Surface Analysis of Liquid Gallium

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Outline

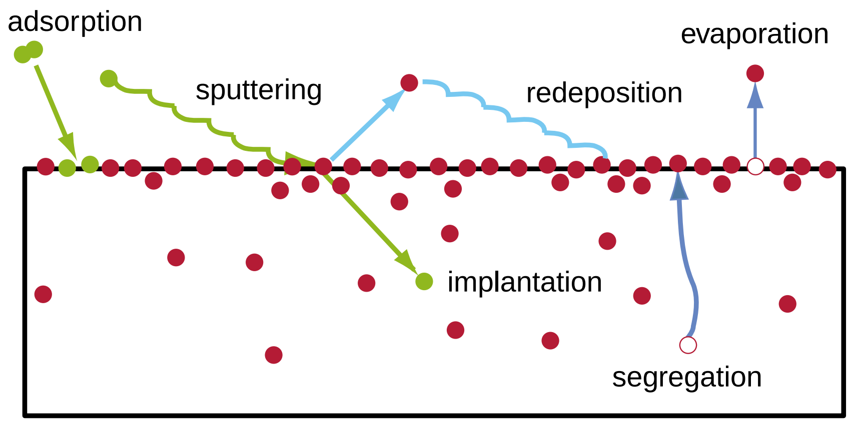
- **Introduction, some properties of Ga**
- **Surface composition data on Ga**
- **Adsorption of deuterium on Ga**
- **Comparison with Li and Sn, summary**

Surface studies of plasma-facing liquids

Issue: What comprises the surface seen by the plasma?

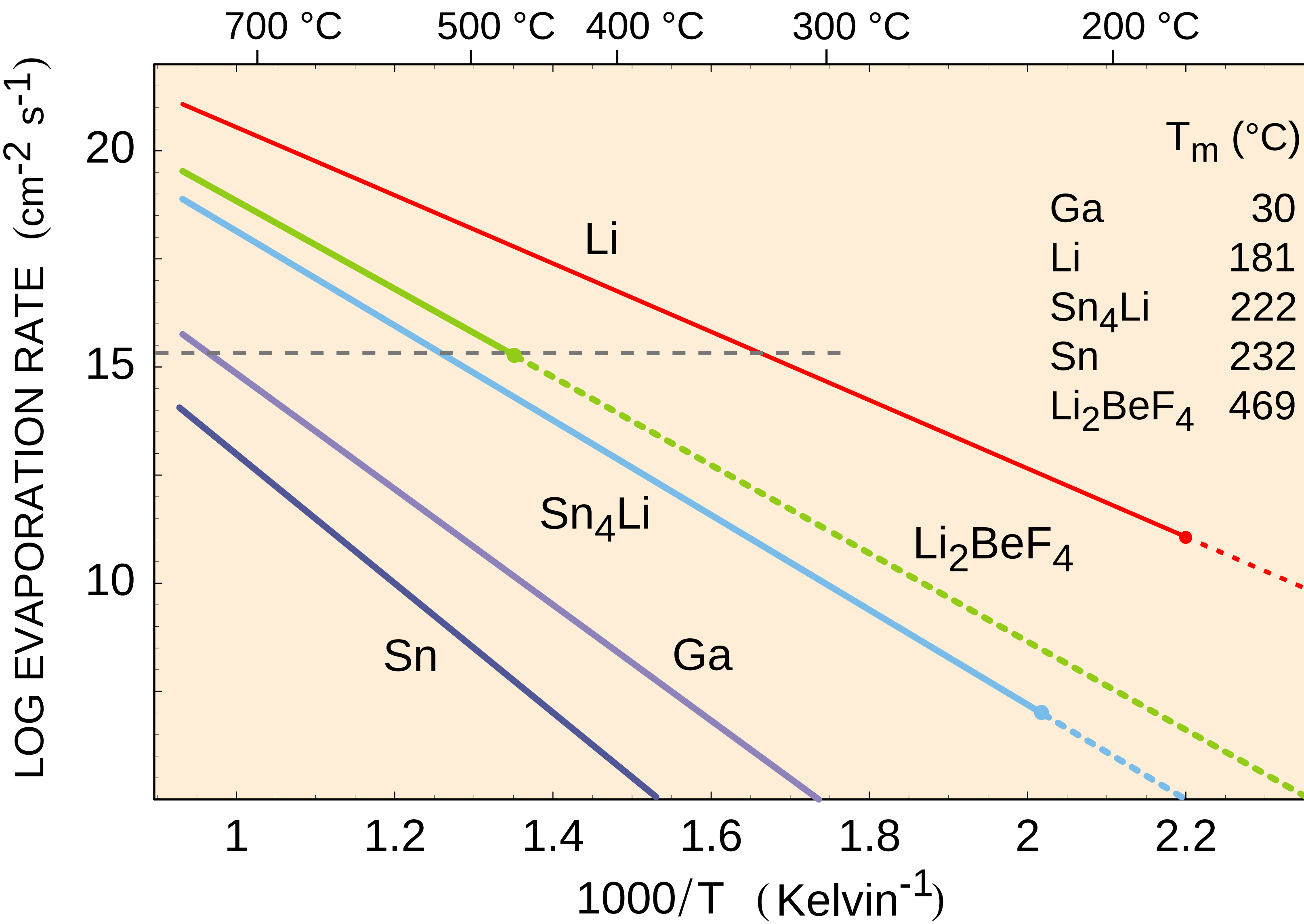
Need: Experimental data on liquid surfaces needed to properly model conditions that will exist in a fusion reactor.

Tasks:
- Examine surface composition of candidate liquids
- Consider how surface composition will evolve during plasma exposure due to combined effects of:



> evaporation
> sputtering / redeposition
> segregation
> adsorption / implantation.

Evaporation rates for candidate liquids



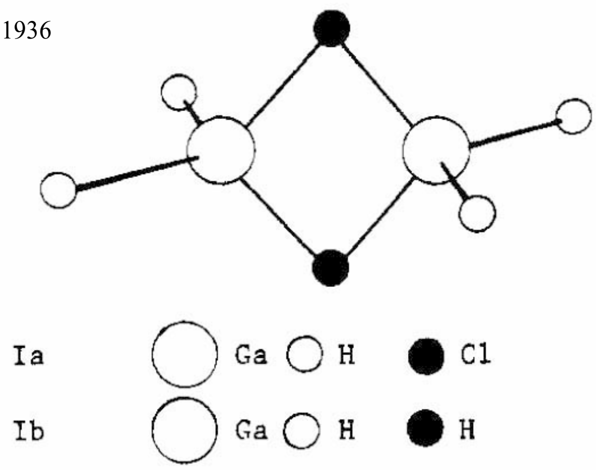
Melting points and densities of some Li, Ga, and Sn containing materials

material	melting point (°C)	density (g/cm^3)
SnH_4	–146	
⇒ Ga_2H_6	– 50	
⇒ Ga	29.76	5.91
Li	180.5	0.534
Sn_4Li	222	
Sn	231.93	7.265
LiH	688.7	0.78
Li_7Sn_2	783	
Li_2O	1570	2.013
SnO_2	1630	6.85
⇒ Ga_2O_3	1807	6.0

Gallium hydride exists, but is not easily formed.

1936

J. Am. Chem. Soc. **1989, *111*,** 1936-1937



Gallane at Last! Synthesis and Properties of Binary Gallium Hydride

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The uncoordinated binary hydride of gallium is terra incognita beyond the vapor-phase transients GaH[1a] and GaH_3.[1b] This has not been for want of exploration. As early as 1941 Wiberg et al. laid claim to the synthesis of the free hydride via two routes[2] Neither stood the test of subsequent reexamination[3a],but Greenwood and Wallbridge[3b] presented analytical and spectroscopic evidence for displacement reaction 1. More recent studies,

$$Me_3N{\cdot}GaH_3 + BF_3 \xrightarrow{-15\ C} 1/x[GaH_3]_x + Me_3N{\cdot}BF_3 \quad (1)$$

viscous liquid

Gallane first isolated in 1989

but **Ia** is also a liquid even at quite low temperatures and therefore susceptible to more efficient mixing with the hydride ion source ($MGaH_4$). We find that **Ia** reacts in vacuo with freshly prepared $LiGaH_4$ at -30 C to give not only substantial quantities of elemental gallium and hydrogen but also a volatile product, shown to be gallane, typically in amounts of 4-40 mg and yields of ca. 5% based on eq 2. Operations were carried out at a pressure of

$$1/2[H_2GaCl]_2 + LiGaH_4 \xrightarrow[\text{neat reagents or n-octane}]{-30\ C} 1/x[GaH_3]_x + LiGaH_3Cl \quad (2)$$

$< 10^{-4}$ mmHg in an all-glass apparatus which had been preconditioned by heating under continuous pumping, with short distillation paths and the maintenance of all glassware to which the gallane had access at temperatures < -20 C. Gallane condenses as a white solid which melts at ca. -50 C and has a vapor pressure at -63 C of ca. 1 mm Hg.

(a) Elemental analysis confirmed that the compound contained no chlorine, only gallium and hydrogen. The reaction with an excess of anhydrous HCl at -95 C resulted in the quantitative formation of $GaC1_3$ and H_2 in accordance with eq 3.

$$1/x[GaH_3]_x + 3HC1 \longrightarrow GaC1_3 + 3H_2 \quad (3)$$

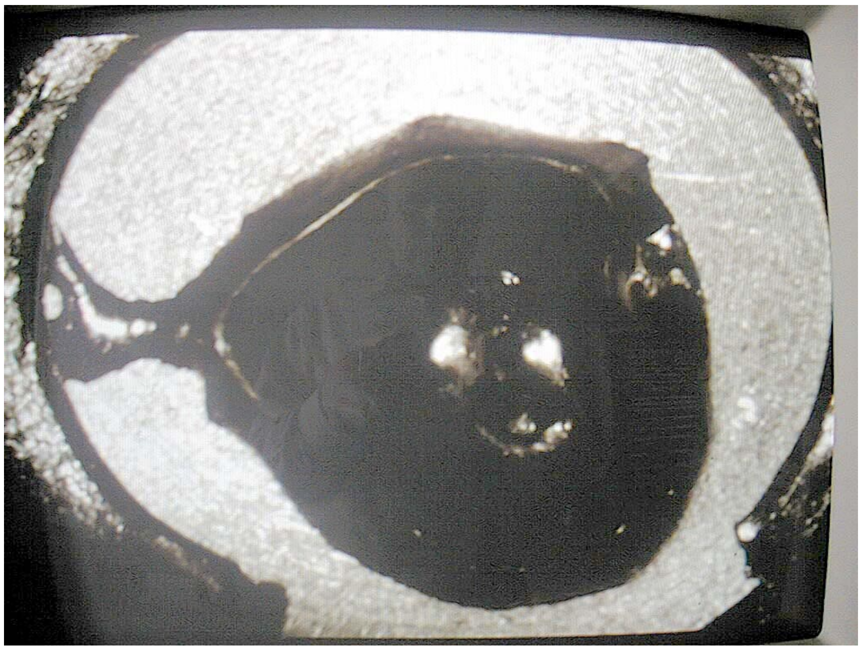
(b) IR Spectrum. A film of the annealed solid compound at 77 K displayed an IR spectrum resembling that of the condensate formed by the vapors derived from the reaction of an excess of NaGaH, with GaC13,5with three main absorptions at 1978 **(s),** 1705 (**s,** br), and 550 cm-1 (**s,** br), which shifted to 1422, 1200, and 400 cm-', respectively, for the perdeuterated compound. Very different spectra were exhibited by the vapor (Figure 1) or by solid matrices formed by codepositing the vapor with an excess of Ar, Kr, or N2 at ca. 20 K. Here the pattern and energies of the absorptions-with two distinct features near 2000 cm-l attributable

Surface analysis of liquid gallium

- Liquid Ga was prepared by melting sputter-cleaned, high-purity Ga in vacuum.
- The composition of the liquid Ga surface was measured using an ion beam probe for both:
  - low-energy ion scattering (LEIS)
  - direct recoil spectroscopy (DRS).
- Surface composition measurements were obtained from 25 °C up to 500 °C.
- Clean liquid Ga surfaces were examined during exposure to molecular D_2(g) and atomic D.

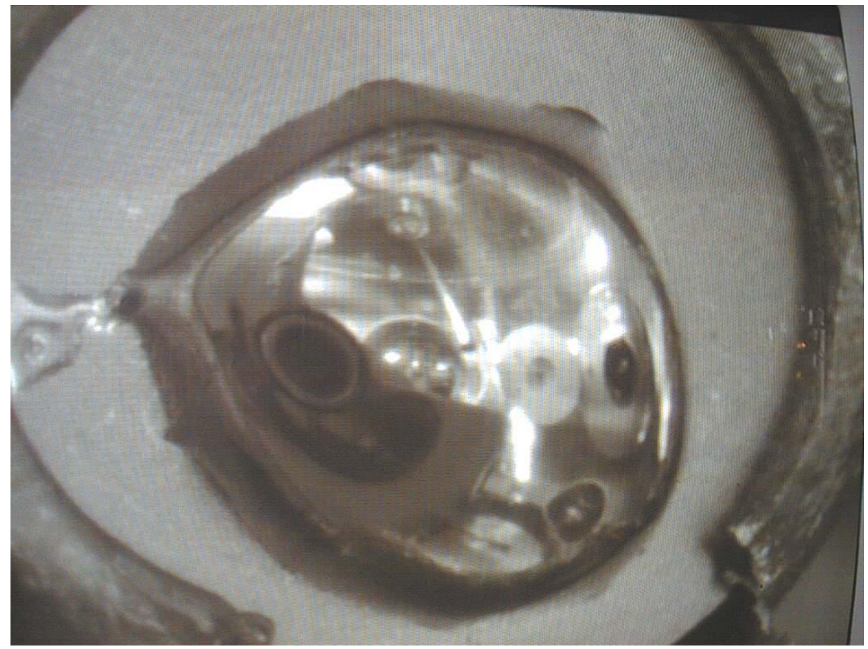
Appearance of solid and liquid Ga surface

solid



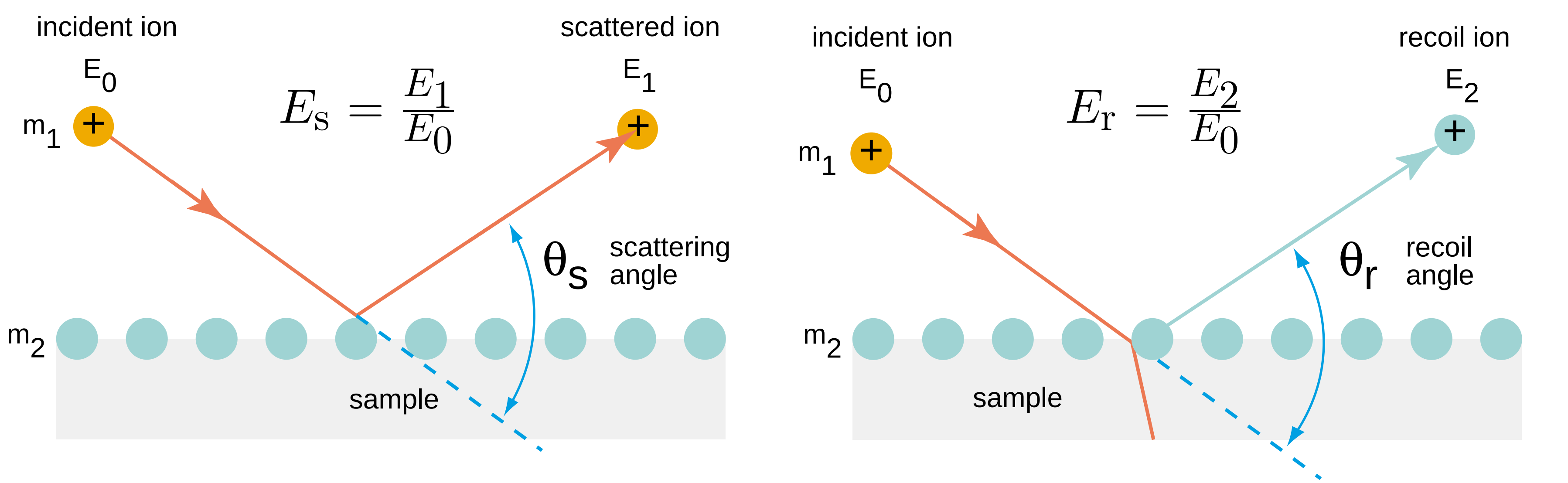
≈25 °C

liquid



≈100 °C

Surface measurements consist of aiming an ion beam at the surface and measuring the energy of scattered and recoiled ions.

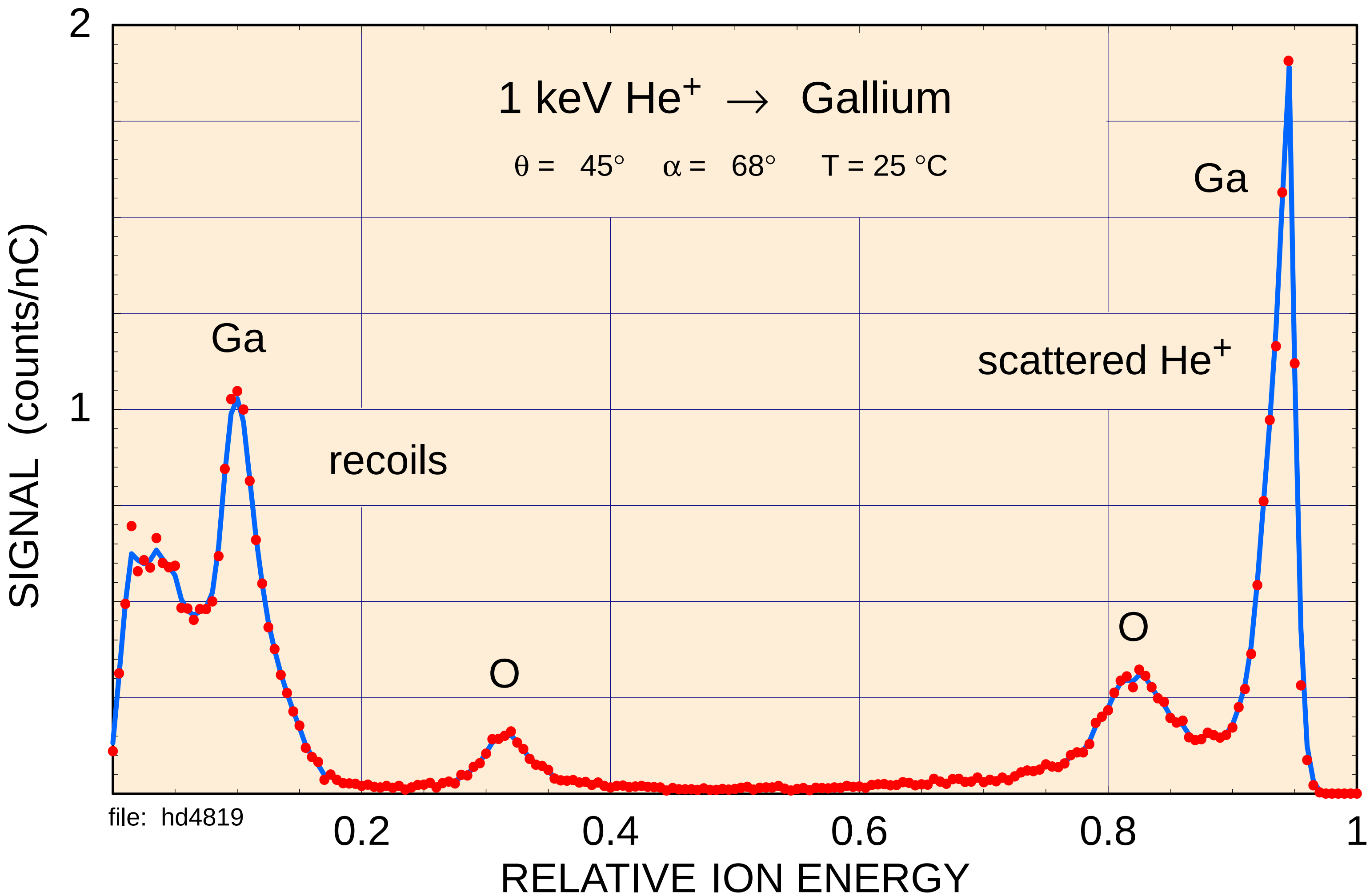


$$m_2 = m_1 \frac{1 + E_s - 2\sqrt{E_s}\cos\theta_s}{1 - E_s - Q_n}$$

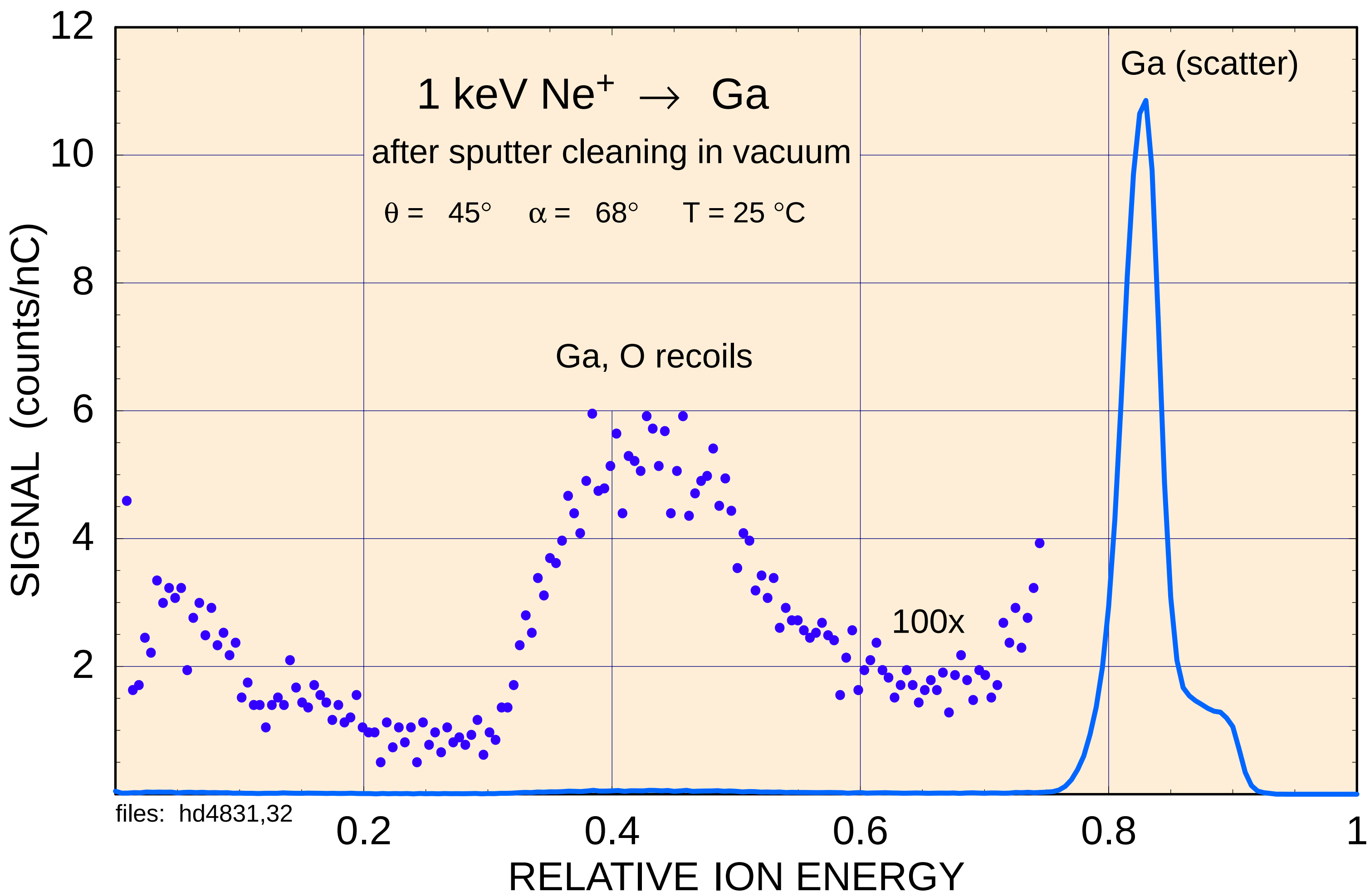
$$m_2 = m_1 \frac{\left(\cos\theta_r \pm \sqrt{\cos^2\theta_r - E_r - Q_n}\right)^2}{E_r}$$

Q_n = inelastic energy loss

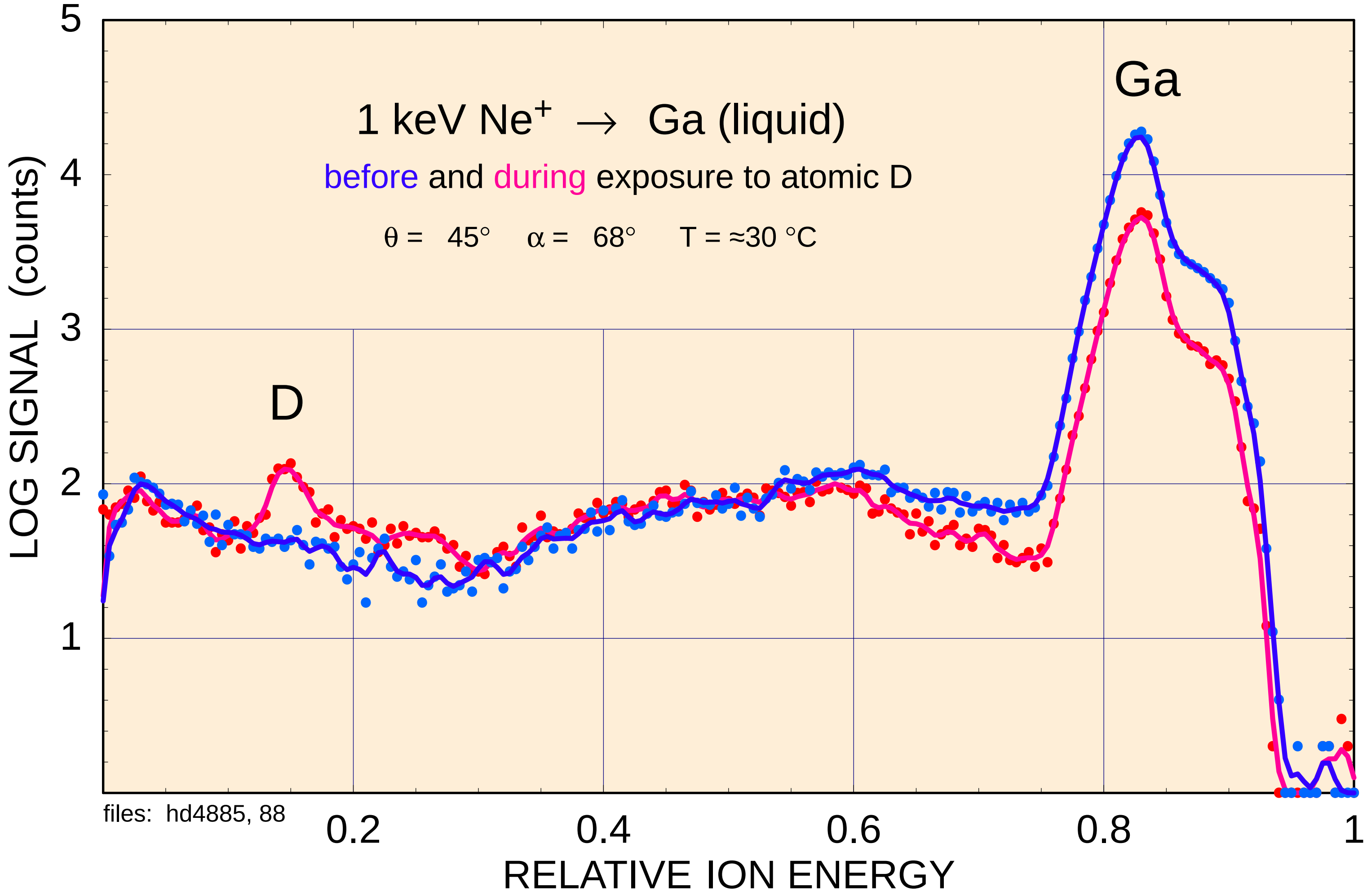
Oxygen is initially present on the Ga surface.



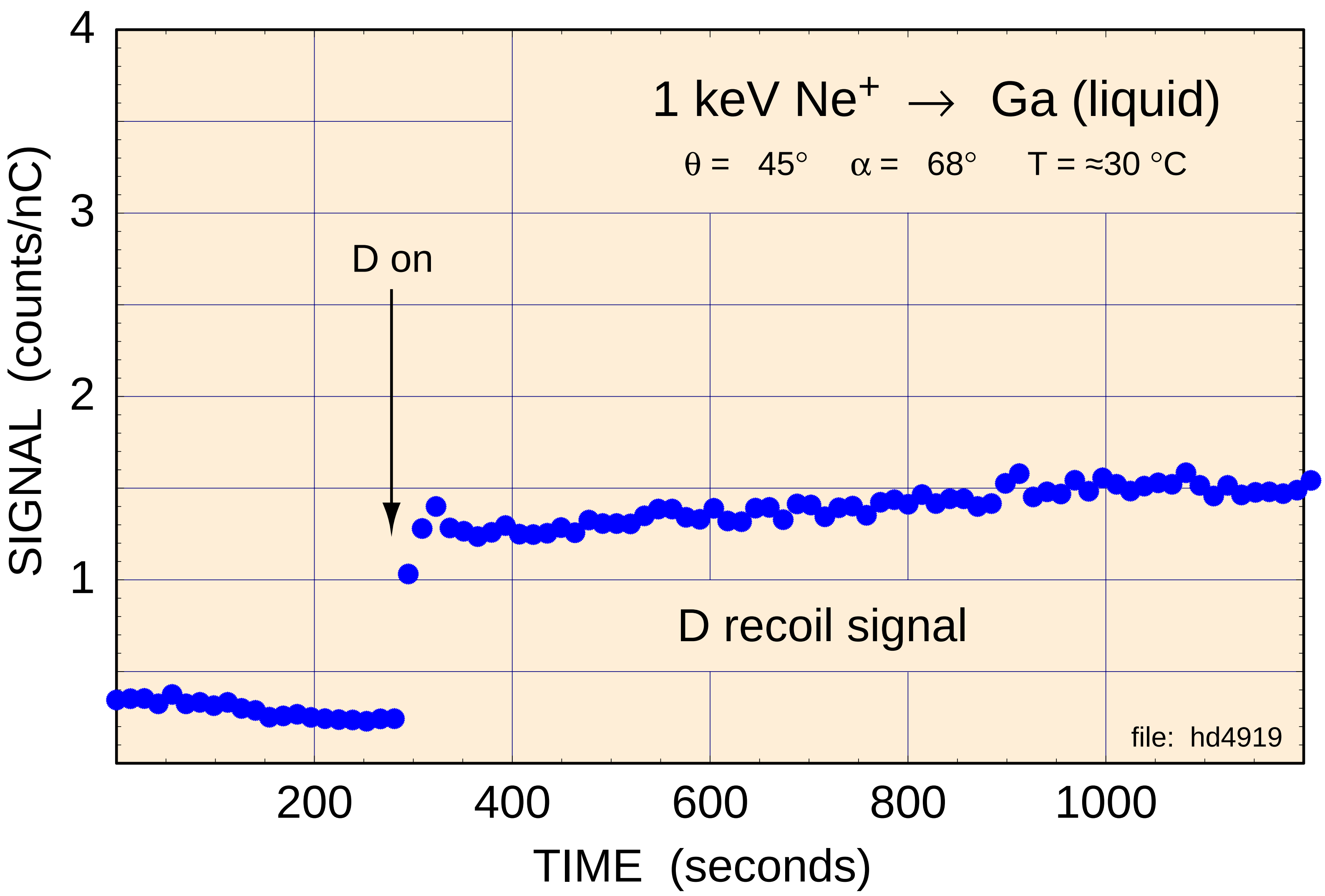
Surface of sputtered Ga in vacuum is clean.



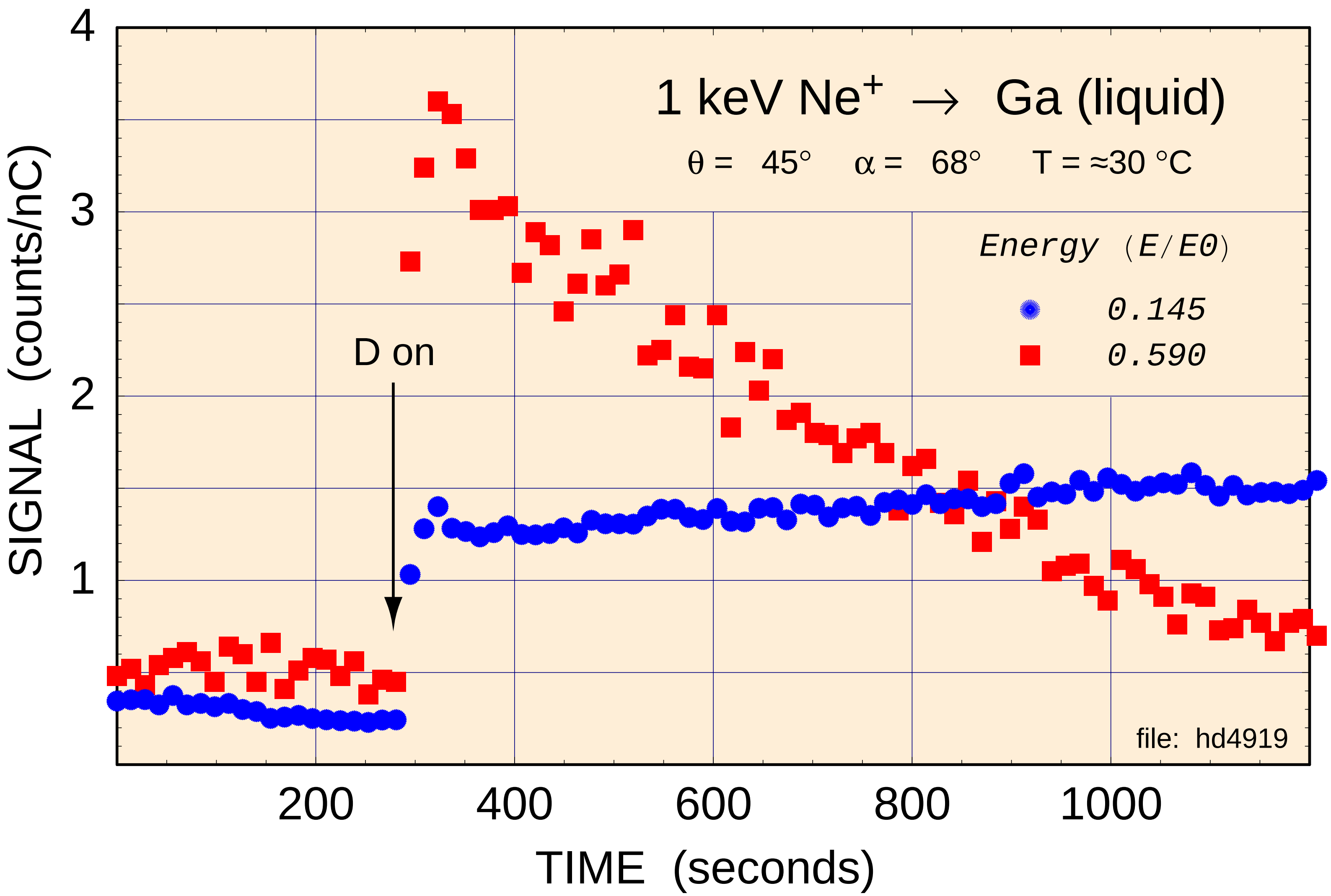
Atomic D adsorbs on liquid Ga at 30 °C.



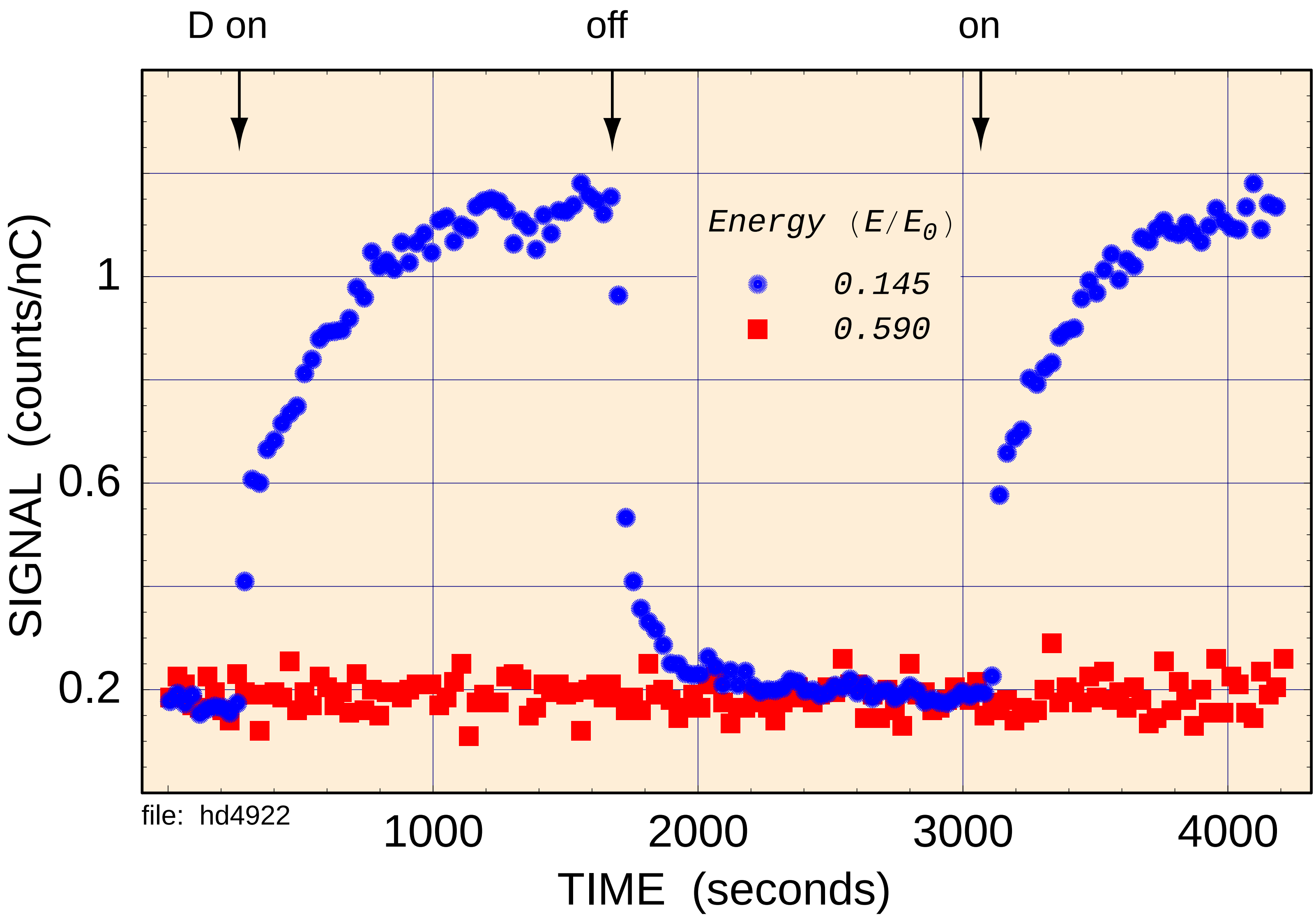
Surface D level rises during D exposure.



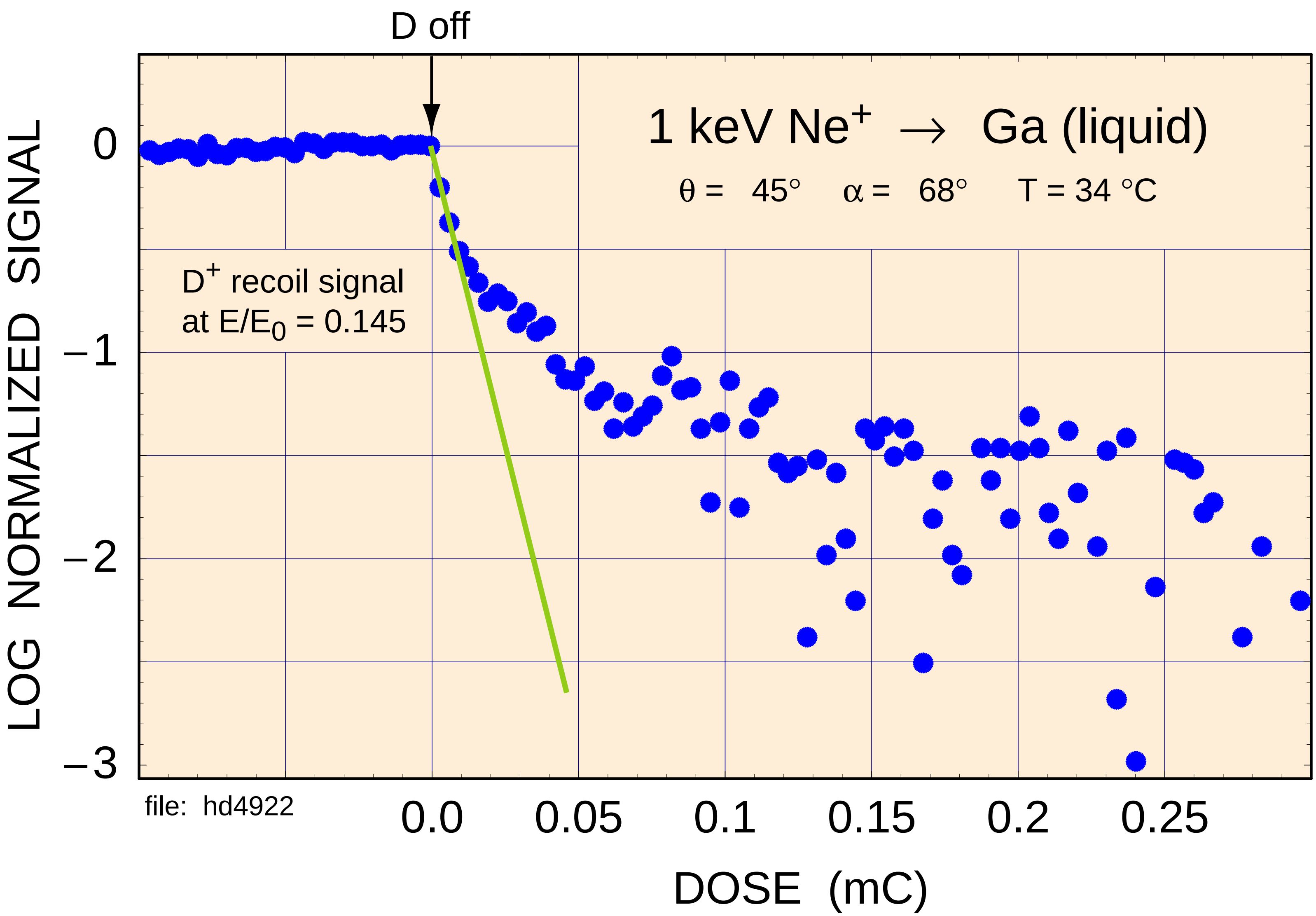
A transient feature appears with D exposure.



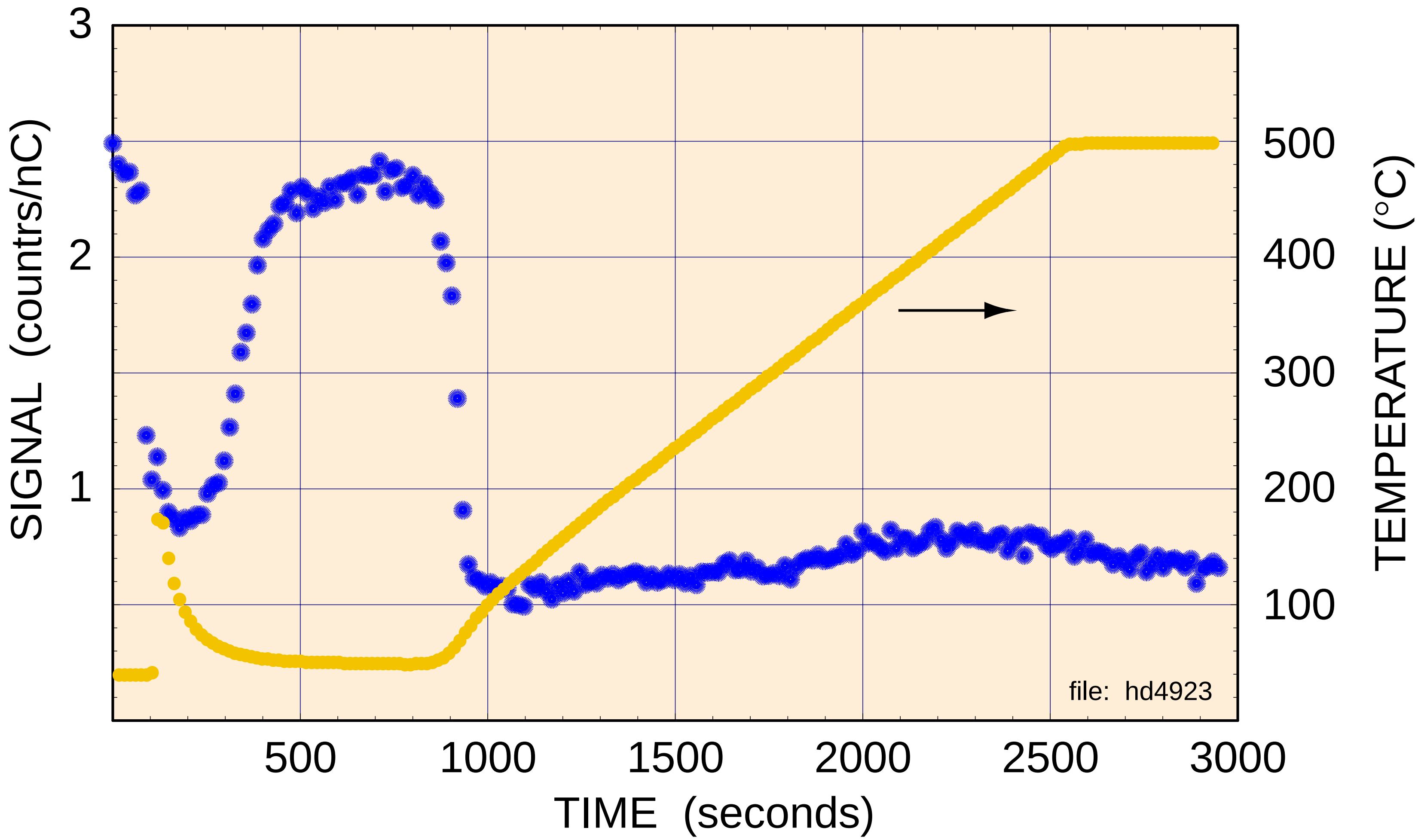
D adsorption is clearly observed on clean Ga.



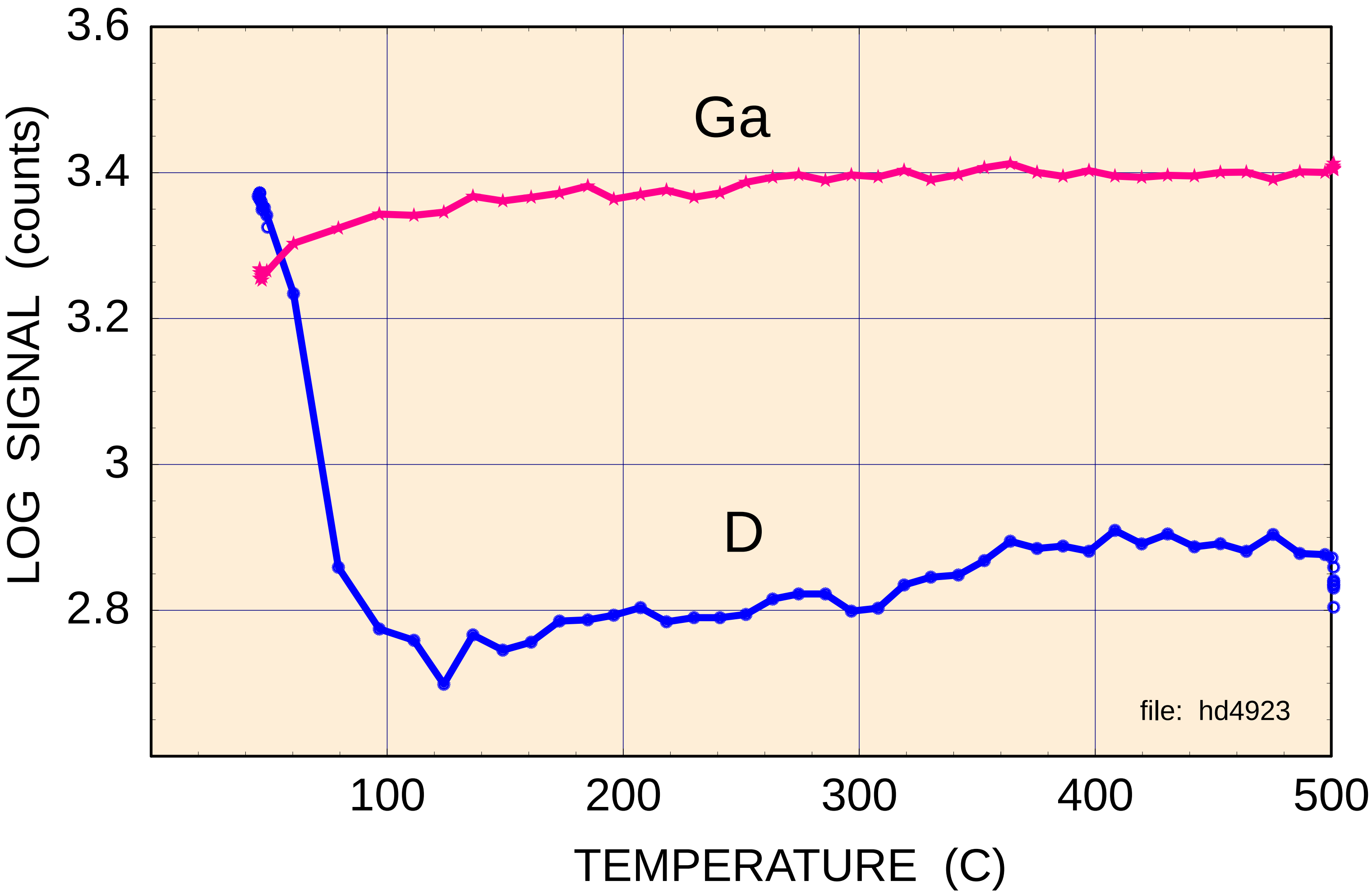
D signal decay gives IID cross section.



D disappears from Ga surface above 100 °C.



Temperature dependence of D on Ga surface



D_2 and D adsorption on Li, Ga, and Sn

Adsorbed D is found under the following conditions:

during exposure to D_2		
material	*solid*	*liquid*
Li	Yes	Yes
Ga	No	No
Sn	No	No

during exposure to D		
material	*solid*	*liquid*
Li	Yes	Yes
Ga	?	Yes
Sn	Yes	No

Summary

- No adsorption of molecular D_2 on Ga observed.
- Atomic D adsorbs on liquid Ga surface at $\leq$100 °C.
- Almost no D seen on surface at higher temperatures (up to 500 °C).
- Surface D efficiently removed by ion impact.
- Surface contamination of liquid Ga may be an issue.

$\Rightarrow$ With respect to H isotopes, liquid Ga surfaces appear to be less reactive than Li, but more reactive than Sn.

Future work

- Measure D re-emission from D loaded Ga.
- Examine contamination effects in more detail.
- Evaluate the cross section for ion impact desorption of D from Ga.
- Explore detection of He on liquid metal surfaces by LEIS.