LITES: rotational Raman spectra of air molecules measured by high-resolution-spectroscopy lidar

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We present the first, to the best of our knowledge, measurements from a new lidar facility that was designed and built at the University of Hertfordshire since 2012. LITES (Lidar Innovations for Technologies and Environmental Sciences) allows testing, developing, and measuring of a multitude of climate-change relevant parameters of atmospheric particulate pollution and photochemically reactive trace gases. The core of LITES consists of a lidar spectroscopy instrument. In this first contribution, for example, we present the design and specifications of this instrument, its performance, and potential applications. First, we show examples of the measurements of range-resolved pure rotational Raman spectra and rotational-vibrational Raman spectra of air molecules with a spectral resolution better than 5 cm⁻¹. We also present day-time temperature profiles obtained from pure rotational spectroscopic lidar signals. In future work, we aim to explore the potential of our multi-channel high-resolution spectrometric lidar to obtain vertically resolved chemical characterization of aerosols and trace gases.

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Lidar is the method of choice for measuring atmospheric state parameters, photochemically reactive trace gases and particulate pollution on a vertically highly resolved scale [1,2]. The combination of various lidar techniques (nitrogen Raman [3] and high spectral resolution lidar [4]) with mathematical inversion algorithms today allows for temporally and vertically resolved observations of aerosol optical and microphysical properties on a routine basis [5,6]. This approach of using Raman lidar and an inversion algorithm for particle characterization is limited to nighttime observations because of the weak intensity of Raman signals in the visible wavelength range (VIS). To the best of our knowledge, only NASA Langley’s airborne multiwavelength high spectral resolution lidar (HSRL-2) allows for carrying out this type of combined optical and microphysical particle characterization also under daytime conditions [6,7]. Lidar and passive remote sensing instruments currently cannot provide us with vertically resolved information regarding the chemical composition of aerosols under ambient conditions.

Pure rotational Raman (PRR) lidar techniques and data analysis have been developed in the past 40 years and commonly used for atmospheric temperature measurements [8–10]. PRR lidar also allows for independent measurements of profiles of aerosol extinction and backscatter coefficients [11]. Both approaches, i.e., temperature and aerosol measurements, are usually based on the use of two or three separate channels for detecting different parts of the PRR spectra (PRRS) of air molecules. These traditional systems use combinations of interference filters, single or double monochromators, or Fabry–Perot etalons. Although these lidar show good performance with regard to temperature and aerosol profiling, they have several significant disadvantages: (1) these lidars are not able to provide simultaneous measurements of the entire PRRS; (2) the hardware is fixed in the sense that only one pumping wavelength can be used; (3) worldwide, only a few systems with very specific design are capable of carrying out day-time observations.

The long-term goal of our work is to explore the potential of using a multi-channel high-resolution spectrometric lidar for the vertically resolved chemical characterization of aerosols and gases based on the measurements of range-resolved Raman spectra. For that purpose, we have been developing a new remote sensing facility called Lidar Innovations for Technologies and Environmental Sciences (LITES). The facility combines a unique lidar spectroscopy instrument (LiSsI) with in situ instruments such as Raman and fluorescence microscopes, and gas and aerosol chambers.

In this Letter, we present the setup of LiSsI and show the results of the first measurements. The design of this lidar allows for the profiling of trace gases, chemical components in particles, and bio-aerosols in atmospheric aerosol pollution in the troposphere. The long-term goal can be achieved by combining different linear and nonlinear spectroscopy techniques, i.e., photoluminescence, fluorescence, Raman, and coherent anti-Stokes Raman spectroscopy in a single measurement platform.

The specifications of the system are listed in Table 1. The main components of the lidar include
- an ultra-high-energy seeded Nd:YAG laser (Continuum Powerlite Furie LD) with a second-harmonic generator and a third-harmonic generator. The system emits laser light with
| Table 1. Technical Specifications of the Lidar System |
|----------------------------------------------------|
| **Continuum Powerlite Furie LD**                    |
| Laser type                                          | Nd:YAG, injection seeded |
| Pulse energy                                        | 8000 mJ at 1064 nm       |
|                                                    | 5000 mJ at 532 nm        |
|                                                    | 2500 mJ at 355 nm        |
| Beam divergence                                     | 0.5 mrad                |
| Repetition rate                                     | 10 Hz                   |
| Linewidth                                          | <0.003 cm⁻¹             |
| Pulse duration                                      | <15 ns                  |
| **Horizon Optical Parametric Oscillator**           |
| Pump wavelength                                     | 355 nm                  |
| Wavelengths                                         | from 192 to 2750 nm     |
| Resolution/scan step                               | 0.01 nm                 |
| Pulse energy                                        | 120 mJ at 400 nm        |
|                                                    | 60 mJ at 600 nm         |
|                                                    | 25 mJ at 300 nm         |
|                                                    | 5 mJ at 200 nm          |
| Beam divergence                                     | <2 mrad (both axes)     |
| Repetition rate                                     | 10 Hz                   |
| **HORIBA 1250M Research Spectrometer**             |
| Focal length                                        | 1.25 m, F/9             |
| Spectral range                                     | 0–1500 nm at 1200 g/mm |
| Grating size                                        | 110 mm × 110 mm         |
| Dispersion @500 nm                                  | 0.65 μm/nm              |
| Accuracy/repeatability                             | ±0.15 nm/ ±0.005 nm     |
| Gratings and blaze                                  | max resolutions at 313.183 nm |
| 2400 gr/mm at 250 nm                               | 0.003 nm                |
| 1800 gr/mm at 400 nm                               | 0.004 nm                |
| 1200 gr/mm at 330 nm                               | 0.006 nm                |
| 600 gr/mm at 500 nm                                | 0.012 nm                |
| **Detection Units**                                |
| Mie and Rayleigh                                    |
| Scattering                                          | 355 nm, PMT HV-R9880U-20 532 nm, |
| Spectroscopic 1 Licel                               |
| SP32-20                                             | 0.8 mm × 7 mm × 32 anodes spectral |
| Princeton Instruments                               |
| PI-MAX4                                             |
| ICCD camera                                         |
| Spectroscopic 3                                     |
| ANDOR iXon 3                                        |
| EMCCD camera                                        |
| **Schmidt–Cassegrain Telescope**                    |
| Primary                                             | f/10, FL = 3910 mm, D = 391 mm |
| Second                                              | f/10, FL = 2000 mm, D = 200 mm |
| Third (planned)                                     | f/11, FL = 11000 mm, D = 1000 mm |
| **Data Acquisition System**                         |
| Mie and Rayleigh scattering                         |
| Multi-anode PMT                                     |
| ICCD                                                |
| EMCCD                                               |

For this lidar system, we specifically developed an optical sub-system that delivers light signals from a set of signal-receiving telescopes (that will provide signals from approximately 100 m to 100 km height above ground, once the setup of three telescopes is complete) to the entrance slit of the main spectrometer. The optical sub-system is based on a commercially available doublet and triplet achromatic lens.

The design of the optical sub-system was developed based on ZEMAX simulations and experimental tests that were carried out subsequently. The optical components allow for focusing the backscattered light that comes from the receiver telescopes on the entrance slit of the spectrometer with a minimum focal point size. In this way, we are able to obtain an optimal ratio between spectral resolution and intensity of the Raman signals within the spectral range from UV (300 nm) to NIR (1500 nm).

The system allows for using three types of data acquisition modes. We can detect lidar signals on the basis of (a) the use of single detectors, (b) the simultaneous detection of multi-channel spectrally resolved lidar signals, and (c) swapping the range of the wavelengths for the imaging detectors.

Depending on the setup of the experiment, the lidar instrument can be used as a (a) multiwavelength elastic backscatter lidar for the measurements of aerosols and temperature from the troposphere to the mesosphere, (b) multi-channel spectroscopic Raman lidar (using Stokes and anti-Stokes, rotational, and rotational-vibrational Raman scattering), (c) multi-channel spectroscopic photoluminescence/fluorescence lidar, (d) high spectral resolution lidar (HSRL), (e) polarization lidar, (f) infrared absorption lidar by scanning the wavelengths generated by an OPO, and (g) differential absorption lidar based on simultaneous emissions from the OPO and one of three main wavelengths of the laser (355, 532, or 1064 nm).
The spectra in Fig. 1 clearly show scattering from main air compounds – molecular oxygen (O$_2$) and nitrogen (N$_2$). The results are in good agreement with model calculations and experimental results obtained under laboratory conditions (presented on page 282 in [12]) in the spectral range from 20 to 200 cm$^{-1}$. The PRRS have local maximums in the range from 2030 and 2359 UTC on 19 October 2018 and averaged over 125576 shots (209 min). Laser pulse energy, 1100 mJ at 354.9 nm. The lidar signals/spectra were obtained by the 32-channel lidar system.}

The results presented in Fig. 1 demonstrate some significant advantages of this spectroscopic approach over the traditional method of using two-channel (or multi-channel) lidars for detecting PRRS of air molecules: (1) LiSsI allows for the direct, range-resolved measurements of entire PRRS of (trace) gases with high spectral resolution; (2) spectra can be taken simultaneously at 1024 channels without the need for scanning across the required wavelength range; (3) the system is designed in a way that allows for observations of PRRS for any excitation wavelength from 300 to 700 nm. With this design, we can easily change to another pumping wavelength without changing significant parts of the experimental setup, which would become necessary in the case of using an interference filter or Fabry–Perot etalons, for example.

Figure 2 shows an example of rotational-vibrational Raman spectra (RVRS). Shown are the experimentally measured distributions of the (1-0) rotation-vibration Raman band of nitrogen molecules as a function of the wavenumber corresponding to the Stokes shift. The spectra represent the altitude range from 150 m to 10 km. The vertical resolution is 15 m. Figure 2 clearly shows three typical spectra taken at 1200, 2700, and 4005 m above ground. The emitted laser pulse energy was 1100 mJ at 354.9 nm. The lidar signals/spectra were obtained by the 32-channel lidar detector (Licel SP32-20). The measurements were carried out at nighttime on October 19, 2018, after sunset (18:50 UTC). The signal-integration time was 209 min (125576 laser shots). The system conditions are described in the figure caption.

The center of the Q branch of the (1-0) band was observed at approximately 2330 cm$^{-1}$ in all altitude levels. Figure 2 clearly shows the O- (2175−2300 cm$^{-1}$) and S- (2355−2555 cm$^{-1}$) rotational-vibrational branches, separately from the Q branch. The obtained spectra are in good agreement with RVRS measured under laboratory conditions by Barrett and Adams [14], as well as numerical calculations [15]. The relative ratios of the O and S branches to the Q branch are also in good agreement with theoretically calculated values.

The spectral resolution achieved under experimental conditions in the case of Fig. 2 (1200 g/mm entrance slit, and Licel SP32-20 detector with 0.8 mm) is insufficient to separate the individual rotational-vibrational lines. However, the resolution and signal intensity of the RVRS of nitrogen are sufficiently high for measurements of 15 cm$^{-1}$ at ambient atmospheric pressure and temperature [13].
atmospheric temperature profiles up to several kilometres above ground. The Q branch of the Stokes nitrogen component (2330 cm\(^{-1}\)) is widely used for aerosol extinction and backscatter profiling. The results presented in Fig. 2 show the potential of using high-resolution spectroscopic lidars. This type of lidar allows for the simultaneous, vertically resolved profiling of temperature, aerosol extinction, and backscattering.

The technical specifications of this spectroscopy lidar result in a significantly increased signal-to-noise ratio and thus allow for carrying out daytime Raman signal observations at VIS and the near UV spectral range. We can use two methods. One is the use of ultra-high pumping energy. The energy of these pulse energies is approximately 10 to 100 times higher than the pulse energy of commonly used Raman lidar systems. The second method is the use of a considerably better bandwidth of the signal receiver system than what is typically used. The receiver system of the spectrometric lidar system has a spectral resolution of better than 1 cm\(^{-1}\). The entrance slit was set to 50 µm. The spectral resolution was approximately 0.325 nm, obtained experimentally by measurements of the spectral difference between the 576.96 and 579.07 nm lines of a mercury pencil lamp. Figure 3 shows daytime PRRS at 1200, 2700, 4005, and 6000 m height above ground.

Figure 4 presents the daytime profile of atmospheric temperature for the altitude range from 1 to 10 km. The values were obtained using the methods developed by Arshinov et al. [9]. The temperature profile is obtained by high-J transmission at 41 cm\(^{-1}\) (533.26 nm) and low-J transmission at 115 cm\(^{-1}\) (535.36 nm). For comparison, we show the two temperature profiles obtained with radiosondes launched at Nottingham, about 200 km north (black curve) of Hatfield and at Larkhill, about 200 km west (blue curve) of Hatfield. The results show good agreement to the data acquired with both radiosondes in the height range from 1 to 15 km. The difference is less than ±2 K in the height range from 1–6 km and ±10 K from 6 to 11 km height above ground for both meteorological stations.

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Disclosures. The authors declare no conflicts of interest.

Data Availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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