# Supporting information (SI) for: Direct molecular level characterization of different heterogeneous freezing modes on mica

Ahmed Abdelmonem[1]

[1]Institute of Meteorology and Climate Research – Atmospheric Aerosol Research (IMKAAF), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

Correspondence to: Ahmed Abdelmonem (ahmed.abdelmonem@kit.edu)

**Abbreviations**

SHG: second-harmonic generation,

SFG: sum-frequency generation

IMG: index-matching gel

TIR: total internal reflection

RH: relative humidity

**Details on experimental setup**

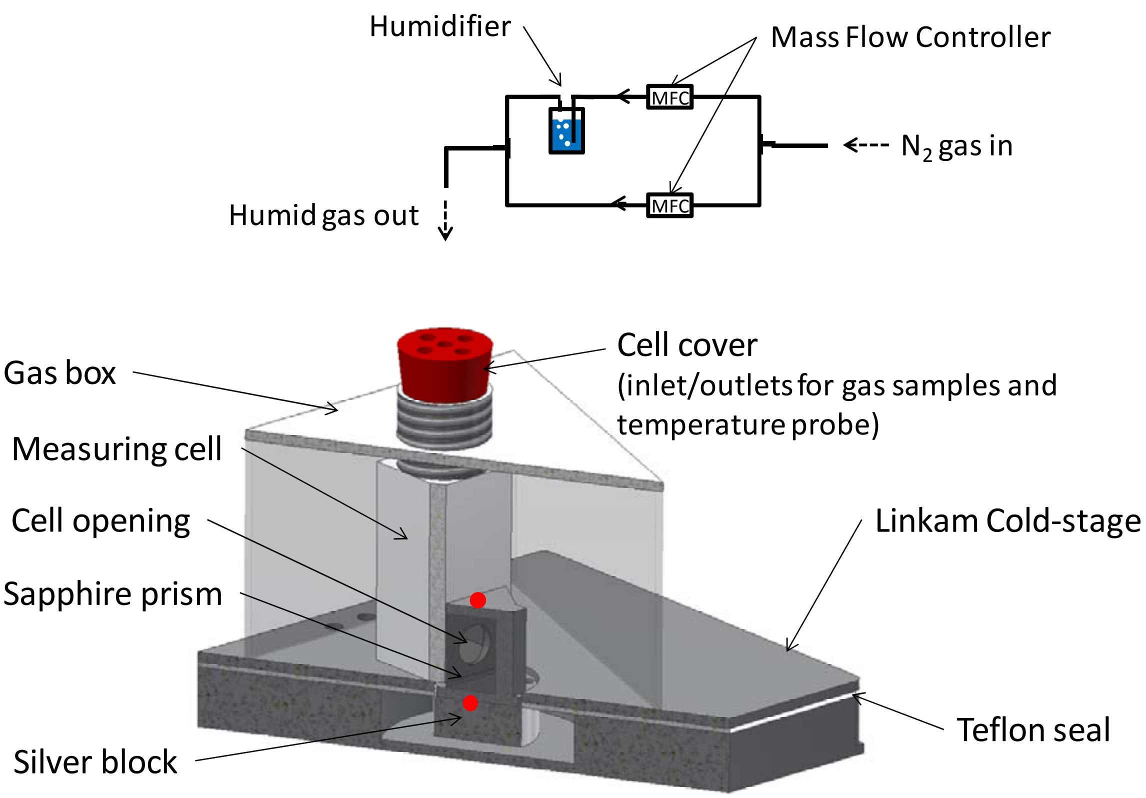


**Figure S1: The measuring cell configuration, humidification and temperature sensors. The red dots are the position of the sample temperature sensors. There is a temperature sensor inside the measuring cell (not shown)**

Figure S1 shows the assembly of the measuring cell. The sapphire prism is place in a cupper adaptor which is fixed on the silver block of the Linkam cold-stage. The cold stage can perform controlled heating and cooling ramps, applied to the silver block, at rates between 0.01 and 100 °C/min. Temperature stability of the cold stage is better than 0.1 K. The temperatures of the air inside the cell and the sapphire prism top and bottom are measured using four-wire-Pt100 elements. The temperature of the probed spot on the surface is considered to be the average of the sample top and sample bottom. However, I emphasize here that the exact onset condition of freezing was not the focus of this work, but rather the study of the qualitative behavior of water molecules during the freezing process. During the experiments, the gas box was filled with $N_2$ gas to avoid condensation on the outer surfaces of the prism during cooling. The humid air pumped to the measuring cell was obtained by mixing dry gas and 100 % humid gas with different ratios at 21 °C using two mass flow controllers (MFC). The continuous flow of the gas (either dry or humid) during the experiment set the temperature inside the cell to 21 °C ± 0.5 °C. The corresponding fluctuation of the relative humidity was less than 0.2%. The corresponding fluctuation in the dew point, at RH = 5 ±0.2 for instance, is ±0.5 °C. The gas mixing ratio versus RH was calibrated by setting a mixing ratio, cooling the sample and recording the condensation/freezing temperature at which the reflectivity at an angle equals to the critical angle of TIR for air-mica interface starts to drop due to the violation of TIR condition. This temperature was used to define the corresponding RH using Arden Buck equation. The same method was used to differentiate between liquid-film and liquid-bulk in this work.

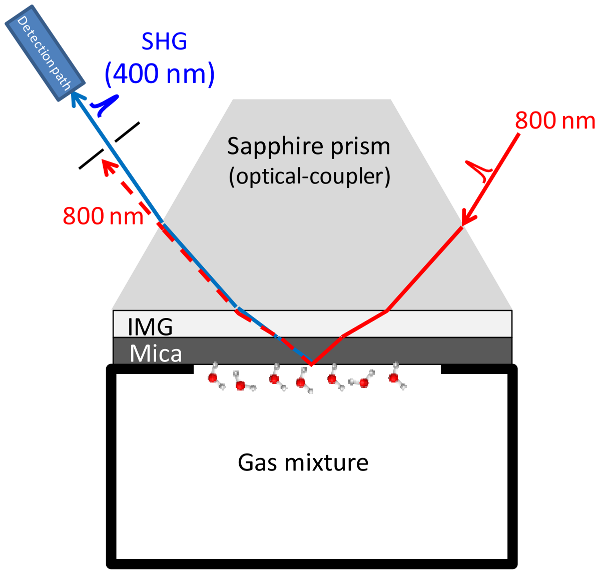


**Figure S2: The sample and beams geometry**

Figure S2 shows the sample and beam geometry. The fundamental beam (800 nm) was incident on the outer side of the prism at an incident angle of 15° with its surface normal. Under this geometry, the reflected 800 nm and generated SHG (400 nm) beams co-propagate to the sapphire-air interface at the other side of the prism at which both beams are refracted at two different angles. Only the SHG signal was allowed to reach the detection path. The detection path included a band pass filter for 400 nm, polarization analyzer and photo-multiplier tube (PMT). The polarization of the incident beam was adjusted using a half-wave plate followed by cube polarizer.

**SFG and SHG: Theoretical background**

SFG and SHG are highly sensitive nonlinear optical probes of surfaces and interfaces where light is generated at a frequency equals to the sum of frequencies of two incident optical fields. The basic theory of SHG and SFG has been described elsewhere (Bain, 1995;Eisenthal, 1996;Richmond et al., 1988;Shen, 1989a;Shen, 1989b;Shen, 1994;Shen and Ostroverkhov, 2006) and will not be repeated here. However, a brief background will be given here. SFG/SHG signal is generated when the incident beams are spatially and temporally overlapped at a point of broken inversion-symmetry (e.g. an interface between two isotropic media). The experiments are usually carried out with definite polarization combinations of incident and generated beams. Such experiments are rich of information, particularly about concentrations and orientations of the entities which contribute to the signal. Unlike SHG, SFG can specify the different entities from their resonance frequencies. SHG and SFG have been used to probe the aqueous/air, aqueous/solid and solid/air interfaces. The overall signal strength depends on 1) intensity and polarization of the incident beams, 2) the optical properties of the media at the interface manifested in the Fresnel factors and 3) the concentrations and orientations of the molecules and the response of the existing dipoles at the interface.

Generally the SFG signal, of frequency $\omega_{SF} = \omega_v + \omega_{IR}$, generated at the interface, Figure (S3), is given as bellow:

$$I(\omega_{SF}) \propto \left|L(\omega_{SF})\,\chi^{(2)}\,L(\omega_v).L(\omega_{IR})\right|^2 I_v I_{IR} \qquad (1)$$

where, $L(\omega_i)$ is the nonlinear Fresnel factor at $\omega_i$ and $\chi^{(2)}$ is the second order nonlinear hyperpolarizability tensor. $\omega_v$ and $\omega_{IR}$ are the frequencies of the incident beams. <u>In SHG, the two incident frequencies are equal</u>. Polarization dependent measurements probe specific tensor element of the hyperpolarizability tensor and yield detailed information about the degree of ordering and angular orientation of the molecules (Abdelmonem, 2008;Shen, 1989a;Shen, 1989b;Jang et al., 2013;Rao et al., 2003;Zhuang et al., 1999;Fordyce et al., 2001;Goh et al., 1988;Luca et al., 1995).

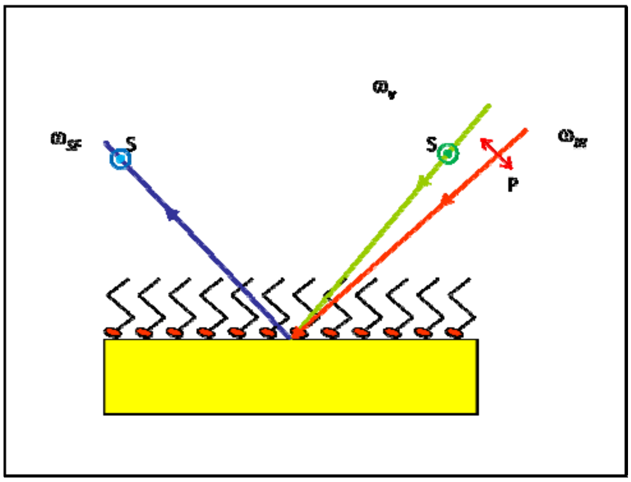


**Figure S3: Simple scheme of SFG generation in co-propagating geometry. S and P indicate light polarized light perpendicular and parallel to the plane of incidence respectively.**

## Data analysis and Fresnel factors (SHG)

The SHG signal with a frequency $\omega_{SH} = 2\omega_{in}$ under SM polarization, (S-polarized SHG and 45°-polarized incident light), generated from an incoming visible light with a frequency $\omega_{in}$ can be described with the equation:

$$S_{SM}(\omega_{SH}) \propto \left| L_{yy}(\omega_{SH}) L_{yy}(\omega_{in}) L_{zz}(\omega_{in}) \chi^{(2)}_{yyz} \right|^2 I_{in}^2 \qquad (2)$$

where, $L(\omega_i)$ is the nonlinear Fresnel factor at $\omega_i$ and $\chi^{(2)}_{yyz}$ is the surface second order nonlinear susceptibility tensor for SM polarisation combination (equivalent to SSP in SFG) (Shen, 1989b;Zhuang et al., 1999) and a measure of the degree of molecular ordering. To obtain the molecular quantity $\chi^{(2)}_{yyz}$ the measured SHG intensities have thus to be normalized to the Fresnel factors which are optical constants dependent. Figure S4 shows the change of Fresnel factors as a function of refractive index in the range of refractive indices covering the involved media in this work. The SHG intensities reported in Figures 1 and 2 in the manuscript are Fresnel corrected and thus directly proportional to$\left|\chi^{(2)}_{yyz}\right|^{(2)}$.

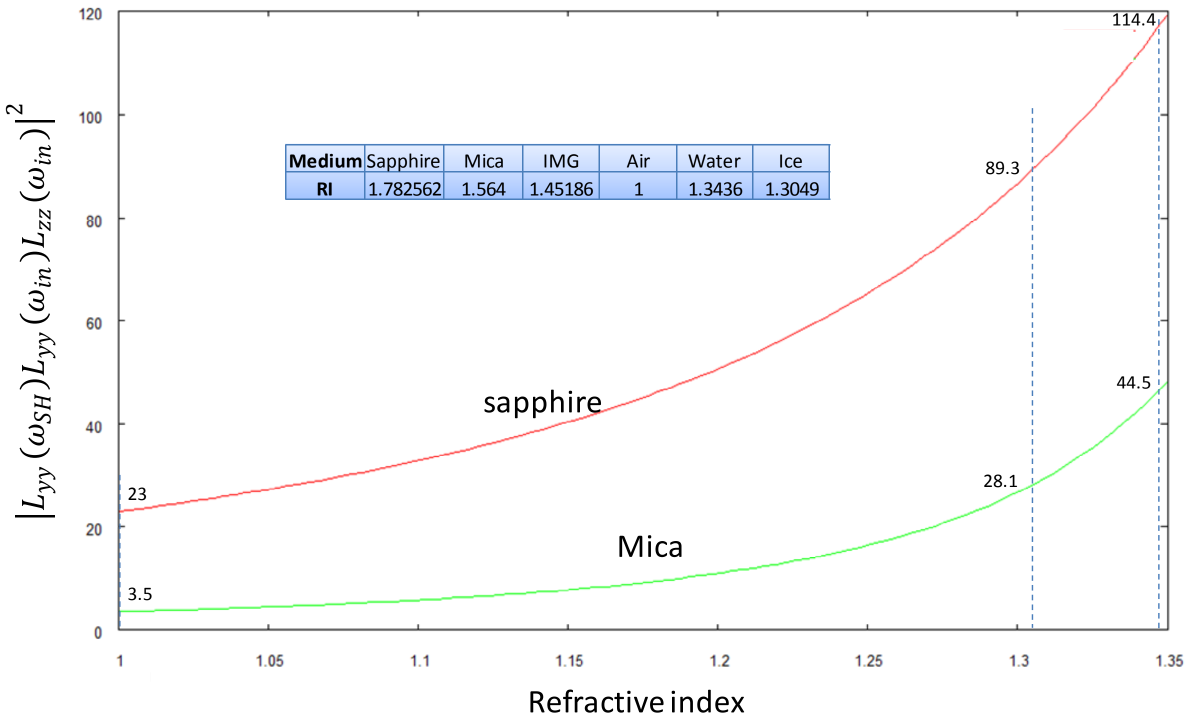


**Figure S4: Theoretically calculated Fresnel factors for sapphire-water (red line) and mica-water (green line) interfaces at incident angle of 15° from air to the sapphire prism. Optical geometry can be found in (Abdelmonem et al., 2015;Abdelmonem et al., 2017).**

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