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Identification of short and long-lived atmospheric trace gases from IASI space observations

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Key Points:

- The whitening transformation allows analyzing anomalies in hyperspectral infrared spectra
- In a biomass burning plume we identify nine compounds including a first observation of glycolaldehyde
- On spectra observed a decade apart we identify atmospheric changes in eight long-lived halocarbons

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Abstract

In recent years, major progress has been made in measuring weakly absorbing atmospheric trace gases from high spectral resolution space observations. In this paper, we apply the so-called whitening transformation on spectra of the Infrared Atmospheric Sounding Interferometer (IASI), and show that it allows removing most of the climatological background from spectra, leaving a residual that contains those spectral signatures that depart from normality. These can subsequently be attributed to changes in the abundance of trace species. This is illustrated for two diverging cases: (1) a biomass burning plume from the 2019/2020 Australian bushfires, leading to the unambiguous identification of nine reactive trace gases, including a first observation of glycolaldehyde; (2) spectra observed a decade apart, from which changes in eight long-lived halogenated substances are identified; three of them never observed before by a nadir sounder.

Plain Language Summary

In recent years, several techniques have been developed for the detection of gases present in very small quantities in the atmosphere, which has significantly improved our knowledge on atmospheric composition and chemistry. In this paper, we describe a powerful complementary technique that transforms atmospheric spectra to highlight and attribute the spectral signatures of different species. We apply it on spectra measured by the spaceborne IASI (Infrared Atmospheric Sounding Interferometer) for two different cases: (1) a plume from the 2019/2020 Australian bushfires leading to the clear identification of nine rare gases including a first observation from space of glycolaldehyde; (2) spectra observed a decade apart, of which eight long-lived halogenated substances were identified; three of them never observed before by a nadir sounder. The detection of these reactive and long-lived trace gases is very promising for the monitoring of their temporal evolution and the attribution of their sources.

1 Introduction

The outgoing longwave radiation spectrum of the Earth-atmosphere system features strong absorption bands of CO₂, H₂O, CH₄, N₂O, O₃ and CO. Routine measurements of several of these strong absorbers are now available from nadir observing polar orbiting infrared sounders, which have led over the years to major advances in our understanding of their distribution (Crevoisier et al., 2014). Unexpectedly, hyperspectral nadir sounders have also proven most useful for the measurements of other, much weaker, absorbers. Harries et al. (2001) for instance demonstrated that infrared sounders can be used to monitor long-term changes of the ozone depleting halocarbons CFC-11 and CFC-12 (see also Coheur et al. (2003)). Beer et al. (2008) and Coheur et al. (2009) showed the first observations of NH₃, C₂H₄, HCOOH, CH₃OH and PAN in fire plumes and above highly polluted urban areas. Progress in retrieval techniques (see Franco et al. (2018) and references therein) has now allowed measuring these and other compounds also outside of highly concentrated plumes, in turn leading to major discoveries on their emission sources, e.g. Stavrakou et al. (2011) and Van Damme et al. (2018). Noticeable progress has been made using the Infrared Atmospheric Sounding Interferometer (IASI) on-board the Metop-A/B/C platforms (Clerbaux et al., 2009). The IASI instrument measures a very large continuous part of the thermal infrared (645–2760 cm⁻¹) and, thanks to its high radiometric performances, high spectral resolution (0.5 cm⁻¹, apodized) and bi-daily global coverage, has played a major role in the monitoring of weakly absorbing trace gases (e.g. Clarisse et al. (2011), Hilton et al. (2012) and Franco et al. (2019)). As a summary of past achievements, the list of 29 species that have been observed with IASI, either globally or in concentrated plumes is given in Table 1.

In recent years, remote sensing of weakly absorbing trace gases has benefited greatly from the discovery of improved algorithms for detecting very small features in spectra. In

particular, the method introduced by Walker et al. (2011) increased drastically the detection sensitivity over traditionally approaches and formed the basis of several quantitative retrieval techniques (Franco et al., 2018; Taylor et al., 2018; Clarisse et al., 2019). In this paper, we introduce a complementary technique based on ‘whitening’ spectra, which is suitable for analyzing spectra with unknown signatures. In the next section, we review briefly the detection method of Walker et al. (2011) and show how it naturally leads to the concept of whitening spectra. In section 3, we apply it on spectra from the 2019/2020 Australian fires and show that it enables, much easier than with alternative methods, to highlight and identify the different trace gas signatures, leading to the unambiguous identification of nine reactive trace gases. An entirely different application of whitening occurs when spectra are compared to those of a different period. As we show in section 4, whitening allows in this instance, highlighting small changes in a series of long-lived halogenated substances, most of which have until now never been identified in IASI spectra.

Table 1. Chemical species observed by IASI. The species reported in this paper which are observed for the first time with a nadir sounder are indicated in italics.

Greenhouse gases and ozone-related substances (14)	H ₂ O, CO ₂ , CH ₄ , N ₂ O, O ₃ , HNO ₃ , CFC-11, CFC-12, HCFC-22, CCl ₄ , CF ₄ , <i>HCFC-142b</i> , <i>HFC-134a</i> , <i>SF₆</i>
Air quality and VOCs (12)	CO, CH ₃ OH, HCOOH, CH ₃ COOH, CH ₃ C(O)CH ₃ , C ₂ H ₂ , C ₂ H ₄ , NH ₃ , HCN, PAN, SO ₂ , OCS
Concentrated plumes (7)	HCl, H ₂ S, C ₃ H ₆ , C ₄ H ₄ O, HONO, HCHO, <i>HOCH₂CHO</i>

2 Whitening transformation

The detection method presented in Walker et al. (2011) is based on a formula that quantifies in a single number the integrated spectral contributions of a target species, in a given spectral range. It relies on the mean \bar{y} and the associated covariance matrix S of a set of spectra that are representative for IASI observations in the absence of enhancements of the target species. The pair $\{\bar{y}, S\}$ describes the distribution of spectra and how they are expected to vary (driven mostly by differences in temperature, surface emissivity, water vapor and interferences with other absorbers). The single number is sometimes referred to as a hyperspectral range index (HRI) (Van Damme et al., 2014) and is defined as

$$\text{HRI} = \frac{K^T S^{-1} (y - \bar{y})}{\sqrt{K^T S^{-1} K}}, \quad (1)$$

with K the Jacobian of the target species calculated from radiative transfer simulations (Van Damme et al., 2014). This formula was originally derived from the least squares estimate, and in that context the covariance matrix can be interpreted as a generalized noise covariance matrix, where all background variability is treated as noise. Note that, by construction, the HRI is normalized to provide a mean of zero and a standard deviation of one on the set of background spectra. Its value can therefore be interpreted in terms of standard deviations from the mean. Higher values (typically above 4σ in absolute value) usually indicate the presence of an anomalous abundance of the target species (or at least an anomaly in the spectrum that sufficiently resembles its Jacobian). The expression can be interpreted geometrically as the weighted projection of the Jacobian onto the zero-centered observed spectrum.

It turns out that Equation (1) has been known since the 1970s (Reed et al., 1974) under the name ‘matched filter’ and is used very frequently in the domain of hyperspectral imagery

(Manolakis et al., 2016). In this field, the covariance matrix is appropriately referred to as the background clutter matrix, the HRI as the signal-to-clutter or signal-to-noise ratio, and its expression is sometimes written as (Manolakis et al. (2016), p520)

$$\text{HRI} = \frac{\tilde{K}^T \tilde{y}}{\|\tilde{K}\|}, \quad (2)$$

with

$$\tilde{K} = S^{-\frac{1}{2}} K \quad (3a)$$

$$\tilde{y} = S^{-\frac{1}{2}} (y - \bar{y}) \quad (3b)$$

92 The operation $y \rightarrow \tilde{y}$, transforms the spectra into a set of spectra with a zero mean and
 93 an identity covariance matrix. As this transforms the generalized noise into white noise,
 94 the operation is referred to as whitening or pre-whitening (Scharf, 1991; Rodgers, 2000;
 95 Manolakis et al., 2016; Kessy et al., 2018). Whitening transforms the spectral channels to
 96 uncorrelated random variables with unit variance and zero mean. In this form, the HRI is
 97 simply the projection of the whitened spectrum \tilde{y} onto the normalized whitened Jacobian
 98 \tilde{K} .

99 Instead of the HRI, one can also analyze the entire unprojected whitened spectra.
 100 Whitening removes most of the background signal. Therefore, on background spectra, each
 101 channel of a whitened spectrum has an expected mean value of zero and a standard de-
 102 viation of 1 (this is a property inherited from the HRI). Conversely, a whitened spectral
 103 channel with an absolute value above 4 indicates a significant departure from Gaussian nor-
 104 mality. Large negative values indicate an anomalous large absorption, while large positive
 105 values indicate either an emission signal or a decrease of a given trace gas with respect to
 106 background conditions (defined by the set of spectra used to generate \tilde{y} and S). So rather
 107 than associating with each spectra a single number like the HRI, whitening a spectrum
 108 produces another spectrum in which all spectral aberrations are exposed. The strength
 109 of the whitening technique is that it allows highlighting anomalies without knowing the
 110 spectral signature (Jacobian) in advance. Once a candidate species is suspected, it can be
 111 unambiguously assigned by comparing the shape of the whitened Jacobian with the spectral
 112 signatures in the whitened spectrum. Unambiguous identification is another clear advantage
 113 over the HRI, which can be prone to false detections caused by a partial match of a spectral
 114 signature with the Jacobian of the target species. Note that by weighting with the inverse of
 115 the covariance matrix, the spectral components that normally exhibit the largest variability
 116 (e.g. the baseline, due to variation in the surface temperature and clouds, or the absorption
 117 features due to O₃, H₂O or CO₂) will carry the least weight in the whitened spectrum.

118 When we talk about departure from normality, this is with respect to a set of spectra
 119 taken from a reference time period and/or geographic area of our choice. This freedom gives
 120 rise to at least two important applications: (1) when the covariance is representative for the
 121 entire set of IASI spectra, whitening can be used to study special events such as volcanic
 122 eruptions or large fires; (2) when the covariance matrix is representative for a specific time
 123 period and used on spectra from another time period, whitening, as we will show, can
 124 reveal small changes in the concentrations of long-lived compounds. A case study of each
 125 application is presented next.

126 As a side comment, the HRI formula can also be derived from standard linear discrimi-
 127 nant analysis, and through the use of the covariance matrix, is also closely linked to principal
 128 component analysis (PCA). We refer to Clarisse et al. (2013) for a detailed discussion of
 129 this. Whitening can be seen as an alternative to PCA-based analysis of anomalies in spectra
 130 (Grainger et al., 2013).

131 Whitening can be seen as an alternative to analyzes based on principal components
 132 (PC) (Hurley et al., 2009; Grainger et al., 2013). In such approaches, the signatures of
 133 interest are contained in the orthogonal part to the PC. A key difference between the two

134 approaches, is that whitening disregards no components but instead weights them inversion-
 135 ally proportional to their weight in the covariance matrix (see also Clarisse et al. (2013)).
 136 As a consequence of this, it can more readily be used for the detection of species already
 137 present in the set of spectra that was used to create the covariance matrix, as illustrated
 138 in the following sections. Other statistical transformations of the spectra or residuals exist,
 139 such as the random projections technique used for quantifying OCS in the IASI spectra (see
 140 Camy-Peyret et al. (2017) and references therein).

141 3 Short-lived gas detection in Australian bushfires

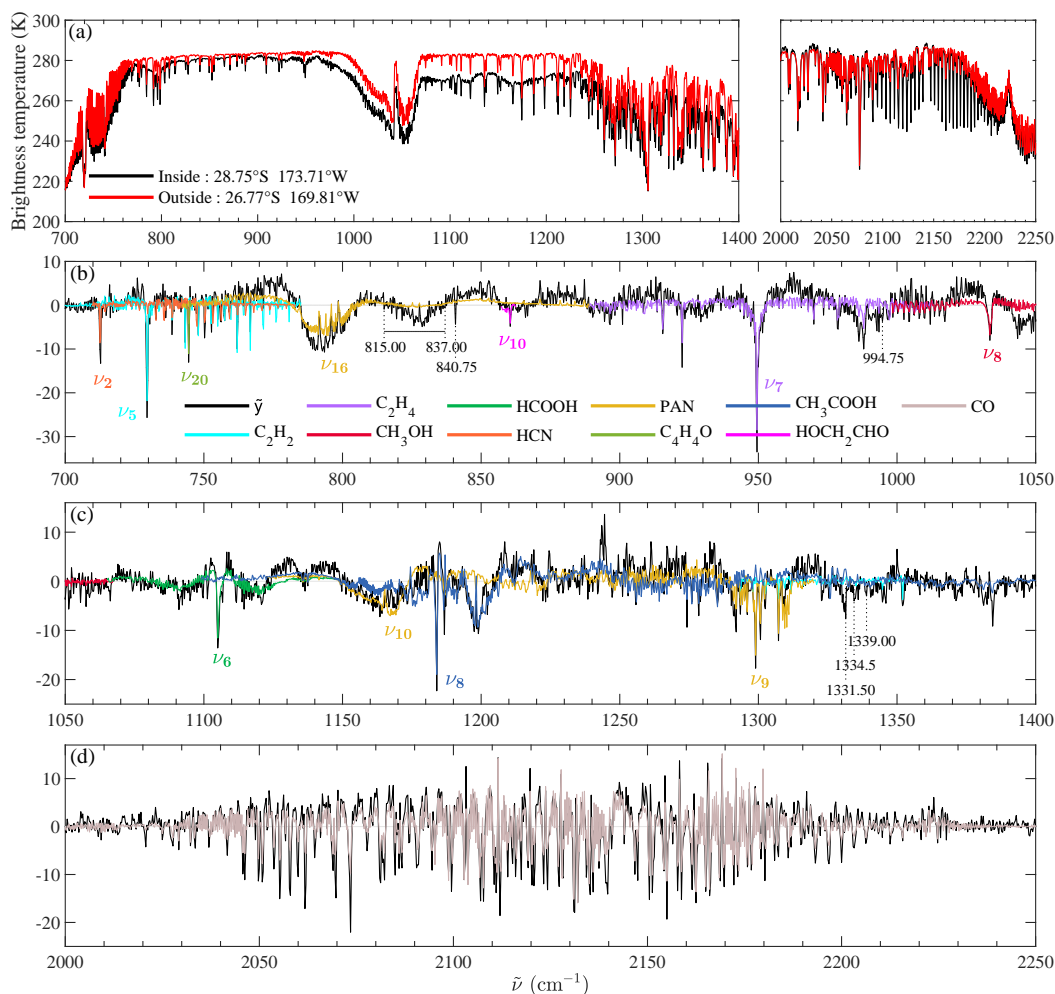


Figure 1. Spectrum from the Australian bushfires of 5 January 2020 revealing nine trace gas species and carbon monoxide. Panel a shows the spectrum as measured by IASI before the whitening transformation (in black), together with a spectrum measured just outside the plume (in red). The whitened spectrum is shown in panels b to d for selected spectral ranges.

142 This first case study concerns the massive bushfires which took place in Australia
 143 around the turn of year 2019–2020 (Nolan et al., 2020; Boer et al., 2020). IASI spectra
 144 of similarly large fires in Australia in 2009 were analyzed in Clarisse et al. (2011) with a
 145 physical retrieval approach, and revealed very strong spectral signatures of some well-known
 146 fire tracers. Here we will focus on a particular spectrum that was observed over the South

147 Pacific Ocean (28.75°S, 173.71°W) on January 5, 2020. This spectrum was selected on the
148 basis of HRI-maps of C₂H₄ (see Figure A1 of Annex A). These indicate that the observation
149 was made in the central part of a large fire plume originating from South-East Australia
150 two or three days earlier. Calipso measurements (Winker et al., 2009) reveal that the plume
151 was located between 4 and 6 km above sea level.

152 The chosen (untransformed) spectrum is shown in Figure 1a together with a spec-
153 trum measured outside the fire plume (their location is indicated in Figure A1 of Annex
154 A). Immediately obvious is the strong absorption band of CO in the 2100–2200 cm⁻¹ re-
155 gion, and the large absorption in the atmospheric window between 1080 and 1230 cm⁻¹
156 due to smoke aerosols and other broadband absorbers. Figure 1b–d shows the whitened
157 spectrum calculated with $\{\bar{y}, S\}$ built using a subset of around 10⁷ IASI spectra measured
158 throughout 2013 and across the globe, from (Franco et al., 2018). From this spectrum,
159 we identified nine species between 700 and 1400 cm⁻¹, namely acetylene (C₂H₂), ethylene
160 (C₂H₄), methanol (CH₃OH), formic acid (HCOOH), hydrogen cyanide (HCN), peroxyacetyl
161 nitrate (CH₃C(O)O₂NO₂, abbreviated as PAN), furan (C₄H₄O), acetic acid (CH₃COOH)
162 and glycolaldehyde (HOCH₂CHO or hydroxyacetaldehyde). The identification was made
163 with Jacobians obtained from a forward model (with temperature and main absorbers of
164 the US standard atmosphere (NASA-USAF, 1976), where each whitened Jacobian was scaled
165 to match its maximum absolute value with the observed signature in the whitened spectrum.
166 Note that for the figures, the scaling factor was slightly offset, so that the whitened spectra
167 and the whitened Jacobian would not obscure each other.

168 The observation of HOCH₂CHO is the first from space to our knowledge. The detection
169 of the Q-branch associated with the ν_{10} vibrational mode at 860.5 cm⁻¹ (Johnson et al.,
170 2013) is promising for future exploitation, as HOCH₂CHO measurements are very limited
171 at the moment (Treadaway et al., 2018). HOCH₂CHO, as well as all the other detected
172 species, are well-known products of biomass burning (see e.g. Akagi et al. (2011); Andreae
173 (2019) and references therein). In the troposphere it is formed from the oxidation of alkenes,
174 in particular isoprene and several of its degradation products, and it is a key intermediate
175 in the formation pathways of oxygenated compounds such as HCOOH and glyoxal (Paulot
176 et al., 2009; Taraborrelli et al., 2012). Strong Q-branches of HCN, C₂H₂ and C₄H₄O are
177 observed between 700 and 800 cm⁻¹, as well as several R lines for HCN and C₂H₂. Note
178 that the strong ν_2 band of CO₂ present in this spectral region is completely removed by
179 the whitening transformation. For C₂H₂, a weaker signal is also detected around 1300–1352
180 cm⁻¹. C₂H₄ is the species that exhibits the largest signal in the whitened spectrum with
181 a value of -33 at 949.5 cm⁻¹ and several other features on both sides. The detection of
182 the ν_8 band of CH₃OH is also straightforward with the removal of the large ozone band.
183 At longer wavenumbers, HCOOH is observed in its ν_3 band around 1105 cm⁻¹. Finally,
184 we observe the broadband absorbers PAN and CH₃COOH, which partially overlap between
185 1150 and 1170 cm⁻¹. PAN also has a remarkable broadband absorption between 780 and
186 800 cm⁻¹. The remaining part of the spectrum (1400–2760 cm⁻¹) was analyzed carefully,
187 but apart from the large CO absorption features in the region at 2000–2250 cm⁻¹, no other
188 spectral anomalies were identified. However, there are several notable enhancements in the
189 800–1350 cm⁻¹ range which we were unable to attribute to a specific species. The strongest
190 features are identified by dotted lines in Figure 1, and in particular those that we could
191 also observe in other spectra of the fire plume. Some are very sharp, such as the feature at
192 840.75 cm⁻¹; others are wider (815–837 cm⁻¹) and these could be due to heavier molecules
193 or a combination of different absorbers. Note that in general, heavier molecules tend to
194 have broader absorption features, for which unambiguous identification can become more
195 difficult, especially when only one feature is identified or when its magnitude is weak.

196 We also analyzed the whitened spectrum of a fresh fire plume (measured at 39.28°S,
197 153.48°E on December 30, 2019), as displayed in Figure B1 of Annex B. The fresh plume
198 exhibits very strong signatures of nitrous acid (HONO) and ammonia (NH₃) that are not
199 seen in the transported plume. This makes sense as these species are known to be emitted

200 in very large quantities by fires (Whitburn et al., 2017; Theys et al., 2020), but are quickly
 201 degraded to form secondary products. A weak absorption feature compatible with the pres-
 202 ence of propene (C_3H_6) is also detected. In contrast, $HOCH_2CHO$, $HCOOH$ and PAN are
 203 only seen in the transported plume. Whereas these three species are well-known secondary
 204 products, $HOCH_2CHO$ is also primarily emitted by fires; the fact that it is not observed in
 205 the fresh plume could be explained by the overlapping prominent HONO absorption feature.

206 4 Long-lived gas analysis over the Pacific Ocean

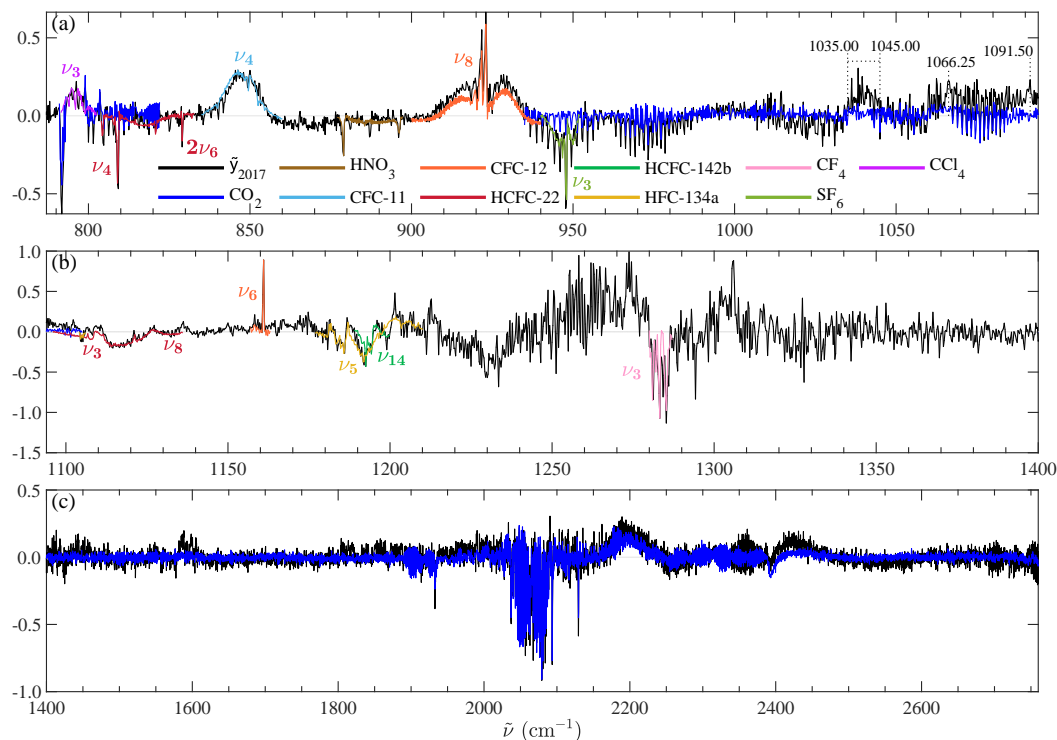


Figure 2. Whitenened spectrum of Pacific Ocean from October 2017 revealing eight halocarbons, carbon dioxide and nitric acid.

207 In this section, we show how small spectral changes that appear over longer time periods
 208 in mean spectra can be exposed with the help of the whitening transformation. Focusing
 209 over an area in the North Pacific Ocean (25° – 45° N; 170° – 165° W), we chose 120,000 clear-sky
 210 spectra measured in 2008 to calculate a reference mean spectrum and associated covariance
 211 matrix. 2008 is the first complete year where IASI L1c reprocessed data are available
 212 (Bouillon et al., 2020). The spectrum on which we applied whitening was calculated from
 213 $N = 20,000$ clear-sky spectra measured in October 2017 over the same area. Using a mean
 214 rather than an individual spectrum is not strictly needed, but it helps focusing on long-
 215 lived compounds, as an individual spectrum might always exhibit anomalies compared to
 216 the reference due to natural variations in short-lived trace species. For instance plumes of
 217 volatile organic compounds are regularly observed in the North Pacific Ocean (Franco et
 218 al., 2018, 2019). The whitenened mean spectrum is shown in Figure 2. As we work with mean
 219 spectra, the maximum values observed in the whitenened spectrum are much lower than in
 220 the previous example. However, for the same reason, a significant value is in theory already
 221 obtained for values as low as $4/\sqrt{N} \approx 0.03$.

222 Changes in eight halocarbons were identified, these are: CFC-11 (CFCl_3), CFC-12
223 (CF_2Cl_2), HCFC-22 (CHF_2Cl), HCFC-142b ($\text{CH}_3\text{CF}_2\text{Cl}$), HFC-134a (CH_2FCF_3), carbon
224 tetrafluoride (CF_4), sulfur hexafluoride (SF_6) and carbon tetrachloride (CCl_4). Halocarbons
225 are synthetic halogenated compounds used in many industrial and domestic applications
226 (Martinerie et al., 2009). Most of them are powerful greenhouse gases and contribute,
227 for chlorinated and brominated compounds, to the depletion of stratospheric ozone and to
228 the development of ozone hole (World Meteorological Organization, 2010). Of these eight
229 species, five of them (CFC-11, CFC-12, HCFC-22, CCl_4 and CF_4) have been observed in
230 IASI spectra before (Clerbaux et al., 2009; Liuzzi et al., 2016).

231 The absorption bands of the two CFCs, located around 849 cm^{-1} for CFC-11 and at
232 ~ 923 and $\sim 1161\text{ cm}^{-1}$ for CFC-12 (here and also later, the wavenumbers refer to the position
233 of strong Q-branches), have whitened signals of 0.3, 0.7 and 0.9 respectively. Those positive
234 values indicate that their atmospheric abundance was smaller in 2017 than in 2008, which is
235 consistent with independent satellite measurements (Chen et al., 2020), independent in-situ
236 measurements (Prinn et al., 2018) and a direct consequence of the 1987 Montreal Protocol
237 to limit the use and production of CFCs (World Meteorological Organization, 2018). The ν_3
238 band of CCl_4 shows up at $\sim 796\text{ cm}^{-1}$ with a whitened signal's value of 0.2. The production
239 of CCl_4 has been controlled by Montreal Protocol as long as CFCs, explaining its decrease
240 between 2008 and 2017.

241 The other halocarbons in Figure 2 are all detected with a negative value, indicating
242 an increase in their atmospheric concentration between 2008 and 2017. Four absorption
243 bands of HCFC-22 are observed: ν_4 ($\sim 809.25\text{ cm}^{-1}$), $2\nu_6$ ($\sim 829.00\text{ cm}^{-1}$), ν_3 (~ 1114.00
244 cm^{-1}) and ν_8 ($\sim 1132.25\text{ cm}^{-1}$). In the spectral region between 1178 and 1200 cm^{-1} ,
245 HFC-134a and HCFC-142b are both absorbing. Although the detection of HFC-134a is
246 unambiguous, the detection of HCFC-142b is less certain, but still very likely considering
247 the presence of a sharp feature at 1192.50 cm^{-1} that would correspond to its ν_{14} Q-branch.
248 Note that constraints on the production of both HCFCs and HFCs were only added in later
249 amendments of the Montreal Protocol (World Meteorological Organization, 2018). The
250 signatures of SF_6 and CF_4 are clearly observed at 947.75 cm^{-1} (Q-branch of the ν_3 band
251 with value of -0.6) and around 1283.25 cm^{-1} (value of -1.1) respectively, and are consistent
252 with increases observed from ground-based measurements (Prinn et al., 2018).

253 The region 1220 – 1370 cm^{-1} is quite complicated for a definite analysis of the individual
254 trends of the atmospheric species contributing to the absorption: CH_4 , N_2O , H_2O , HDO,
255 HNO_3 , O_3 . However, in this region the (negative) spectral signatures of CF_4 around 1283
256 cm^{-1} clearly indicate an increase of its abundance over the considered time frame i.e. 2008
257 (for the reference) compared to 2017 (for the Pacific data set).

258 Apart from the halocarbons, Figure 2 highlights several absorption lines of CO_2 ; the
259 signal shows up at 791.5 cm^{-1} with a succession of rovibrational features around 800 , 950 ,
260 975 , 1050 , 1070 and 2100 cm^{-1} . The negative values indicate an increase in the CO_2 signal,
261 and thus a rise in concentration between 2008 and 2017. The CO_2 features in these spectral
262 regions are less saturated than below 750 cm^{-1} , and are less affected by small changes in
263 atmospheric temperatures. There are also absorption features of nitric acid (HNO_3) in its
264 ν_5 and $2\nu_9$ bands: the corresponding signatures are stronger around the two Q branches
265 centered at 879.00 and 896.00 cm^{-1} indicating an increasing atmospheric abundance of
266 HNO_3 . This is consistent with a recent study that reported a small positive trend for HNO_3
267 (Bernath et al., 2020).

268 A number of smaller features remain unidentified in this spectrum, of which the strongest
269 are spotted by dotted lines in Figure 2. Most of the observed features are found in the at-
270 mospheric window between 800 and 1300 cm^{-1} . The broad feature between 1215 and 1240
271 cm^{-1} could possibly due to the spectral contribution of COF_2 . As a caveat, some of these
272 unidentified features could still be due to natural variations of short-lived trace gases. In
273 addition, while the IASI L1c reanalyzed dataset was used for this study, small changes in

274 the IASI instrument that occurred in the last decade could also play a role. No major fea-
275 tures were identified in the regions impacted by water vapor and CO₂ (645–790, 1300–2000,
276 2200–2400 cm⁻¹).

277 5 Conclusion

278 In this letter, we have shown that the whitening transformation allows analyzing anoma-
279 lies in high resolution infrared spectra. It enables elimination of the large absorption features
280 that usually dominate a spectrum and accentuates those channels which are incompatible
281 with the background norm. We have presented two different applications: an analysis of an
282 extreme event (the 2019/2020 Australian fires) and an analysis of long-term mean changes
283 in IASI spectra. These exploit respectively the spatial variability of reactive species and the
284 temporal variability of long-lived compounds. We have provided spectroscopic evidence of
285 the occurrence of nine fire tracers and eight halocarbons. This includes four species (gly-
286 colaldehyde, HCFC-142b, HFC-134a, SF₆) which have never been observed before with a
287 nadir sounder. Their detection is very promising, especially for the determination of their
288 source emissions and the study of their temporal evolution.

289 The advantages of the whitening approach compared to more traditional techniques are
290 numerous. For instance, Clarisse et al. (2011) analyzed spectra from the 2009 Australian
291 fires using a fitting approach, which aims at reconstructing the observed spectrum by means
292 of forward simulations. Especially in extreme cases, it is very difficult and time consuming
293 to obtain reasonable fits of the corresponding spectra, and often fitting windows need to be
294 restricted to narrow spectral ranges. In contrast, whitening is immediate, does not require
295 an inverse model nor the ability of a forward model to account for all the observed features,
296 and can be applied on spectral ranges of any size. Likewise, in a more traditional analysis of
297 trends in high resolution infrared spectra (Brindley et al., 2015; Strow & DeSouza-Machado,
298 2020), it is very challenging to deal properly with variations of O₃, CH₄, CO₂ or H₂O due
299 to e.g. natural temporal variations, variations in temperature or sampling biases related to
300 clouds; whereas these are dealt with automatically using the whitening technique.

Appendix A

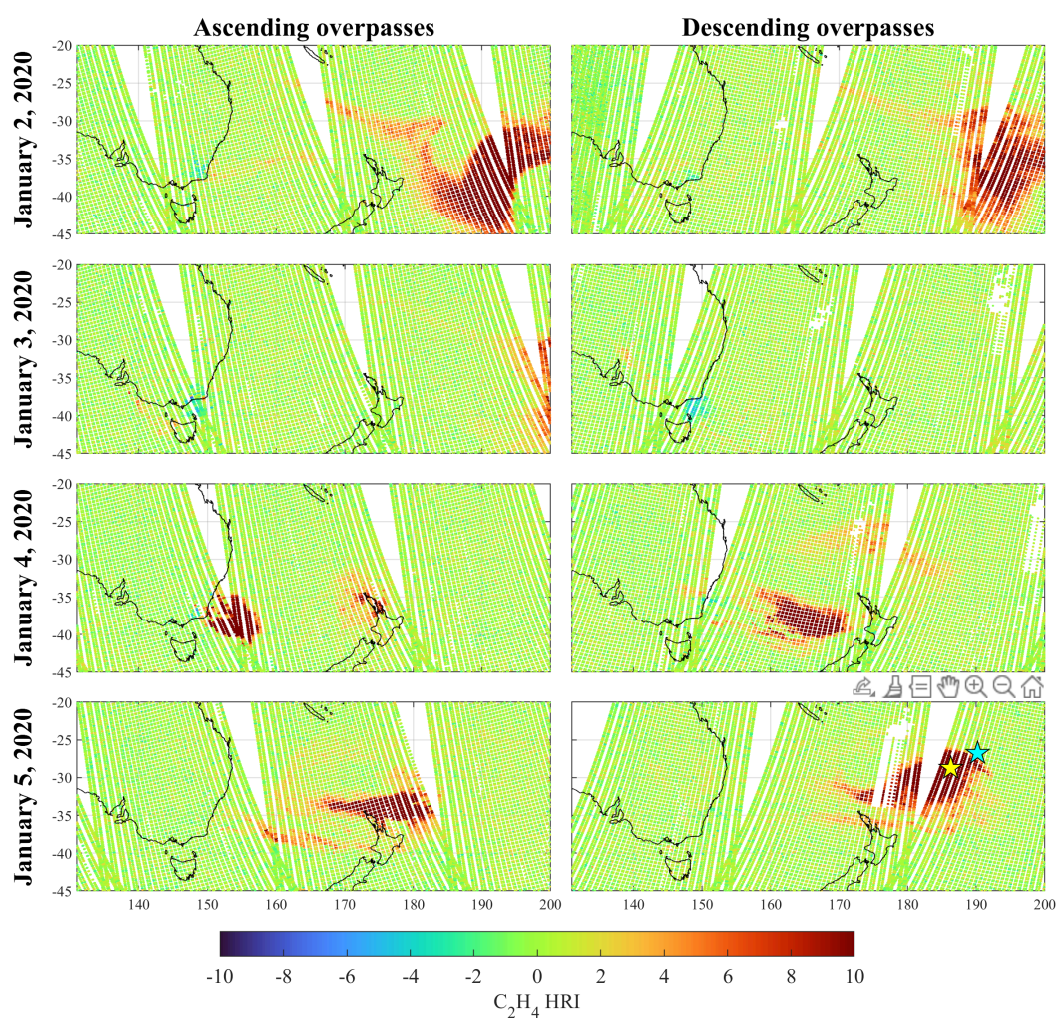


Figure A1. HRI maps of C_2H_4 of the 2020 Australian bushfires on selected days. The size of the IASI footprint has been slightly exaggerated for visualization purposes. (\star and \star respectively mark the spectra selected inside and outside the fire plume)

302 Appendix B

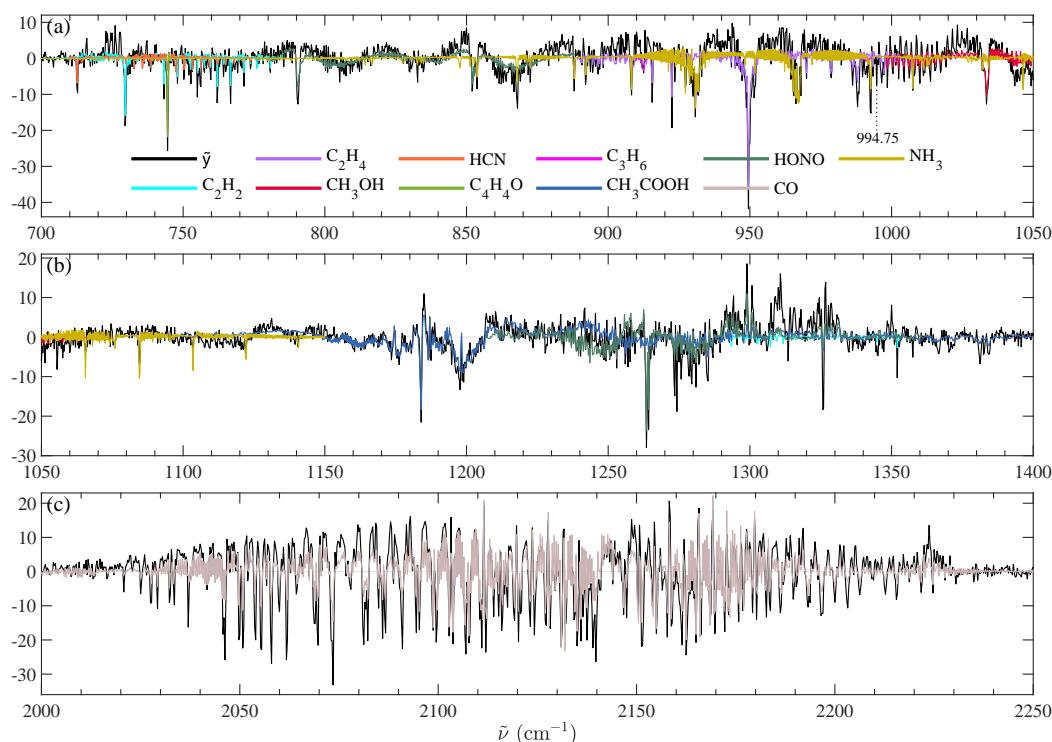


Figure B1. Whitenened spectrum of Australian bushfires from December 30, 2019 revealing 8 trace gas species and carbon monoxide.

303 **Acknowledgments**

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