A spectrometer for height-resolved measurements of the Raman backscatter-coefficient spectrum of water in its gaseous and condensed phases is presented. The spectrometer is fiber coupled to the far-range receiver of the Raman Lidar for Atmospheric Moisture Sensing (RAMSES) of the German Meteorological Service and consists of a Czerny–Turner spectrograph (500-mm focal length) and a 32-channel single-photon-counting detection system based on a multianode photomultiplier. During a typical measurement (transmitter wavelength of 355 nm), the spectrum between 385 and 410 nm is recorded with a spectral resolution of 0.79 nm; the vertical resolution is 15 m and the height range is 15 km. The techniques outlined are those that are applied to calibrate the spectrum measurement and to monitor fluorescence by atmospheric aerosols that have the potential to interfere with the water observation. For the first time, Raman spectra of liquid-water, mixed-phase, and cirrus clouds are reported, and their temperature dependence is investigated by means of band decomposition. The spectrum-integrated condensed-water Raman backscatter coefficient strongly depends on cloud particle volume, but it is not tightly correlated with the cloud optical properties (particle extinction and backscatter coefficient), which implies that retrieval of cloud water content from optical proxies is likely impossible. Aerosol measurements are also discussed. Depending on type, aerosols may show no backscattering in the spectrometer range at all, or a featureless spectrum that stems quite likely from fluorescence. Finally, the example of a cloud forming in an aerosol layer demonstrates that the new instrument not only opens up new perspectives in cloud research but also contributes to studies of cloud–aerosol interaction.

1. Introduction

The explanation of excess humidity in Raman lidar measurements of liquid-water clouds with contributions of Raman scattering from water droplets (Melli et al. 1997) sparked research efforts devoted to remotely measuring atmospheric water in all of its three phases because of the alluring prospect of providing much-needed information on cloud microphysics and bulk properties (such as effective radius and cloud water content) to weather and climate models (Randall et al. 1984; Stephens et al. 1990; Baker 1997; Turner et al. 2007; Chen et al. 2011; Cheng et al. 2012).

Conventional water vapor Raman lidars usually operate in the spectral region that covers the ro-vibrational Raman spectra of molecular nitrogen (N$_2$, centered at a Stokes shift of 2331 cm$^{-1}$) and of the water molecule (H$_2$O) around 3654 cm$^{-1}$ (Penney and Lapp 1976; Murphy 1978; Avila et al. 1999). As illustrated by Fig. 1, the vibrational spectra of both liquid and frozen water exhibit Stokes shifts roughly between 2800 and 3800 cm$^{-1}$ (Gabrichidze 1965; Scherer et al. 1974; Slusher and Derr 1975; Scherer and Snyder 1977; D’Arrigo et al. 1981). This spectral region lies between the nitrogen and water vapor Raman features, and thus expansion of such instruments to also measure the condensed-water phases seemed feasible. Over the years, two different approaches to water measurements have been followed. The first technique employs two discrete receiver channels for the detection of Raman scattering by condensed water and water vapor (Veselovskii et al. 2000; Wang et al. 2004; Rizi et al. 2004; Park et al. 2010; Sakai et al. 2013); the second technique employs a spectrometer for recording the full Raman spectrum of water (Arshinov et al. 2002; Kim et al. 2009; Park et al. 2010; Sakai et al. 2013). While an advantage of the former is the comparatively strong return signals, it suffers from difficulties in calibration, and from the fact that contributions to the signals from other sources than water, such as atmospheric or inner-instrument fluorescence, are difficult to handle (Whiteman et al. 2010; Sakai et al. 2013). The
latter, on the other hand, can overcome these obstacles in principle but requires the spectrometer to be implemented in a lidar with a powerful laser, a large telescope, and efficient optics for meaningful measurements because of the weak Raman backscatter cross sections per detection channel.

This paper presents the first lidar measurements of calibrated Raman backscatter-coefficient spectra of liquid-water, mixed-phase, and ice clouds. The measurements were performed with a water spectrometer that was added to the high-performance Raman Lidar for Atmospheric Moisture Sensing (RAMSES) of the German Meteorological Service, located at the Richard Aßmann Observatory in Lindenberg, Brandenburg, Germany (Reichardt et al. 2012). After initial tests and experimental characterization (Reichardt 2012), the water spectrometer became operational in April 2012 and is now used for cloud spectroscopic studies on a routine basis.

The experimental setup of the water spectrometer and its implementation in the RAMSES far-range receiver is described in section 2. Section 3 details how the spectrometer data are processed, especially the procedure that is applied to calibrate the measured spectra. In section 4 measurement examples are presented that illustrate the scope of the water spectrometer. First, profiles of spectrum-integrated Raman backscatter coefficients of condensed water are compared to those of the cloud optical properties, and the apparent differences are discussed. Second, the evolution of the spectral features of a descending cloud is analyzed in terms of penetration depth, temperature, and water phase. It is demonstrated that Raman band decomposition can be applied to estimate the contributions of liquid and frozen water to the observed Raman spectra. Finally, spectra of atmospheric aerosols are presented. The dependence of the spectral signal strength on the origin and the type of the aerosol is examined. The spectrum of a cloud forming in an aerosol layer is also shown. In section 5 the results of the current studies are summarized and research areas are suggested to which the water spectrometer may make valuable contributions.

2. Water spectrometer

The water spectrometer was added to the multiparameter Raman lidar RAMSES. Details of the lidar instrument are summarized here as much as it is necessary to understand the experimental setup and operation of the spectrometer. For a full description of RAMSES prior to the addition of the water spectrometer, see Reichardt et al. (2012).

a. RAMSES overview

RAMSES is a UV Raman lidar operating at a primary wavelength of 354.7 nm. A 30-Hz injection-seeded frequency-tripled Nd:YAG laser is used as the radiation source; average UV output power is about 15 W. The laser beam is expanded tenfold, steered to the center axis of the main telescope, and transmitted vertically into the atmosphere.

RAMSES has two optical receiving systems, the near-range receiver and the far-range receiver. The near-range receiver consists of a 20-cm telescope and a fiber-coupled three-channel polychromator. It provides, among other parameters, profiles of the water vapor mixing ratio, which are used to calibrate the concurrent measurements with the water spectrometer (section 3); it is thus an indispensable component of the spectroscopic experiment.

The far-range receiver employs a nine-channel polychromator that is, because of limitations in space, split into two horizontal layers. The confocal main telescope (80-cm diameter) delivers the atmospheric signal in a horizontal direction toward this polychromator stack on its lower level. A motorized iris diaphragm in the focal plane of the telescope is used to set the field of view, after which the light is collimated. A dichroic beamsplitter directly after the collimator transmits light <370 nm and
reflects the remainder. It thus separates elastic and rotational Raman signals, which are processed further in the lower level for observations of particle backscattering, depolarization ratios, and rotational Raman and Rayleigh-integration temperatures, from the vibrational Raman signals of N\textsubscript{2} and water, which are analyzed in the upper level for extinction coefficient and water vapor mixing ratio. The part of the polychromator's upper level that is relevant to the implementation of the water spectrometer is shown in Fig. 2.

All Raman detection channels of RAMSES are protected by steep long-wave-pass edge filters against elastic backscattering. Further, to suppress cross talk between the channels, each photomultiplier tube (PMT) detector is placed in a light-proof chamber into which light can enter only through a narrowband interference filter (IF). Each Raman channel is also equipped with a set of five motor-driven neutral-density filters (NDF) for individual intensity adaptation of the optical receiver signals.

RAMSES performs measurements autonomously according to the preselected operation mode of the measurement and systems control software. The lidar can be scheduled to operate continuously or only at nighttime; the automatic beam-alignment system can be activated; and, since the implementation of the water spectrometer, the time frame can be chosen during which spectroscopic measurements are carried out. Because of the weak Raman signals, the spectrometer portion of the lidar system can only be used at night.

**b. Spectrometer setup and integration**

The only minor mechanical modification of the original far-range receiver that was necessary to add the water spectrometer to RAMSES was to install bending mirror M on a motorized translation stage (Fig. 2). Mirror M deflects light around 400 nm, so now when it is pulled back, the fiber optic bundle that transmits light to the water spectrometer is illuminated and the (discrete) water vapor (WV) Raman detection channel is deactivated, and vice versa.

The first optical element in the optical path between the collimator and the water spectrometer is the dichroic beamsplitter BS\textsubscript{a} (not shown in the figure) in the lower level of the polychromator, which reflects light >370 nm upward into the upper level. BS\textsubscript{b} (tilted to direct the signal horizontally), BS\textsubscript{c}—dichroic beamsplitters, EF—edge filter, LP—linear polarizer (optional), WP—wave plate (optional), M—mirror (moveable), FC—fiber coupler, FB—fiber bundle, NAA—numerical-aperture adaptor, D32—32-channel detector, IF—interference filter, L—lenses, NDF—set of five neutral-density filters (moveable), WV—RAMSES water vapor Raman detection channel, N\textsubscript{2}—to RAMSES N\textsubscript{2} Raman detection channels (not shown).

![Fig. 2. Schematic view of the experimental setup used for water measurements.](http://journals.ametsoc.org/doi/abs/10.1175/JTECH-D-13-00188.1)
which has to be taken into account in the calibration of the spectrometer data: see section 3.

Between BSc and the fiber coupler (FC), there is enough room to accommodate additional optical elements, if needed. For example, a linear polarizer (LP; Codixx, Barleben, Germany) and a half-wave plate (WP; VLOC, New Port Richey, Florida) were inserted when the spectrometer was inspected for polarization effects. The atmospheric return signals then impinge on the FC’s focusing lens system (optics built to specification by Licel GmbH, Berlin, Germany), which images the primary telescope mirror onto the circular front face (1.7-mm diameter) of a fiber bundle (FB; 0.12 numerical aperture, 150 individual quartz/quartz fibers with protective coating and 100-μm core, manufactured by LEONI Fiber Optics GmbH, Stromberg, Germany). This optical design concept was adopted because it proved successful in the case of the discrete RAMSES detection channels (Reichardt et al. 2012). It avoids range-dependent effects beyond the point of full overlap (between 1 and 2 km, depending on the field of view), which could occur if the shifting image of the light pulse propagating through the atmosphere were used instead.

The fiber bundle, now in the form of an upright rectangle (4.4 mm × 0.5 mm), is connected to an optical adaptor [numerical-aperture adaptor (NAA)] that projects its image in the plane of the entrance slit of a spectograph with the correct numerical aperture (optics custom built by Licel GmbH). The spectograph (Shamrock SR-500i by Andor Technology, United Kingdom) is based on the Czerny–Turner optical design, has a focal length of 0.5 m, and a numerical aperture of f/6.5. The detector D32 in the spectograph focal plane is the Licel SP32-03 32-channel multianode photomultiplier (Hamamatsu H7260-03) single-photon-counting detection system. Two gratings, 2400 grooves per millimeter (SR5-GRT-2400-GH, holographic, optimized for 400 nm, Andor Technology) and 3600 grooves per millimeter (SR5-GRT-3600-AH), are available. To avoid the effect of the slit on the polarization transition of the spectograph (Romanov and Shuklin 1975), the slit width was chosen as wide as possible without degrading the spectrometer resolution (0.05 and 0.1 mm for entrance and exit slit, respectively). Experimental testing confirmed that the response of the spectograph-detector system is indeed insensitive to the polarization state of the optical input. The wavelength scale of the water spectrometer was calibrated using the intense spectral line at 404.66 nm of a mercury pencil lamp (Sansonetti et al. 1996). Optical properties of all optical elements that determine the wavelength-dependent optical efficiency of the receiver (dichroic beamsplitters) or that were used for characterizing the spectograph (linear polarizers, half-wave plates) were measured with a Varian Cary 400 spectrophotometer.

Default spectrometer settings for water measurements are the grating with 2400 grooves per millimeter and a spectograph center wavelength of 397 nm. The measured spectrum then covers the wavelength range from 384.81 (detector 1) to 410.01 nm (detector 32) with a resolution of Δλ = 0.79 nm. The advantages of these settings are twofold. First, the Q branches of the ro-vibrational Raman spectra of water vapor and N2 are both included, which simplifies the spectrum calibration considerably. Second, sharp features like the spectral peak of ice around 3150 cm⁻¹ and the Q branch signals impinge the photocathodes near their centers and not in between, which is important because detector sensitivity falls off to the cathode edges, and neighboring cathodes are not mounted side by side but with a gap of 0.2 mm.

Figure 3 gives an idea of how challenging the measurement of Raman signals of clouds is. The observation during the night of 25–26 April 2012 is selected as an example. Presented spectrometer data are corrected for pulse pileup, background, range, and Rayleigh extinction. Only the spectral range of Raman scattering by water is shown. The towering spectral feature in the background is the ro-vibrational Raman band of water vapor. At shorter wavelengths, the spectrum of boundary layer aerosol (<2.5 km) and the vibrational Raman bands of a predominantly liquid-water cloud (3–4 km) and a cirrus cloud (5–7.5 km) are visible. Shown are raw data corrected for pulse pileup, background, range, and Rayleigh extinction.
(<2.5 km) and the vibrational Raman bands of a predominantly liquid-water cloud (3–4 km) and a cirrus cloud (5–7.5 km) are visible. As compared to the signal strength of the ice cloud, the Q branch signals of water vapor and N2 are up to a factor of 400 and 5000 more intensive, respectively.

3. Signal processing

a. Data preprocessing

For spectroscopic analysis of clouds or aerosol layers, 15 min or more of measurement time are necessary. First, the selected spectrometer data are corrected for pulse pileup (Whiteman 2003) and integrated. Then, the vertical resolution is reduced (from initially 15 to 60 m) and the background, obtained at the far end of the signal range, is subtracted. Next, the signals are corrected for range and light extinction by molecular scattering and, finally, smoothed with a height-dependent sliding-average length.

The set of the 32 preprocessed spectrometer signals $N_i$ can be written in aggregate form as

$$ M(z) = \{N_1(z), N_2(z), \ldots, N_{32}(z)\}. \quad (1) $$

Signal $N_i$ is the product of the spectrometer efficiency $c$, the optical receiver efficiency $\eta_{rec}$, the spectral backscatter coefficient $\beta$, and the two-way transmission term $T_{i,\text{par}} T_{L,\text{par}}$, which is related to light extinction by particle scattering (and, secondarily, absorption) in the atmosphere:

$$ N_i(z) = N(\lambda_i, z) = c(\lambda_i) \eta_{rec}(\lambda_i) \beta(\lambda_i, z) T_{i,\text{par}}(\lambda_i, z) T_{L,\text{par}}(\lambda_L, z), \quad (2) $$

with $\lambda_L$ the laser wavelength. The overlap function is omitted here because it is assumed to be similar for all spectrometer channels and, thus, to cancel out during the calibration process. Two-way transmission can be considered as wavelength independent in clouds, but not necessarily in aerosols.

The spectral backscatter coefficient $\beta$ encompasses variable contributions from inelastic scattering by gases (e.g., molecular nitrogen, water vapor), condensed water (liquid and solid), and other sources (e.g., aerosol fluorescence):

$$ \beta(\lambda, z) = \beta_{\text{init}}(\lambda, z) + \beta_{\text{vap}}(\lambda, z) + \beta_{\text{con}}(\lambda, z) + \beta_{\text{aer}}(\lambda, z). \quad (3) $$

The optical efficiency of the receiver $\eta_{rec}$ can be written as the product of the two terms, $\eta_{\text{DBS}}$ and $T_{\text{rec}}$, of which the former characterizes the three dichroic beamsplitters—BSa, BSb, and BSc—of Fig. 2 and the latter the remaining optical elements. Term $T_{\text{rec}}$ can be considered as wavelength independent over the spectrometer spectral range between 380 and 410 nm, while $\eta_{\text{DBS}}$ exhibits a pronounced dependence on wavelength and the polarization vector at wavelengths < 393 nm (see Fig. 4):

$$ \eta_{rec}(\lambda_i) = \eta_{\text{DBS}}(\lambda_i) T_{\text{rec}}. \quad (4) $$

The spectrometer efficiency $c$ includes detector responsivity, spectrometer throughput, and shadowing effects on the outer cathodes (because of a mismatch between the focal-plane width of the spectrograph and the length of the detector row). Except for detectors 1 and 32, $c(\lambda_i)$ values vary by 14% (data provided by Licel).

The final step in data preprocessing is the correction for the wavelength dependence of efficiencies $c$ and $\eta_{\text{DBS}}$ in the range of the water spectrum as a prerequisite for quantitative measurements. The spectrometer efficiency is taken into account by multiplying $N(\lambda_i)$ of Eq. (2) by the factor $c(\lambda_{\text{vap}})/c(\lambda_i)$, with $c(\lambda_{\text{vap}})$ the efficiency of the detector channel that contains the Q branch of ro-vibrational Raman scattering by water vapor [$N(\lambda_{\text{vap}})$].

Fig. 4. Spectra averaged over the cloud-free height range (2.5–2.75 km) and the cirrus height range (5.5–6.5 km), and in-cloud spectrum corrected for Raman water vapor scattering of the observation shown in Fig. 3. Bars indicate statistical errors of the lidar measurement. Note that the wavelength range from 392 to 395 nm between the S branch of the N2 ro-vibrational Raman band and the onset of the condensed-water Raman spectrum (396–406 nm) is unaffected by Raman scattering by either N2 or condensed water. This spectral region, which is called the reference spectrum, is monitored for signs of inelastic aerosol scattering (e.g., fluorescence) that may interfere with the water measurement. Note the scale break and the change from linear to logarithmic scale at 1 Tm$^{-1}$sr$^{-1}$ nm$^{-1}$. The combined optical efficiency of the three dichroic beamsplitters (DBS) in the spectrometer setup is also presented. Cross-polarized (cr) and copolarized (co) components with respect to the laser polarization vector are shown.
Term $\eta_{\text{DBS}}$ is considered by dividing $N(\lambda_i) \text{ by } \eta_{\text{DBS}}$ (mean of $\eta_{\text{DBS}}$ for copolarized light and $\eta_{\text{DBS}}$ for cross-polarized light). The corrected signal $N'(\lambda_i)$ can then be written as

$$N'(\lambda_i, z) = \frac{c(\lambda_{\text{vap}})}{c(\lambda_i)\eta_{\text{DBS}}(\lambda_i)} N(\lambda_i, z) \quad (5)$$

For all detection channels with wavelengths $\lambda \approx 393$ nm, $k(\lambda_i)$ is independent of wavelength [$k(\lambda_i) = k_{\text{wat}}$] because $\eta_{\text{DBS}} / \eta_{\text{DBS}}$ is, in good approximation, equal to one.

**b. Spectrum calibration**

Calibration of signal set $M$ is achieved with the aid of the concurrent RAMSES measurement of the water vapor mixing ratio $m_{\text{vap}}$, which is available from the near-range receiver.

Let $N'(\lambda_{\text{nit}})$ be the signal of the detection channel that spans the $N_2$ Raman $Q$ branch. Then, one obtains for the signal ratio $N'(\lambda_i)/N'(\lambda_{\text{nit}})$ the following expression ($\lambda_i \approx 393$ nm):

$$N'(\lambda_i, z) / N'(\lambda_{\text{nit}}, z) = k_{\text{cal}} \beta(\lambda_i, z) T_{\text{par}}(\lambda_i, z) \quad (8)$$

with $k_{\text{cal}} = k_{\text{wat}} / k(\lambda_{\text{nit}})$.

In a height range without clouds or aerosols, one then finds for the ratio $N'(\lambda_{\text{vap}})/N'(\lambda_{\text{nit}})$ (neglecting the wavelength dependence of $T_{\text{par}}$):

$$N'(\lambda_{\text{vap}}, z) / N'(\lambda_{\text{nit}}, z) = k_{\text{cal}} \beta_{\text{vap}}(\lambda_{\text{vap}}, z) \beta_{\text{nit}}(\lambda_{\text{nit}}, z) \quad (9)$$

and for $k_{\text{cal}}$:

$$k_{\text{cal}} = 287.19 \text{ g kg}^{-1} \left( \frac{N'(\lambda_{\text{vap}}, z)}{N'(\lambda_{\text{nit}}, z)} \right) \frac{1}{m_{\text{vap}}(\lambda_{\text{vap}})} \quad (10)$$

with $m_{\text{vap}}$ the water vapor mixing ratio of the clear air. The number in Eq. (10) combines the nitrogen-to-air ratio (by volume), the Raman differential backscatter cross sections of $N_2$ and water vapor, and the factor associated with the unit conversion of the mixing ratio. Calibration constant $k_{\text{cal}}$ is determined by averaging the ratio of $N'(\lambda_{\text{vap}})/N'(\lambda_{\text{nit}})$ and $m_{\text{vap}}^0$ over the particle-free height range. The profile of the calibrated backscatter-coefficient spectrum $S$ can then be written in aggregate form as

$$S(z) = \{ \beta(\lambda_1, z), \beta(\lambda_2, z), \ldots, \beta(\lambda_{32}, z) \}$$

with

$$\beta(\lambda_i, z) = k_{\text{cal}}^{-1} \frac{N'(\lambda_i, z)}{N'(\lambda_{\text{nit}}, z)} \beta_{\text{nit}}(\lambda_{\text{nit}}, z) \quad (12)$$

[from Eq. (8) assuming $T_{\text{par}}(\lambda_i, z) / T_{\text{par}}(\lambda_{\text{nit}}, z) = 1$].

The $N_2$ Raman backscatter coefficient is calculated from the air number density profile obtained from the 6-hourly radiosonde soundings at Lindenberg and the known differential backscatter cross section. Note that $k_{\text{cal}}$ is applied to all spectrometer channels, which can lead to calibration errors in the $\beta$ measurement at wavelengths $\approx 393$ nm, depending on the depolarization ratio of the lidar signal. For water measurements, however, the effect is irrelevant because of the very high transmission and polarization insensitivity of the receiver at these wavelengths.

Figure 4 illustrates the results of the calibration process for the measurement night of 25–26 April 2012. The $N_2$ Raman band is by far the dominant spectral feature, followed by the $Q$ branch of the ro-vibrational Raman spectrum of water vapor. The $\beta$s of the condensed water are at most 2% of the water vapor peak.

Between 392 and 395 nm, no Raman scattering by $N_2$ or water is observed. So, this spectral range is ideally suited for monitoring interferences, which are frequent and mostly related to the presence of fluorescence by aerosols as past experience shows (see section 4c). For this reason this so-called reference spectrum,

$$S_{\text{ref}}(z) = \{ \beta(\lambda_i, z) | 392 \text{ nm} < \lambda_i < 395 \text{ nm} \} \quad (13)$$

has to be evaluated always along with the water measurement.

**c. Determination of condensed-water spectra**

The vibrational Raman spectrum of condensed water (liquid and solid) starts at about 395 nm. It extends to approximately 407 (ice) or 409 nm (liquid water), but here it is overwhelmed by the ro-vibrational Raman
spectrum of water vapor (Fig. 1). The condensed-water Raman spectrum can thus only be determined accurately at wavelengths <406 nm, but even at these shorter wavelengths the vapor spectrum has to be taken into account although its scattering cross sections are weak, since water molecules in the gas phase are more plentiful. The correction is performed in the following way. Let
\[ S_{\text{wat}}(z) = \{ \beta(\lambda_i, z) \mid 396 \text{ nm} < \lambda_i < 406 \text{ nm} \} \]  
be the measured backscatter-coefficient spectrum of a cloud. If \( S_{\text{ref}} \) indicates that interferences are negligible, \( S_{\text{wat}} \) consists of inelastic scattering contributions from condensed and gaseous water:
\[ S_{\text{wat}}(z) = S_{\text{con}}(z) + S_{\text{vap}}(z). \]  

Basically, there is a theoretical and an experimental approach to solving Eq. (15) for \( S_{\text{con}} \). The theoretical method would involve the calculation of \( S_{\text{vap}} \) for ambient \( m_{\text{vap}} \) and temperature at every cloud height, and the subsequent convolution of the theoretical spectrum with the spectrometer function. The advantage of these ab initio computations is that they could be applied under all atmospheric conditions. On the downside, however, they are prone to errors in the spectroscopic data and require the exact characterization of the spectrometer. To avoid these difficulties, the experimental method is used. It requires a height range, ideally just below or above the cloud, where cloud particles are absent. For this cloud-free interval, the backscatter-coefficient spectrum is determined and assigned to the water vapor spectrum of clear air \( S_{\text{air}} \) with mixing ratio \( m_{\text{air}} \). The \( S_{\text{con}} \) profile (including the cloud layer) is then computed according to
\[ S_{\text{con}}(z) = S_{\text{wat}}(z) - \frac{m_{\text{vap}}(z)}{m_{\text{air}}} S_{\text{air}}. \]  

The effect of the vapor correction is exemplified in Fig. 4. The cirrus ice Raman spectrum emerges clearly as a separate entity, and the vapor spectrum is reduced to a small statistics-related residual around its Q branch. As past experience shows, the experimental correction approach works satisfactorily in most measurement cases, which is particularly important for warm liquid-water clouds. The presence of a height interval that is particle free turns out to be a requirement not too stringent. If the meteorological conditions are favorable for lidar observations, then such ranges can generally be found.

d. Spectrum-integrated parameters

The integral condensed-water Raman backscatter coefficient is calculated from \( S_{\text{con}} \) according to
\[ \beta_{\text{con}}^R(z) = \Delta \lambda \sum_{\beta \in S_{\text{con}}} \beta(\lambda, z). \]  
The superscript R is introduced to accent the nature of the scattering process (Raman scattering), and \( \Delta \lambda \) is the spectral width of a detection channel (0.79 nm).

The mean condensed-water Raman spectral backscatter coefficient is defined as \( \bar{\beta}_{\text{con}}^R \) per total spectral width (\( \Delta \lambda_{\text{con}} \)) of the condensed-water spectrum \( S_{\text{con}} \):
\[ \bar{\beta}_{\text{con}}^R(z) = \frac{\beta_{\text{con}}^R(z)}{\Delta \lambda_{\text{con}}} \]  

Vertical integration of \( \bar{\beta}_{\text{con}}^R \) yields the layer-integrated mean condensed-water Raman spectral backscatter coefficient:
\[ \mathcal{B}_{\text{con}}^R = \Delta z \sum_{z_{\text{layer}}} \bar{\beta}_{\text{con}}^R(z), \]  
with \( \Delta z \) the width of a height bin.

The parameters \( \beta_{\text{ref}}, \mathcal{B}_{\text{ref}}, \) and \( \mathcal{B}_{\text{ref}} \) of the reference spectrum \( S_{\text{ref}} \) are defined analogously. For all measurement products, the statistical errors are deduced from those of the raw signals (Poisson statistics assumed) following Gauss’ error propagation law.

e. Perspective: Estimation of cloud microphysical properties

With the water spectrometer, calibrated measurements of the backscatter-coefficient spectrum between the Raman bands of molecular nitrogen and water vapor are possible for the first time. This capability enables one to study quantitatively the spectral characteristics of clouds and aerosols, as will be demonstrated in section 4.

Derivation of cloud microphysical properties from the calibrated Raman spectra is also possible (and straightforward), and it can be accomplished in two different ways. One approach is to apply spectroscopic data for the Raman differential backscatter cross sections of liquid water and ice obtained in laboratory experiments (Slusher and Derr 1975; Faris and Copeland 1997; Ahmad and Iles 2001) to convert the integral condensed-water Raman backscatter coefficient to cloud water content [under proper consideration of resonance effects related to the small sizes and symmetry properties of the atmospheric particles; see the discussions by Melfi et al. (1997), Whiteman and Melfi (1999), and Veselovskii et al. (2002)]. Alternatively, the water spectrometer measurement can be related to cloud water content with the help of observations by other instruments. For instance, this method was used by Sakai et al. (2013) to calibrate their two-channel liquid-water measurements. The retrieval results
obtained with a dual-field-of-view Raman lidar (Schmidt et al. 2013) could also be used for this purpose.

From the profiles of cloud water content and either the particle extinction coefficient (Korolev et al. 2001; Rizi et al. 2004) or the backscatter coefficient (Whiteman and Melfi 1999), one then derives other microphysical properties, such as effective radius and particle concentration in liquid-water clouds. First microphysical studies based on the water spectrometer show encouraging results, but a full description and discussion of the microphysical analysis would be beyond the scope of this article and will have to be the topic of a follow-up publication.

Finally, for the discussion that follows it is important to note that the above-mentioned resonance effects do not compromise spectroscopic analysis of clouds. The laboratory experiments by Suzuki et al. (2012) prove that the shape of the Raman spectrum is the same for water drops and bulk liquid water, and so the cloud Raman spectra obtained with RAMSES can be interpreted physically.

4. Measurements

Measurement examples are presented that illustrate the capability of the water spectrometer. First, profiles of the spectrum-integrated condensed-water Raman backscatter coefficient and the optical properties are discussed for liquid-water and ice clouds. Then, Raman backscatter-coefficient spectra $S_{con}$ of mixed-phase clouds are analyzed. Finally, aerosol measurements are investigated.

a. Cloud profiles

Figure 5 combines the measurement results obtained with the RAMSES water spectrometer and far-range receiver for the example measurement of 25–26 April 2012. Profiles of particle properties are shown, and smoothing is the same for all profiles to facilitate comparison. Three particle layers are observed that exhibit distinct optical characteristics. Boundary layer aerosols below 2.5 km show $\beta_{ref}$ values that are larger than those of the free-troposphere clouds, even though the particle extinction coefficient $\alpha_{par}$ and the particle backscatter coefficient $\beta_{par}$ suggest a comparatively smaller particle mass. Another difference is that only the aerosol possesses significant $\beta_{ref}$, which likely indicates aerosol fluorescence (for a general discussion of aerosol measurements, see section 4c).

In the free troposphere, identical cloud boundaries are seen in all profiles, except for the extinction coefficient, which stretches to higher altitudes because of the multiple-scattering effect (Whiteman et al. 2001; Reichardt and Reichardt 2006). Coefficient $\beta_{ref}$ is zero within statistical errors throughout the cloud ranges, indicating the absence of fluorescence or other interfering effects. The Raman backscatter-coefficient spectrum $S_{con}$ (not shown), ambient temperatures between $-10^\circ$ and $-5^\circ$C, and particle depolarization ratios $<0.08$ confirm that the cloud at 3–4 km consists mostly of supercooled liquid-water droplets mixed with some ice particles. In contrast, the higher cloud (5–7.8 km, temperatures $<-15^\circ$C) contains only frozen water particles.
Fig. 6. Particle volume-to-projection-area ratio $V_{\text{par}} / G_{\text{par}}$ as function of particle maximum dimension for different particle shapes (random spatial orientation assumed). Values are indicated for droplets with a diameter of 20 $\mu$m and for columnar crystals of 200-$\mu$m length. Length-to-width relations of Mitchell and Arnott (1994) and Auer and Veal (1970) are used for hexagonal columns and plates, respectively.

So, the optical properties ($\alpha_{\text{par}}$ and $\beta_{\text{par}}$) depend differently on particle size and morphology than $\beta_{\text{con}}$, and the spatial orientation of the particles matters as well, because upon horizontal alignment the projection area increases, while the volume remains unchanged. In the case of platelike crystals, for example, this effect can amount to 20%–80%, depending on size. For column-like crystals it is smaller but still significant (<20%). For these reasons it is hardly surprising that the profiles of $\alpha_{\text{par}}$ and $\beta_{\text{par}}$ depicted in Fig. 5 bear little resemblance with the $\beta_{\text{con}}$ profile. In summary, both observations and theoretical considerations suggest that no simple relation exists between the optical properties of a cloud, for example, $\alpha_{\text{par}}$ and $\beta_{\text{par}}$. By extension, retrieval methods of cloud water content that exploit optical proxies, such as the technique proposed for cirrus clouds by Heymsfield et al. (2005), are likely to be inaccurate.

b. Cloud spectra

1) OBSERVATIONS

Figure 7 presents the RAMSES measurement of the night of 23–24 September 2012. The sky was overcast. Cloud base descended from 4 to 2 km over time and cloud top could not be observed because of massive light extinction by particle scattering. For the same reason, measurements of particle optical properties and Raman backscatter-coefficient spectra were limited to penetration depths of about 1 and 0.5 km, respectively. Labels M1–M3 indicate measurement segments that are discussed in detail.

The cloud segment labeled M1 was mixed phase, with ice contributing approximately 4 times more to the total cloud Raman signal than supercooled liquid water [see the spectrum analysis in section 4b(3); Fig. 9]. Particle depolarization ratio $\delta_{\text{par}}$ and $\beta_{\text{par}}$ are inversely correlated, which can be a sign of partial horizontal alignment of the ice particles.

The most striking difference between liquid-water cloud and ice cloud is seen in the profile of $\beta_{\text{con}}$. While the optical coefficients $\alpha_{\text{par}}$ and $\beta_{\text{par}}$ are of similar magnitudes for the two clouds, values of $\beta_{\text{con}}$ are more than 4 times larger for the cirrus as compared to the liquid-water cloud. The effect is likely being caused by the difference in particle size. Coefficient $\beta_{\text{con}}$, as the product of the molecular Raman differential backscatter cross section and the number of condensed H$_2$O molecules, is proportional to the particle volume in an air parcel, while $\alpha_{\text{par}}$ and $\beta_{\text{par}}$ are proportional to the particle projection area of the same air parcel (the proportionality holds for both mono- and polydisperse size distributions). Because the ratio of particle volume to projection area generally increases with size, a size increase favors $\beta_{\text{con}}$ over $\alpha_{\text{par}}$ and $\beta_{\text{par}}$. The relationship is illustrated in Fig. 6 for spheres and hexagons, the principal shapes of cloud particles. For example, consider a liquid-water cloud composed of droplets with a diameter of 20 $\mu$m and a cirrus cloud of hexagonal columns of 200 $\mu$m. For this example, the volume-to-projection-area ratio ($V_{\text{par}} / G_{\text{par}}$) for 20-$\mu$m spheres and 200-$\mu$m columnar hexagons is shown in the figure to be 13.4 and 70 $\mu$m, respectively. Therefore, the volume of the hexagonal columns compared to the volume of the spheres would be 5.2 (70/13.4) times greater for the same $\alpha_{\text{par}}$ (since $\alpha_{\text{par}}$ is proportional to $G_{\text{par}}$).
because of strong multiple scattering in the optically thick cloud (Sassen and Petrilla 1986). Even though $\beta_{par}$ is up to more than $14 \times 10^6$ times stronger than $\beta_{con}$ and $\beta_{ref}$, profiles of these two quantities are unaffected by elastic backscattering from the cloud, which demonstrates the efficient suppression of laser light in the water spectrometer. Interfering inelastic scattering is absent also, as can be seen from $\beta_{ref}$. The marginally elevated $\beta_{ref}$ values just below 2.9 km are considered an artifact of the data processing because of low signal levels.

The dependence of the cloud Raman backscatter-coefficient spectrum on penetration depth, and hence temperature, for cloud segment M2 is depicted in Fig. 8 as well. All spectra lack evidence of the ice peak around 399.3 nm (see Figs. 1 and 9), indicating that this cloud segment consisted of liquid droplets throughout. Interestingly, according to the midnight radiosounding, temperatures dropped below freezing at 2.7 km, so the cloud liquid was supercooled above this altitude. A slight shift of the spectrum to shorter wavelengths with height is discernable, which implies that the detection sensitivity of the water spectrometer is sufficient to observe the temperature dependence of Raman scattering by liquid water. This temperature dependence is further explored in section 4b(3), after a short review of the relevant theoretical background.

2) REVIEW: TEMPERATURE DEPENDENCE OF THE RAMAN SPECTRA OF LIQUID WATER AND ICE

Upon condensation of water vapor, hydrogen bonds form between the H$_2$O molecules, and depending on their number, the corresponding vibrational modes vary in frequency. At warm temperatures, the modes of weakly hydrogen-bonded H$_2$O (higher frequencies) are favored, while at colder temperatures those of strongly bonded molecules dominate (lower frequencies). As a result, the vibrational Raman spectrum of liquid water depends on ambient temperature, and is relatively broad (Scherer et al. 1974; D’Arrigo et al. 1981; Whiteman et al. 1999). On the phase transition from liquid to frozen water, the H$_2$O molecules form the tetrahedral structure of ice, and the Raman spectrum changes accordingly (Pershin and Bunkin 1998). Like in liquid water, in ice all vibrations are weakly active, which gives rise to a similar broad vibrational spectrum. However, the number of highly coupled H$_2$O molecules is significantly higher and thus the characteristic spectral maximum of Raman scattering by ice around 3150 cm$^{-1}$ develops at the expense of modes with higher frequencies (Gabrichidze 1965; Slusher and Derr 1975; Scherer and Snyder 1977).

To explain the temperature dependence of the Raman spectrum of liquid water, different models have been suggested over the years that have in common a finite number of discrete vibration bands with fixed spectral shapes (the bands are assumed to be associated with specific vibrating H$_2$O molecular structures). These bands are populated depending on temperature and thus a superposition of the bands is needed to obtain the overall spectral shape. The observed Raman spectra can be decomposed as the sum of the vibration bands of the selected model and interpreted in terms of the relative band strengths (Gabrichidze 1965; Walrafen 1967; Scherer et al. 1974; D’Arrigo et al. 1981; Pershin et al. 2007; Suzuki et al. 2012). For example, the model of D’Arrigo et al. (1981) assumes three coexisting molecular structures to explain the Raman spectrum of (supercooled) liquid water. These are 1) H$_2$O molecules that are hydrogen bonded with their four neighbors, 2) H$_2$O molecules with fewer than four hydrogen bonds, and 3) H$_2$O molecules bound as ice that is postulated to exist because of heterophase fluctuations. Unfortunately, similar elaborate mode models are not available for studies of the temperature dependence of the Raman spectrum of ice.

3) INTERPRETATION OF OBSERVATIONS: CLOUD VIBRATIONAL RAMAN MODES

Spectral band decomposition is applied to determine the vibrational Raman modes of the observed clouds. The relative strengths of the modes are used to identify
the phase, or phases, of the cloud, and to show the dependence of the liquid-water cloud spectrum on temperature. Four measurements are selected for the analysis. Arranged in order of mean cloud temperature, these are the cirrus cloud of 25–26 April 2012 (height between 5.5 and 6.5 km, temperatures below −21.8°C; Fig. 5), and the ice-containing cloud segment M1 (3.1–3.2 km, −20.3°C) and the liquid-water cloud segments M2 (2.7–2.8 km, −0.2°C) and M3 (2.0–2.1 km, 3.7°C) of the measurement of 23–24 September 2012 (Fig. 7).

Band decomposition is performed by fitting mode model data to the measurement with an automated least squares algorithm. Liquid-water spectra are analyzed using the model of D’Arrigo et al. (1981). The model was selected for its simplicity. As compared to Suzuki et al. (2012), only three modes are defined, and mode spectral shapes and positions are fixed. Further, it is applicable to supercooled liquid water which, for example, the model of Wallraff (1967) is not. The D’Arrigo et al. (1981) modes are shown in the top-right panel of Fig. 9; labels I, Lo, and Lc indicate Raman bands of water molecules bonded as ice, with four and fewer than four hydrogen bonds, respectively. The model of D’Arrigo et al. (1981) is not ideal for decomposing the Raman spectra of ice and mixed-phase clouds. Test runs show that it especially fails to reproduce the short-wavelength part of the cloud spectrum, and significant residuals remain. So, other mode models are necessary in these cases. Unfortunately, these are not available, as mentioned earlier. Nevertheless, to study ice and mixed-phase clouds, the corresponding Raman spectra are decomposed based on the laboratory data of Slusher and Derr (1975) obtained for bulk liquid water and solid water (ice). The modes are denoted L and S, respectively, and are depicted in the top-left panel of Fig. 9. Note that the selection of the models underlying the Raman band analysis is in a sense arbitrary, as no scientific consensus seems to exist on the most appropriate model.

The results of the Raman band decomposition are also presented in Fig. 9. First, the Raman spectra of ice-containing clouds are discussed. The spectral data provided by Slusher and Derr (1975) can be successfully applied to the measured data to determine the inelastic scattering contributions by liquid and frozen water to the cloud Raman spectrum. In the case of cloud M1 (bottom-left panel), 80% of the integral condensed-water Raman backscatter coefficient originates from ice. Interestingly, mean temperatures of clouds M1 and M2 are almost equal, yet cloud water of the former is mostly frozen, while that of the latter is not. This observation underscores the known fact that near the 0°C level, atmospheric temperature alone is not a sufficient indicator of particle phase and that other processes, such as supercooling of droplets and sedimentation of ice particles, have to be considered as well. In the case of the cold cirrus cloud of 25–26 April 2012 (middle-left panel), the measured Raman spectrum agrees very well with the ice spectrum of Slusher and Derr (1975). The best fit of the inversion algorithm yields exactly 100% ice with marginal residual.

Raman spectra of liquid-water clouds M2 and M3 are discussed next. The three-mode model can be applied successfully to the water spectrometer measurements. Observation and the fitted model agree within the measurement uncertainties. Modes Lo and Lc dominate the spectra of M2 and M3, as can be seen in Fig. 9, while
mode I accounts for only 0.6% and 2.3% of inelastic scattering, respectively, which is, in view of the measurement errors, statistically insignificant. Mode Lo is favored at colder temperatures as more H₂O molecules form four hydrogen bonds. As a result, the backscatter-coefficient-weighted center of the M2 Raman spectrum is shifted to shorter wavelengths by approximately 0.1 nm as compared to the M3 spectrum. This example suggests that the model of D’Arrigo et al. (1981) is suited for interpreting the Raman spectra of liquid-water clouds, but more studies are necessary to substantiate this hypothesis. Particularly interesting would be cases with strongly supercooled cloud liquid because these would allow one to investigate the postulated mode I.

c. Aerosols

1) Observations

Figure 10 presents three aerosol measurements of summer 2012. The cases were selected to give an overview of the additional information one can expect to derive from the water spectrometer under different atmospheric conditions.

On 18 August 2012, the atmosphere below 4 km was dry, and the δₚₑₚ and βₚₑₚ profiles indicate two distinct aerosol layers at heights of <1 km and >2 km, respectively. Boundary layer aerosol shows elevated values of the mean condensed-water Raman and reference spectral backscatter coefficients (βₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑ廨data}
levels of $\beta_{\text{con}}^R$ and $\beta_{\text{ref}}$. The corresponding backscatter-coefficient spectra for altitude regions S1 and S2 seen in Fig. 10 are presented in Fig. 11.

Two days later, on 20 August 2012, the air was much moister and a cloud formed in the free troposphere. The spectrum shown in Fig. 11 for the 3–4-km height range of the cloud (S3 in Fig. 10) is evidence for the presence of liquid water, but unlike the cloud cases of Fig. 5, considerable signal is observed at the reference wavelengths < 395 nm as well (Fig. 11). Because this scattering contribution has a spectral shape that is similar to those of aerosol layers S2 and S4 (Fig. 11), it appears plausible to assume that it stems from atmospheric aerosol particles that coexisted with the cloud or were within the cloud droplets.

Finally, on 16 September 2012, aerosols were observed in dry air masses between the ground and 4 km (relative humidity < 60%). Mean $\delta_{\text{par}}$ and the optical properties ($\delta_{\text{par}}$ and $\beta_{\text{par}}$) suggest a change in aerosol type around 1.4 km (see Fig. 10). The upper layers are characterized by higher $\delta_{\text{par}}$ (0.05 as compared to <0.03), and by $\beta_{\text{con}}^R$ and $\beta_{\text{ref}}$ values that are twice as large as those of the boundary layer even though $\beta_{\text{par}}$ indicates a lower aerosol content. The spectrum shown in Fig. 11 of the aerosol lamina between 2.3 and 3 km (S4) is broad and featureless with a small linear increase with wavelength.

In all measurement examples, the aerosol spectroscopic characteristics are different from those of pristine clouds. Spectrum shape, especially the elevated values of $\beta_{\text{ref}}$, and the low relative humidity (except for the cloud-formation case) all indicate that they cannot result from Raman scattering by water molecules. The following review of inelastic scattering by aerosols strongly supports the conclusion that fluorescence by aerosol is observed instead.

2) REVIEW: INELASTIC SCATTERING BY AEROSOLS

In situ field and laboratory studies show, that depending on their composition, most atmospheric aerosols scatter light inelastically, either by the Raman process or by fluorescence, and have thus the potential to interfere with the water measurement if the emission lies within the spectrometer range. Most important in this context is organic material, be it as relatively simple chemical compounds constituting or contributing to the composition of the aerosol particles (Baustian et al. 2012; Liu et al. 1958).
or as complex biogenic particles (O’Connor et al. 2011; Pan et al. 2011). Its vibrational Raman bands of the C–H bonds and the ammonium and hydroxyl functional groups overlap the water spectrum (Baustian et al. 2012), but given its much larger scattering cross section, the dominant effect of organic material is fluorescence. Pan et al. (2007) grouped fluorescence spectra of airborne particles in clusters with characteristic spectral features to which they tentatively assigned the fluorescent materials or particle types. It was found that when excited at a wavelength of 263.5 nm, fluorescence spectra of monomeric compounds, compound mixtures, bacteria, and marine aerosol tend to fall off in intensity over the spectral range of the spectrometer (around 400 nm), while those of humic acid and humic-like substances (HULIS) exhibit an intensity increase. Spectra obtained for pollen and fungal particles show characteristics that are similar to HULIS when excited at ultraviolet wavelengths. Furthermore, these so-called bioaerosols (a group of airborne particles that also comprises whole organisms like bacteria and algae, biopolymers, plant debris, and insect parts) are particularly potent fluorophores (Pößner and algae, biopolymers, plant debris, and insect parts) are particularly potent fluorophores (Pößner et al. 2012), fluorescing much more strongly than soot or inorganic particles like mineral dust, or dry salt particles (Pan et al. 2003; Pößner et al. 2012). So, in atmospheric measurements the water spectrometer should be most sensitive to the presence of bioaerosols even when the particle concentrations are low. However, one should also expect a fluorescence background of varying intensity in the case of predominantly inorganic aerosols because of internal or external mixing with organic matter that is observed for sea salt aerosol or Saharan dust (Cavalli et al. 2004; Aymoz et al. 2004). In fact, fluorescence of the latter type of aerosol has been detected by Toprak and Schnaiter (2012).

In the absence of organic material, Raman scattering by aerosols might pose a secondary source of systematic error for the water measurement, but probably only a weak one and only for certain types of aerosols. For instance, clay minerals, such as kaolin, and other hydrated minerals exhibit characteristic OH Raman spectra with compound-specific peak positions within the spectrometer range (Wang et al. 2003). Most inorganic aerosols, however, should not interfere with the water measurement because the Stokes shifts of many main constituents are too short. To these belong, for example, anhydrous carbonates, such as calcite and dolomite (1087 cm$^{-1}$), gypsum (1005 cm$^{-1}$), feldspar (513 cm$^{-1}$), and quartz (474 cm$^{-1}$) (Wang et al. 2003), as well as inorganic salt particles, such as sulfates and nitrates, irrespective of whether the salts are dry or in solution (Tang and Fung 1989; Ivleva et al. 2007).

3) INTERPRETATION OF OBSERVATIONS: AEROSOL TYPE CLASSIFICATION

To get a better understanding of the aerosol measurements shown in Fig. 10, the origins of the observed air masses were investigated using the Flexible Particle (FLEXPART) Lagrangian particle dispersion model (Stohl et al. 2005). The results are summarized in Table 1, along with the particle optical properties ($\delta_{\text{par}}$ and $S_{\text{par}}$) of the observed aerosol layers. In most cases it was sufficient to trace back the air masses for 10 days to obtain source regions that would reconcile the inferred aerosol types with the optical properties, except for the elevated layer of 18 August 2012. Here the 10-day backtrajectories circled over the Atlantic Ocean most of the time, and then followed the English Channel and made landfall only shortly before the measurement, indicating predominantly maritime aerosol. However, the reported lidar properties of this aerosol type—that is, $\delta_{\text{par}} < 0.03$ and $S_{\text{par}}$ around 20 sr (Groß et al. 2011)—do not match the observations of 0.1–0.18 and 25–35 sr, respectively. Especially the substantial depolarization ratios indicate that mineral dust particles were present, because it is the only aerosol type that is known to cause significant depolarization (Müller et al. 2003; Groß et al. 2011). For this reason, the FLEXPART model runs were extended to 20 days for this measurement case, and indeed the results suggest that the air masses were previously advected from northern Africa to the western Atlantic by the easterly trade winds. So, it is reasonable to assume that actually a mixture of maritime aerosol and Saharan dust was observed at Lindenberg during that night.

The findings suggest the following basic idea for the interpretation of measurements of aerosol fluorescence with the water spectrometer. The relative strength of the fluorescence signal may serve as an indicator of the aerosol type. Signal strength depends on the species and the amount of the fluorescent compound, and the chemical environment of the fluorophore is important as well because the quenching of the fluorescence intensity depends on the substrate or solution (Putikiranta et al. 2010). It is instructive in this context to study the relation between the layer-integrated mean condensed-water Raman and reference spectral backscatter coefficients ($\overline{B}_{\text{con}}^R$ and $\overline{B}_{\text{ref}}^R$) and the layer-integrated particle (elastic) backscatter coefficient $B_{\text{par}}$:

$$B_{\text{par}} = \Delta z \sum_{z \in \text{layer}} \beta_{\text{par}}(z).$$ (20)

The width of a height bin is denoted by $\Delta z$. If $B_{\text{par}}$ is viewed as an approximate measure of aerosol content, then the ratios $\overline{B}_{\text{con}}^R/B_{\text{par}}$ and $\overline{B}_{\text{ref}}^R/B_{\text{par}}$ indicate the fluorescence capacity of the aerosol. Observed values are
presented in Table 1. On all three days, $B_{\text{con}}^R/B_{\text{par}}$ and $B_{\text{ref}}^R/B_{\text{par}}$ of mixed boundary layer aerosols are similar, but seem to be higher when particles with continental sources outweigh those of maritime origin. The free-troposphere measurements of 18 August and 16 September 2012 show that the fluorescence capacity of continental aerosols can vary widely. Ratios of 18 August and 16 September 2012 demonstrate, elevated aerosol interaction is possible. As the observation of dust (and maritime aerosol) are minimal, while maximum values are measured in the plume of wild fires that ravaged the western territories of the contiguous United States in September 2012. This result is to be expected because complex organic matter, which should abound in biomass-burning or biogenic aerosol, fluoresces strongly, while simple organic compounds that may be found in maritime or mineral dust, or minerals themselves, show little fluorescence. The perception that fluorescence may be generally associated with the presence of continental aerosols may serve as a working hypothesis for future studies.

The discussion of the aerosol measurements can be summarized as follows. First, investigation of cloud–aerosol interaction is possible. As the observation of 20 August 2012 demonstrates, elevated $B_{\text{con}}^R$ values would clearly indicate the presence of aerosols even in clouds (see Fig. 10). Second, measurements of cloud condensed-water content require monitoring of the reference spectrum, so that the Raman spectrum can be corrected for aerosol interference if necessary. For the cloud case presented here, the derived liquid-water content would be 25% too high if the water spectrum were not corrected for fluorescence (see S3; Fig. 11). Third, simultaneous measurements of the fluorescence capacity and of the particle optical properties may help to identify, or further characterize, aerosol type.

5. Summary and outlook

A spectrometer for lidar measurements of atmospheric water in all three phases has been presented. The instrument has been integrated in the far-range receiver of the RAMSES lidar at the Lindenberg Observatory of the German Meteorological Service. The experimental setup is described in detail, and the signal processing that is performed in order to obtain calibrated Raman spectra of vaporous, liquid, and frozen water is explained. Measurement examples are discussed that demonstrate the scope of the water spectrometer. Spectrum-integrated condensed-water Raman backscatter coefficients and optical properties (particle backscatter coefficient and particle extinction coefficient) of clouds are found to be only weakly correlated because of their different dependence on particle size, shape, and spatial orientation, and thus retrieval of cloud water content from optical proxies is likely to be unreliable without additional information on the cloud. Further, the case is made that for accurate water measurements, it is absolutely necessary to monitor a spectral region outside the water Raman band for interfering inelastic light scattering, such as aerosol fluorescence. Moreover, it is shown that decomposition of measured condensed-water Raman spectra allows one to determine unambiguously the cloud phase and to study temperature effects. Finally, aerosol spectra are presented that can be linked to fluorescence, most likely of biogenic material. Dispersion-model simulations suggest that the fluorescence capacity of the aerosol is correlated with its source region and, hence, aerosol type. As spectra of aerosols and clouds are distinctly different, simultaneous observation is possible.

The results of this study demonstrate that the water spectrometer holds promise for several fields of atmospheric research, for example, the characterization and classification of aerosols, and the interaction between aerosols and clouds. Moreover, the water spectrometer can be used to improve our understanding of mixed-phase clouds. Questions that could be addressed include, among others, the fraction of water ice and its relation to the optical properties of the cloud. Another important
issue that needs to be studied more carefully is the effect of aerosol fluorescence on water vapor measurements with Raman lidar. Its error potential is particularly pronounced if the filter bandwidth of the vapor detection channel is large and humidity is low (Immler et al. 2005; Sakai et al. 2013).

Finally, preliminary studies suggest that the RAMSES lidar with the addition of the water spectrometer may also be used to derive cloud microphysical properties such as particle effective radius and particle concentration in liquid-water clouds, and cloud water content. Ideally, the lidar measurements would go hand in hand with laboratory experiments to provide suitable and reliable spectroscopic data. Especially, measurements of the Raman backscatter cross sections of liquid water and ice, studies of structural resonances, and systematic investigations of the temperature dependence of the ice spectrum are required.

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