Electronic supplementary information for

Radical theory of hydride atomization confirmed after four decades –
determination of H radicals in the quartz hydride atomizer by two-photon absorption laser-induced fluorescence

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ESI includes:

Materials and methods
Fig. S1
Notes and references
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Reagents. Compressed gases Ar (99.996%), H₂ (99.95%) and O₂ (99.5%) were produced by SIAD Czech, Ltd., Czech Republic. Kr diluted in Ar (from 1:50–1:400) obtained from Linde, Czech Republic was used for calibration measurements.

Atomizer. T shaped externally heated quartz atomizer identical as described in Refs.²⁷,⁸¹-⁸² having a rectangular cross-section of the optical (longitudinal) arm was employed (see Fig. 2). It was fused from two quartz microscope slides 15 mm × 75 mm (1 mm thick) and two quartz spacers 3 mm × 3 mm (75 mm long) so that the horizontal and vertical, respectively, walls of the optical arm were 3 mm and 1 mm thick. The slides and spacers were purchased from UQG Optics Ltd., England. A deactivated fused silica capillary (Supelco, Germany, 0.53 mm i.d., 0.74 mm o.d.) was centered inside the inlet arm. The optical arm was resistively heated by a kanthal wire (4.17 Ω m⁻¹, 0.65 mm in diameter powered by a laboratory power supply source (PS 3065-10 B; E-A, Elektro-Automatik GmbH, Viersen, Germany). The wire, not shown in Fig. 2, was spiraled around the optical arm to maintain the distance between neighboring wire coils 2 to 3 mm and no thermal insulation was used to keep the optical arm walls transparent for the fluorescence radiation. The temperature distribution inside the optical arm was rather homogeneous, ca 850 °C, in the 50 mm long central section (± 25 mm longitudinally from the optical arm centre). Towards optical arm ends, the temperature decreased to ca 800 °C at coordinates ± 30 mm to reach 420 °C close to the optical arm ends (± 35 mm from the optical arm centre). The inlet arm served to deliver Ar, H₂ and Kr diluted in Ar. If not explicitly stated otherwise the flow rates of Ar and H₂, respectively, were 125 and 15 ml min⁻¹. The capillary was used to deliver O₂ flow rates up to 12 ml min⁻¹. If explicitly stated O₂ was delivered not to the
capillary but to the inlet arm together with Ar and H₂. The temperature inside the inlet arm decreased steeply with the distance from the junction of both arms: from 700 °C at the junction (vertical coordinate 0 mm) to 500 °C at the coordinate of 10 mm, to reach 200 °C at the coordinate of 20 mm. All the temperatures were measured by a thermocouple under flow rate of neat Ar - the determined temperatures were not significantly influenced by varying the gas flow rate between 0 and 125 ml min⁻¹.

**TALIF instrumentation.** The scheme of the experiment is shown in Fig. 1. A three component laser system consisting of a Q-switched pumping laser (Quanta-Ray PRO-270-30), a dye laser (Sirah, PRSC-D- 24-EG) and a frequency tripling unit was used to produce short laser pulses at the frequency of 30 Hz, with duration 8 ns, spectral width 0.06 cm⁻¹ and wavelength of 205 or 204 nm for the two-photon excitation of atomic hydrogen or krypton, respectively.

Inside the whole optical arm, the dimensions of the laser beam profile were significantly smaller than the inner dimensions of the optical arm cavity (7 mm × 3 mm). Due to the principle of krypton calibration, each spatial variation of laser beam profile was taken into account and compensated during the processing of measured data.

The fluorescence radiation at 656.3 nm passing through the vertical wall was recorded perpendicularly by an intensified charge coupled device camera (Princeton Instruments - MAX 1024RB- 25-FG43) with an interference filter. The spatial resolution of the camera was 0.04 mm. The image never included the optical arm sections at the longitudinal distance higher than ± 15 mm from the optical arm centre. If not explicitly stated otherwise, the image was corrected to the radiation from the hot resistance wire by subtracting the signal measured without laser. In order to increase the signal-to-noise ratio, typically 500 accumulations of the signal on the camera chip were used.
The energy of each pulse was detected by the pyroelectric energy sensor (Ophir PE9). The energy of laser pulses was varied between 20 and 300 μJ. No saturation effects originating from depletion of the ground state, photoionization of the excited state or stimulated emission from the excited state were observed.

**Uncertainty of H concentration values.** The standard deviation of experimental data measured at identical conditions in one experiment was a few percent, which indicates good reliability of measured trends. Uncertainty of absolute concentration values was higher due to effects like slow variations of laser-beam profile which manifest themselves by typically 20% variation of concentration values measured on different days. Finally, the uncertainty of results is increased by the uncertainties of published constants that were used for the calculation of H concentration. All these factors together lead to the uncertainty of absolute H concentration values around 50%.
**Fig. S1.** Vertical laser-beam profile. This distribution of relative laser intensity was estimated from square root of TALIF signal of homogeneously distributed Kr atoms. The zero position is placed to the inner surface of the bottom wall of the optical arm.

**Notes and references**