Surface interaction of selected transition metals and semiconductors with H_2 plasma generated species

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Introduction

Plasmas are convenient sources of radiation and energy for driving chemical and physical processes. The interaction between plasma constituents and matter results in a multitude of pathways for e.g. ionization and/or the initiation of chemical reactions.

The reactivity of excited hydrogen towards tin and in general elements of the 14th group of the periodic table (Carbon group, group IV) has been described in the literature for decades. Likewise, the thermodynamic instability of the resulting metal hydrides and the catalytic effect of metal surfaces regarding their decomposition is known since long. This chemistry has recently gained importance for the modeling of high energy H_2 plasmas in the presence of tin, which requires knowledge of the neutral and ionic reaction channels and mechanisms.

The initial interaction in the formation of metal hydrides is a heterogeneous gas/surface reaction of excited atomic H and metal atoms M, in which successive H-M bonds are formed. The volatile metal hydrides thus formed subsequently desorb and may subsequently adsorb on other (metal) surfaces and decompose.
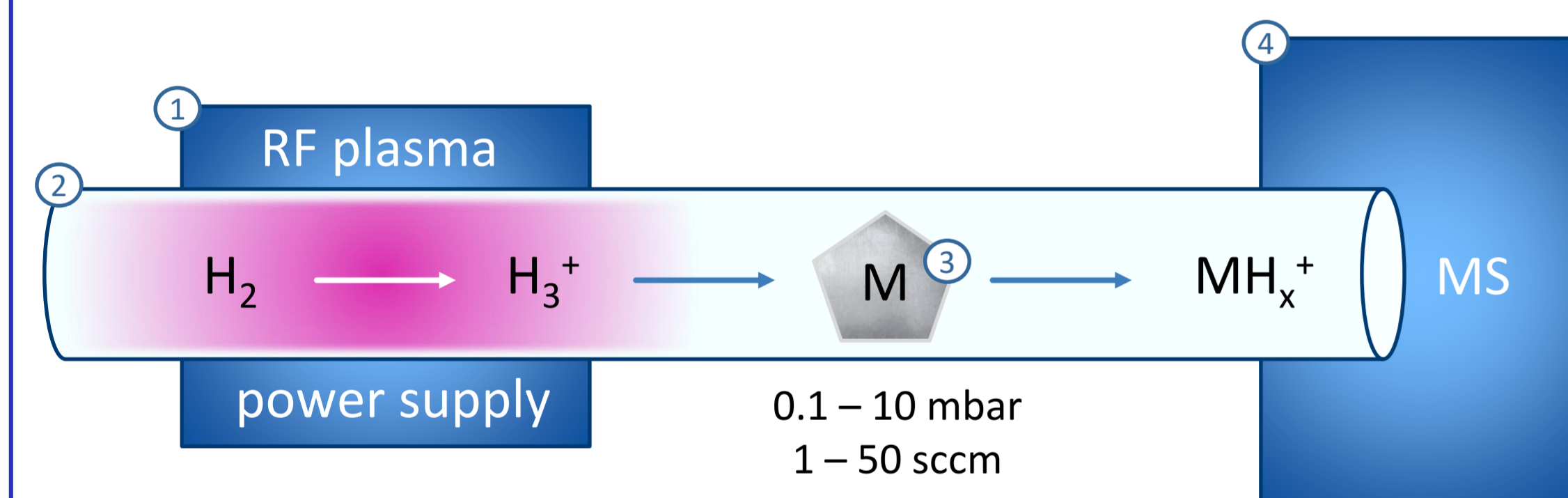
Experimental setup

Fig. 1: Schematic setup and simplified mechanism of metal hydride formation

A custom low-pressure RF discharge generates the reagent ions H_3^+ within a hydrogen plasma fed by an adjustable continuous gas flow (**1**). The plasma source consists of an electrode-less, helical coil resonator (HCR) providing the RF energy to sustain the discharge, which is classified as a high density plasma [**1**]. Typical operation pressures range between 0.1 and 10 mbar.

The continuously generated ions are brought into contact with the solid metal samples (**3**) by the gas flow within the glass tube (**2**). The tube itself is additionally pumped by the first differentially pumped stage (0.1 – 10 mbar) of the used time of flight mass spectrometer (TOF-MS) (**4**).

Methods

Mass spectrometer:	C-TOF time of flight mass spectrometer equipped with custom ion transfer stage (TOFWERK AG, Thun, Switzerland)
RF power supplies:	Modified VUV lamp RF power supplies (Heraeus GmbH, Hanau, Germany)
Gases:	Hydrogen 5.0 and Argon 5.0 (Messer Group GmbH, Krefeld, Germany)
Software:	Gaussian 16. [5] and GaussView 6.0.16
UV-Vis spectrometer:	iHR 320 (Horiba, Kyoto, Japan)

Basic chemical assumption

The RF discharge primarily generates electronically excited H species and H^+ ions. The latter react with molecular hydrogen to form H_3^+. In the presence of N_2 or synthetic air N_2H^+ and also N_4H^+ are readily formed. In contrast to H_2, the adsorption of reactive H species leads to a subsequent formation of stannane (SnH_4), which either decomposes on the surface or desorbs into the gas phase [**2,3**].

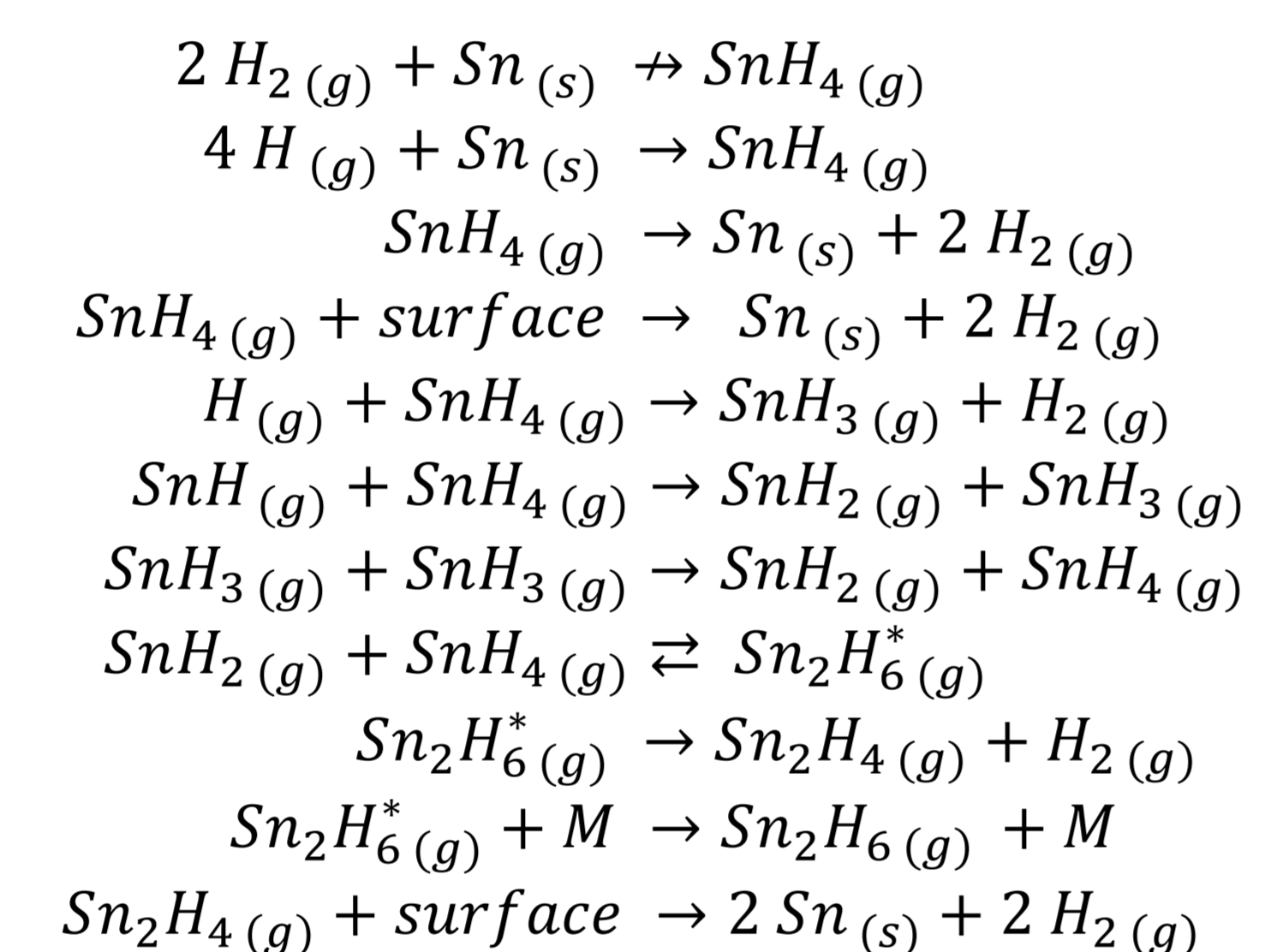Tin oxide is reduced by atomic hydrogen to tin metal and water. In the gas phase, a reaction cascade leads to a multitude of tin hydrides, which is shown in **Fig. 2**.

In this scheme (Eley-Rideal mechanism), more H is consumed than expected by a simple recombination of adsorbed and newly penetrating H atoms.

Stannane tends to spontaneously decay into the elements, a process which is accelerated by reactive surfaces (1st order kinetics [**2**]).

**Fig.3** shows schematically the reaction channels of these tin compounds [3].

$$2\ H_{2\,(g)} + Sn_{(s)} \nrightarrow SnH_{4\,(g)}$$
$$4\ H_{(g)} + Sn_{(s)} \rightarrow SnH_{4\,(g)}$$
$$SnH_{4\,(g)} \rightarrow Sn_{(s)} + 2\ H_{2\,(g)}$$
$$SnH_{4\,(g)} + surface \rightarrow Sn_{(s)} + 2\ H_{2\,(g)}$$
$$H_{(g)} + SnH_{4\,(g)} \rightarrow SnH_{3\,(g)} + H_{2\,(g)}$$
$$SnH_{(g)} + SnH_{4\,(g)} \rightarrow SnH_{2\,(g)} + SnH_{3\,(g)}$$
$$SnH_{3\,(g)} + SnH_{3\,(g)} \rightarrow SnH_{2\,(g)} + SnH_{4\,(g)}$$
$$SnH_{2\,(g)} + SnH_{4\,(g)} \rightleftharpoons Sn_2H_{6\,(g)}^*$$
$$Sn_2H_{6\,(g)}^* \rightarrow Sn_2H_{4\,(g)} + H_{2\,(g)}$$
$$Sn_2H_{6\,(g)}^* + M \rightarrow Sn_2H_{6\,(g)} + M$$
$$Sn_2H_{4\,(g)} + surface \rightarrow 2\ Sn_{(s)} + 2\ H_{2\,(g)}$$

Fig 2: Cascade of elementary reaction steps involving hydrogen and tin hydride compounds [**2**].
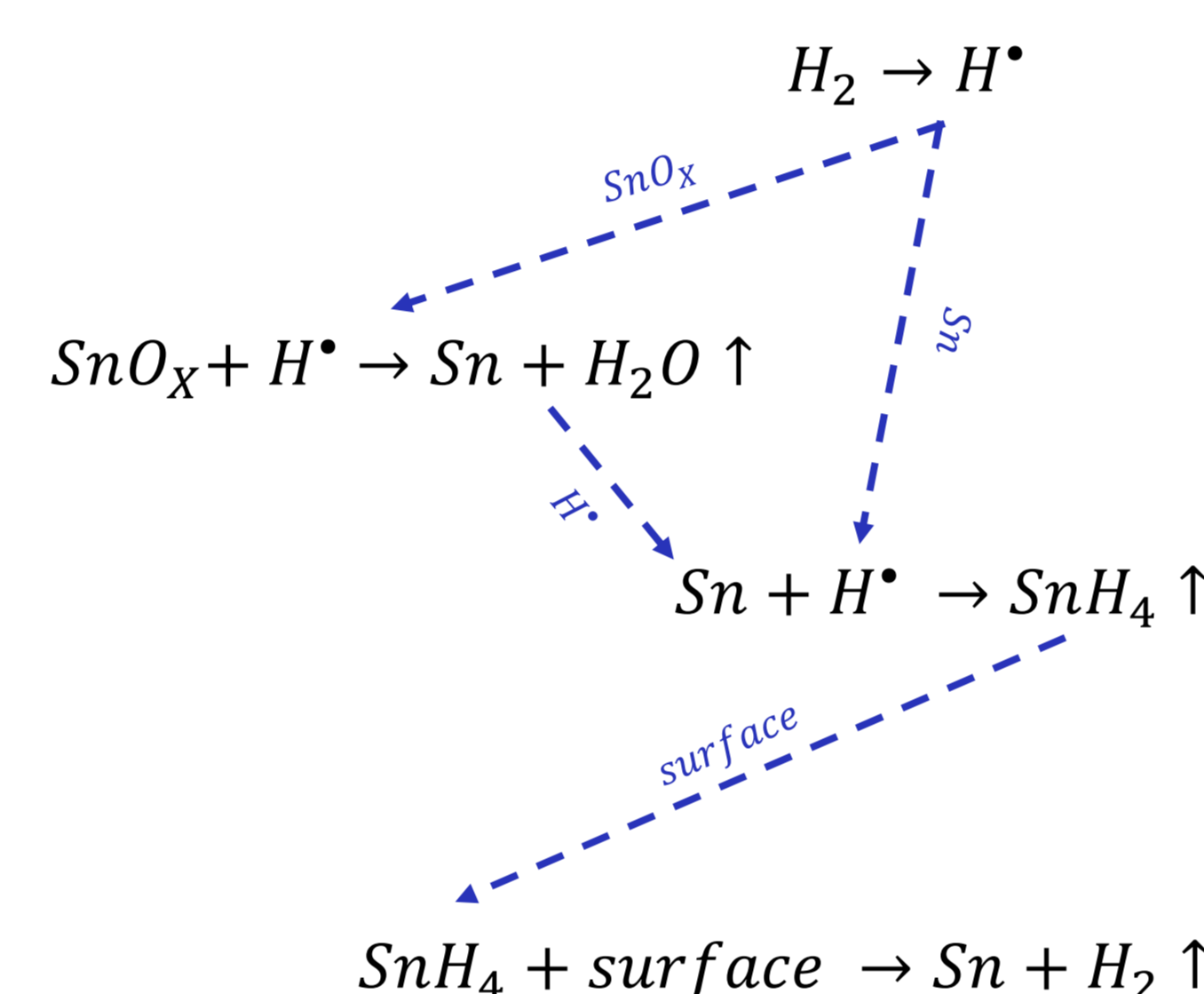
Fig 3: Schematic representation of the reactions channels shown in Fig. 2.

Ab-initio calculations of molecular stabilities

Molecule	SnH_4	SnH_3^+	SnH^+	Sn^+
Energy relative to stannane		+24.549 eV	+56.125 eV	+72.480 eV
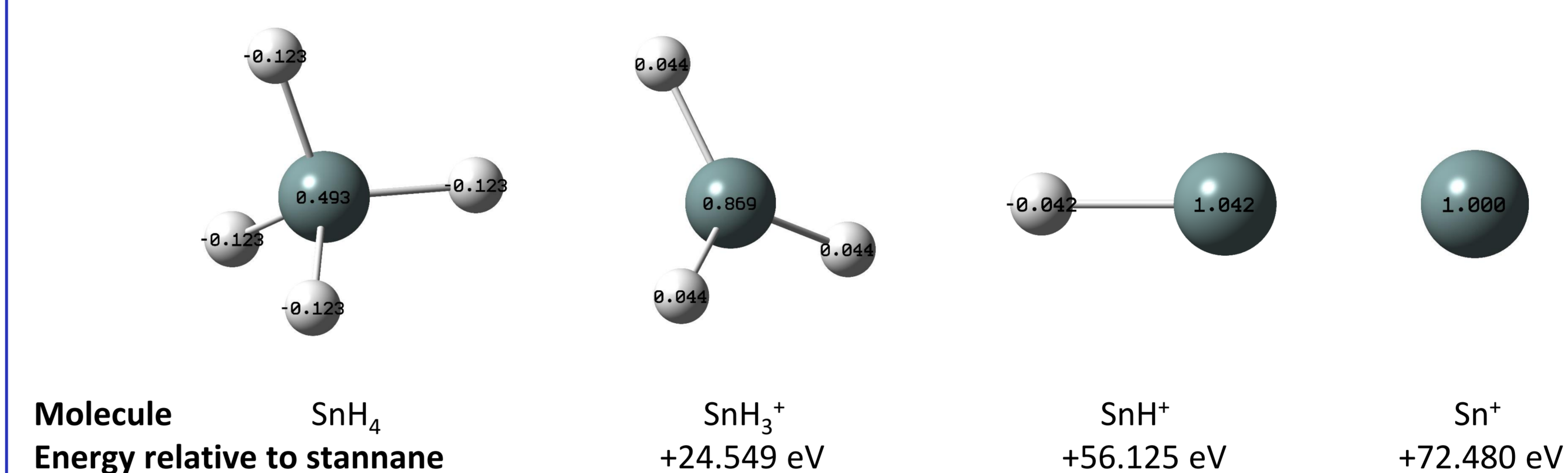
The molecules are labeled with the Mullikan charges. Ab initio calculations of SnH_2^+ and SnH_4^+ did not lead to any stable structures – this is experimentally verified.

Why are SnH_2^+ and SnH_4^+ not detectable?

The Plasma discharge continuously generates a large number of excited hydrogen species. The recombination of these species becomes "visible" through the emission spectrum. The Balmer series is identified in the UV-Vis spectrum, higher transitions of the series are not unambiguously assignable. The broad continuum presumably originates from a combination of Bremsstrahlung and electron recombination emission. The large number of H atoms present causes the inherently unstable tin hydride species to react quickly, presumably forming H_2 and more stable tin hydrides, which are detected by MS.
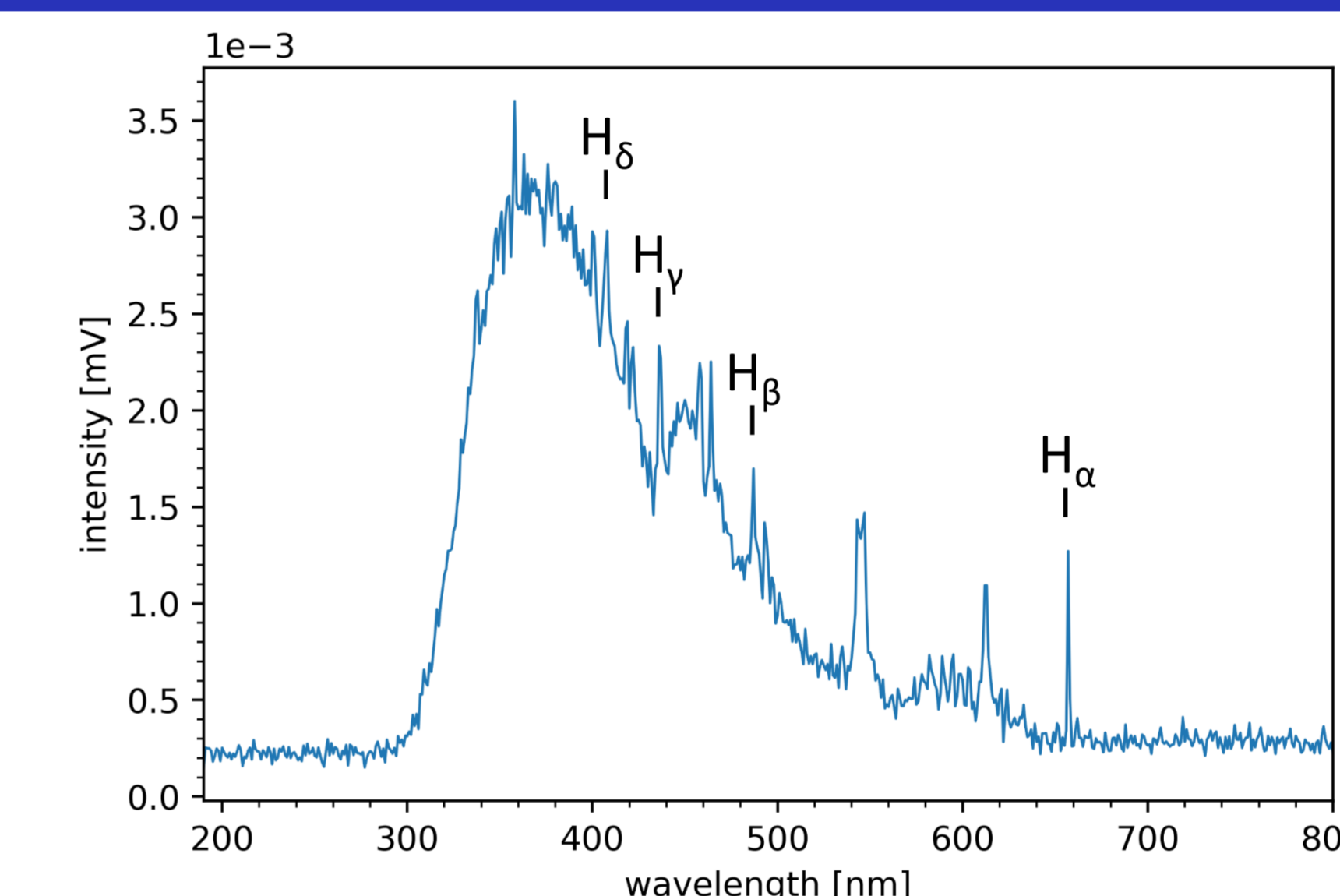

Fig.5: UV-Vis spectrum of the RF hydrogen plasma with marked transitions of the Balmer series.
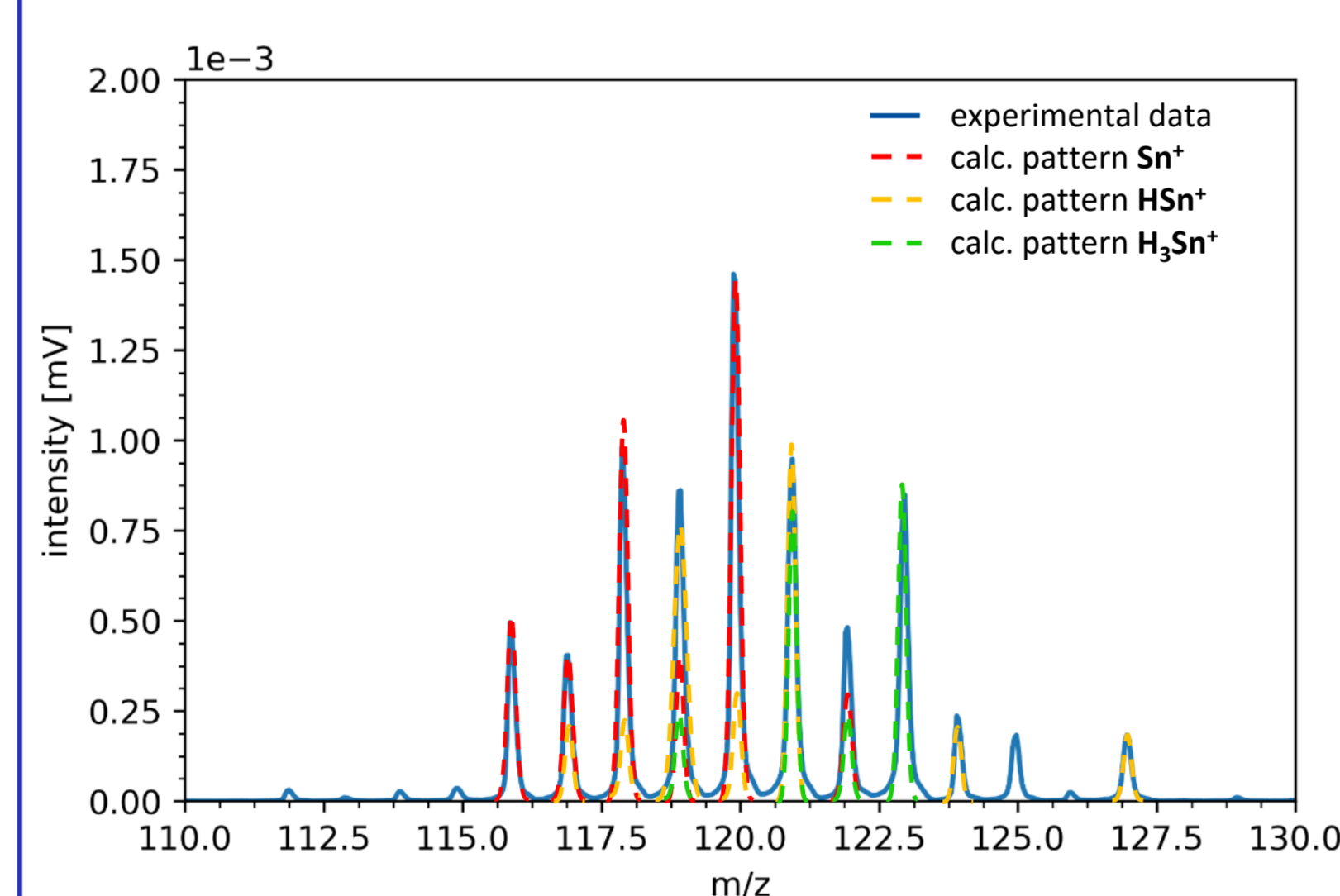
Mass spectra

Fig 6: Recorded mass spectrum of H-plasma generated tin hydrides and calculated isotopic patterns.
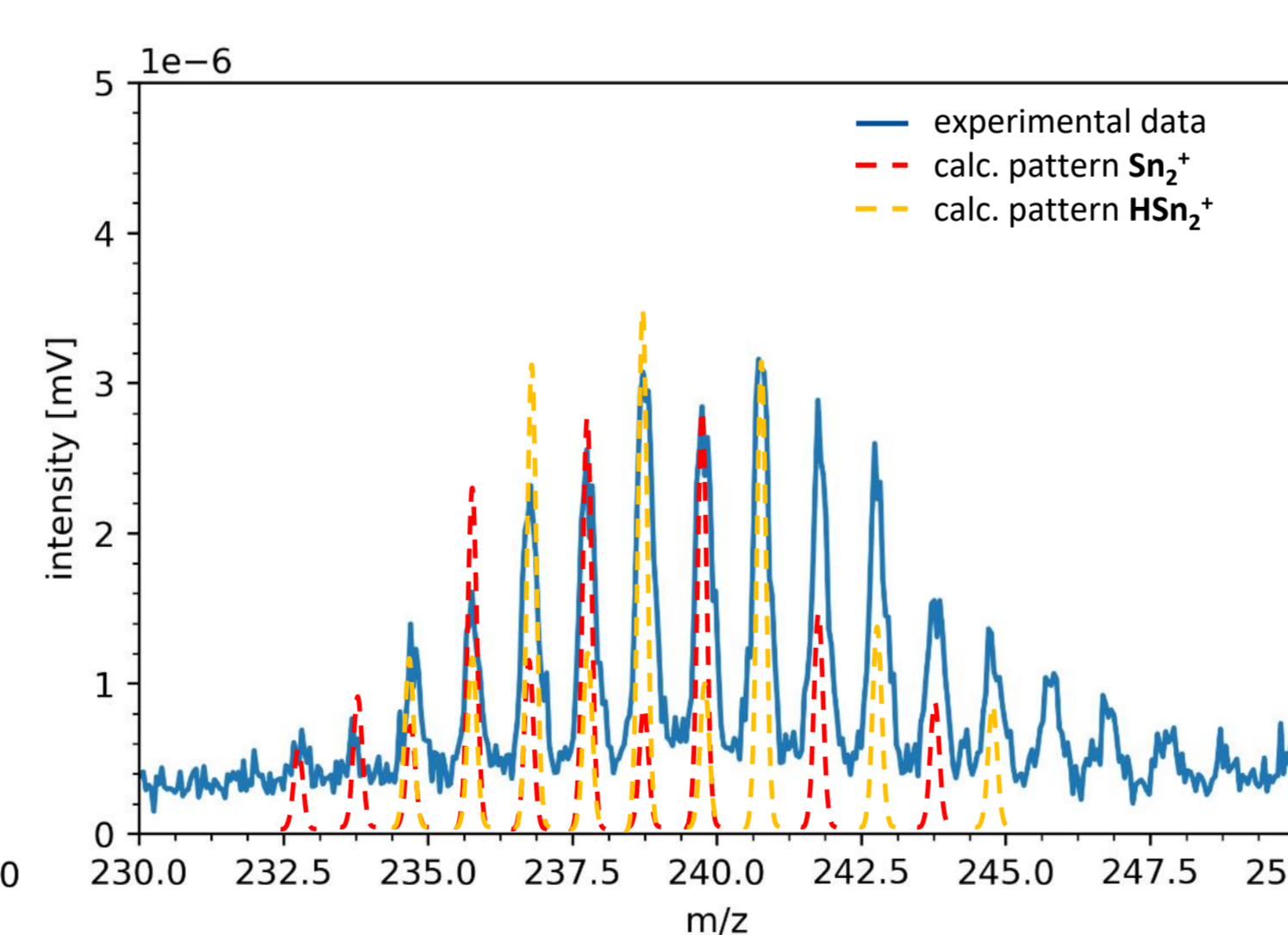
Fig 7: Recorded mass spectrum of H-plasma generated dimeric tin hydrides and calculated isotopic patterns.
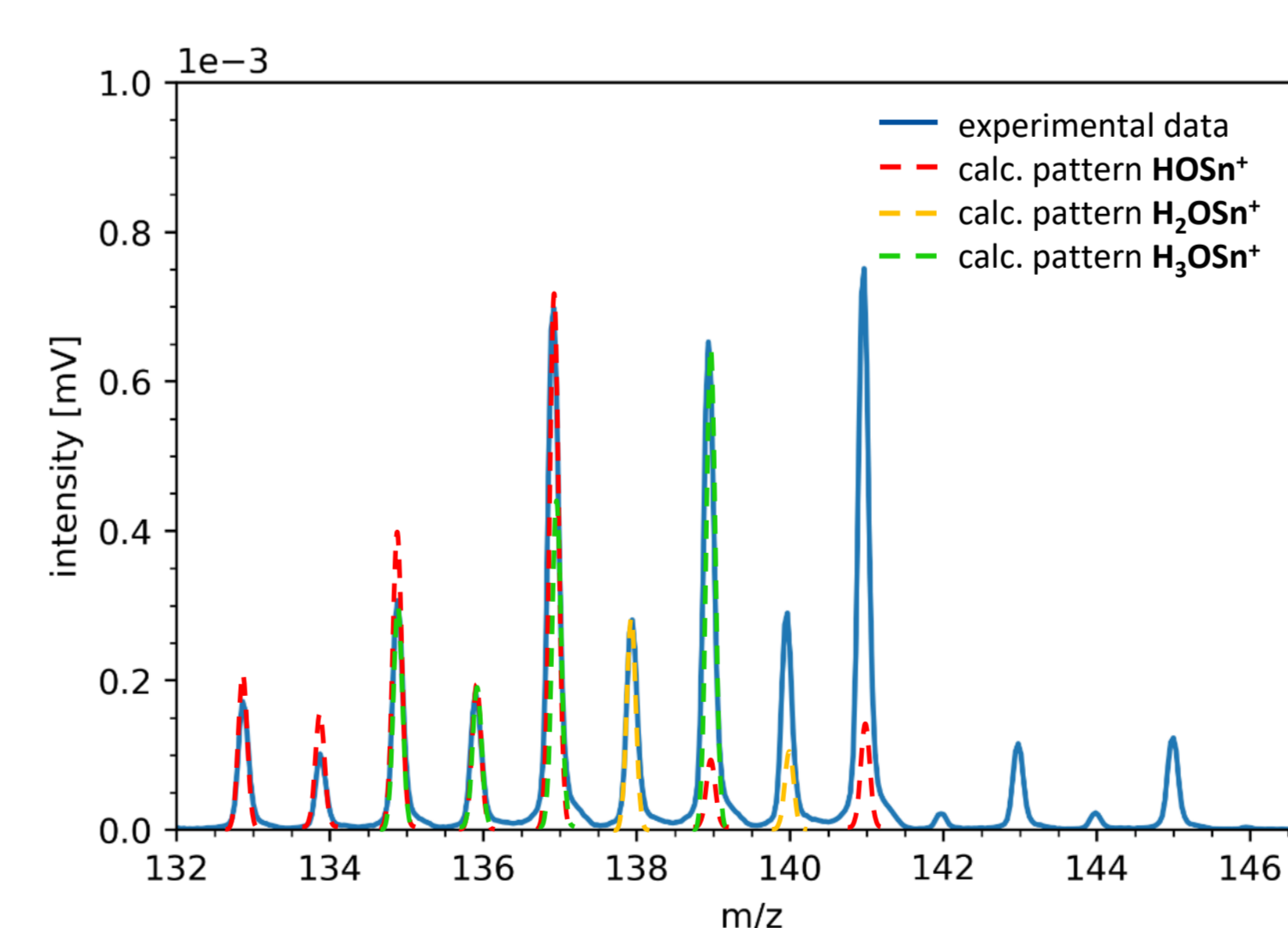
Fig 8: Recorded mass spectrum of H-plasma generated oxygenated tin hydrides and calculated isotopic patterns.
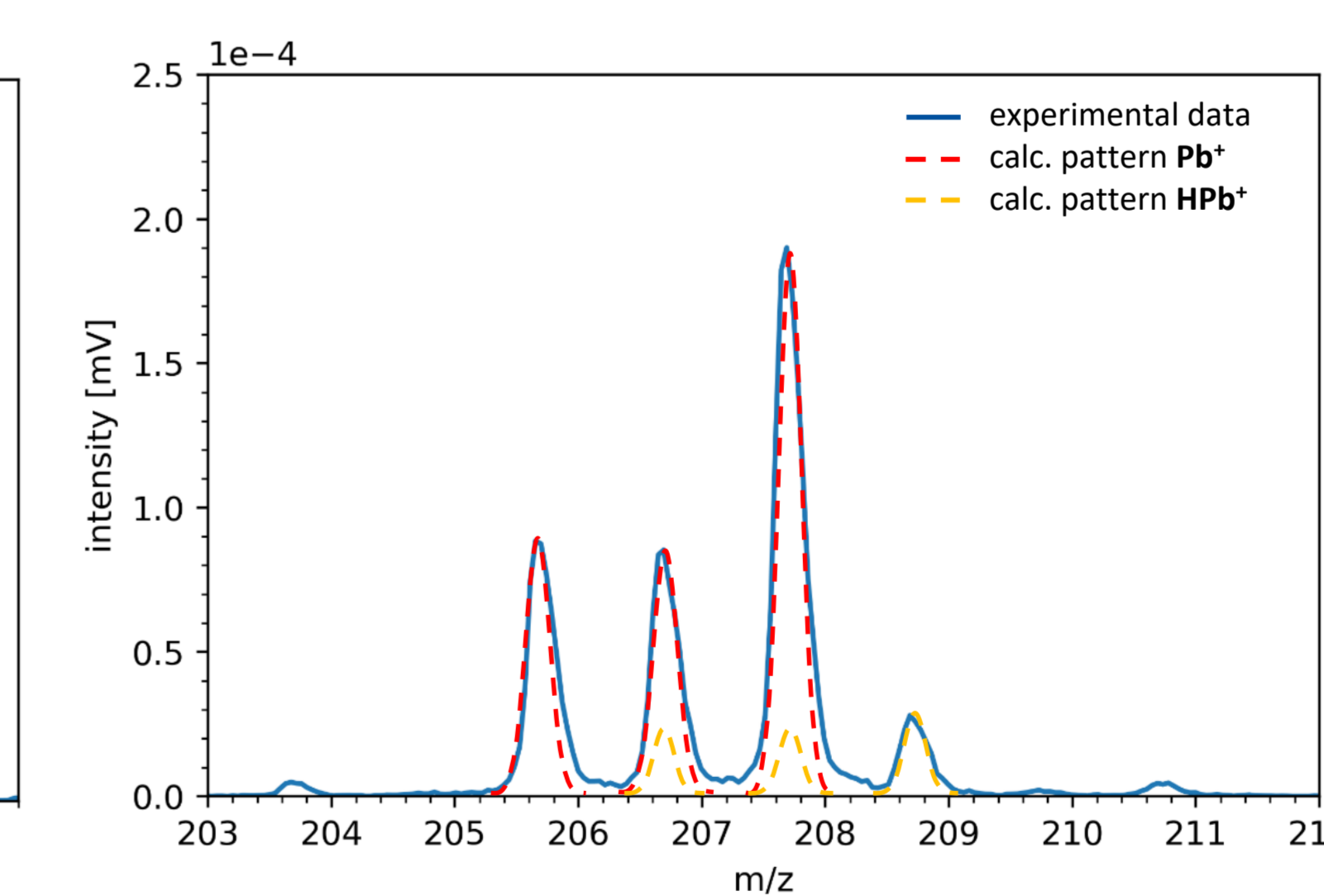
Fig 9: Recorded mass spectrum of H-plasma generated lead hydrides and calculated isotopic patterns.

In the spectra, ionic tin hydrides and oxygenated tin compounds were detected. The comparison of the recorded mass spectrum with calculated isotopic patterns [4] reveals the distinctive patterns of various ionic tin hydrides of the type SnH_x^+, especially SnH_3^+ and SnH^+, while the more unstable SnH_4^+ and SnH_2^+ are absent (see **Fig. 6**).

The dimeric Sn_2H_x compounds formed are also detected but with lower intensities. However, only Sn_2^+ and Sn_2H^+ are present in the mass spectrum, dimers with additional hydrogen atoms were not detected or only to a very small extent (see **Fig. 7**).

The oxygenated compounds of the type H_xOSn^+ mainly originate from the oxidized target surface, rather than from the gas matrix oxygen, as only very high purity gases were used. Most prominently $HOSn^+$ is detected, whereas H_2OSn^+ and H_3OSn^+ are detected to a much lesser extent (see **Fig. 8**).

The characteristic patterns of the Sn isotopes are fully reproduced and thus used for compound identification.

The recorded mass spectra of lead (Pb) compounds are in very good accordance with the calculated isotopic patterns [4]. In addition to Pb^+, only mono plumbane (PbH^+) is observed (see **Fig. 9**). Experiments with nickel (Ni), tantalum (Ta) and silicon (Si) did not result in detectable ionic species, probably due to i) the formation of a protective oxide surface layer, ii) low stability of the corresponding ionic hydrides, or iii) insufficient sensitivity of the experimental setup.

Conclusion / Outlook

Conclusions:
- It has been confirmed that plasma generated excited hydrogen species are capable of generating gas phase metal compounds via hydride formation.
- The experimental data agree with the expected isotope patterns of stannane and its dimer, as well as with plumbane.
- Ab initio calculations show the relative decreasing stability of the ionic tin hydrides as compared to the molecule SnH_4. SnH_4^+ and SnH_2^+ appear to be extremely unstable, which is most probably the reason why the are not detected in the recorded mass spectra.
- Experiments with nickel, tantalum, and silicon reveal no signals of the corresponding ions, most probably due to a strong protective oxide layer, very low stability of the ionic hydrides, or insufficient sensitivity of the employed set-up.

Outlook:
- Optimization of the ion transfer from formation to analyzer injection.
- Measurement of neutral metal hydrides species
- Images of metal surfaces with SEM before and after treatment with H-plasma and their generated species.
- Further ab-initio calculations regarding the stability of metal hydrides and simulations of the formation of hydrides on metal surfaces with MD simulations.

Literature

[1] H. Kersten, T. Kutsch, K. Kroll, K. Haberer, T. Benter; H_2 plasma for the generation of protonation reagents with a standard APPI power supply, 64th ASMS Conference on Mass spectrometry and Allied Topics, Indianapolis, IN, USA, 2017.

[2] D. J. Aaserud, F. W. Lampe, Journal of Physical Chemistry, 100, 10215-10222, 1996.

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[5] Frisch et al., Gaussian16, Revision A.03, Gaussian, Inc., Wallingford CT. 2016.

Acknowledgement