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# Accurate absolute measurements of the Raman backscattering differential cross-section of water and ice and its dependence on the temperature and excitation wavelength

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## ABSTRACT

Measurements of Raman backscattering spectra between  $-15\text{ }^{\circ}\text{C}$  and  $22\text{ }^{\circ}\text{C}$  in liquid water (including its supercooled state) and in polycrystalline ice ( $-35\text{ }^{\circ}\text{C}$  to  $0\text{ }^{\circ}\text{C}$ ) at two excitation wavelengths (407 and 532 nm) are presented. It is found that the spectrum-integrated backscattering cross-section of the  $3400\text{ cm}^{-1}$  band is about 1.2 times larger for ice in comparison to liquid water. The excitation-wavelength dependence of the cross-section in ice is very close to that in water. A discontinuous change of the spectrum is observed upon phase transition at  $0\text{ }^{\circ}\text{C}$ . The results are applicable to preliminary calibration of lidar systems designed for water content surveys in the atmosphere.

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## 1. Introduction

Raman scattering in water is important for many applications but, in particular, for lidar studies of the atmospheric water cycle as its understanding is critical for weather and climate modeling and prognosis. Instrument development aimed at first at accurate and continuous observation of the humidity profile for experimental ease, relative abundance of atmospheric water in its vapor phase, and straight-forward calibration [1–4]. Later, measurement of the condensed water phases became the research focus because it holds the promise to directly determine the water content of clouds [5–10]. With the most advanced water Raman lidars such as [10,11] it is now possible to measure the Raman backscattering coefficients of atmospheric water vapor, ice, and liquid water. While the humidity measurement is routinely calibrated using radiosondes, no such opportunity to compare exists for water content profiles. Consequently, water content has to be determined *ab initio* from the backscatter coefficients, which requires accurate knowledge of the molecular Raman backscattering differential cross-section in frozen and liquid water at the excitation wavelength of the lidar for small ice particles or droplets.

Because Raman scattering in water depends on intermolecular interactions (in particular, on the hydrogen bonding), theoretical

calculations of the Raman spectra are very difficult. Significant deviations between theoretical modeling and experiments are observed despite the use of adjustable parameters and an extensive computing power. For bulk liquid water, the agreement between theory and experiments is rather semi quantitative [12–14]. The situation is even more complex for small water droplets and ice crystals because their morphology (shape) affects the scattering [15–18] unless their sizes are an order of magnitude smaller than the wavelength of light or so large that the surface effects can be either ignored or accounted for (reflection from a large flat surface is an example where the calculations are simple). Generally, the morphology especially of the ice crystals can be very diverse. In icy samples, the scattering is also affected by the birefringent nature of crystalline materials and tensor nature of the scattering in the crystals [19]. At normal conditions, ice forms uniaxial crystals where the ordinary and extraordinary refractive indices at 546 nm are  $n_o = 1.3105$  and  $n_e = 1.3119$  respectively [20]. The difference is small but far from being negligible. Because of the difficulty with theoretical estimations and modeling, the backscattering cross-section should be measured accurately in a laboratory environment.

Despite of a very long history [21], the published values of the cross-section deviate up to a factor of 5 from each other even for bulk liquid water [22] but generally the accuracy of the most reliable values for this case has been estimated to be about 20%. The relatively large uncertainty of the best available estimate has, perhaps, prevented water from being included in the list of

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photometric standards for Raman spectroscopy [23]. The situation for bulk liquid has improved recently with publication of the scattering cross-section measured at 532-nm excitation with 1.5% absolute accuracy [24]. Impurities in atmosphere and water, if present, do not affect the scattering cross-section directly but may obscure the Raman signal. This can be mitigated by using spectrally resolved Raman spectroscopy instead of measurements of spectrally integrated intensity (see [25] and references therein).

In ice, the situation is more complex. Due to the difference  $n_e - n_o \approx 0.0014$ , the path length required to achieve the phase shift of  $180^\circ$  between the two orthogonally polarized beams is on the order of 0.1 mm. Therefore it is likely that light will be depolarized inside a polycrystalline ice sample even if it is only a few millimeters thick. This, in turn, will affect Raman scattering especially if the scattering is measured in the *orthogonal geometry* (perpendicular to the exciting beam of light), which is historically the most frequently used in the laboratory measurements. In such a geometry, the rotation of polarization of the exciting laser beam by 90-degree aligns it parallel to the direction in which the scattering is observed. The induced-dipole emission in the direction of the dipole axis is zero and therefore the detected scattering in the direction orthogonal to the exciting beam is significantly reduced. This effect is hard to take into account quantitatively and is a possible reason for a reported 1.6 times larger cross-section in liquid water than in ice [26]. In the case of backscattering, the rotated polarization stays perpendicular to the scattering direction and therefore the backscattered intensity will not be affected by the birefringence in the first approximation. For this reason, the measurements of the scattering cross-sections will be more reliable in the backscattering geometry, also the main mode of operation for lidar systems. By preparing ice samples of good optical quality, we have also rectified the use of Raman spectroscopy for detecting the water-ice phase transition. In our experiments, the transformation of the Raman spectrum at the phase transition shows a discontinuity instead of about 3 °C-wide transient as observed in [27].

This paper starts a series of experimental and theoretical publications aiming at clarifying Raman scattering of different forms of water in atmosphere and continues our previous work on accurate measurements of Raman scattering in bulk water [24].

## 2. Experimental

A simple confocal measurement scheme described earlier [24] has been used also here. Such a design helps to deal with polarization dependent factors. The measurements have been done at two excitation wavelengths, 532 nm (CW laser, Verdi, Coherent) and at about 407 nm (CW diode laser, Thorlabs). The wavelengths are chosen so that they span a significant range of the excitation wavelengths (a factor of 1.3 difference between the two) and the corresponding Stokes regions (the water band is shifted by about  $3400 \text{ cm}^{-1}$  from the pumping light) are covered by good luminescent standards of the quantum yield [28]. Most details of the experimental setup have been described in [24]. A new feature essential for the measurement of the Raman spectra of ice and supercooled liquid water is a home-designed microscope chamber where the samples can be cooled from room temperature down to  $-35^\circ\text{C}$  with a carefully controlled cooling rate.

### 2.1. Sample preparation

The preparation of high-quality ice samples involves two main steps. First, water (UltraPure, Invitrogen) is fast cooled down to approximately  $-18^\circ\text{C}$  to form ice. These low-quality and milky samples are then heated up to about  $1^\circ\text{C}$  to start melting. Note

that supercooled liquid water can be easily obtained and maintained in our cold chamber for a long time in the temperature range between  $0^\circ\text{C}$  and  $-15^\circ\text{C}$ . The moment only a few tiny crystals of the ice are left in the sample chamber, the temperature is reduced again to about  $-0.2^\circ\text{C}$  to start slow formation of the crystal phase from the ice nuclei. The dynamics of this process at constant temperature of  $-0.15^\circ\text{C}$  is illustrated in Fig. 1. After 43 min, the first signs of the growing solid phase can be identified as a small rise of the left wing of the Raman spectrum. The feature, located at about 639 nm (marked by the arrow), is clearly visible at 48 min and growing thereafter. Note that 6 more spectra have been taken between 50 min and 69 min (not shown in this figure), which are identical to the ones at 50 min, and 69 min and indicate that the crystal formation is complete. The spectrum taken at 43 min can be decomposed into a sum of water (spectrum at  $t=5$  min) and ice (spectrum at  $t=69$  min) contributions with weighting factors 0.89 and 0.11 respectively. The final result is a transparent, good optical quality ice block of about 2.5 mm thickness. Note that the onset of melting has been detected at  $-0.1^\circ\text{C}$  according to the chamber thermometer reading which indicates that the temperature of the sample has been correctly measured, with less than  $-0.1^\circ\text{C}$  systematic error. This small offset has been subtracted from the sensor readings at all temperatures. The accuracy of the sensor as specified by the manufacturer is  $\pm 0.25^\circ\text{C}$  in the entire range of the temperatures used in these experiments. The stability of the temperature during the measurement was very high. Generally the temperature fluctuated by approximately  $\pm 0.01^\circ\text{C}$ . Three samples of ice were prepared. For each sample, spectra were measured with two orthogonal orientations of polarization,  $S_H$  and  $S_V$  (vertical and horizontal respectively). The average  $S = (S_H + S_V)/2$  has then been analyzed as described in Section 3.

### 2.2. Spectrum calibration

Luminescence of Rhodamine 6G (R6G) in ethanol dissolved at a concentration of about  $10^{-8} \text{ M}$ , excited at 532-nm wavelength and perylene in cyclohexane ( $10^{-6} \text{ M}$  in cyclohexane, 407-nm excitation) have been used to obtain absolute values of the scattering cross-sections (see [24] for details). The quantum yield values used in the calibration procedure have been taken as  $0.950 \pm 0.005$  for R6G [29] and  $0.94 \pm 0.05$  for perylene. Note that, for example, a decrease of the yield from 0.94 to 0.90 makes the estimate for the cross-section proportionally 5% smaller. The relatively large uncertainty of the quantum yield of perylene is the main contribution to the uncertainty of the scattering cross-section and is briefly discussed in the following.

At ambient partial pressure of oxygen, the luminescence quantum yield of R6G is not affected significantly by the oxygen dissolved in ethanol [29] while luminescence of perylene may be appreciably quenched. The reported quenching by oxygen constant of perylene in dodecane is  $112 \text{ M}^{-1}$  [30]. Given the solubility of oxygen in cyclohexane near room temperature is  $1.16 \times 10^{-3} \text{ mole fraction atm}^{-1}$  [31], the oxygen quenching of perylene in cyclohexane should decrease the yield by a factor of about 1.25 at the ambient partial pressure of  $0.21 \text{ atm}^{-1}$  (assuming that the quenching constants in dodecane and cyclohexane are similar). But a much smaller 5%-increase upon deaeration has been observed experimentally [32]. Nevertheless oxygen related quenching is still a factor of concern because when perylene is dissolved in ethanol or benzene, the reported change of the yield upon deaeration has been about 1.3 [33], in agreement with the above estimate. This sheds some doubts on the 1.05 factor for cyclohexane reported in [32]. To reduce oxygen concentration, our sample of cyclohexane has been placed in a helium atmosphere. This has resulted in a moderate increase (a factor of 1.15) of the

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