Absolute high spectral resolution measurements of surface solar radiation for detection of water vapour continuum absorption

BY T. D. GARDINER1,*, M. COLEMAN1, H. BROWNING1, L. TALLIS2, I. V. PTASHNIK2,3 AND K. P. SHINE2

1National Physical Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, UK
2Department of Meteorology, University of Reading, Earley Gate, Reading RG6 6BB, UK
3V.E. Zuev Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Science, 1, Academician Zuev Square, Tomsk, 634021, Russia

Solar-pointing Fourier transform infrared (FTIR) spectroscopy offers the capability to measure both the fine scale and broadband spectral structure of atmospheric transmission simultaneously across wide spectral regions. It is therefore suited to the study of both water vapour monomer and continuum absorption behaviours. However, in order to properly address this issue, it is necessary to radiatively calibrate the FTIR instrument response. A solar-pointing high-resolution FTIR spectrometer was deployed as part of the ‘Continuum Absorption by Visible and Infrared radiation and its Atmospheric Relevance’ (CAVIAR) consortium project. This paper describes the radiative calibration process using an ultra-high-temperature blackbody and the consideration of the related influence factors. The result is a radiatively calibrated measurement of the solar irradiation at the ground across the IR region from 2000 to 10 000 cm\(^{-1}\) with an uncertainty of between 3.3 and 5.9 per cent. This measurement is shown to be in good general agreement with a radiative-transfer model. The results from the CAVIAR field measurements are being used in ongoing studies of atmospheric absorbers, in particular the water vapour continuum.

Keywords: Fourier transform infrared spectroscopy; radiative calibration; solar irradiation; water vapour continuum

1. Introduction

Water vapour is the most important radiatively active gas in the Earth’s atmosphere. It is responsible for about 55 per cent of the natural greenhouse effect and about 55 per cent of the solar radiation absorbed by the atmosphere [1]. Despite its relatively low abundance in the Earth’s atmosphere, water vapour’s central importance in the radiation balance results from its permanent dipole moment and its asymmetric shape. This leads to a strong and complex

*Author for correspondence (tom.gardiner@npl.co.uk).

One contribution of 17 to a Theo Murphy Meeting Issue ‘Water in the gas phase’.
rotational–vibrational spectrum characterized by discrete highly absorbing bands across the whole of the IR wavelength region (25–14 000 cm\(^{-1}\)), extending into the visible. These bands are made up of discrete rotational and rotational–vibrational spectral lines, about 50 000 of which are catalogued on spectral line databases such as the High Resolution Transmission (HITRAN) database [2].

In addition to the spectral lines, it has long been recognized that water vapour possesses a continuum absorption that varies relatively slowly with wavelength and pervades the entire IR and microwave region. The absorption at wavelengths between the strongly absorbing bands, the so-called ‘windows’, is of particular importance to the Earth’s radiation balance and for remote sensing of the Earth and its atmosphere. Compared with the spectral line absorption in the bands, the continuum in the windows is normally relatively weak (especially in the near-IR region considered here), and also, by definition, rather unstructured; this renders its detection in both laboratory and field measurements challenging.

The work reported here is part of a UK consortium known as Continuum Absorption by Visible and Infrared radiation and its Atmospheric Relevance (CAVIAR), which combines new theoretical developments and co-ordinated state-of-the-art measurement technologies in both the laboratory and the atmosphere to develop a consistent and experimentally validated continuum model across the entire visible and IR wavelength region. The work described in this paper forms a key element of the experimental methodologies developed to enable field validation of the theoretical and laboratory work. The field measurements for CAVIAR took place during two measurement campaigns, one at a low-altitude location at the UK Met Office observation station at Camborne, UK, and the other at a high-altitude site at the International Scientific Station at the Jungfraujoch, Switzerland.

Fourier transform infrared (FTIR) spectrometers provide the ideal technology for making this type of field measurement, with their capability to make high-resolution measurements across the IR region. These instruments have been used for many years for ground-based remote sensing of the atmosphere using the Sun as a source [3–5], and the National Physical Laboratory (NPL) has been involved in various aspects of the validation of these measurements [6–8]. To date, these measurements have not included an absolute radiative calibration of the FTIR signal that is required to study broadband continuum effects. This paper describes the procedure that has been developed to achieve this absolute calibration, and the measurement uncertainties associated with it.

The second section of the paper describes the various instrument configurations used for the solar and calibration measurements. Section 3 discusses the main sources of measurement uncertainty and the experiments that have been conducted to quantify them, with the combined measurement uncertainty discussed in §4. The paper finishes with an example of the absolute calibrated solar spectrum compared with a radiative-transfer model.

2. Measurement configuration

(a) Measurement and calibration concept

The objective here was to provide radiative calibration for solar measurements by a ground-based FTIR spectrometer to enable high-resolution absolute solar

Phil. Trans. R. Soc. A (2012)
irradiance measurements to be made. No calibration standard exists that is directly comparable to the Sun. However, the ultra-high-temperature blackbody (UHTBB) source available at NPL is state-of-the-art for high-temperature emission calibration. The UHTBB operates at around 3000 K and is traceable to primary standards (see §2d). Because the attenuation of the UHTBB power in the laboratory is much smaller than the attenuation of the solar source through the atmosphere, the absolute power levels measured by the FTIR instrument are similar. Hence, this source can be used to calibrate the FTIR instrument so that solar spectra can be quantified in terms of W m$^{-2}$.

Because the UHTBB is only useable within a dedicated laboratory, a transportable integrating sphere was used as a transfer standard so that when the FTIR instrument was used during field campaigns, the continued validity of the calibration was checked.

**(b) Fourier transform infrared instrument configuration**

The FTIR spectrometer used in this work is a Bruker IFS 125 M with OPUS spectroscopy software v. 3.0.1. This follows the standard Michelson design and is a transportable instrument with a resolution of up to 0.0035 cm$^{-1}$. The instrument has previously been used as a mobile transfer standard in a series of intercomparison campaigns of solar FTIR measurements within the Network for the Detection of Stratospheric Change, as well as providing ground-based and aircraft-borne measurements of trace atmospheric species [9–11]. The experimental set-up as used during the CAVIAR campaign is shown in figure 1, with the FTIR instrument in the background of the photograph.

In the configuration described in this paper, a calcium fluoride beam splitter and liquid-nitrogen-cooled indium antimonide detector are used to provide
high-resolution spectral data across the near-IR region from 2000 to 10 000 cm\(^{-1}\). The key instrument parameters for the measurements described here were as follows:

- resolution, 0.03 cm\(^{-1}\);
- aperture size, 0.65 mm diameter;
- apodization, boxcar;
- phase resolution, 10 cm\(^{-1}\);
- phase correction, Mertz; and
- optical filters, none.

A schematic of the optical layout within the spectrometer is shown in figure 2. The key features of the layout are:

- the input beam area is defined by the aperture stop A2;
- the instrumental field of view is defined by the combination of the field stop, aperture A3 and the focal length of the input off-axis parabola (OAP 1A);
- a second image is formed at the focus of OAP 1C, but aperture A4 is always set to be larger than aperture A3, so this second image does not limit the instrumental field of view, but cuts out any stray light;
Figure 3. Schematic layout for the FTIR measurements, with the source in (a) (solar configuration in upper section, calibration configuration in lower section), the external optics in (b) and the FTIR instrument in (c). The angles shown are the orientations used during the calibration measurements. OAP, off-axis mirror; TA, solar tracker A mirror; TB, solar tracker B mirror; BBO, blackbody OAP; Apt, aperture; cal., calibration; BBF, blackbody fold mirror.

— the final image is formed on the detector at the focus of OAP 3; and
— cube-corner reflector CC1 is stationary, while CC2 moves along the scanning arm to provide single-sided interferograms during forward (mirror movement away from the beam splitter) and backward (mirror movement towards the beam splitter) scans.

(c) Solar measurement configuration

The optical configuration for the measurements is shown in figure 3. In the solar measurement configuration, the solar beam is collected by an externally mounted active solar tracker. This uses a quadrant photo-detector and feedback loop to initially find and then actively track the solar disc throughout the day. This tracker comprises mirrors TA1, TA2 and TA3, as shown in figure 3b, where TA1 is the moving mirror driven by the signal from the quadrant detector. The solar beam is then directed to a second active optical tracker unit, made up of mirrors TB1 and TB2, which is directly mounted on the FTIR instrument. This tracker is used to compensate for any movement between the first solar tracker and the FTIR instrument, as these systems are physically disconnected.

The output beam from TB2 passes directly into the spectrometer. A removable aperture and target assembly is locked into the spectrometer bench prior to measurement and is used to check that the beam passes through the aperture and is imaged concentrically on the target. If necessary, the external optics are adjusted to correct for any misalignment of the input beam. This ensures the consistency of the incident beam alignment and therefore consistent imaging of the solar disc onto the spectrometer field of view aperture.

The power entering the FTIR instrument is the product of the incident solar radiance \( S \) with the area of the limiting aperture \( A_2 \) and the ratio of the aperture area \( A_3 \) over the area of the solar image falling on the FTIR aperture.
wheel. Through simple geometric optics, the power ($P_s$) entering the FTIR instrument during a solar measurement is given by

$$P_s = \frac{A_3}{\pi \times f_{1A}^2 \times \alpha_{\text{solar}}} \times \eta S_p A_2,$$

(2.1)

where $\eta$ is the combined optical efficiency of the transfer optics (TA1, TA2, TA3, TB1, TB2), $S_p$ is the incident solar radiance in W m$^{-2}$ ster$^{-1}$ at wavenumber $\nu$, $f_{1A}$ is the focal length of OAP 1A and $\alpha_{\text{solar}}$ is the solar half-angle divergence in radians.

(d) Calibration configuration

(i) Calibration against an ultra-high-temperature blackbody

The principal calibration source was NPL’s UHTBB. The UHTBB source is a BB3500 blackbody operating at temperatures around 3050K. The source has been extensively investigated and shown to be uniform and stable under active optical stabilization from the front [12,13].

The radiance of the blackbody was determined from Planck’s law, based on a measure of its thermodynamic temperature via calibrated filter radiometers. The geometry is defined by a water-cooled, brass, diamond-turned aperture in front of the blackbody and the aperture on the filter radiometer itself.

The blackbody temperature was measured with an 800nm filter radiometer that had been calibrated against the primary standard cryogenic radiometer to which all UK optical intensity measurements are traceable. The radiometer was used in conjunction with a geometric system to allow it to measure spectral radiance. The filter radiometer comprised a diamond-turned brass aperture, a wedged 10nm bandwidth interference filter, a silicon photodiode and was housed in a water-cooled jacket. A Vinculum trans-impedance amplifier was connected to the silicon photodiode and held in the same water jacket.

A 300mm focal length lens was used at a distance of 600mm to image light from the blackbody aperture so as to overfill the filter radiometer aperture. This aperture and a thin-film aperture on the lens defined the geometry of the measurement. The filter radiometer was used in the same f/55 geometry in which it had been calibrated. The lens transmittance was calculated using the Fresnel equations, which have previously been shown to agree within 0.05 per cent of the measured value at this wavelength.

The optical configuration for the calibration of the FTIR instrument is shown schematically in figure 3, with the calibration source in the lower section of figure 3a. The divergence of the calibration source is defined by aperture A1, and the focal length of the blackbody OAP (BBO). These were selected to be close to the 1/2° full-angle divergence of the solar source. A flat steering mirror, a blackbody fold (BBF) mirror, was required to achieve the required measurement geometry.

The power entering the FTIR instrument from the UHTBB calibration source, $P_c$, can be shown to be

$$P_c = \frac{\eta \eta_{\text{cal}} B_p A_2 A_3}{f_{1A}^2},$$

(2.2)
where $\eta_{\text{cal}}$ is the optical efficiency of BBF and BBO (i.e. the optics that are only used in the calibration measurement), $B_{\nu}$ is the UHTBB radiance (units of \(\text{W m}^{-2} \text{ ster}^{-1}\)) at aperture A1 at frequency $\nu$ and $A_2$ and $A_3$ are the areas of the respective apertures.

The calibration coefficient that can be used to provide absolute power for a solar measurement is found from the ratio of (2.1) over (2.2),

$$\frac{P_s}{P_c} = \frac{\eta_{\text{cal}}}{B_{\nu} \pi \alpha^2_{\text{solar}}} \frac{S_n}{B_{\nu} \pi \alpha^2_{\text{solar}}}.$$ \hspace{1cm} (2.3)

If the electronic gain and processing steps within the instrument is unchanged between the calibration and solar measurements, then the ratio of the powers given in equation (2.3) is equal to the ratio of the measured values ($V_s/V_c$).

Therefore, the solar radiance reaching the FTIR instrument is given by

$$S_{\nu} = \frac{\eta_{\text{cal}} V_S}{V_C} \frac{B_{\nu} \pi \alpha^2_{\text{solar}}}{B_{\nu} \pi \alpha^2_{\text{solar}}}.$$ \hspace{1cm} (2.4)

Equation (2.4) gives the basic radiometric calibration relationship for the solar FTIR measurements.

(ii) Calibration transfer

Because the UHTBB source can only be operated in a dedicated laboratory, a suitable calibration transfer procedure had to be developed to ensure that the performance of the FTIR instrument in the laboratory was maintained when it was moved and deployed for solar measurements.

The NPL Transfer Standard Absolute Radiance Source (TSARS), shown in the foreground of figure 1, has been developed to provide a transportable radiance source for the calibration of field spectrometers. The design is based around a 230 mm diameter integrating sphere from Gigahertz Optik. The sphere coating is Ultralon, which is a form of polytetrafluoroethylene-based diffuser. It is illuminated externally by four dichroic lamps contained in lamp housings, which are fixed to four of the entrance ports. The lamps used are 21V, 150W dichroic lamps, which are gold-plated IR lamps. The heat generated from the lamps burn off any organic matter that the sphere has absorbed during transportation, which would otherwise affect the reflectivity of the Spectralon. Therefore, the sphere can be used in most locations, irrespective of the surrounding environmental conditions.

The key requirement of the TSARS is that it provides a stable and uniform area radiance source. Tests on the TSARS were made using an optical uniformity facility [14, 15], which has a moving stage that can perform uniformity scans of large area sources in the $x-y$ plane. A filter radiometer was set up with a lens to focus the image of the exit port on the plane in which the filter radiometer was moved. These tests showed that the source uniformity of the TSARS is better than $\pm 0.25\%$ across the 50 mm diameter exit port.

Control software receives and records the signal from three filtered detectors mounted together on one port of the sphere. The filters have central wavelengths of 400, 520 and 695 nm and band passes of approximately 100 nm. The 520 nm detector provides the signal for the feedback routine, which alters the current to stabilize the lamps. Other channels are monitored and can provide immediate
information if the lamp output has changed outside its uncertainty limits. The user therefore has information about the current state of the calibration of the TSARS, and this was logged throughout the calibration and solar measurement exercises.

3. Sources of measurement uncertainty

(a) Calibration source

In addition to the underlying uncertainties of the UHTBB source, regular measurements of the UHTBB temperature were made using the calibrated filter radiometer. The temperature uncertainty was determined by calculating the standard deviation in the measured temperatures from each day. The typical level of variability during the calibration measurements was less than 1 K. This corresponds to uncertainties in the emitted flux of the order of 0.15 per cent at 1 μm and 0.08 per cent at 2 μm.

(b) The Fourier transform infrared instrument

The measurement repeatability was measured by monitoring the variability of back-to-back scans of the UHTBB, and this was shown to be approximately 1 per cent with no significant spectral dependence. The reproducibility of the measurement was assessed by moving the FTIR instrument away from the source, then moving it back and repeating the alignment procedure. This gave a reproducibility of better than 3 per cent in those regions of the spectrum not significantly affected by water vapour absorption—see the later discussion of the effect of ambient conditions in §3c. The percentage differences observed were approximately uniform across the spectrum, apart from the localized effect discussed later.

(i) Ice formation on the detector

In addition to the broadband issues discussed earlier, another factor was observed with a strong spectral dependence. This is illustrated in figure 4, which shows a series of repeat measurements made over a 7 h period, all normalized to the initial measurement. This shows the growth of a feature with a distinct spectral signature centred around 3200 cm\(^{-1}\). This feature is due to the formation of an ice layer on the active surface of the detector, as described by Theocharous & Fox [16]. Because the detector is filled with liquid nitrogen at the start of each day, the feature will grow during the course of the day. This effect is of particular relevance to atmospheric radiative balance research as this region of the IR spectrum is the same location as one of the main spectral features in the water vapour continuum.

Up to this point, the detector had undergone annual evacuations to maintain the integrity of its internal vacuum, and this had last been carried out 9 months previously. Following the observation shown earlier, a new ‘bake and vac’ procedure was implemented, which involved the detector being evacuated on a turbo-pump for 3 days while being held at a temperature of 50°C. A set of repeat measurements were carried out following the bake and vac. The results are given in figure 5, which show no significant spectral variation. Regular monitoring of
Figure 4. Series of spectra measured over a 7h period showing the effect of the ice layer growing within the detector. Each spectrum is normalized against an initial measurement at 08.55.

Figure 5. Series of spectra measured over a 5.5h period following bake and evacuation of the detector. Each spectrum is normalized against an initial measurement at 09.15.
Absolute measurements of solar radiation

Table 1. Transmission through FTIR apertures due to diffraction.

<table>
<thead>
<tr>
<th>wavenumber (cm(^{-1}))</th>
<th>fraction of energy transmitted through limiting aperture(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>first image</td>
</tr>
<tr>
<td>10000</td>
<td>0.995</td>
</tr>
<tr>
<td>2000</td>
<td>0.975</td>
</tr>
<tr>
<td>1000</td>
<td>0.952</td>
</tr>
</tbody>
</table>

this region was implemented to assess the degradation of the vacuum, and this showed that with regular implementation of the bake and vac, the effects of ice formation could be reduced to less than 0.5 per cent.

(ii) Diffraction effects

The effect of diffraction on the measurements was also considered. Three images are formed within the FTIR instrument, as shown in figure 2, and the maximum image size is limited at each image. Using the standard calculations for Fraunhofer diffraction through circular apertures, we can estimate the fraction of the total energy that falls within the limiting apertures for a co-axial beam from

\[ E_x = 1 - J_0(x)^2 - J_1(x)^2, \]  

where \( J_0 \) and \( J_1 \) are zero- and first-order Bessel functions and \( x = (2\pi/\lambda) \times \) (beam diameter/focal length) \( \times \) (limiting radius).

The first image is formed on the first aperture wheel, aperture A2, which is at the focus of OAP 1A. The input beam radius, defined by aperture A1, is 11 mm and the beam divergence is 1/2° full angle, defined by the solar disc or the combination of aperture A1 and BBO. The solar image size is 0.96 mm radius, and the typical aperture radius is 0.25 mm (0.26 of solar radius).

The second image is formed on the second aperture wheel by OAP 1C. The input beam radius is unchanged, 11 mm, because OAP 1A and OAP 1B have the same focal length. The limiting radius is set by aperture A3 radius and is typically 0.325 mm.

The final image is formed on the detector by OAP 3. The four to one ratio of the focal lengths of OAP 1C and OAP 2 gives an input beam radius of 2.75 mm, while the detector area is 1 mm\(^2\), therefore, the limiting radius is approximately 0.5 mm.

Table 1 shows the fraction of the total energy of a coaxial beam that is transmitted through each aperture for three different wavenumbers.

The final column in table 1 shows the combined diffraction effect for each of the three images, showing the fraction of the energy in a coaxial beam that reaches the detector. This shows that the diffractive losses in the system are quite high, up to 11 per cent at 10 μm. However, the following points should be considered:

- aperture A2 is overfilled, and therefore light will be diffracted into the aperture as well as out, so the overall effect should give an integrated energy factor of unity as long as the source is uniform and

Phil. Trans. R. Soc. A (2012)
— the diffraction factors for aperture A3 and the detector are the same for the calibration and the solar measurements, as long as the aperture sizes are not changed.

Therefore, the diffractive effects are cancelled out in the calibration process as long as the sources are uniform. The calibration source is uniform, but the solar source is not, due to limb darkening. So the effect of diffraction will depend upon how much of the limb-darkened light is diffracted into the FTIR instrument. See §3d(i) for further discussion of this point.

(c) External optics

The external optics are all those shown in figure 3 that are external to the FTIR instrument. The key difference in the optical configuration between the calibration (laboratory) and solar observations (field) was the removal of mirrors BBO and BBF. This resulted in an increase in the transmission through the system owing to a decreased number of reflections. In addition, the fact that the remaining external optics (the mirrors not within the FTIR instrument) could not be expected to maintain the same level of reflectivity between the calibration and solar observations was taken into account. It was also observed that the reflectivity of the used optics changed with the ambient absolute humidity (AH) level. Three key parameters that could influence the reflectivity between the laboratory and field were taken into account, namely, angle, AH and age. For the solar observations, Tracker A was positioned with an increased displacement from Tracker B, resulting in altered incident beam angles for TB1 and TA3. Similarly, the incident angle upon TA1 changed between the laboratory and the field; only here the difference also varied for each measurement because the Sun was continually moving across the sky.

Figure 6 shows the results of measuring the reflectance of TA1 from new (unused) and following the field work (used) on NPL’s National Reference Reflectometer (NRR) facility [17,18]. This facility provided data between 4000 and 6000 cm\(^{-1}\), and it was necessary to extrapolate the results at the high and low wavenumber ends to cover the complete FTIR spectrum. With unused mirrors, negligible change in reflectance was found with a change in AH; however, after use in the field, in addition to a loss in reflectance due to ageing (unavoidable pick-up of dirt, surface attrition, etc.), a dependency of reflectance on AH was observed. The effect is the subject of further investigation in order to understand the full mechanism; however, for the purposes of this work, the effect was characterized and so it could be accounted for in the calibration function.

A series of measurements on the NRR were carried out on TA1 at a range of angles and AH values on the unused and used mirrors. Interpolation between these data allowed the algorithm to determine the reflectance for a gold mirror at any angle and AH either during the calibration (unused) or during the solar observations (used). Hence, for any given solar observation, the algorithm determines the change between the laboratory and the field in reflectance owing to angular alteration across TA1, TA3 and TB1 based on unused mirror data (i.e. independent of any AH change or ageing). Then, the contribution from ageing was determined using NRR measurements of the unused and used mirror at the same angle and AH. The contribution from the AH change was determined from
the used mirror data. The loss in reflectance due to the removal of BBF and BBO was taken into account by combining the NRR results with data from additional reflectance measurements between 1000 and 4000 cm\(^{-1}\).

The algorithm was run using extreme changes between the laboratory and field in order to assess the relative sensitivity of the calibration to the effects of angle, AH and age. It was found that for the most extreme angular change, the change in reflectance was of the order of 0.003 per cent. The change due to humidity was approximately 0.7 per cent, and the change due to mirror ageing was up to approximately 4 per cent. Combining all these effects produces an optical efficiency correction as a function of wavenumber, which acts as a change to \(\eta\) in equation (2.2). This means that the \(\eta\)'s in equations (2.1) and (2.2) no longer cancel, and the change in optical efficiency therefore feeds through as a fractional correction to equation (2.4).

**Solar measurements**

(i) **Limb darkening**

It is well known that the brightness of the Sun reduces from the centre to the limb. A frequency-dependent model of solar limb darkening is taken from Hestroffer & Magnan [19]. Figure 7 shows the variation in intensity along the solar radius (relative to the intensity at the centre) at a series of different frequencies (in wavenumbers). For reference, the equivalent radius of the FTIR field-of-view aperture, \(A_2\), is 0.26 of the solar radius. Figure 7 shows the potential significance of limb darkening. The effect must be taken into account, particularly when extrapolating measurements made in the centre of the solar disc to the total solar radiance. For example, if an FTIR measurement is made with the aperture centred on the solar image, then the fraction of the total direct solar radiation...
Figure 7. Modelled solar limb darkening as a function of radius at various wavenumbers (from 9555 to 4164 cm\(^{-1}\)), showing more darkening with increasing wavenumber.

at 4164 cm\(^{-1}\) (2.4 \(\mu\)m) within the FTIR aperture radius is 0.074. The equivalent fraction that would be captured if the solar disc was uniform is 0.068, a difference of more than 12 per cent.

The fraction of light captured is not particularly sensitive to the precise centring of the solar image on the FTIR aperture. A 10 per cent error in the alignment (i.e. aperture centred at 0.1\(R_s\) not 0) would lead to a reduction in the fraction of light captured of approximately 0.4 per cent.

As discussed in §3b(ii), limb darkening could also affect the measurement through diffraction. However, the calculated change in the measured fraction as a result of diffraction is only \(1.5 \times 10^{-6}\) at 1.24 and \(1.1 \times 10^{-5}\) at 2.4 \(\mu\)m. These values assume that the solar image is correctly centred on the FTIR aperture, and that the limb-darkening model is correct.

In order to give confidence to the use of the limb-darkening model, some observations of the actual limb darkening were made at NPL on 21 April 2005. During a period of clear skies around noon, measurements were made with the aperture \(A_2\) aligned to different parts of the solar image. This was achieved by adjusting the horizontal angular alignment of the final steering mirror (TB2 in figure 3). The measurements were made by starting at the centre of the Sun, traversing to one edge of the solar disc, then back through the centre to the other edge.

Figure 8 shows a comparison between the measured and modelled limb-darkening results. The error bars on the measured results are an estimate of the uncertainties in the location of the FTIR field of view relative to the solar disc. The agreement between measurement and model is generally very good with results at all but one position within the basic uncertainties, particularly given the undetermined uncertainty related to the required assumption that the atmospheric conditions have remained stable during the series of measurements.
Figure 8. Comparison of solar limb darkening as measured at 3000 cm\(^{-1}\) (black diamonds) and 6000 cm\(^{-1}\) (grey squares) and modelled at 4167 cm\(^{-1}\) (solid line). Measurements made at NPL around noon on 21 April 2005.

Note that a further effect influencing whether the narrow field of view observations represent the entire solar disc could occur in the presence of sunspots and bright networks. However, the field campaigns in CAVIAR were performed in the summers of 2008 and 2009, close to a minimum in solar activity with sunspots virtually absent.

(ii) *Cloud variability*

Another potential source of uncertainty is variability of the atmospheric transmission during the course of a scan, as this would change the effective apodization of the interferogram measurement. Clouds and/or aerosols are the usual source for such short-term variability. In order to minimize the potential impact of this effect, all solar measurements are recorded during days that appear cloud free to the naked eye. In addition, the DC component of the InSb detector signal is monitored throughout the measurements to give a direct measure of the light intensity variation. The results from these DC measurements showed that, during cloud-free conditions, the received solar intensity varied by less than 1 per cent, and this level of stability is therefore taken as a guideline for reliable solar measurements.

(e) *Calibration transfer*

The stability of the NPL TSARS was tested using a calibrated 800 nm filter radiometer. The filter radiometer was positioned to focus on the centre of the exit port of the sphere and left to monitor the sphere over a period of 5 hours. The sphere is stabilized by its own detector, but the filter radiometer was used to
monitor the NPL TSARS externally, verifying the sphere detectors were correctly stabilizing the sphere. The result of these tests revealed that the output of the NPL TSARS was stable to $\pm 0.50\%$ over a period of 5 h.

The relatively low intensity of the TSARS compared with either the solar or UHTBB sources means that the instrument configuration is significantly different, and the results are therefore not directly comparable to the main measurements. The TSARS results therefore provide a good indication of significant changes to the FTIR instrument performance, but are not immediately suitable for direct adjustment of the calibration factors. The TSARS results are therefore not included directly in the combined measurement uncertainty discussed in the following section.

4. Combined measurement uncertainty

As described in the previous section, there are four main aspects of the measurement that contribute to the overall uncertainty: the UHTBB calibration source, the solar source, the FTIR instrument and the external optics. Figure 9a–d shows the spectral distributions of the combined ($k = 1$, 67% confidence limit) uncertainties for each aspect.

The UHTBB calibration source uncertainties are dominated by the uncertainty in the reflectance of the two gold-coated transfer optics and in the divergence of the beam. However, it also includes factors due to the spatial and temporal uniformity of the UHTBB emission, the traceability of the monitoring radiometer and the temperature stability of the UHTBB itself.
The solar source uncertainties are made up of four main factors: the solar solid angle, the radiative uniformity of the solar disc, the potential impact of clouds and the spectral dependence of the limb-darkening effect.

The FTIR instrument uncertainties include the influence of the main aperture location, the detector stability, the localized spectral effects of potential ice formation and the basic noise level on the measurements. It should be noted that this does not include the potential influence of phase errors on the FTIR data, and this may be an area for further investigation.

The external optics uncertainties include contributions from the uncertainty in the intensity limiting aperture area, the effect of humidity on the mirror reflectance, the alignment reproducibility and the effect of ageing on the reflectance of all the external gold-coated mirrors.

It can be seen from figure 9 that the uncertainties from each of the four aspects are of similar magnitude; so they all contribute to the overall measurement uncertainty that is shown as a function of wavenumber in figure 10. Figure 10 shows a minimum value of around 3.3 per cent in the central region of the spectrum where the mirror reflectivity had been directly measured, rising to a maximum of 5.9 per cent at the high-frequency end of the spectrum.

5. Comparison against a radiative-transfer model

Measurements of the solar radiation reaching the surface made at a UK Met Office observation station in Camborne, UK, during summer 2008 are now compared with those predicted using a line-by-line (LBL) simulation. From the Beer–Lambert–Bouguer law, assuming instrumental resolution much higher than the typical line width of atmospheric gases in the lower troposphere, the observed
irradiance, $F_m(\nu)$ as a function of wavenumber $\nu$ can be presented as the product of the top of atmosphere irradiance, $F_s(\nu)$, the transmittance of the atmosphere and the calibration factor, $k(\nu)$, such that

$$F_m(\nu) = F_s(\nu) \exp\left[-\frac{\tau_m(\nu)}{\cos \theta}\right] k(\nu).$$

(5.1)

$F_s(\nu)$ is taken from Kurucz [20] at 0.01 cm$^{-1}$ resolution, corrected for the Sun–Earth distance on the observation day. The solar zenith angle, $\theta$, is calculated from the time, date and location of the measurement, and the optical depth, $\tau_m(\nu)$, of the atmosphere is simulated using the LBL code developed by Mitsel et al. [21]. The fine mesh resolution of the LBL calculations was 0.001 cm$^{-1}$ with an instrument resolution set to 0.03 cm$^{-1}$; the output step of the LBL calculation was set to match that of the spectrometer, 0.015 cm$^{-1}$. Provided $F_s(\nu)$, $k(\nu)$ and the vertical profile of the concentrations of absorbing and scattering species are known with sufficient accuracy, these measurements should allow the strength of gaseous absorption to be derived.

The recent H$_2$O linelist UCL08 [22] was applied for the spectral line parameters of water vapour, with HITRAN 2008 [2] used for other gases. The UCL08 linelist contains many weaker lines not catalogued in HITRAN 2008. It also makes significant changes to the line intensities of strong water vapour lines in the 8000–9500 cm$^{-1}$ spectral interval, which our measurements indicate are improvements over HITRAN 2008 [23]. In addition to water vapour, the following gases are included in the simulation: CO$_2$, O$_3$, N$_2$O, CO, CH$_4$, O$_2$, NO and N$_2$. Profiles for gases other than water vapour are taken as climatological values.

Water vapour profiles are from Vaisala RS92 radiosonde launches that were routinely performed at Camborne. These profiles are corrected for relative humidity bias using the empirical corrections of Miloshevich et al. [24]. Errors in the water vapour profile present some of the largest uncertainties in this technique; we make an assumption that the distribution of the water with height is well characterized by the radiosonde, and confirm total column amount by comparison with measurements from a co-located, global-positioning-system-integrated, water vapour instrument. We measure the aerosol optical depth using a handheld aerosol optical depth monitor and include this in our simulation. At wavelengths of interest here, this optical depth is always small (less than 0.1 at 10,000 cm$^{-1}$).

For the simulation of the continuum absorption of H$_2$O, CO$_2$, O$_3$, O$_2$ and N$_2$, we use a recent update (v. 2.5) of the Mlawer Tobin-Clough Kneizys Davies (MT-CKD) continuum model [25].

Figure 11 shows an example of the measured irradiance by the FTIR instrument reaching the surface on 22 August 2008 at 14:32 coordinated universal time (UTC) (with a water column of 17.1 kg m$^{-2}$ and solar zenith angle of 46.7$^\circ$) compared with the modelled irradiance. Figure 12 shows four example window regions (centred on 2500, 4500, 6500 and 8500 cm$^{-1}$) of this comparison. It can be seen that there is generally good agreement between the measured and modelled irradiance, and that in three of the four window regions, the two results lie within the $(k = 1)$ measurement uncertainty. In the 2500 cm$^{-1}$ region, the modelled result lies slightly above the measured, although it is still within the $k = 2$ (95%) uncertainty limits and in a region where the irradiance is low. In addition, this
Figure 11. Comparison between measured (grey) and modelled (black) solar irradiance at the ground. Measurements made at Camborne on 22 August 2008 at 14.32 UTC.

Figure 12. Comparison between measured (grey) and modelled (black) solar irradiance at the ground in four windows centred on 2500, 4500, 6500 and 8500 cm\(^{-1}\), with the \(k = 1\) measurement uncertainty limits indicated by the dotted grey lines.
comparison makes no allowance for any uncertainty in the model and its input data. A further general point to note is that it can be seen in these figures that the high resolution (0.03 cm$^{-1}$) of these measurements means that even narrow lines can be individually well resolved.

6. Conclusions

In this paper, we have demonstrated the potential for an FTIR instrument to make high-resolution measurements of the solar irradiance reaching the ground across wide bandwidths of the IR spectrum. In order to achieve this, it is necessary to radiatively calibrate the FTIR response, including the many factors that influence the measurement owing to the solar source, the calibration source, the FTIR instrument and the external optics. The spectral variation of the measurement uncertainty for these factors has been assessed across the IR band from 2000 to 10 000 cm$^{-1}$, giving a combined ($k=1$) measurement uncertainty of between 3.3 and 5.9 per cent.

The FTIR measurements are being used to study the various factors affecting radiative transmission through the atmosphere. The measurements are particularly relevant for studies of water vapour as they provide simultaneous data on the fine structure of the water monomer absorption and the broadband continuum absorption across the entire spectral region. The results from this work are being used with field measurements made during the CAVIAR programme to compare with the latest laboratory and theoretical studies of water vapour, including validating updates to the monomer linelists [23] and recent laboratory measurements [26,27]. It is recognized that the absolute uncertainty as presented here may not be low enough to exploit the full potential of the measurements; so additional information is being used in these assessments, such as the broad spectral correlation of many of the uncertainties, which enables more localized regions to be studied with lower uncertainties, and the evolution of measurements over the course of a day, where the main change is the solar zenith angle, which can provide information on the top of the atmosphere solar irradiance.

In conclusion, this work has shown that high-resolution absolute solar irradiance can be measured with a ground-based FTIR instrument, once the measurement influence factors have been accounted for. This then provides an important tool for studying atmospheric absorbers such as water vapour, particularly when combined with other information about the atmospheric state.

The CAVIAR project is jointly funded by the Natural Environment Research Council and the Engineering and Physical Sciences Research Council, and some of the initial work on the radiative calibration was carried out under the NPL’s Strategic Research Programme. The authors acknowledge the contribution of various NPL colleagues to the practical aspects of the optical calibration activity, particularly Barry Scott, Emma Woolliams, Chris Chunnilall and Andrew Deadman. We also thank Rob Boast and the other Met Office staff at the Camborne site for their help during the field campaign.

References


Phil. Trans. R. Soc. A (2012)
21 Mitsel, A. A., Ptashnik, I. V., Firsov, K. M. & Fomin, A. B. 1995 Efficient technique for line-

22 Shillings, A. J. L., Ball, S. M., Barber, M. J., Tennyson, J. & Jones, R. L. 2011 A upper limit
for water dimer absorptions in the 750 nm spectral region and a revised water line list. *Atmos.
Chem. Phys.* 11, 4273–4287. (doi:10.5194/acp-11-4273-2011)

23 Tallis, L., Coleman, M., Gardiner, T., Ptashnik, I. V. & Shine, K. P. 2011 Assessment of
the consistency of H2O line intensities over the near-infrared using sun-pointing ground-
(doi:10.1016/j.jqsrt.2011.06.007)

and correction of Vaisala RS92 radiosonde water vapor measurements. *J. Geophys. Res.* 114,
D11305. (doi:10.1029/2008JD011565)

25 Clough, S. A., Shephard, M. W., Mlawer, E. J., Delamere, J. S., Iacono, M. J., Cady-
Pereira, K., Boukabara, S.-A. & Brown, P. D. 2005 Atmospheric radiative transfer
(doi:10.1016/j.jqsrt.2004.05.058)

self-continuum absorption in near-infrared windows derived from laboratory measurements.