Molecular emissions in the laser-induced plasma in simulated Martian conditions – calibration models and new insights from plasma imaging

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Introduction

Molecular emissions in LIBS can be used to detect elements that do not have strong emission lines, such as chlorine and fluorine. This is interesting for Martian exploration, where chlorine and fluorine offer important clues about past environments [1]. CaCl and CaF have been detected in Martian LIBS spectra by ChemCam [2, 3], the first LIBS instrument on Mars, and were used to estimate the halogen concentrations [1]. In this study, we investigate the relationship between the reactant concentrations and the intensities of the molecular emissions of MgCl, CaCl, and CaF.

Methods

LIBS measurements are conducted with the high-resolution LIBS setup at DLR Berlin and with a new plasma imaging setup that allows for time- and space-resolved measurements. All measurements are made in simulated Martian atmospheric conditions. Pure samples of MgCl2, CaCl2, and CaF2 are investigated as well as mixtures of salts with different relative concentrations of Ca, Cl, and F. Numerical simulations are made to calculate results for plasma in equilibrium.

Results

The most intense MgCl band is too weak for the detection of Cl due to a low population density of the excited electronic level. The CaCl and CaF bands are much more intense and can be described well by a reaction model with only two fit parameters. In contrast to predictions by the equilibrium model, their intensities are skewed towards lower Cl and F concentrations, respectively. This indicates a strong influence of non-equilibrium effects in the plasma. Plasma imaging measurements show that the molecules only form in a small region around the plasma center.

Conclusion

CaCl and CaF emissions are promising for the detection of chlorine and fluorine on Mars. Their intensity can be described well by the reaction model presented here. Plasma imaging experiments show that the molecules only form close to the center, suggesting that the plasma temperature is unexpectedly low there, potentially due to rarefaction and radiative losses.

References

[1] Gaft et al. 2014. Spectrochim. Acta B 98: 39-47.
[2] Maurice et al. 2012. Space Sci. Rev. 170: 95–166.
[3] Wiens et al. 2012. Space Sci.Rev. 170: 167–227.