Self-absorption in laser-

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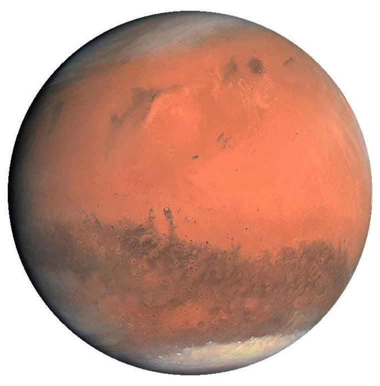
(1) Introduction

- LIBS has been used for exploring the Martian surface since 2012 [1].
- Two more LIBS instruments will follow in 2020 [2,3].
  - ➢ Important to understand capabilities and challenges of LIBS in extraterrestrial atmospheric conditions.
- One challenge of LIBS, known from terrestrial plasmas, is *self-absorption* (SA):
  - Breaks linearity of calibration curves → limits accuracy.
  - Expected to be lower at reduced pressures such as in Martian atmospheric conditions.

(2) Research questions



What is the effect of SA in LIBS data measured in Martian atmospheric conditions?

- Which lines are affected?
- To what extent are they affected?

To answer this, LIBS spectra were measured in simulated Martian atmospheric conditions and the effect of SA was investigated using doublet ratios and plasma parameter estimates by fits of simulated spectra.

(3) About self-absorption

- SA is the effect of emitted light being absorbed by other atoms within the plasma. When the effect of SA is non-negligible, the plasma is said to be optically thick.
- Assuming *local thermal equilibrium* (LTE), the effect of SA can be modeled by the **radiative transfer equation** and a set of **plasma parameters** :

$$\frac{\mathrm{d}I}{\mathrm{d}s} = \boldsymbol{\alpha(T, n_e)} - I \cdot \boldsymbol{\beta(T, n_e)} \qquad (1)$$

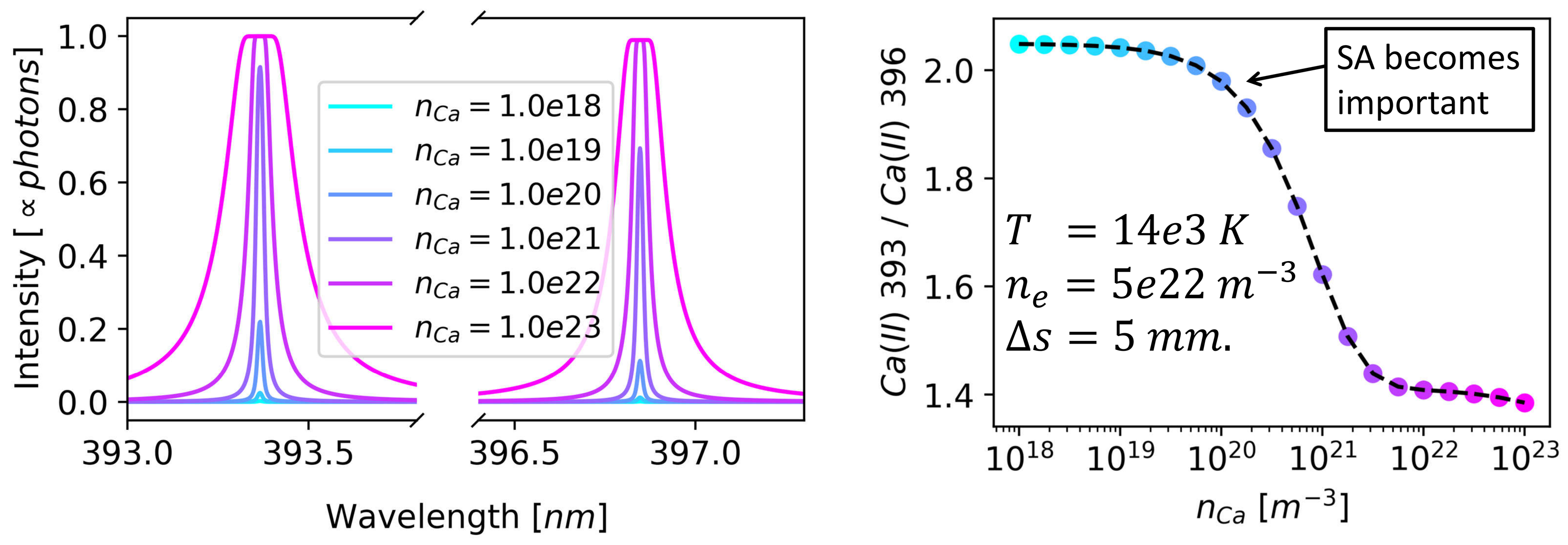
spontaneous emission *absorption & stimulated emission*

- SA can also be probed by **doublet line ratios**, where the dependence on plasma temperature and electron density cancels out:

→ Optical thin limit (negligible SA): $\frac{I^{(1)}}{I^{(2)}} = \frac{gA_{lu}{}^{(1)}}{gA_{lu}{}^{(2)}} = const.$

→ Optical thick limit: $\frac{I^{(1)}}{I^{(2)}} = blackbody\ ratio \sim 1$

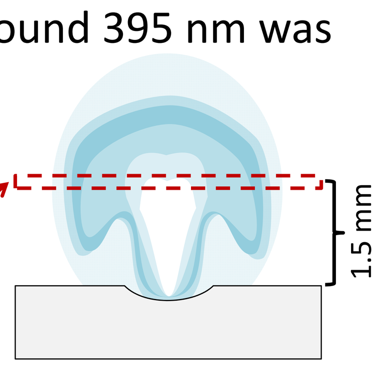
- Example of solving radiative the transfer equation for the strong Ca(II) doublet:

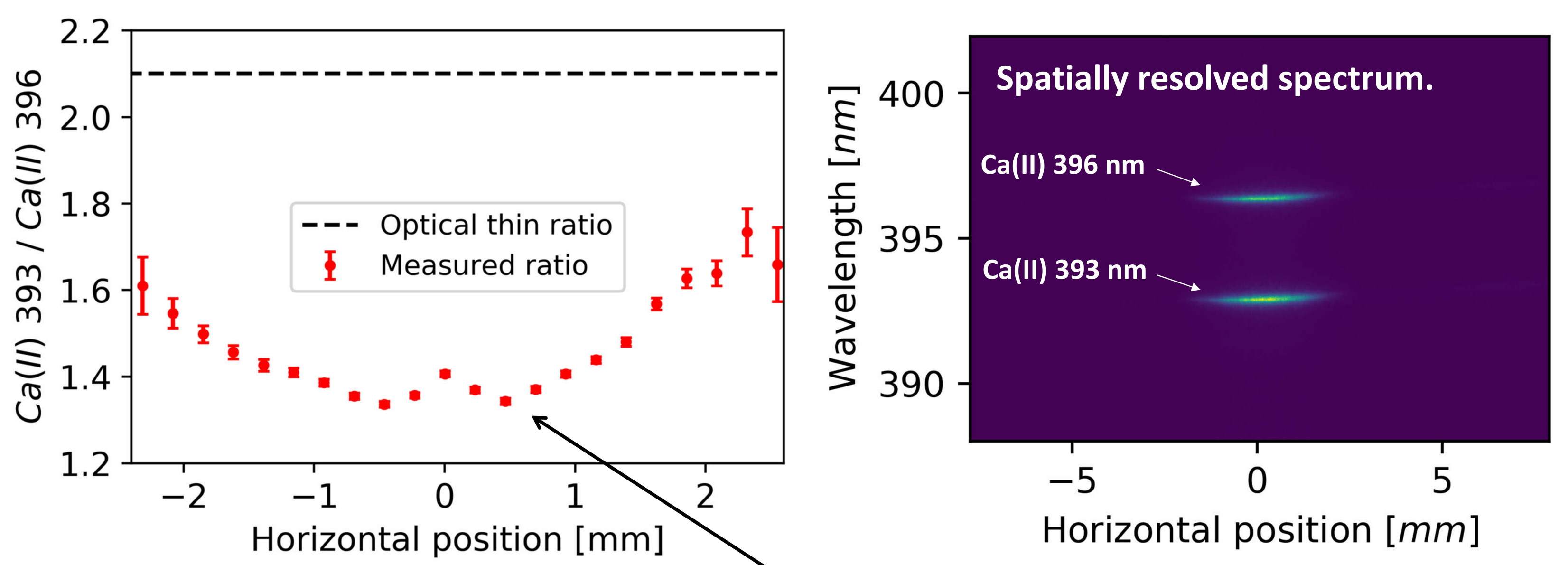


(4) Probing of SA with spatially resolved LIBS

Using a plasma imaging set-up[4], the SA of the Ca (II) doublet around 395 nm was investigated qualitatively.

- Temporal interval: [500;600] ns.
- Target: pressed pellet of pure $CaCO_3$.
- Different lines of sight in a thin slice
- Atmosphere: Mars-analog gas (mainly CO_2) @ 7 mbar pressure.



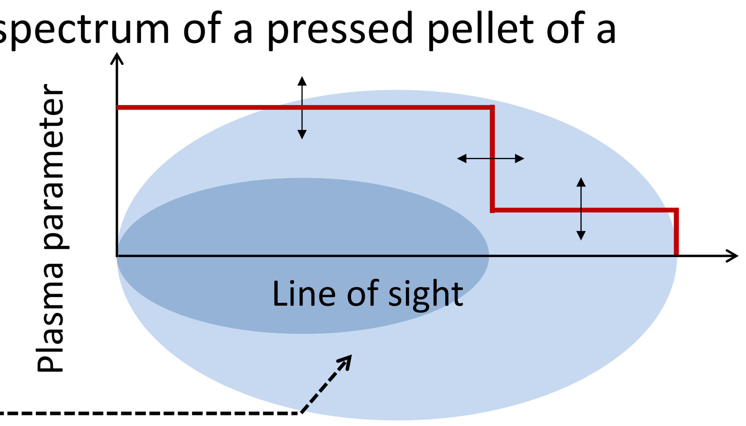


Large deviation from optical thin ratio → large degree of self-absorption.
Strongest deviation for lines of sight near plasma center.

(5) Plasma parameter estimates by fits of simulated spectra

Using a high resolution LIBS set-up (*Aryelle Butterfly, LTB*), the spectrum of a pressed pellet of a carbonate mixture was measured.

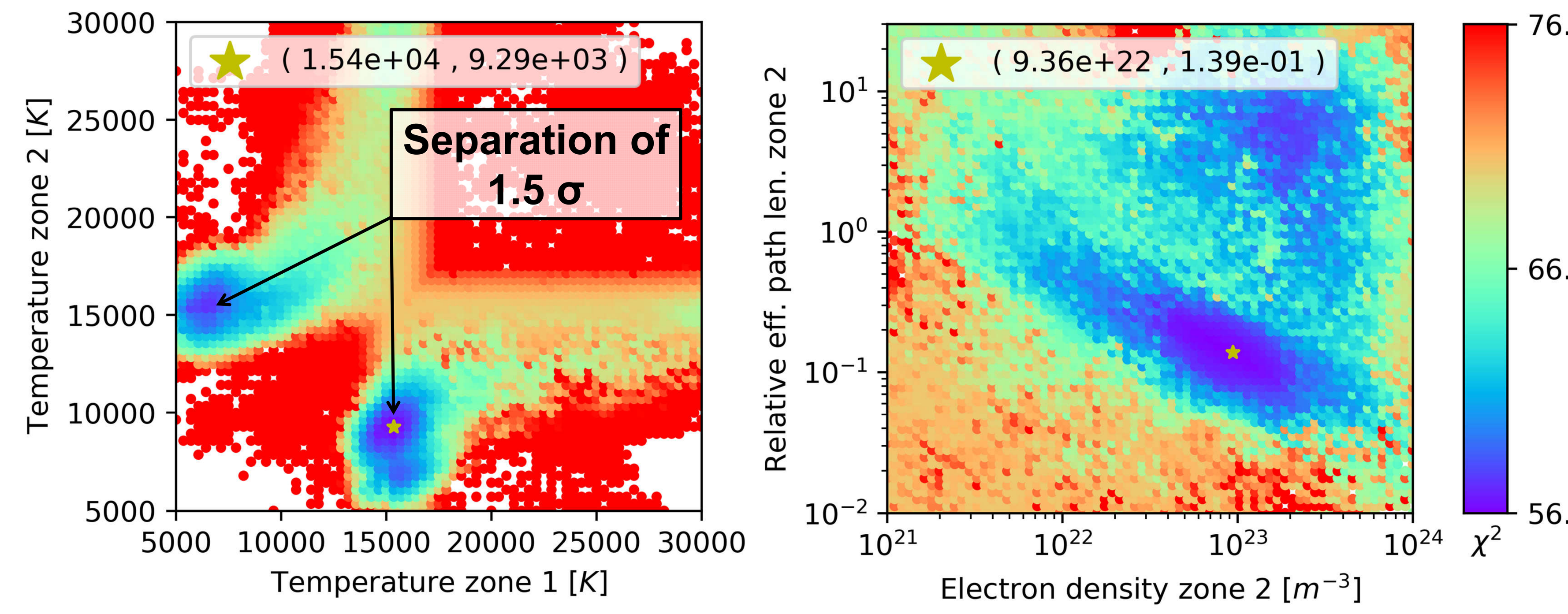
- Temporal interval: [500;550] ns.
- Large spectral range: [273;800] nm.
- Atmosphere: Mars-analog gas (mainly CO_2) @ 7 mbar.
- Light collection geometry: top view with small field of view.



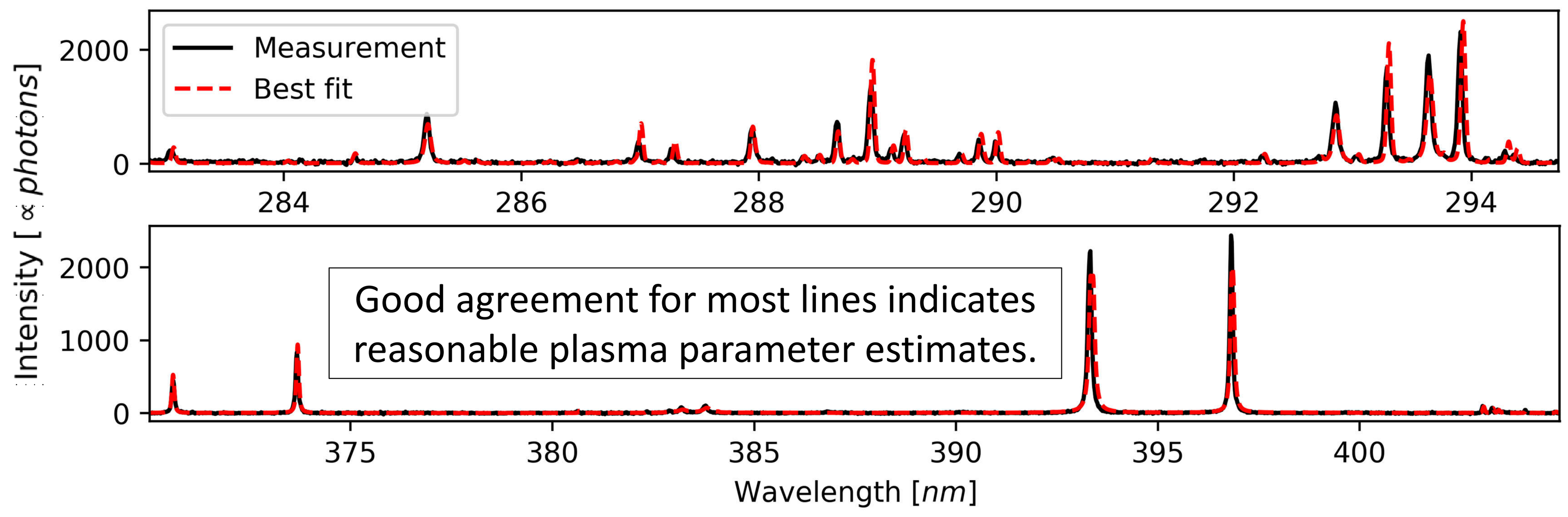
In the approximation of a "**two-zone plasma model**" spectra are simulated and fitted to the measured spectrum in order to estimate the plasma parameters and later evaluate the amount of SA.

- Simulated spectra are based on LTE and the radiative transfer eq.
- 6 fit parameters for describing the plasma parameters:
  - 2 x Temperature, 2 x Electron density, 2 x Eff. path length (density × distance).

Color plots showing goodness of fit (χ^2) for different parts of the fit-parameter space (best solution marked by the star):



Best fitted spectrum plotted together with the measured data:

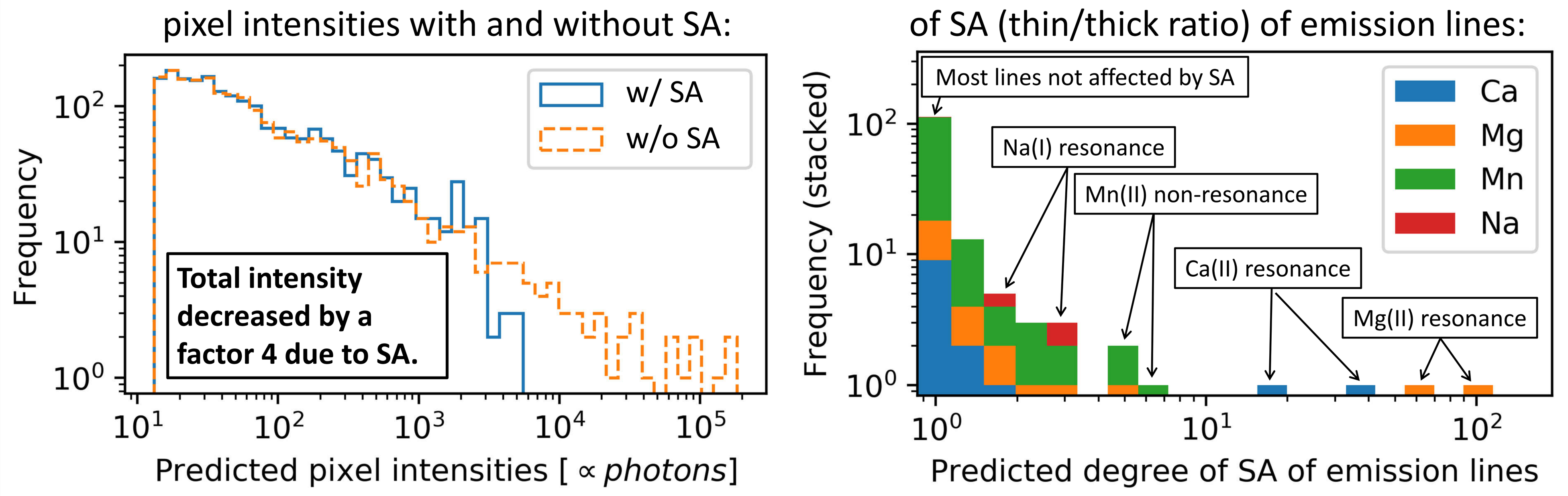


(6) Quantifying the effect of SA using fit results

Using the plasma parameter estimates from the fits of simulated spectra, the effect of SA in the carbonate spectrum was evaluated by comparing the predicted intensities with and without the absorption term in the radiative transfer equation (β in eq. (1)).

Histogram showing the distribution of pixel intensities with and without SA:

Histogram showing the distribution of degree of SA (thin/thick ratio) of emission lines:



(7) Conclusion

- Probing the SA from the Ca (II) doublet indicated a strong effect on these lines. This was expected since the doublet is very strong and involves the ground state.
- Using plasma parameter estimates in the approximation of a two-zone model, the amount of self-absorption was derived. Even though most of the emission lines were found not to be affected, some strong effects were noted:
  - Total intensity decreased by a factor of ~4.
  - Strongest emission lines decreased in intensity by a factor of ~100.
  - Strong non-resonant emission lines are also affected, but more moderately.

→ In Martian atmospheric conditions, SA still affects the emission lines.
→ Consider the effect when estimating plasma parameters or extrapolating calibration models in elemental concentrations.

References

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[4] D. S. Vogt, et al., *Time-resolved spectral imaging of LIBS plasma at low pressures for the exploration of Solar System bodies,* 2018, EPSC Abstracts, Vol. 12, EPSC2018-754.