

$$\eta_{ph} \approx A \cdot E_c^{\beta} \qquad 0{,}74 < \beta < 1{,}12$$

The orders of magnitude of η_{ph} for E_c of about 0.5 ÷ 1 KeV are:

for well cleaned and in situ baked Cu, and st. steel:

$\eta_{H_2} \approx 10^{-3}$ molecules/photon

$\eta_{CO} \simeq \eta_{CO_2} \approx 10^{-3} \div 10^{-4}$ molecules/photon

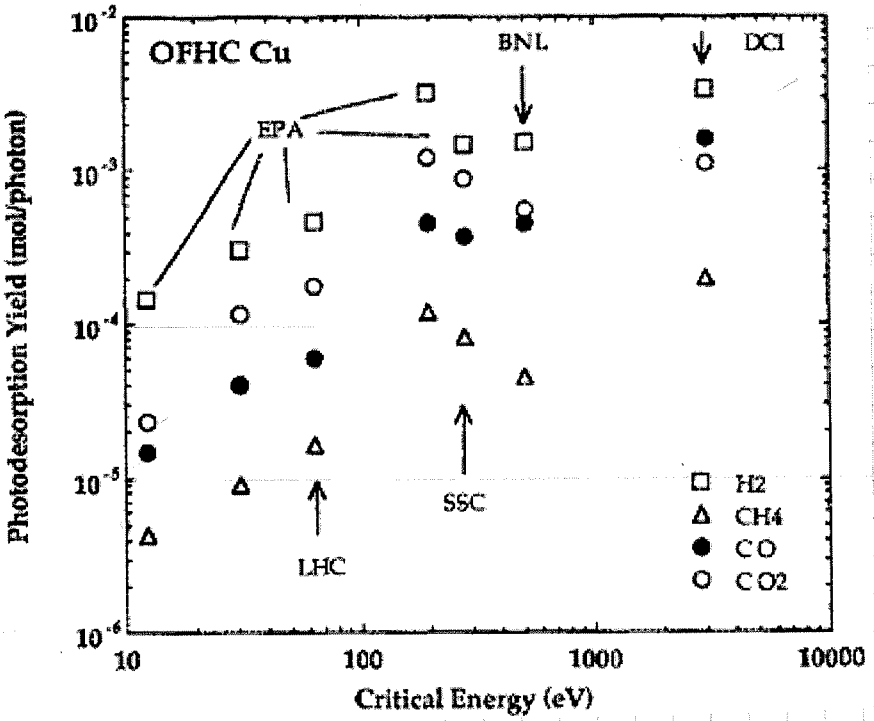
$\eta_{CH_4} \approx 10^{-5}$ molecules/photons

EASY TO REMEMBER: η_{PH} are about 2 orders of magnitude lower than η_e.

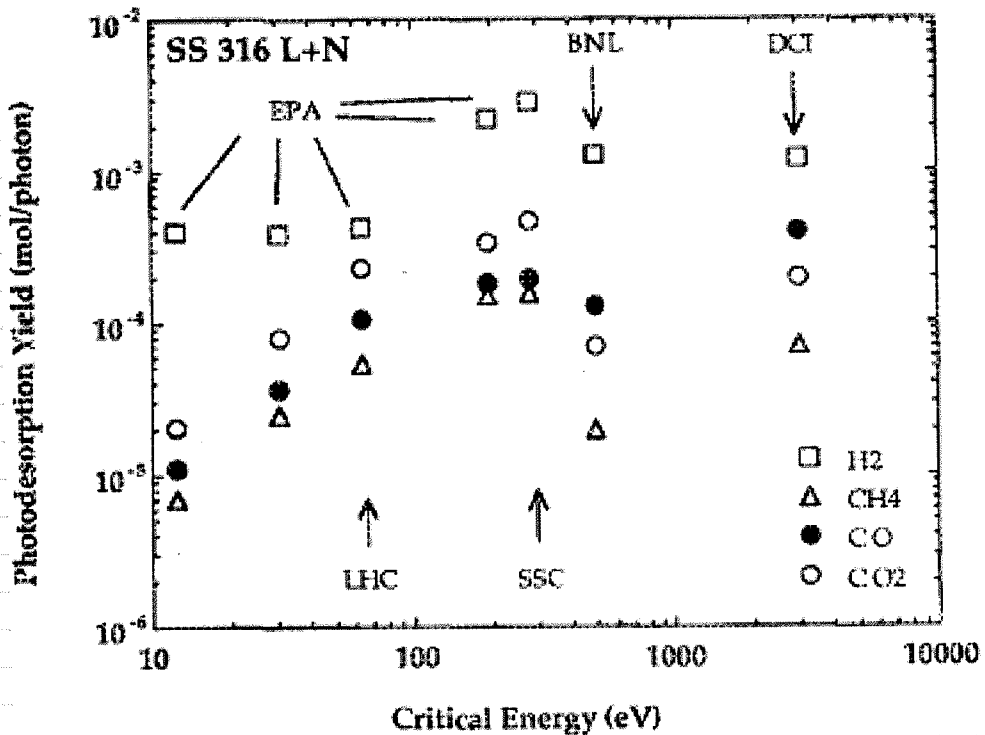
$\Rightarrow$ photoelectron yields $\approx 10^{-2}$ electrons/photon for the material of interest.

Photons with energy lower than a threshold value should not contribute to the desorption process. The threshold should be equivalent to the photoelectron extraction threshold (work function):

$E_{min} \approx 5$ eV } for typical metals



J. Gomez-Goñi et al. J. Vac. Sci. Tech A12, 1714 (1994)



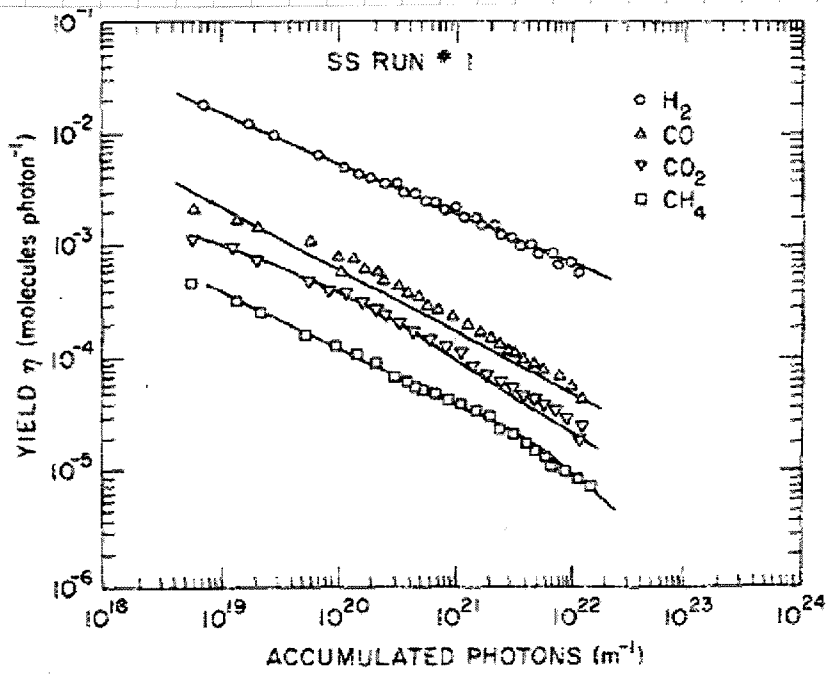


FIG. 2. Molecular desorption yields for prebaked stainless steel.

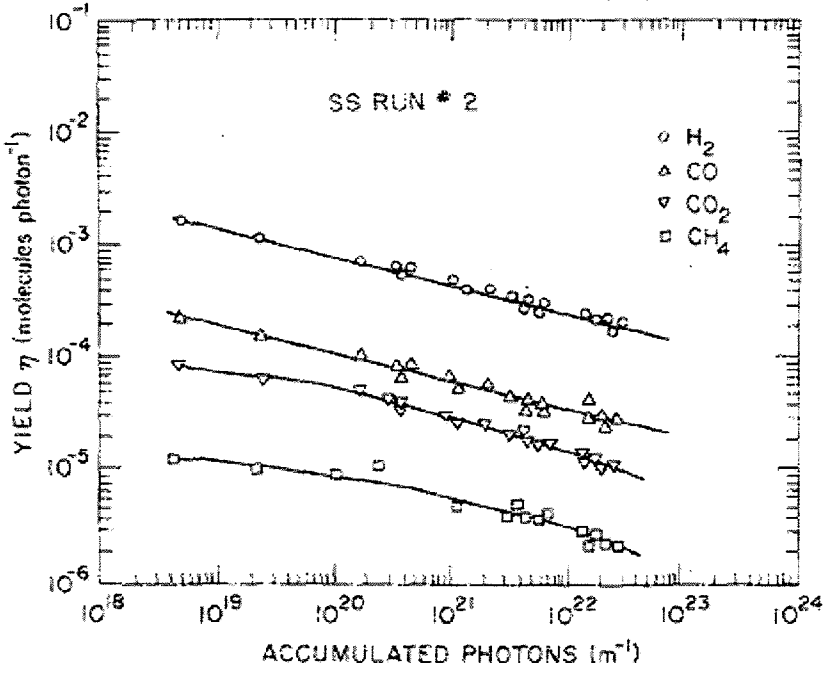


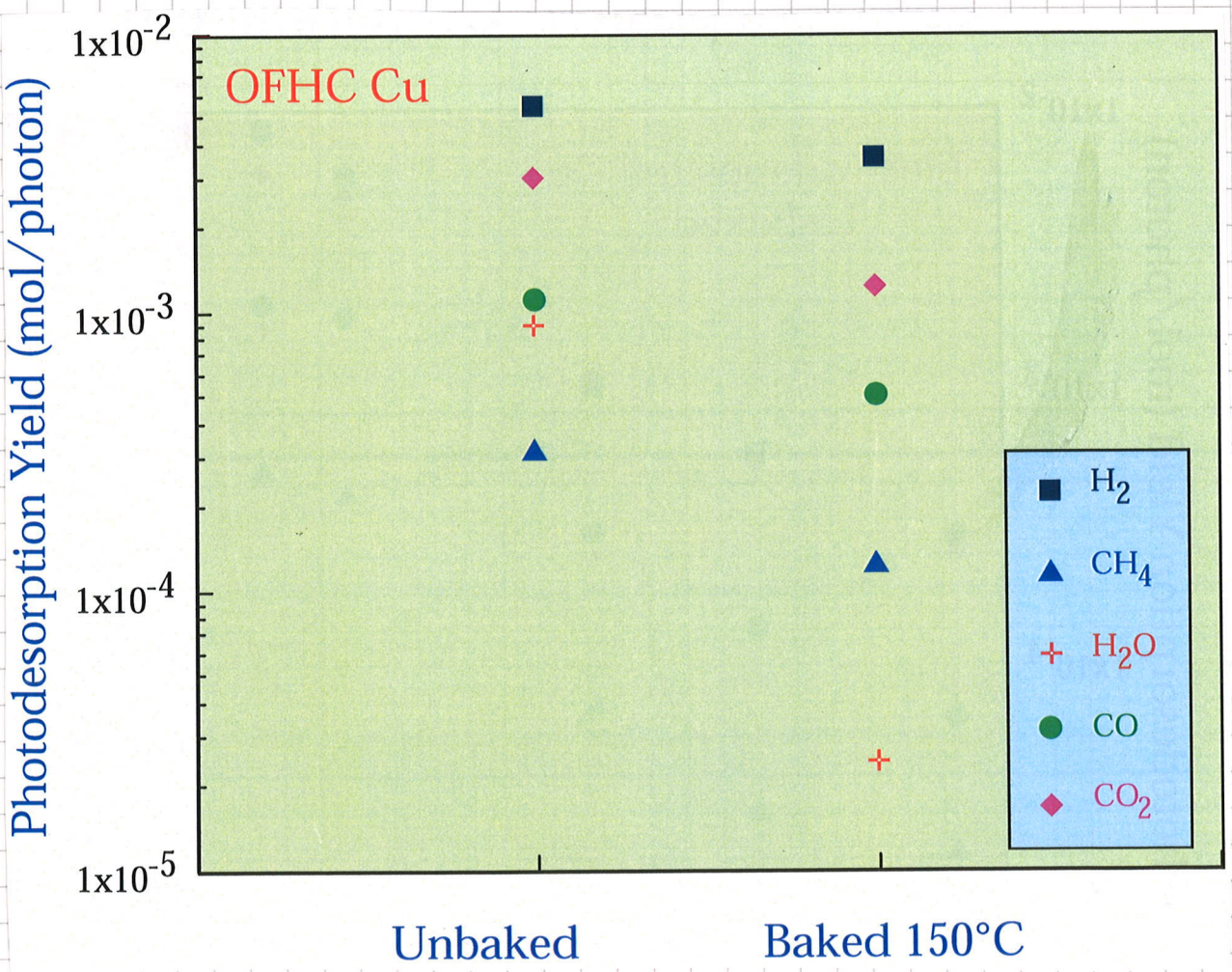
FIG. 3. Molecular desorption yields for *in situ* baked stainless steel.

Foster, Havana, Lam, J. Vac. Sci. and Tech A, vol 8, p. 2858, 1990
2/15

7.3 METHODS FOR THE REDUCTION OF ELECTRON AND PHOTON INDUCED DESORPTION.

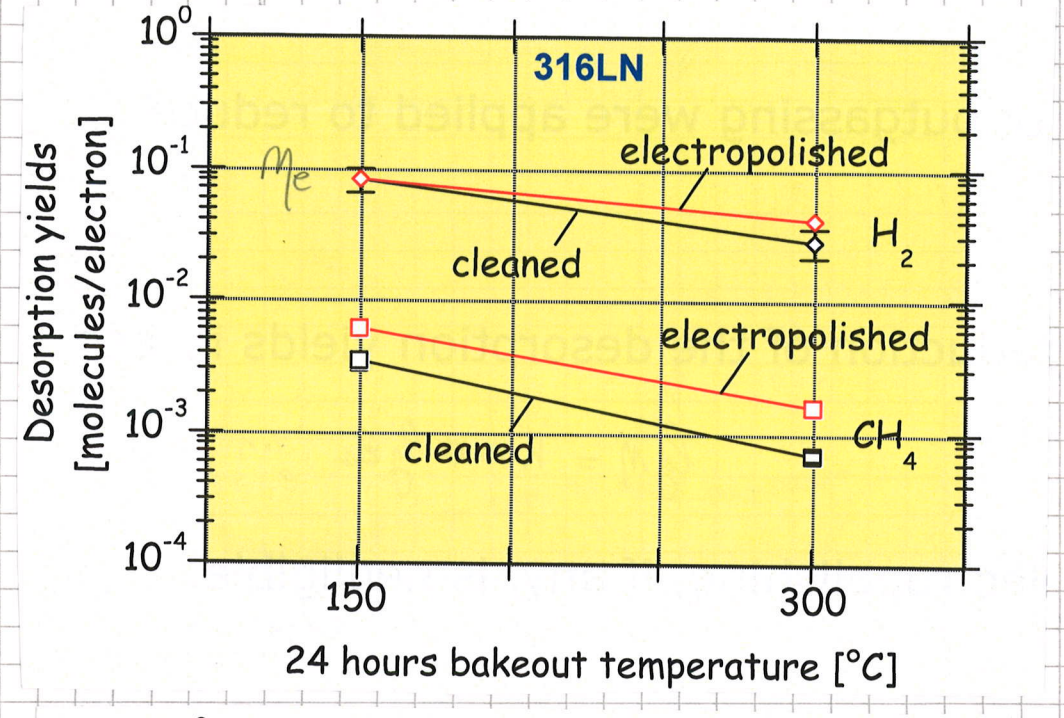
The gas desorbed by electrons or photons is located on the surface of the vacuum chamber materials or very close to it. It goes without saying that a state of art surface cleaning is essential to avoid excessive induced desorption.

An additional mitigation is provided by in situ bakeout at temperature in the range 120°C ÷ 350°C. Heating the vacuum material results in a reduced quantity of gas onto the surface and in the oxide layer. However, the effect on the η values is limited and in general less than an order of magnitude.



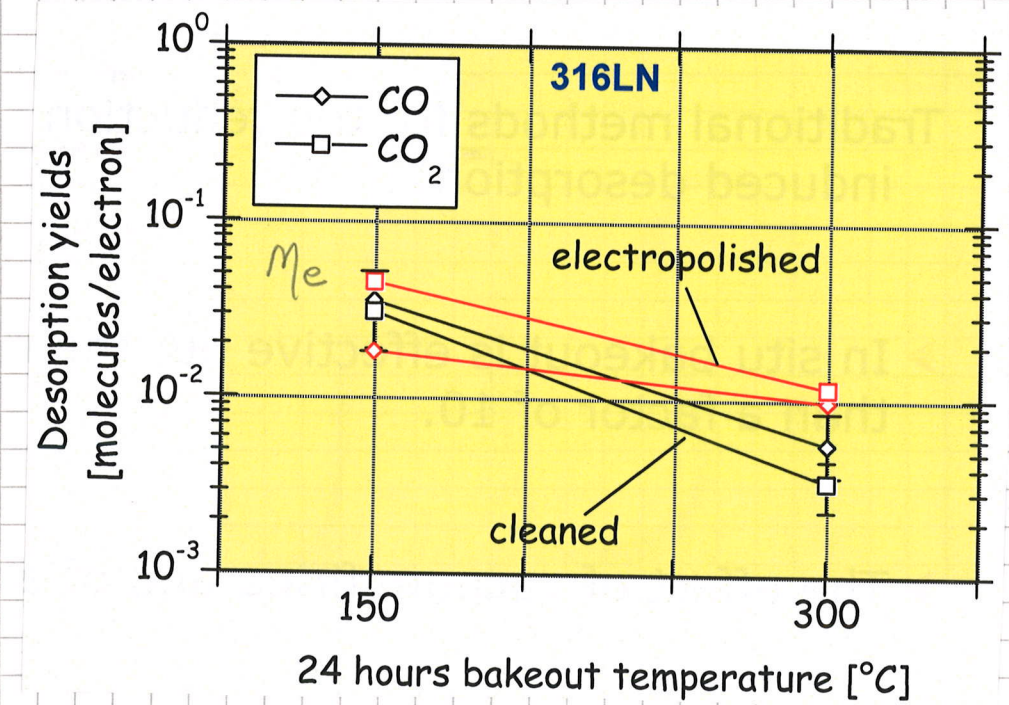
H_2 : 1,5 CH_4 : 2,5 H_2O : 36,7 CO : 2,2 CO_2 : 2,5

Electropolishing and vacuum firing have a very limited effect on η.

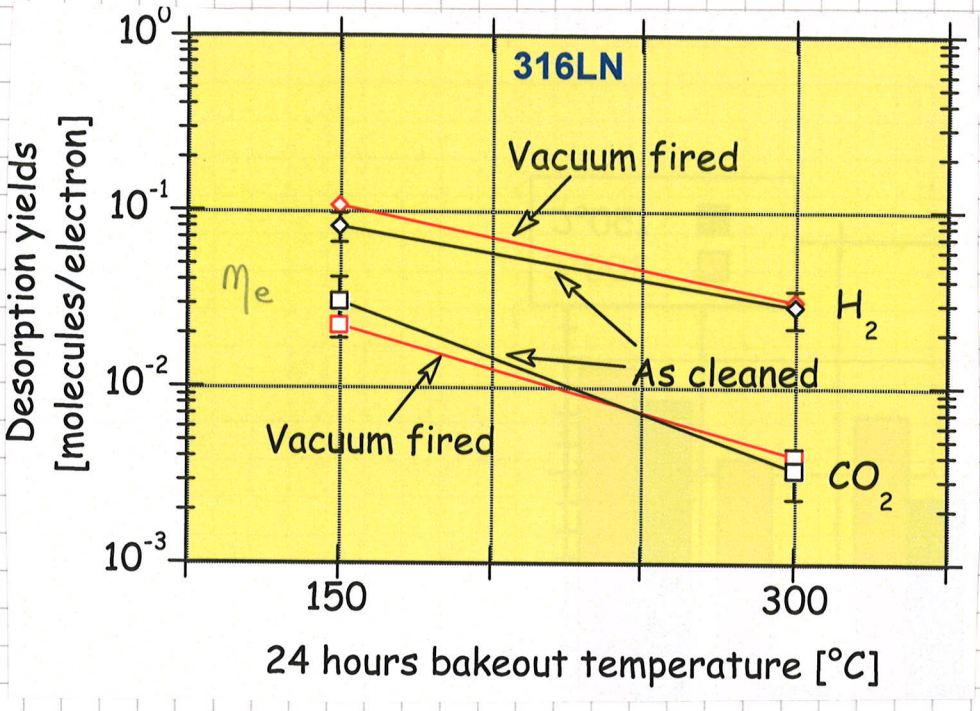


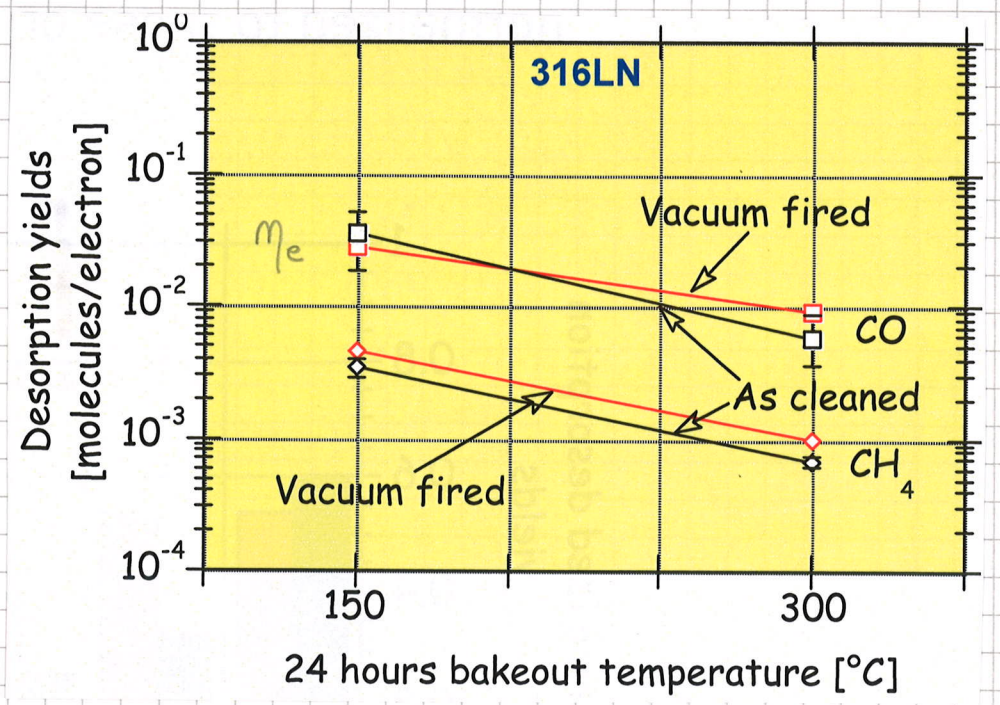
Austenitic st. steel

E_e = 500 eV



After these treatment, vacuum materials are re-exposed to air. A new oxide layer is formed, which is considered as the source of gas.





Stainless steel components that are preliminarily air baked shows η sligtly lower than those reported for as cleaned surfaces, despite a thicker oxide layer.

- The accumulation of electron or photon doses is very effective in the reduction of η as shown above for Cu. The particle bombardment produce an additional surface cleaning and a change in the surface chemistry.