

Mass Spectrometric Product Study in the Interaction of Selected Metal Surfaces with H₂ Plasma Generated Species

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Introduction

During the past decades, plasmas have gained a considerable interest in diverse research and development areas. Generally, they are utilized to initiate chemical and physical processes [1,2]. This includes the interaction of highly energetic hydrogen plasmas in the presence of metals leading to the formation of the corresponding metal hydrides. The initial step in the hydride formation mechanism is a heterogeneous gas/surface reaction of electronically excited hydrogen (H) atoms and metal atoms (M), successively forming H-M bonds. The volatile metal hydrides eventually desorb and consequently adsorb on another (metal) surface, involving the decomposition into a metal atom and hydrogen [3]. This presentation, focuses on the element tin (Sn) and the corresponding plasma generated mainly (SnH₄).

To investigate the involved reaction mechanisms, mass spectrometric studies of plasma-generated stannane were carried out, both using ions directly sampled from the plasma and electron ionization (EI) of the neutral molecules. Results from these studies are compared with a reference mass spectrum of synthesized stannane. Furthermore, the fragment distributions of the different mass spectra are compared and considerations about the underlying mechanisms are presented.

Experimental

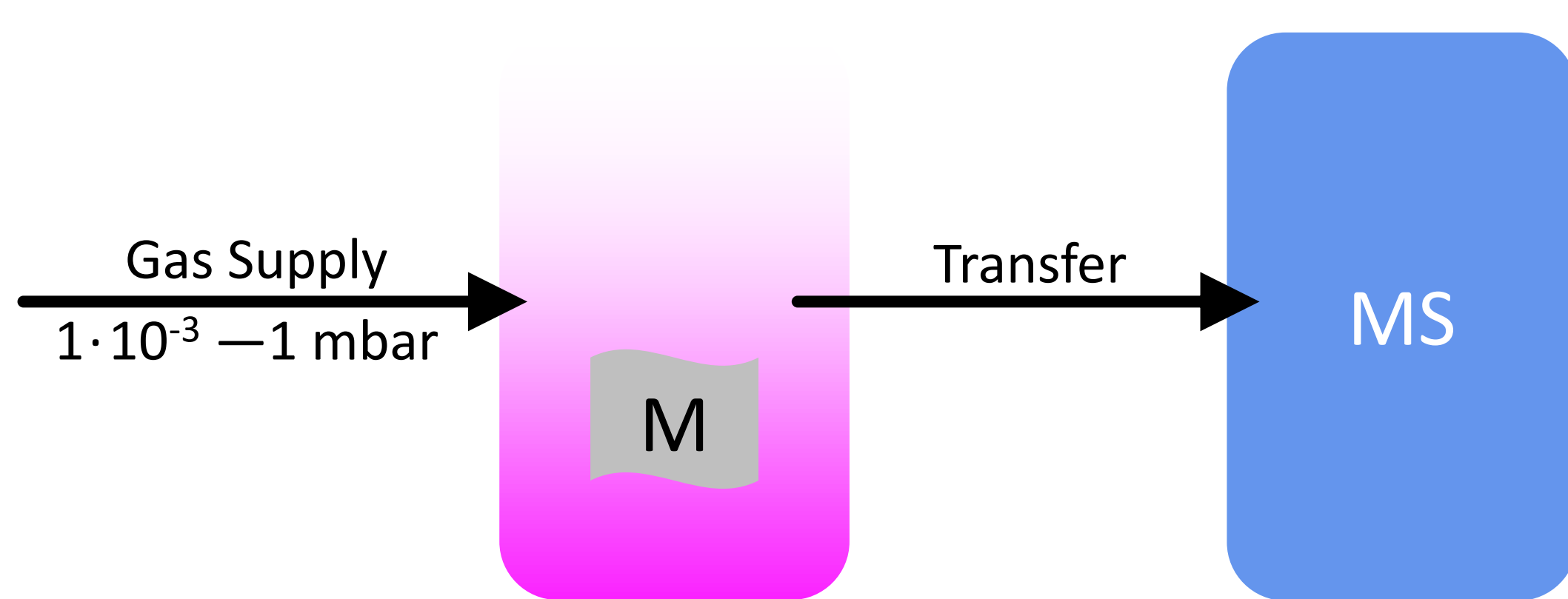


Fig.1: Schematic illustration of the experimental setup. The hydrides formed by the interaction between the hydrogen plasma and the metal target (M) enter a mass spectrometer as neutral molecules or ions via a transfer.

Hydrogen plasma created by an RF power supply generates excited hydrogen species, such as the reagent ion H₃⁺. Volatile metal hydrides are formed via heterogeneous reactions on the surface. The typical operation pressures range between 1 · 10⁻³–1 mbar, which is compatible with the conditions in the different stages of the coupled mass spectrometers.

The metal hydrides generated in the hydrogen plasma enter the MS as neutral molecules via viscous transport or as ions via a custom hexapole transfer.

Methods

Mass Spectrometers

- LTOF & CTOF time of flight mass spectrometer, custom ion transfer stage; TOFWERK AG, Thun, Switzerland (abbr. LTOF, CTOF)
- MAT95XP double-focusing sector field mass spectrometer; Thermo Fisher Scientific, Waltham, MA, USA (abbr. SF)
- HPR-60 MBMS molecular beam mass spectrometer; Hiden Analytical, Warrington, UK (abbr. Hiden)

RF Power Supply

- RF-13-100 13.56 MHz RF generator 100 W; Barthel HF Technik, Aachen, Germany (abbr. PC, plasma chamber)
- Modified VUV lamp RF power supply; Heraeus GmbH, Hanau, Germany (abbr. HCR, helical coil resonator)

Chemicals

Plasma:

- Hydrogen 5.0; Messer SE & Co. KGaA, Krefeld, Germany

Stannane Synthesis [4,5]:

- Tin(IV)-chloride (SnCl₄); Lithium aluminium hydride (LiAlH₄); 1,2-Dimethoxyethan; Dibutyl ether; Merck KGaA, Darmstadt, Germany

Software

- Python 3 [6] based custom analysis script: RASP—Reverse Analysis of Superimposed Signal Patterns in Mass Spectra

Versatile Mass Spectra of Stannane SnH₄

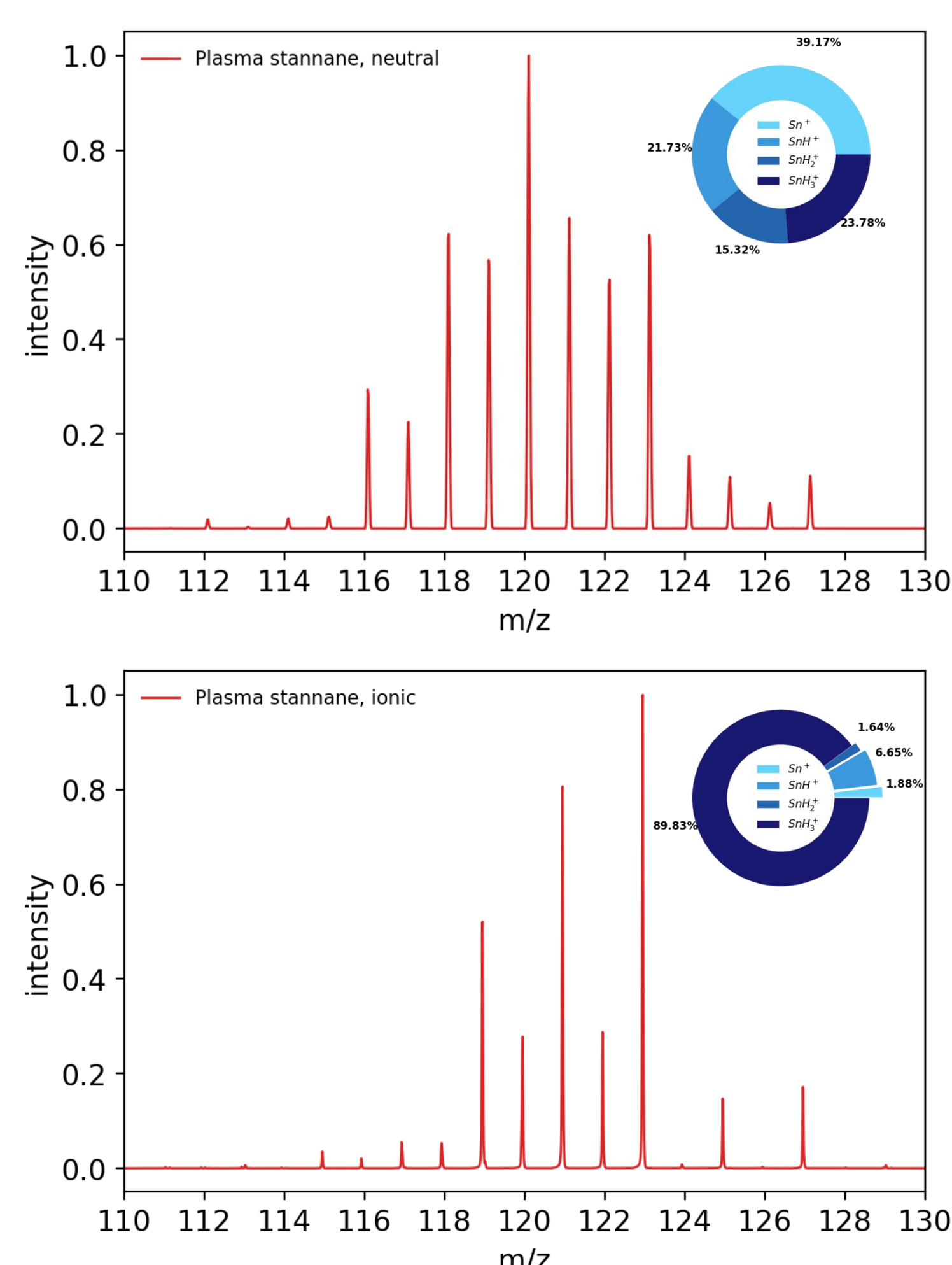


Fig.2: Mass spectra of the plasma generated neutral fragments via sector field MS (top) and the plasma-generated ionic species of stannane via LTOF (bottom), each with the composition calculated via RASP.

Tin (Sn) has ten naturally occurring isotopes and subsequently a multitude of species is generated in the interaction between tin and hydrogen, as there are several possible products (Sn⁺, SnH⁺, SnH₂⁺ and SnH₃⁺). The complex experimental mass spectra are composed of superimposed signals of the isotope pattern of tin, tin hydrides and the corresponding fragments.

Fig.2 shows two mass spectra of stannane, the upper one showing the mass spectrum of the neutral molecules stemming from the plasma region, ionized in the MS and the lower one that of species that are directly ionized in the plasma region. However, in addition to the complexity, the figure also shows the diversity of the stannane mass spectra, which depends significantly on the relative distribution of the tin hydrides.

The Python 3-based custom analysis script RASP (Reverse Analysis of Superimposed Signal Patterns in Mass Spectra) is used to calculate the relative ratio of the experimental acquired signals. RASP is an algorithm to generate a theoretical mass spectrum of expected ions and adapt the ratios of said ions using a Nelder-Mead [7] algorithm to achieve the highest congruence with experimental data. The optimized distributions are shown as donut charts within the displayed mass spectra in Fig.2.

The calculated distributions also highlight how fundamentally different the two mass spectra are. The upper MS consists mainly of Sn⁺ and almost equal parts of the other three species. The lower MS, on the other hand, consists almost exclusively of SnH₃⁺.

A Comparison of Calculated Distributions

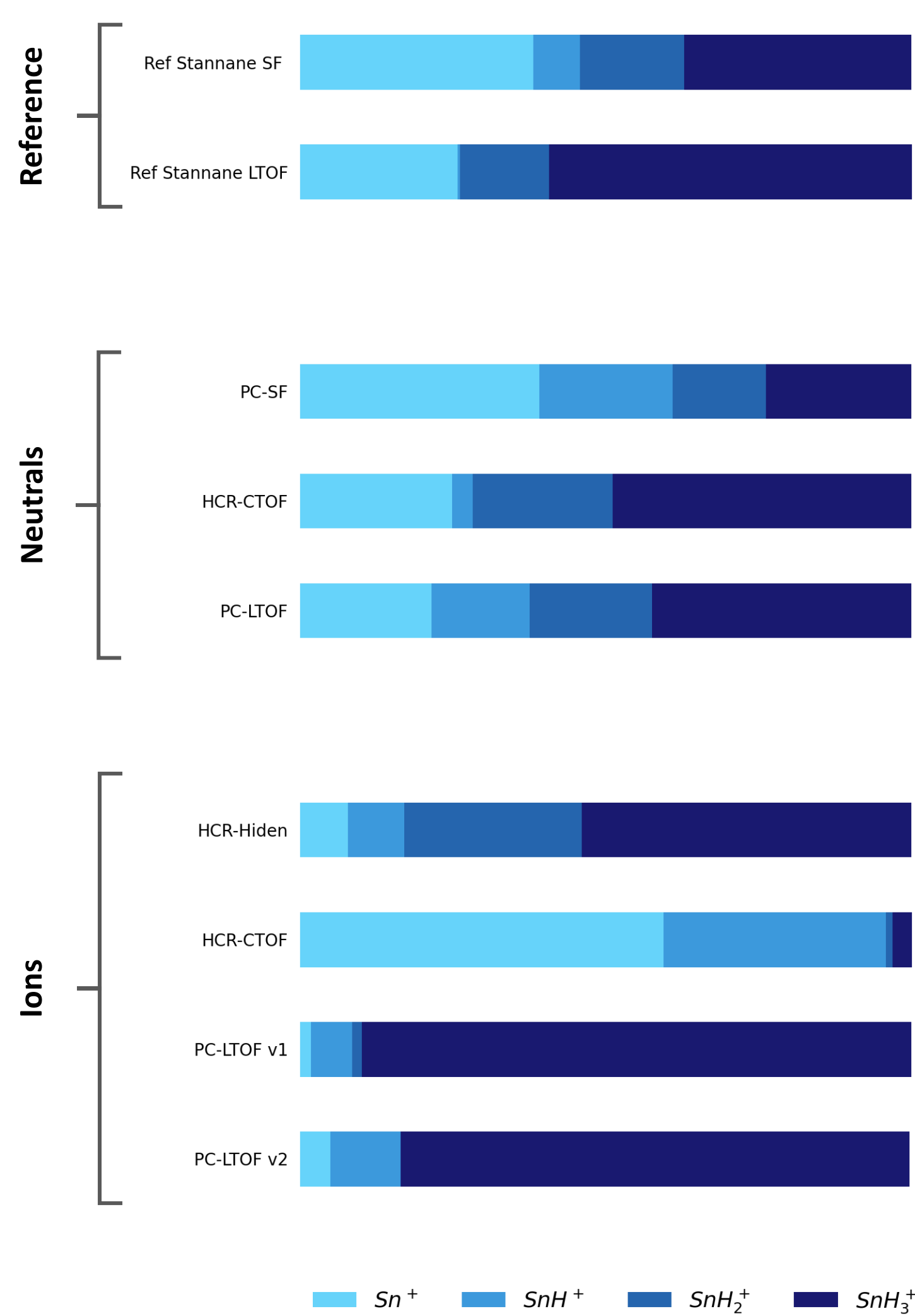


Fig.3: Distributions of tin hydride fragments calculated via RASP. Top: Synthesized stannane ionized by EI (70 eV) as reference. Center: Plasma generated neutral tin hydrides ionized by EI (70 eV). Bottom: Plasma-generated tin hydride ions.

As shown above, the mass spectra respectively distributions highly depend on the measurement scenario, the used mass spectrometer and the prevailing plasma conditions.

Fig. 3 shows the calculated distributions of Sn⁺, SnH⁺, SnH₂⁺ and SnH₃⁺ via RASP. There are certain variations in the respective compositions, depending on the employed plasma, the mass spectrometer and whether neutral molecules are ionized via EI (70 eV) or detected directly as ions. The distributions of the synthesized stannane (Fig.3 top) and the neutrals (Fig.3 center) show a similar behavior, although differences in composition are discernible. These differences most likely originate from the different conditions during ionization transfer and detection, such as pressure, temperature and exact electron energy.

The results of the ions (Fig.3 bottom), which are sampled directly from the plasma are remarkable. The distributions of the respective fragment ions are a lot more on the extreme. For example, the mass spectrum of the HCR plasma with the CTOF consists mainly of Sn⁺ and SnH⁺, whereas the mass spectrum of the plasma chamber with the LTOF consists almost exclusively of SnH₃⁺.

Further assuming that all ionic tin hydride fragments originate from neutral SnH₄, the distribution shows the “history” of stannane up to detection. The exact circumstances influencing the distribution deserve more research. Data suggests that the conditions in the plasma region and in the ion source might have an influence, as well as the “hotness” of the transfer optic. In general, the goal is to be able to make a prediction about the mechanism from the formation of stannane to detection of the respective fragments based on the distribution of a measured mass spectrum.

Conclusion and Outlook

Conclusion

- Mass spectra of stannane SnH₄ applicable as a reference
- Strong evidence was gathered that hydrogen plasmas are capable of forming stannane with metallic tin
- Using the custom program RASP it is possible to calculate the superimposed signals back to the distribution
- The distributions of the fragments depend strongly on the measurement scenario, the mass spectrometer, the conditions in the plasma and ion source and the pressure
- Initial conclusions about the “history” of the stannane are possible based on the calculated distribution

Outlook

- Further systematic investigation of the various dependencies will shed lighter onto the involved mechanisms
- Ample research is planned towards the elucidation of the homogeneous/heterogeneous chemical processes taking place in gas phase and surface
- Application to different metal hydride systems

Literature

Acknowledgement

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