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Raman spectra of frozen salt solutions relevant for planetary surfaces

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Abstract

The confocal Raman spectroscopy is a non-destructive method to analyze the chemical composition of materials. The aim of this study is to examine frozen salt solutions with Raman spectroscopy and to identify and distinguish different kinds of salts.

1. Introduction

The existence of liquid water is a necessary condition for the presence of life [1]. Hydrogen and Oxygen are elements that can be found in many different locations in our planetary system [1]. Hence, there is a high probability to find water especially in its solid phase because temperatures of the outer solar system do not allow otherwise [2]. Exceptions are subsurface oceans on Europa [3] and Enceladus [4, 5].

Regarding Mars, the temperature (215 K) and pressure (6 hPa) conditions imply that the only possibility to find liquid water would be as a mixture of water and salt (brines) [6]. Therefore, this study deals with salts and salt solutions which reduce the freezing point of water and could allow the existence of liquid water on Mars (metastable phase) [7].

2. Samples

Different salts and frozen salt solutions are measured with Raman spectroscopy. The samples are examined as pure salt powder and as frozen salt solutions. The salt types are chosen according to their extraterrestrial existence. Remote sensing and in-situ measurements of Mars and the icy moons of Jupiter and Saturn indicate the possible existence of, for example, Ice + $Na_2SO_4 \cdot 10H_2O$ [7, 8], Ice + $K_2SO_4 \cdot H_2O$ [7, 8], Ice + LiCl [7], Ice + $Fe_2(SO_4)_3$ [7], Ice + $CaCl_2 \cdot 6H_2O$ [7, 8], Ice + $MgCl_2 \cdot 12H_2O$ [7, 8], Ice + $NaCl \cdot 2H_2O$ [7, 8], Ice + KCl [7], Ice + $MgSO_4 \cdot 7H_2O$ [7] on Mars, $MgSO_4 \cdot 7H_2O$ [9], NaCl [9], KCl [9], $MgCl_2$ [9] and Na_2SO_4 [4] on Europe and NaCl [4, 5] on Enceladus.

The 14 salts examined can be divided into chlorides (NaCl, KCl, LiCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$), sodium salts (NaBr, NaI), sulfates (Na_2SO_4, K_2SO_4, $MgSO_4 \cdot H_2O$, $MgSO_4 \cdot 7H_2O$, $CaSO_4 \cdot 2H_2O$) and iron salts ($Cl_3Fe \cdot 6H_2O$, $Fe_2(SO_4)_3 \cdot xH_2O$).

3. Experimental Setup

The samples are investigated with a Witec Alpha 300 Raman spectrometer. The laser excitation wavelength is 532 nm and the spot size on the sample is approximately 1 µm. The spectral range goes from 100 cm^{-1} to 3800 cm^{-1} and the spectral resolution using a 600 l/mm grating is about 4 cm^{-1}. The measurements of the frozen salt solutions were done at three different temperatures (about 120 K, 220 K, 250 K) and with a laser power of 3 - 5 mW. The salt powder samples are examined at the same temperatures as well as room temperature. The samples are placed in a cryostat that was evacuated to a pressure of $4 \cdot 10^{-1}$ hPa. Afterwards, it is cooled with liquid nitrogen to about 120 K.

4. Results and Conclusions

Since the frozen salt solutions are a mixture of water and different kinds of salts, it is expected that the Raman spectra consist of salt features that are located in the water signal region [10]. In this study the position of the five identified water peaks in the O-H-stretching region (2800 cm^{-1} - 3800 cm^{-1}) are determined with a Gaussian distribution using the advanced fitting tool of the WiTec Project 2.10 software. The recorded Raman spectra show a shift to smaller wavenumbers and a decrease of the half width with decreasing temperature. A reason for the decrease of the half width is a reduced thermal broadening [11].

The dependence on temperature is examined with the symmetric O-H-stretching mode $\Delta\nu_1$ (main ice peak at 3139 cm^{-1}). The comparison of $\Delta\nu_1$ of the different frozen salt solutions show a maximum shift to smaller wavenumbers of about 50cm^{-1} in the temperature range of [120 K to 250 K]. The change in peak positions represents a structural change, whereby a decrease in temperature results in a strengthening of hydrogen bonds [11].

The influence of the salt hydrates on the main ice peak is very small. Exceptions are KCl, Na_2SO_4 and $CaSO_4$ at 120 K where the shift is only 32 cm^{-1} for KCl and 36 cm^{-1} for Na_2SO_4 and $CaSO_4$.

The salt features of the diatomic frozen salt solutions are located in the O-H-stretching region of water (Figure 1). Exceptions are LiCl and NaI. LiCl does not possess any salt signals and NaI has well defined peaks in the H-O-H-bending region of water (1500cm^{-1} - 1700cm^{-1}). The peaks differ in their relative intensities. This can be explained by the interaction of polarized light with differently oriented crystals [10]. There is a change in form, number and position of the water and salt peaks with decreasing temperature. The influence of temperature is rather small regarding the position of the salt signals. Most peaks appear at 120 K. This is probably because of a reordering of the water molecules within the crystal lattice [11].

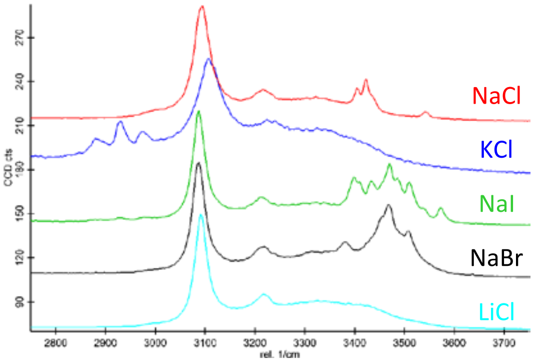

Figure 1: The Raman spectra of diatomic frozen salt solutions in the O-H-stretching region of water.

There are no characteristic salt peaks in the O-H-stretching region of the polyatomic frozen salt solutions ($MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$ and $Cl_3Fe \cdot 6H_2O$). The freezing process did probably not allow the formation of a stable solid phase [12] of $MgCl_2 \cdot 12H_2O$ and $CaCl_2 \cdot 6H_2O$ which would result in numerous peaks [10].

The Raman spectra of the sulfates $CaSO_4$ and Na_2SO_4 show characteristic peaks in the O-H-stretching region of water. Besides, there appears a well-defined peak around 980 cm^{-1} in all sulfate samples, with the exception of $CaSO_4$ where it is located at 1010 cm^{-1}. This peak is the result of the symmetric stretching mode of the SO_4^{2-} ion. It is shifted to higher wavenumbers with decreasing temperature.

There is a huge difference when comparing the diatomic frozen salt solutions to the pure salts. The diatomic pure salts samples consist of two ions. Therefore, the only bonding existing is the ionic bonding which prohibits the existence of Raman active modes [12]. This can be seen in the Raman spectra which consist mainly of noise.

Most of the frozen salt solutions can be distinguished from each other. This is also confirmed by the principal component analysis (PCA) and the partial least square regression (PLS).

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