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Spaceborne estimate of atmospheric CO₂ column by use of the differential absorption method: error analysis

Emmanuel Dufour and François-Marie Bréon

For better knowledge of the carbon cycle, there is a need for spaceborne measurements of atmospheric CO₂ concentration. Because the gradients are relatively small, the accuracy requirements are better than 1%. We analyze the feasibility of a CO₂-weighted-column estimate, using the differential absorption technique, from high-resolution spectroscopic measurements in the 1.6- and 2- μ m CO₂ absorption bands. Several sources of uncertainty that can be neglected for other gases with less stringent accuracy requirements need to be assessed. We attempt a quantification of errors due to the radiometric noise, uncertainties in the temperature, humidity and surface pressure uncertainty, spectroscopic coefficients, and atmospheric scattering. Atmospheric scattering is the major source of error [5 parts per 10⁶ (ppm) for a subvisual cirrus cloud with an assumed optical thickness of 0.03], and additional research is needed to properly assess the accuracy of correction methods. Spectroscopic data are currently a major source of uncertainty but can be improved with specific ground-based sunphotometry measurements. The other sources of error amount to several ppm, which is less than, but close to, the accuracy requirements. Fortunately, these errors are mostly random and will therefore be reduced by proper averaging. © 2003 Optical Society of America

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1. Introduction

The rise of atmospheric CO₂, the primary anthropogenic contribution to the greenhouse effect, is documented at many observing sites around the world.¹ Over the past 200 years, CO₂ concentration has increased by 30% in response to industrial emissions and land-use change. Climate models predict a global warming between 1.5 °C and 4 °C, for a doubling of the current concentration. To make reliable predictions of future CO₂ levels and set up apposite CO₂ emission-mitigation strategies, it is of paramount importance to quantify the factors that control atmospheric CO₂.

Observations over the past decades indicate that, on average, only approximately half of the anthropogenic emissions end up being stored in the atmo-

sphere; the rest is reabsorbed by two natural reservoirs: the oceans and the continental biosphere.² Net CO₂ removals by these two sinks have different time scales. Carbon dissolved in the oceans has a time scale of several hundred years, whereas carbon taken up by trees and soils is stocked only for a few years, with a residence time depending on the type of ecosystem. To predict the future rate of increase of atmospheric CO₂ concentration, there is a strong need to quantify carbon sources and sinks at a regional scale (i.e., finer than a 10⁶ km²).

It is possible to infer the spatial distribution of the carbon sources and sinks by using repeated CO₂ measurements on a global network of observatories. The atmosphere is a powerful integrator of the surface fluxes at large scale, which makes it possible to relate small but persistent concentration gradients to sources and sinks, provided that the air-mass transport is known. Hence atmospheric transport models can be used to interpret atmospheric measurements in terms of surface fluxes by using inverse methods.^{3–5} At present, the atmospheric CO₂ observation network consists of approximately 100 ground stations around the globe providing *in situ* concentration measurements [with flasks or infrared (IR) analyzers]. In addition, a few vertical profiles are

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acquired from airborne measurements. Unfortunately, the limited horizontal density and uneven distribution of the current network hinders the geolocation of the CO₂ fluxes at a resolution better than the continent and ocean basin scales.^{6,7} Furthermore, the current temporal frequency of the observations used in the inversions (monthly averages of CO₂ data) is insufficient to capture sporadic sources, such as fires, whose signals get severely damped by atmospheric diffusion after approximately a week. Therefore there is a strong need for a sampling network with much denser coverage in space and time than currently achieved with the existing surface network, and this suggests the use of satellite-based observations. Simulations show that spaceborne measurements could dramatically improve the determination of carbon fluxes, provided that the precision of the measurement is sufficient. As atmospheric CO₂ is a long-lived gas, its background concentration is large compared with the spatial and temporal variations that need to be measured. In an individual satellite measurement, a precision of better than 1% [<3 parts per 10⁶ (ppm)] is needed to reasonably detect fluxes.⁸ Above a threshold of approximately 5 ppm, there is no substantial gain in flux uncertainty reduction from that obtained with the current surface network. Ideally, a vertical profile would be desirable, but a column-integrated amount or column-weighted amount is also valuable, provided that the lower troposphere contributes significantly.

Three main technologies can be envisioned to monitor the CO₂ concentration from space. (1) Analysis of CO₂ emission bands in the thermal IR region such as conducted with measurements from the TIROS (Television Infrared Operational Satellite) operational vertical sounder on board the National Oceanic and Atmospheric Administration's series of polar meteorological satellites.⁹ In the near future this technique will be applied to much higher spectral resolution radiometers^{10,11} such as the atmospheric infrared sounder, launched onboard the NASA Aqua platform, and the infrared atmospheric sounding interferometer to be launched onboard the Meteorological Operational satellite. (2) Active differential absorption, envisioned for the Celsius mission proposed, but not selected, for the NASA Earth System Science Pathfinder 3 (ESSP-3) call.¹² (3) Passive differential absorption, measuring the solar light reflected by the Earth's surface after a double atmospheric path. This method is used with the SCIAMACHY (scanning imaging absorption spectrometer for atmospheric cartography) instrument, onboard the Environmental Satellite (ENVISAT) platform and is envisioned for the Orbiting Carbon Observatory mission, recently selected in the NASA ESSP-3 call. In the scope of this paper we propose to focus on an instrumental concept reliant on the last technique.

From the ground, the determination of atmospheric gas column abundance by using direct sunlight is a mature technique. By reanalyzing high-resolution spectra records measured at the Kitt Peak National Solar Observatory, Yang *et al.*¹³ retrieved column-

averaged amounts of CO₂ with a precision better than 0.5%. For satellite-based measurements, the question is whether an individual precision of 1% is feasible. In recent years, several sensitivity studies have investigated the attainable precision of the sunlight-based technique with a spaceborne instrument. Tolton and Plouffe¹⁴ have considered a radiometer consisting of 22-cm⁻¹-wide bandpass filters tuned around the 1.6- μ m CO₂ band. Buchwitz *et al.*¹⁵ have evaluated the potential of the SCIAMACHY spectrometer, which provides 0.5-cm⁻¹ spectral resolution scans in a 250-cm⁻¹-wide window around the 2.0- μ m CO₂ band. O'Brien and Rayner¹⁶ have focused on the error due to undetected atmospheric scattering by optically thin cirrus and aerosol. They propose a procedure by which the scattering problem may be overcome by using simultaneous measurements at selected wave numbers around 1.6 μ m and an oxygen band around 1.27 μ m. Finally, in an introductory study, Kuang *et al.*¹⁷ projected the retrieval of atmospheric CO₂ by using three short-wavelength infrared (SWIR) spectrometers operating in the A band at 0.76 μ m, and in the 1.6- and 2.0- μ m CO₂ bands, indicating a potential accuracy of 0.3–2.5 ppm. The 0.76- μ m band is used to correct for the effect of atmospheric scattering on the measurement. This oxygen band was chosen rather than the 1.27- μ m band suggested by O'Brien and Rayner¹⁶ because the latter is strongly affected by airglow and therefore appears to be unusable for scattering correction unless the measurements are made at high spectral resolution as proposed by O'Brien and Rayner.¹⁶ In the present paper we investigate the CO₂ column inversion from the analysis of high-resolution spectra in optimized microwindows at 1.6 and 2.0 μ m. We attempt to list and quantify all uncertainty sources individually to provide a detailed budget of baseline errors and propose potentials for error reduction. We first recall the principle of differential absorption spectroscopy, then we propose an optimized instrument and retrieval algorithm designed for the recovering of CO₂ column abundance, and, finally, we discuss the sources of incertitude.

2. Measurement Principle

A. General Theory

The measuring principle (Fig. 1) relies on the spectral analysis of the solar radiance reflected on the Earth's surface back to the top of the atmosphere (TOA) in the SWIR domain. In the measured spectrum, each atmospheric molecular species leaves a characteristic set of absorption lines by which it can be identified and quantified, provided that the spectral resolution is adequate. In the absence of scattering by the atmosphere, the radiance L reflected to space is proportional to the TOA atmospheric transmittance t_{atm} according to

$$L = E_s \mu_s R_{\text{surf}} t_{\text{atm}} / \pi, \quad (1)$$

where the other parameters are defined in Table 1. Let $k(\lambda, P, T)$ be the molecular absorption coefficient

Fig. 1. CO₂ column estimation relies on the measurement of the solar radiance reflected on the Earth's surface back to the TOA. Atmospheric scattering, which allows photons to be measured that have not traversed the full double atmospheric path, is a source of bias for the column estimates.

where λ , P , and T , respectively, denote the wavelength, pressure, and temperature. The spectrum of transmission may be written as

$$t_{\text{atm}}(\lambda) = \exp \left[-m N_{\text{air}} \int_0^{P_{\text{surf}}} r(P) k(\lambda, P, T) dP \right], \quad (2)$$

where m is the air-mass factor, N_{air} is the number of molecules of dry air in the atmospheric column per unit pressure, r is the volume mixing ratio of the gas, and P_{surf} denotes the surface pressure.

The column-averaged volume mixing ratio, defined as the total mass of gas normalized by the total mass of air in an atmospheric column, is

$$\bar{r} = \frac{1}{P_{\text{surf}}} \int_0^{P_{\text{surf}}} r(P) dP. \quad (3)$$

If we consider, in a first approximation, that the absorption coefficient is constant with height, then, after Eqs. (2) and (3),

$$t_{\text{atm}}(\lambda) = \exp[-m N_{\text{air}} k(\lambda) P_{\text{surf}} \bar{r}], \quad (4)$$

Table 1. Variables and Constants Used in This Paper Together with Typical Values When They Exist

Symbol	Definition	Unit	Typical Value
L	Radiance	$\text{W m}^{-2} \text{sr}^{-1} (\text{cm}^{-1})^{-1}$	
R_{surf}	Surface reflectance	—	0.1–0.2
t_{atm}	Double-path atmospheric transmission	—	
m	Air-mass factor	—	$2 < m < 6$
N_{air}	Number of dry-air molecules in atmospheric column per unit of pressure	$\text{hPa}^{-1} \text{cm}^{-2}$	212×10^{20}
r	CO ₂ volume mixing ratio	—	370×10^{-6}
k	Molecular absorption coefficient	cm^2	
P_{surf}	Surface pressure	hPa	900–1050
T^0	Standard air temperature	K	296
T	Air temperature	K	200–300
ν	Wave number	cm^{-1}	4940, 6357
λ	Wavelength	μm	2.0, 1.6
P_{ws}	Probability of surface slope	—	
ρ	Fresnel reflection coefficient	—	0.02
μ_s, μ_v	Cosines of solar and view zenith angles	—	
S_i^0	Normalized line intensity	—	
S_i	Line intensity	$\text{cm}^{-1}/(\text{cm}^{-2})$	
c_2	Second radiation constant	cm K	1.439
Q	Partition sum function	—	
E_i''	Lower state energy of the transition	cm^{-1}	
SNR	Signal-to-noise ratio	—	200
n_e	Spectral flux of electrons	$\text{s}^{-1} (\text{cm}^{-1})^{-1}$	
$\delta\nu$	Spectral resolution	cm^{-1}	0.1
$\Delta\nu$	Width of the band-limiting filter	cm^{-1}	15
E_s	Band-averaged solar irradiance	$\text{W m}^{-2} (\text{cm}^{-1})^{-1}$	$43 \times 10^{-3}, 65 \times 10^{-3}$
z	Satellite altitude	m	700×10^3
h	Planck constant	Js	6.6262×10^{-34}
c	Speed of light	ms^{-1}	300×10^6
A	Diameter of the instantaneous field of view (supposed circular)	m	
$\bar{t}_{\text{atm}}$	Band-averaged double-path atmospheric transmittance	—	0.4/0.8
t_{ins}	Band-averaged transmittance of the instrument ^a	—	0.715
t_{opt}	Band-averaged transmittance of the optics ^a	—	0.5
t_{filter}	Band-averaged transmittance of filters ^a	—	0.3
D	Side of the collecting area ^a	m	0.1
Δt_i	Integration time ^a	s	0.6
η	Quantum efficiency ^a	—	0.6

^aInstrumental parameters values are the results of a spaceborne Fourier-transform spectrometer concept study conducted at Centre National des Études Spatiales.¹⁸

which reveals a quasi-linear relation between the logarithm of the measured radiance and the column-averaged concentration, at a given wavelength. In practice, the absorption coefficient k varies along the atmospheric column through pressure and temperature so the measurement depends not only on the total amount of gas but also on its vertical distribution. The sensitivity to the CO₂ vertical distribution (weighting function) will be established in Subsection 5.A.

Because the TOA radiance is also dependent on the surface reflectance through Eq. (1), at least two frequencies are needed for the concentration estimate. In the so-called differential absorption technique, the difference of optical depth between a sensitive frequency, chosen to lie near the center of an absorption line of the target species, and a nonsensitive frequency, outside the absorption line, is measured. In the proposed method this principle is extended to spectral measurements (differential absorption spectroscopy). If the absorption is a good measure for the concentration of the target molecule, it is also driven by the other parameters in Eq. (2) (surface pressure, temperature vertical profile, and air-mass factor). As these parameters are known only to a finite accuracy, they are potential sources of error, whose effect will be assessed further in Subsections 5.B to 5.F.

B. Main Limitations and Constraints

The principle of atmospheric column estimate by differential absorption requires that most of the measured radiance goes through a full atmospheric path. Over the oceans, in the near IR, the only significant contribution to the surface reflectance is the glint. As a consequence, the instrument must point roughly toward the specular direction. The glint pattern depends on the wind speed and is typically of the order of a few to 20 deg. Thus the pointing tolerance is of the order of 1 deg. In Subsection 3.B we discuss the order of magnitude of glint reflectance over the oceans.

Another consideration is the cloud cover. A reliable retrieval requires the absence of clouds in the instrument's field of view. Thus the footprint size must be limited to minimize the probability of cloud contamination.

Finally, the measurements at low-elevation Sun angles must be avoided because (1) the incoming irradiance is then lower, which reduces the signal-to-noise ratio (SNR) and (2) the atmospheric scattering contribution (see Fig. 1) that is unwanted for the proposed method gets larger both because of a slant-path effect and because of the scattering phase function. In practice, solar zenith angles (SZAs) larger than 75 deg (elevation angles less than 15 deg) are probably not usable.

C. Optimal Transmission

In the SWIR the atmospheric transmission spectrum is the result of overlapping H₂O and CO₂ bands (Fig. 2). Favored regions are CO₂ absorption bands that

Fig. 2. Simulated spectrum of atmospheric transmission in the SWIR region showing regions of CO₂ absorption around 1.6 and 2.0 μm . In the calculation the densities of the absorbers in the atmosphere were supposed to follow typical tropical profiles. The SZA and view zenith angle (VZA) were set to 45 deg.

are less contaminated by the H₂O absorption lines. Using this approach, we identified two potential spectral regions around 1.6 and 2.0 μm .

After Eq. (4), for a single spectral grid-point measurement, a perturbation Δt_{atm} of the measured transmission, due to radiometric noise, would produce a relative estimation error:

$$\frac{\Delta \bar{r}}{\bar{r}} = \frac{\Delta t_{\text{atm}}}{t_{\text{atm}}} \frac{1}{\ln(t_{\text{atm}})}. \quad (5)$$

The most favorable spectral elements are those that minimize the impact of radiometric noise. As demonstrated by Eq. (5), regions of transparent transmission (t_{atm} close to 1) or with large absorptions (t_{atm} close to 0) yield the largest retrieval errors. This suggests the need for a measurement at intermediate transmission. Typically, if we suppose the perturbation is caused by a spectrally white noise (a realistic assumption for a Fourier-transform spectrometer), the best-suited spectral elements are for $t_{\text{atm}} = 0.37$, but a measurement is still acceptable for a large range of transmission around this optimal value (the error does not degrade by more than a factor of 2 as long as $0.07 < t_{\text{atm}} < 0.79$).

3. Instrument Design

A. Orbit and Time of Acquisition

The satellite should be polar orbiting to provide a large coverage of the Earth. Owing to scattering in the atmosphere, low SZAs are needed for a proper measurement, which implies a local time of observation around midday. This suggests the satellite should be launched on a Sun-synchronous orbit with equator-crossing time close to noon.

B. Viewing Geometry

Surface reflectance directly affects the quality of the CO₂ retrievals. First, measurements benefit from a better SNR over bright surfaces. Second, high surface albedo limits the relative effect of scattering processes taking place in the atmosphere, as it decreases

Fig. 3. Simulated glint reflectances in the specular direction as a function of wind speed for various SZAs θ_s .

the proportion of the atmosphere-scattered rays over the surface-reflected ones. Over the oceans, the reflectance consists of a diffuse component (by back-scattering of seawater mass) and a specular component (Sun glint). Because water is highly absorbing in the IR, the diffuse contribution is extremely small (less than 10^{-3}) and therefore can hardly be used. The specular component of the reflectance can be exploited but is significant only in the vicinity of the glint direction. The bidirectional glint reflectance R_{surf} is related to Fresnel's reflection coefficient ρ according to

$$R_{\text{surf}} = \pi^* \rho(i) / [4^* \cos^4(\beta) \mu_s \mu_v] P_{\text{ws}}, \quad (6)$$

where P_{ws} is the wave-slope distribution, β is the tilt of the plane so inclined it would reflect the incident solar ray specularly to the satellite, and i is the angle of incidence of the ray on that plane. By use of the nondirectional approximation for the slope probability distribution proposed by Cox and Munk,¹⁹

$$P_{\text{ws}}(\beta) = 1/(\pi\sigma^2) \exp[-\tan^2(\beta)/\sigma^2], \quad (7)$$

where the variance σ^2 is related to the wind speed v (in meters per second):

$$\sigma^2 = 0.003 + 5.12 \times 10^{-3} v. \quad (8)$$

Figure 3 shows reflectances predicted by Eqs. (6)–(8) in the specular direction (i.e., β is null, and i is equal to the SZA) for typical oceanic wind stress and various Sun angles. The specular reflectance decreases with increasing wind speed (the glint pattern spreads out on rougher sea surfaces) and increases toward a large SZA with a marked ascent above 40 deg owing to the variation of Fresnel's coefficient.

To assess the statistics of the Sun-glint intensity observed from a polar orbiting satellite, we used a database of clear-sky measurements of glint reflectance observed by the spaceborne radiometer POLDER²⁰ (polarization and directionality of the Earth's reflectance) in the vicinity of the specular direction. The measured reflectances have been corrected for scattering by molecules and aerosols as well as gaseous absorption. The database consists of 37,074 glint reflectances and covers a wide range of

Fig. 4. Cumulative histograms of Sun-glint reflectance over ocean surface produced by POLDER. The histogram functions were computed from a complete database of 37,074 observations and different subsets of this database arranged by SZA θ_s .

wind speed from approximately 1 to 15 m s^{-1} and Sun angles as great as 55 deg. One should point out the relative dimness of the Sun glint for most of the observations. As shown by the cumulative histogram in Fig. 4, 45% of the observed reflectances are below 0.1 and 85% are below 0.3. The average reflectance is 0.12, which is much smaller than cloud reflectance (typically, 0.6). Figure 4 also presents cumulative histograms of the database subsets classified according to SZA. The observed magnitudes are in agreement with the model prediction in Fig. 3. Furthermore, the nonlinear behavior of the reflectance with SZA is perceptible (strong increase above 45 deg).

The direction of maximum reflectance is easily predictable. It coincides roughly with the specular direction with a slight shift toward larger view zenithal angles (VZAs) in the principal plane. Indeed, for a given SZA, facets inclined such that the angle of incidence is more grazing are relatively more reflecting (the Fresnel coefficient increases with the angle of incidence). The direction follows a smooth and slow evolution with respect to the satellite referential. For a heliosynchronous satellite with an equatorial crossing time close to midnight or noon, the specular direction is close to the satellite forward or nadir plane at all times.

Over land, surface reflectance has a less marked directional signature so there is no particular constraint on the viewing geometry. On the other hand, land reflectance varies strongly with wavelength and with the surface type. The moderate-resolution imaging spectroradiometer (MODIS) channels at 2.105–2.155 μm and 1.628–1.652 μm give an indication of the reflectances at 2.0 and 1.6 μm , respectively. Cloud-free composite maps of surface reflectance produced with the spaceborne MODIS were analyzed for several types of surface cover. Figure 5 presents histograms of reflectance over a vegetated area (Amazonian forest), a snow- and ice-covered surface (Greenland), and a mineral surface (Sahara desert) at the wavelengths of interest. The average values around 2.0 and 1.6 μm

Fig. 5. Histograms of surface reflectance in cloud-free composite images produced by MODIS for the spectral bands 1.628–1.652 μm (dotted curve) and 2.105–2.155 μm (solid curves) over different land surface covers. The two well-packed histograms are for the Amazonian forest. The two histograms with a maximum at 0.7 are for the desert. The two histograms with a broad distribution around 0.15 are for Greenland.

have been reported in a summary table (Table 2) after empiric correction for the wavelength disparity with the MODIS channels.

C. Spatial Resolution

Establishing the optimal satellite spot size results from a trade-off. Large spot size permits good SNR measurements but increases the probability of cloud contamination and the spatial heterogeneity in the instrument's instantaneous field of view. Therefore the most favorable spot size is such that the SNR requirement is just met. Computation of the spectrum SNR differs according to the type of interferometer.²² Typically, in the case of a Fourier-transform spectrometer, if we suppose the detectors are limited only by the Poisson statistics of discrete electron events, the band-averaged SNR is

$$\text{SNR} = n_e \delta \nu \Delta t_i / (n_e \Delta \nu \Delta t_i)^{(1/2)}, \quad (9)$$

where n_e is the spectral flux of electrons.

Table 2. Comparative Study of the Two Envisioned Spectral Windows

	2.0 μm	1.6 μm
Range (cm^{-1})	4932–4947	6350–6365
Solar spectral irradiance [$\text{W m}^{-2} (\text{cm}^{-1})^{-1}$]	43×10^{-3}	65×10^{-3}
Spectral flux of solar photons [$\text{s}^{-1} \text{m}^{-2} (\text{cm}^{-1})^{-1}$]	44×10^{16}	51×10^{16}
Band-average double transmission ^a	0.40	0.84
Surface-reflectance vegetation ^b	0.10	0.18
Surface-reflectance snow and ice ^b	0.02	0.15
Surface-reflectance desert ^b	0.35	0.40

^aCalculated by assuming the same atmosphere and observation geometry as for Fig. 6.

^bEstimated after MODIS reflectance products at 2.105–2.155 μm and 1.628–1.652 μm (Fig. 5). To account for the difference of wavelength with the MODIS channels, given values have been decreased by 5% to 60% in agreement with typical spectral profiles of land reflectance.²¹

When we assume that most of the photons arise from solar reflection, n_e can be written as a function of the diameter A of the spot as

$$n_e = A^2 \bar{t}_{\text{ins}} \bar{t}_{\text{opt}} \bar{t}_{\text{filter}} \bar{t}_{\text{atm}} R_{\text{surf}} E_s \mu_s D^2 \eta / (4z^2 h c \nu). \quad (10)$$

Equations (9) and (10) permit us to relate the SNR and the spot size. As shown further in Subsection 5.B, the CO_2 concentration rms error resulting from instrumental noise can be contained below 1 ppm by use of a SNR of 200 (Fig. 8). If we assume the typical parameter values of Table 1, a need for a SNR of 200 would impose a spot size of approximately 5 km.

D. Spectral Interval Selection

In spaceborne atmospheric spectroscopy, it is common for the measurement to be bound to small spectral regions, so-called microwindows, dedicated to the retrieval of the target species rather than to scan the whole absorption band. Establishing the microwindow spectral width is a subtle step in the design of the retrieval method. The extension of the spectral interval to a region in which the signal is sensitive to a change of the target parameter tends to decrease the overall retrieval error, provided that this does not occasion the increase of the number of unknown parameters and that the additional spectral elements are little affected by the nontarget parameters.²³ On the other hand, within narrow spectral intervals, parameters with broadband spectral signatures, such as scattering by aerosol and surface reflectance, the H_2O continuum can be assumed constant. Furthermore, at a given sampling rate, a narrower spectrum will be acquired faster and thus less contaminated by the artifacts due to the spatial variation of surface reflectance, pressure, temperature profile, and gas abundances as the instrument's instantaneous field of view moves across the Earth. In the present study we assume that the spectrometer scans are 15 cm^{-1} wide.

The microwindow boundaries were adjusted in the previously identified CO_2 absorption bands so as to maximize the number of absorption lines within the bandwidth. As pointed out earlier, favored microwindows contain prominent but nonsaturated absorption lines of the target species. In addition, it was ensured that the spectral signature of the interfering species be minimum and noncorrelated to the target species's signal. This finally led us to consider two optimized microwindows (Fig. 6): 4932–4947 cm^{-1} (2.0214–2.0276 μm) and 6350–6365 cm^{-1} (1.5711–1.5748 μm), labeled, respectively, as the 2.0- and the 1.6- μm channels in Subsection 3.E.

E. Spectral Resolution

As can be observed in the two simulated spectra of Fig. 6, the spectral interval between two consecutive strong CO_2 transitions is of the order of 1 cm^{-1} . High spectral resolution and good knowledge of the instrument's spectral response are required to separate the individual CO_2 lines and resolve the atmospheric CO_2 and H_2O lines and solar lines. These

Fig. 6. Spectral transmissions for the 2.0- μm channel (top) and the 1.6- μm channel (bottom), as simulated by our radiative transfer model. The CO_2 , H_2O , and solar transmissions are shown by the solid, dashed, and dotted lines, respectively. In the calculation, CO_2 concentration was fixed to 370 ppm throughout the atmospheric column. The SZA and VZA were set to 45 deg. The solar spectrum was produced at the Kitt Peak National Observatory by the National Science Foundation, National Optical Astronomy Observatories.

observations have suggested the need for a spectral resolution of 0.1 cm^{-1} (resolving power of 50,000) and a 0.05-cm^{-1} spectral sampling interval. Furthermore, in the radiative transfer simulations below, the apodized instrument's spectral response was assumed to have a Gaussian shape.

F. Advantages and Shortcomings of the Selected Intervals

Owing to larger CO_2 line intensities, the 2.0- μm channel contains more spectral elements at intermediate transmissions than the 1.6- μm channel does. The 2.0- μm channel appears better suited in this respect to capture the changes of CO_2 abundance. In addition, the sensitive spectral elements of the 2.0- μm channel are located farther away from the line centers than those of the 1.6- μm channel. Therefore inversion in the 2.0- μm channel is driven by the regions of smoother slope and is then more robust with respect to incorrect spectral calibration (shift or drift of the detectors) and uncertainties on

the instrument's spectral response. On the other hand, the signal (that is, the flux of photons from solar reflection) is expected to be larger in the 1.6- μm channel. As shown in Table 2, the 1.6- μm channel profits from higher flux of solar photons and a more transparent atmosphere. Furthermore, land surfaces are usually brighter in the 1.6- μm channel (Table 2). Ocean reflectance is similar in the two bands.

Though the retained microwindows are optimized in this regard, the 2.0- μm channel suffers from significant H_2O contamination (Fig. 6). The inversion procedure supposes fixed vertical distribution of CO_2 and H_2O concentrations, with variable total columns. The vertical profile of H_2O is given by numerical weather prediction (NWP) centers with significantly large error margins. Water-vapor content has large spatial and temporal variabilities in the atmospheric column. Although the H_2O column is adjusted in the inversion, uncertainty in the relative humidity profile could induce uncorrected error in the synthetic spectrum (mostly through the alteration of the absorption line shape).

Fraunhofer lines can be a potential source of error when they interfere with the atmospheric signatures in the measured spectrum. However, the spectral position of the Fraunhofer lines are well known from astronomical observations and can be screened off in the inversion procedure. On the basis of the high-resolution solar atlas produced by Livingston and Wallace,²⁴ we synthesized solar spectra degraded to the spectrometer resolution (0.1 cm^{-1}) in the bands of interests (Fig. 6). Solar contamination remains limited in both envisioned bands with relatively more prominent lines in the 1.6- μm channel compared with the 2.0- μm channel.

4. Error Analysis: Method and Models

Spaceborne sensing of CO_2 poses a difficult challenge of accuracy: A satellite mission would be essentially worthless if the typical uncertainty on the retrievals was significantly larger than 1% (3–4 ppm). For such required precision, many causes of uncertainty must be analyzed that could be neglected for other gases with lower requirements (owing to a larger relative variability). The objective of this section and the next section is to draw up a complete error budget. Section 4 presents our general approach for assessing the error associated with a given parameter uncertainty and describes the forward and inverse models used in this paper. In Section 5 we discuss and quantify the impacts of all the sources of uncertainty that we have identified.

A. General Approach

Let $\mathbf{x}$ be the state vector describing all the unknowns to be estimated from the measurement (i.e., the column-averaged concentration of CO_2 and several by-products). We suppose that for a given $\mathbf{x}$ a forward model F can accurately produce a synthetic satellite measurement of TOA radiance spectrum $F(\mathbf{x}, \mathbf{b})$, where $\mathbf{b}$ is a vector of model parameters that

are not retrieved by the measurements (temperature profile, surface pressure, and spectroscopic data).

Furthermore, we consider an inverse model, I , which permits the exact restitution of $\mathbf{x}$ from the analysis of one spectrum, providing knowledge of the model parameters:

$$\mathbf{x} = I[F(\mathbf{x}, \mathbf{b}), \mathbf{b}]. \quad (11)$$

In practice, the model parameters $\mathbf{b}$ are known only to a finite accuracy. Departures of the model parameters from their assumed state induce an erroneous retrieval. Model parameters can be sources of random errors (e.g., temperature) or systematic errors (e.g., spectroscopic data). In our error analysis the retrieval error due to a given parameter was calculated as follows. For a representative perturbation ϵ_b of the parameter, the forward model produces an altered spectrum $F(\mathbf{x}, \mathbf{b} + \epsilon_b)$. Then, assuming no perturbation, the altered spectrum is input through the inverse model to calculate the retrieved state vector:

$$\mathbf{x}' = I[F(\mathbf{x}, \mathbf{b} + \epsilon_b), \mathbf{b}]. \quad (12)$$

The retrieval error ϵ_x is the difference between the retrieved and the true states:

$$\epsilon_x = \mathbf{x}' - \mathbf{x}. \quad (13)$$

B. Radiative Transfer Model

A numerical radiative transfer model was developed to perform the forward and inverse simulations. In the radiative transfer model, the atmosphere is discretized in 40 vertical layers of equal pressure thickness, each of which is considered homogeneous in temperature, pressure, and densities of the absorbing gases. In each layer the elementary transmission spectrum is computed with a line-by-line scheme by using spectroscopic parameters provided by HITRAN 2000.²⁵ The absorption line shape follows Voigt's profile and is numerically calculated by using the approximation by Humlicek.²⁶ The Earth's surface is assumed a spectrally white reflector.

As the error analysis relies on the comparison of synthetic spectra calculated with the same forward model (i.e., the radiative transfer model), it is not a priority in the scope of this study that the forward model be absolutely accurate. On the other hand, operational inversion from actual spectra will require very accurate models to moderate the biases in the CO₂ concentration measurements. Ideally, the forward model should be accurate to the relative precision that is pursued for the CO₂ concentrations (0.3%). Given this challenging precision, the effects of several second-order physical processes were investigated.

(1) Radiance scattered by molecules in the atmosphere (Rayleigh) back to the spaceborne instrument is less absorbed than radiance that goes through a

full atmospheric path and, as a consequence, leads to a lower apparent CO₂ column. The efficiency of the Rayleigh decreases rapidly with wavelength and is much weaker in the near IR in comparison with the visible region. Nevertheless, its effect in the bands of interest may be nonnegligible over dark surfaces and for low Sun angles. For a VZA and SZA of 60 deg and a reflectance of 0.1, simulation predicts an error of 2 ppm at 1.6 μm and 1.5 ppm at 2.0 μm . Because Rayleigh scattering is small and invariant, its effect can be modeled with the single-scattering approximation and accounted for in the inversion procedure.

(2) In the assumption of a plane-parallel atmosphere, the air-mass factor is systematically overestimated, which yields an underestimation of the CO₂ column. The bias is rather small for SZAs less than 50 deg and increases rapidly for larger angles. Simulations show that the error in the CO₂ concentration reaches 1.3 ppm at VZAs and SZAs of 60 deg. In the calculation, the curvature of the Earth was assumed constant (spherical shell atmosphere approach²⁷). Also influent on the optical path, the water-vapor effect on the air refractive index causes a variation of 0.2 ppm on the apparent CO₂ mean column concentration for both VZAs and SZAs of 60 deg. It is therefore necessary to account for the curvature of the Earth's atmosphere and the refractive index for large solar and view angles.

(3) In addition to the broadening of the CO₂ line by dry air and self-broadening (whose coefficients are provided in HITRAN), broadening by the H₂O molecule was considered by using an analytical quantum model based on the work of Rosenmann *et al.*²⁸ For warm and humid regions (oceanic sources and sinks), the simulations predict an overestimation of the CO₂ content by 0.2 ppm if the broadening by H₂O is not modeled.

(4) As shown in Eq. (2), atmospheric absorption can be related to the density of dry air per pressure unit N_{air} , which is usually assumed constant. The latter is, in fact, a function of the Earth's gravity g as $N_{\text{air}} = N_A / (g M_{\text{air}})$, where N_A is the Avogadro constant, M_{air} is the molar mass of dry air, and g decreases with altitude ($-3.10^{-6} \text{ m s}^{-2}/\text{m}$ from 0 to 90 km). Consequently, an approximated constant value of N_{air} would result in a biased estimate through Eq. (2). After investigation, our simulations indicate that omitting the gravity decrease with height results in a minor overestimation of 0.05 ppm.

(5) Thermal emission of the Earth's surface and atmosphere contributes to the radiance at the top of the atmosphere. At 2 and 1.6 μm , the relative effect of the thermal emission process is of the order of 10^{-6} and 10^{-9} , respectively, and can be neglected.

C. Inversion Scheme

The algorithm proposed for the retrieval of the CO₂ column amount from solar-reflected spectra is derived from the differential optical absorption spec-

troscopy (DOAS) technique. The DOAS technique can be traced back to Brewer *et al.*²⁹ and has been used ever since to estimate the column concentrations of many trace gases in the atmosphere.^{30–32} The results from the Global Ozone Monitoring Experiment onboard the second European Remote Sensing Satellite show the capabilities of the technique applied to spaceborne measurements.³³ Similarly, the SCIAMACHY instrument onboard ENVISAT relies on this technique to estimate column concentrations and vertical profiles of various gases.³⁴ The underlying principle of DOAS is that, to the first order, the logarithm of the radiance is a linear function of the vertical column densities to be retrieved as in Eq. (4). In practice, the spectral measurement results from a convolution with the instrument's spectral response, and the linearity does not hold. Nevertheless, it can be supposed that, within the natural variability of the unknowns about their *a priori* state, the logarithm of the measured radiance is linear to the required accuracy of the retrieval. Thus if we pose

$$f = -\ln(F), \quad (14)$$

we can write

$$f(\mathbf{x}) = f(\mathbf{x}^a) + \mathbf{K}(\mathbf{x} - \mathbf{x}^a), \quad (15)$$

where $\mathbf{x}$ is the state vector to be retrieved, $\mathbf{x}_a$ is the *a priori* state vector (independent of the direct satellite measurement), and the Jacobian matrix $\mathbf{K}$ contains the sensitivity $\delta f / \delta \mathbf{x}$ to the state vector parameters.

Consequently, provided that the *a priori* estimation is sufficiently accurate, it is assumed that the negative logarithm of the observed spectral radiance can be written as

$$\mathbf{y} = f(\mathbf{x}^a) + \mathbf{K}(\mathbf{x} - \mathbf{x}^a), \quad (16)$$

with $\mathbf{x} = [\hat{r}_{\text{CO}_2}, \hat{r}_{\text{H}_2\text{O}}, a_0, a_1, a_2]$, $\mathbf{x}^a = [\hat{r}_{\text{CO}_2}^a, \hat{r}_{\text{H}_2\text{O}}^a, a_0^a, a_1^a, a_2^a]$ and $\mathbf{K} = [\delta f / \delta \hat{r}_{\text{CO}_2}, \delta f / \delta \hat{r}_{\text{H}_2\text{O}}, 1, (\lambda - \lambda_0), (\lambda - \lambda_0)^2]$, where λ is the wavelength; λ_0 is a wavelength chosen to lie near the center of the spectral interval; $\hat{r}_{\text{CO}_2}$ and $\hat{r}_{\text{H}_2\text{O}}$ are the estimated CO_2 and H_2O column integral concentrations; a_0, a_1 , and a_2 are constants; and $\hat{r}_{\text{CO}_2}^a, \hat{r}_{\text{H}_2\text{O}}^a, a_0^a, a_1^a$, and a_2^a are the respective *a priori* values. The low-order polynomial accounts for solar energy, surface reflectivity, H_2O absorption continuum, and radiometric calibration, whose effect is assumed to be broadband in the spectral microwindows. The derivatives in the matrix $\mathbf{K}$ were numerically calculated by perturbing the forward model.

If the measurement error is supposed normally distributed with zero mean, with known error covariance $\mathbf{S}_y$, the Bayesian approach³⁵ permits the

following formulation of the retrieved state vector $\mathbf{x}$ and the associated error matrix $\mathbf{S}$:

$$\mathbf{x} = \mathbf{x}_a + (\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1} \mathbf{K}^T \mathbf{S}_y [\mathbf{y} - f(\mathbf{x}_a)], \quad (17)$$

$$\mathbf{S} = (\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1}, \quad (18)$$

where $\mathbf{S}_a$ is the error covariance associated with $\mathbf{x}_a$.

In the present study the *a priori* constraints for the gas concentrations were fixed as follows. (1) The column-averaged CO_2 concentration was attributed a nominal value of 370 ppm with an *a priori* uncertainty of 3% (estimated current knowledge of CO_2 concentration based on the assimilation of surface and airborne *in situ* measurements, i.e., GLOBAL VIEW³⁴). (2) The column-averaged H_2O concentration matched that of a standard tropical atmosphere with an estimated *a priori* uncertainty of 20% (current precision of NWP model outputs).

5. Error Analysis: Results

A. Vertical Weighting Function

The approximated Eq. (4) assumes an absorption coefficient that depends only on wavelength. In practice, it is also a function of pressure and temperature. Therefore we can write that the measured absorption is proportional to a vertically weighted column $\int_0^{P_{\text{surf}}} r(P)w(P)dP$, where $w(P)$ denotes the contribution to the measurement of an atmospheric layer at pressure P (weighting function). By the fitting of the modeled and the observed absorptions, the inversion scheme implicitly states that

$$\int_0^{P_0} \hat{r}w(P)dP = \int_0^{P_{\text{surf}}} r(P)w(P)dP, \quad (19)$$

where $\hat{r}$ is the CO_2 volume mixing ratio to be estimated, P_{surf} is the actual surface pressure, and P_0 is the assumed value of P_{surf} used in the model. For the inversion, $\hat{r}$ is assumed uniform with height in the model, thus

$$\hat{r} = \frac{\int_0^{P_{\text{surf}}} r(P)w(P)dP}{\int_0^{P_0} w(P)dP}. \quad (20)$$

For a proper assimilation of the spaceborne CO_2 measurements in the three-dimensional transport models, it is critical to know the vertical weighting function. The weights can be obtained numerically by finding the relative contribution of each atmospheric layer. We calculated, in turn, the change in the retrieved CO_2 column that results when locally perturbing the CO_2 concentration by some suitable amount (small enough that the forward model response is linear).

The calculated vertical weighting functions are shown in Fig. 7. In the 2.0- μm channel the CO_2 profile is roughly proportional to the pressure down

Fig. 7. Predicted vertical weighting functions as a function of pressure (dimensionless averaging kernels). The dashed and solid curves are for the 1.6- and the 2.0- μm channels, respectively.

to the surface, whereas in the 1.6- μm channel the vertical weighting is more uniform below 250 hPa. The reason for this different behavior is that the inversion procedure relies implicitly on measurements in the line wings of the 2.0- μm channel, whose absorption is proportional to pressure, whereas in the 1.6- μm channel the inversion is constrained by the line-center measurements, which are less sensitive to pressure. The 1.6- μm channel thus provides a good estimate of the tropospheric column amount. On the other hand, the 2.0- μm channel appears superior for sensing the lower atmosphere, where the largest variability is expected and where concentration gradients are more easily related to surface fluxes.

B. Radiometric Noise

The errors in the measurement have different origins (e.g., spectrometer noise, detector noise, and sampling position uncertainty) and depend on the type of instrument (Fourier-transform spectrometer or dispersive spectrometer). The detailed analysis of how different instrument designs affect the retrieval of CO_2 is beyond the scope of this study. In our simulations the radiometric noise is assumed Gaussian, constant, and spectrally uncorrelated (white Gaussian noise), which is a good approximation for a Fourier-transform instrument. The theoretical relationship between CO_2 column rms error and measurement noise is directly given by Eq. (18). Figure 8 shows the attainable CO_2 precision with respect to the instrument SNR, expressed at the maximum atmospheric transmittance ($t_{\text{atm}} = 1$). We observe a strongly linear relation between the inverse of the CO_2 relative precision and the instrument SNR. For an instrument SNR of typically 200, the simulations predict a CO_2 column rms error of 0.9 ppm in the 2.0- μm channel and 1.0 ppm in the 1.6- μm channel. Note that, for a SNR of 0, the rms error has a finite value that corresponds to the *a priori* uncertainty on the CO_2 concentration (set to 11 ppm).

C. Surface Pressure

The estimation of the CO_2 column-weighted concentration supposes knowledge of the surface pressure

Fig. 8. Retrieval error of the CO_2 -weighted concentration as a function of the instrumental SNR. Dashed and solid curves, the 1.6- and the 2.0- μm channels, respectively.

as shown by Eq. (19). Mistaking the surface pressure by ΔP_{surf} induces a relative error on the concentration estimates:

$$\frac{\Delta \hat{r}}{\hat{r}} = \frac{\int_0^{P_{\text{surf}} + \Delta P_{\text{surf}}} r(P)w(P)dP - \int_0^{P_{\text{surf}}} r(P)w(P)dP}{\int_0^{P_{\text{surf}}} w(P)dP} \quad (21)$$

If we assume that CO_2 is uniformly mixed in the column, $r(P)$ can be held constant; thus, to a good approximation,

$$\frac{\Delta \hat{r}}{\hat{r}} = \frac{w(P_{\text{surf}})}{\int_0^{P_{\text{surf}}} w(P)dP} \Delta P_{\text{surf}} \quad (22)$$

or, more simply,

$$\frac{\Delta \hat{r}}{\hat{r}} = w_n(P_{\text{surf}}) \frac{\Delta P_{\text{surf}}}{P_{\text{surf}}}, \quad (23)$$

where $w_n(P)$ is the normalized weighting function.

Accordingly, the more responsive to the lower atmosphere the measurement is, the more it is affected by surface pressure error. In view of the weighting functions (Fig. 7), the impact of surface pressure uncertainty is expected to be larger in the 2.0- μm channel than in the 1.6- μm channel (normalized weights at the surface are 1.9 and 1.1, respectively).

The rms error for mean sea level pressure given by numerical weather centers is 1 hPa. This error is expected to be lower for regions of clear sky, for which valid satellite measurements are available. Thus, over the ocean, the surface pressure is known to better than 1‰ relative rms and the corresponding error in CO_2 -weighted concentration is better than 1‰ or 0.4 ppm.

Over land surfaces, there is an additional uncertainty due to the altitude of the measurement spot. The surface pressure decreases by 1 hPa (or roughly

1‰) for an increase in altitude of around 8 m. Thus the effective altitude of the spot must be known with an accuracy of 8 m. This requirement clearly excludes mountainous regions for which it will not be possible to define an effective altitude to this degree of precision at the expected spatial resolution of a few kilometers. For regions with limited relief (i.e., with a standard deviation of the altitude within the measurement spot that is less than a few tens of meters), digital elevation models are available. The accuracy of these models is currently of the order of a few tens of meters and will improve dramatically within the following years with the release of the data acquired during the Shuttle Radar Topography Mission. Nevertheless, it is clear that surface topography brings an additional error source for measurements made over land surfaces. If we assume a typical error of 30 m on the pixel's surface altitude, and are well aware that this value varies greatly with the area, it results in an additional error on the column-weighted concentration of 4‰, or 1.5 ppm overland. This error is mostly random and may decrease within the coming years with better knowledge of topography. Moreover, using a simultaneous measurement in an oxygen band, such as that envisioned for atmospheric scattering correction (see Subsection 5.E), may significantly reduce the surface pressure impact on the concentration estimate.

D. Temperature Sensitivity

Temperature has an impact on the absorption coefficients of CO₂. Therefore imperfect knowledge of the atmospheric temperature profile yields an error in the CO₂ concentration estimate. The inversion procedure assumes a temperature profile as provided by the reanalysis of the NWP models. Typical rms errors for the temperature profile are currently around 1 to 1.5 K. Note that this may decrease in the future with the constant improvement of weather forecast models and the associated assimilation procedures. These errors are slightly correlated in the vertical and therefore tend to compensate for one another statistically. Thus the assumption of a constant bias of such magnitude on the vertical profile would result in unrealistic large errors on the CO₂ column estimate. Using a correlated noise generator, we simulated a field of 1000 realistic vertical profiles of temperature errors in order that their statistics match the variance-covariance matrix derived by the 60-level European Center for Medium-Range Weather Forecasts (ECMWF) model. Following the method described earlier, we analyzed the mean impact on the CO₂ column estimate (Fig. 9). The concentration rms errors are lower in the tropics, where the rather low temporal and spatial variabilities of the temperature profile facilitate the capture by meteorological models. Temperature is a major source of error in the 2.0-μm channel, but the error is very much lower in the 1.6-μm channel (about six times lower). For measurements at midlatitude (40 deg), we predict typical errors of 0.3 and 1.7 ppm in the 1.6- and the 2.0-μm channels, respectively. This large

Fig. 9. CO₂-weighted concentration rms error due to uncertainty on the temperature profile as a function of latitude in the 2.0-μm channel (solid curve) and the 1.6-μm channel (dashed curve). The dotted curve shows the achievable error by use of simultaneous measurements in both bands. The simulation used 1000 synthetically noised temperature profiles.

difference is inherent to the spectroscopic parameters of the absorption lines in the selected portions of the absorption bands. The integrated absorption coefficient of a line (i.e., the line intensity) S_i is dependent on temperature according to

$$S_i = S_i^0 Q(T^0)/Q(T) \exp[-c_2 E_i''(1/T^0 - 1/T)], \quad (24)$$

where E_i'' is the energy of the lower state of the transition. As shown in Fig. 10, the relative change of CO₂ line intensity caused by a perturbation of temperature is very much a function of the lower state energy of the transition. Typically, for lines with E_i'' below 300 cm⁻¹, S_i varies by less than 1% per unit degree at characteristic atmospheric temperatures. At larger E_i'' , the percentage change increases significantly, especially over the range of stratospheric temperature (200–270 K). For the principal CO₂ isotope, E_i'' lies from 464.17 to 1188.29 cm⁻¹ in the 2.0-μm channel and from 2.34 to 234.08 cm⁻¹ in the 1.6-μm channel. Therefore the absorption lines in the 1.6-μm channel are significantly less sensitive to temperature errors. Note that the percentage changes of line intensity in Fig. 10 slightly differ from

Fig. 10. Relative change of CO₂ line intensity caused by a unit degree perturbation of temperature as a function of temperature for various lower state energies E'' . Partition sum functions used in the computation are issued from HITRAN 2000.

Fig. 11. Dimensionless temperature-averaging kernels for the 2.0- μm channel (solid curve) and the 1.6- μm channel (dashed curve).

those obtained by Park,³⁵ owing to different values of the CO_2 partition functions in the calculation.

Let us point out that the established temperature sensitivities are a direct function of the chosen spectral intervals. If the spectral windows were shifted or chosen wider, they would encompass absorption lines with a different range of E_i , and this would affect the overall dependences on temperature. In addition, if simultaneous measurements in both 1.6- and 2.0- μm channels are performed, the different temperature sensitivities of the bands can be used to reduce the temperature uncertainty on the CO_2 estimate as we now explain: Temperature-averaging kernels of the 1.6- and the 2.0- μm channels (Fig. 11) show a clear anticorrelation. In consequence, it is expected that a given field of error in the temperature profile will affect the CO_2 retrieval of the two channels in a connective manner. The representation of the synthesized 1000 errors in a scatter plot (Fig. 12) reveals a simple linear relation (solid line) in the form

$$\varepsilon_{\text{CO}_2}^{1.6} = \alpha \varepsilon_{\text{CO}_2}^{2.0}, \quad (25)$$

with $\alpha = -0.1670$, where $\varepsilon_{\text{CO}_2}^{1.6}$ and $\varepsilon_{\text{CO}_2}^{2.0}$ denote the CO_2 retrievals in the 1.6- and 2.0- μm channels, respectively.

The constraint that the retrieved CO_2 must be the

Fig. 12. Correlation between $\varepsilon_{\text{CO}_2}^{1.6}$ and $\varepsilon_{\text{CO}_2}^{2.0}$. The calculation used the same field of noised temperature profiles as for Fig. 9.

Fig. 13. Retrieval error of the CO_2 -weighted concentration owing to atmospheric scattering as a function of the scatterer optical thickness. We considered the case of a cirrus cloud distributed around 250 hPa and a boundary-layer aerosol distributed around 900 hPa. The simulation was made for a SZA and a VZA of 45 deg and a surface reflectance of 0.2. The dashed and solid curves are for the 1.6- and the 2.0- μm channels, respectively.

same from both bands suggests the corrected estimate:

$$\hat{r}_{\text{CO}_2} = \frac{\hat{r}_{\text{CO}_2}^{1.6} - \alpha \hat{r}_{\text{CO}_2}^{2.0}}{1 - \alpha}, \quad (26)$$

where $\hat{r}_{\text{CO}_2}^{1.6}$ and $\hat{r}_{\text{CO}_2}^{2.0}$ are the retrieved CO_2 values in the 1.6- and 2.0- μm channels, respectively. Because errors will be mostly compensated for in Eq. (26), the sensitivity to errors in the *a priori* temperature profile will be significantly reduced. Simulations show that, after correction, the rms errors on the CO_2 retrieval are contained below 0.2 ppm at all latitudes (dotted curve in Fig. 9).

E. Atmospheric Scattering

Atmospheric scattering allows photons that have not traversed the full double atmospheric path to be measured. Because this light traverses less material, it is less absorbed by the CO_2 and yields a lower apparent concentration. The quantitative impact is a function of both optical properties and height, which are highly variable in space and time. Observations in the presence of thick clouds can be identified and filtered out, but undetectable scatterers, such as sub-visible cirrus, are a potential source of error that needs to be assessed. In Fig. 13 we present the errors associated with a boundary-layer aerosol distributed around 900 hPa and a cirrus cloud distributed around 250 hPa as a function of optical depth. In this simulation, we assumed a nonabsorbing scatterer and a Henyey–Greenstein^{36,37} phase function.

Aerosol optical properties are now well known thanks to considerable effort during the past decade, including research with surface Sun photometers and satellite measurements. Most aerosols show a rapid decrease of the optical thickness with the wavelength so that it is relatively minor at 1.6 and 2 μm except for specific cases such as dust storms. Moreover, aerosol layers are generally low in the atmosphere. Typically, the presence of a boundary-layer aerosol at

an average height of 1 km with an optical thickness of 0.05 in the spectral range of interest above a surface of reflectance 0.2 is expected to generate an error of approximately 1.5 ppm (0.45%) for a SZA or VZA of 45 deg.

A similar evaluation is more difficult for thin cirrus clouds because it requires a reliable estimate of their optical thickness. Furthermore, assuming it were possible to select observations totally free of thin cirrus clouds, we ignore whether such clear areas would represent a significant fraction. Using MODIS-calibrated radiance products, we processed optical thickness histograms at 1.6 and 2.1 μm over the ocean (not shown). Regions contaminated by clouds or Sun glint were removed so that atmospheric scattering generates the main contribution to the TOA radiance. Our analysis reveals that even the apparently clearest cases over the open oceans seem to be affected by atmospheric scattering with typical optical thickness of 0.02 (after molecular scattering correction). These results indicate that most of the clear cases may, in fact, be contaminated by thin cirrus layers with an unacceptable (over 1%) impact on the CO_2 apparent concentration.

Fortunately, the effect of scattering by thin clouds and aerosols on the estimation of the CO_2 column amount can be largely mitigated by use of dedicated schemes. Promising techniques have been proposed to correct for this error in previous studies.^{16,17,38} One strategy consists of compensating for the scattering error by using supporting measurements in an oxygen band in addition to the CO_2 absorption band.^{16,17} Because oxygen is a well-mixed gas in the atmosphere and its density is mostly constant, its absorption spectrum yields a scattering vertical profile that may be used to correct the apparent CO_2 concentration. O'Brien and Rayner¹⁶ have demonstrated the potential of such a method applied to high-resolution measurements at a few frequencies in the 1.61- μm absorption band of CO_2 and the 1.27- μm absorption band of O_2 . The results indicate that the proposed algorithm allows for scattering error reduction to below the 0.5% level in situations with cirrus and aerosol optical thickness as large as 0.1 and 0.2, respectively. Another method, suggested by Aoki *et al.*,³⁸ relies on the analysis of the polarized radiation in the Sun-glitter region. The difference between the polarization rate of the surface-reflected radiation over Sun glint and that of the scattered radiation in the atmosphere is exploited to eliminate the impact of scattering by appropriately differentiating two components of the polarized light. It is found that the effect of the radiation scattered by thin clouds and aerosol on the estimation of the CO_2 column amount can be reduced to below 0.1%. Similar procedures could be applied to the spectra inversion that is discussed here, although an evaluation of the expected accuracy would be the subject of a full paper.

F. Knowledge of Spectroscopic Parameters

The accuracy of the absorption intensity for the lines of interest is not better than several percentages [HITRAN or GEISA³⁹ (Gestion at Etude des Informations Spectroscopiques Atmosphériques) databases]. The relative accuracy for the other parameters (line width and sensitivity to temperature and pressure) is even lower. Clearly, this accuracy is not sufficient for determining the absolute abundance of CO_2 . There is a strong need to better characterize the necessary coefficients. This can be carried out either in the laboratory or, for better compatibility with the spaceborne measurements, using a spectrometer, aiming at the Sun with a concomitant airborne profile measurement of CO_2 . In view of that, it can be reasonably expected that the error associated with spectroscopic parameter uncertainty will become less than 0.5%. Besides, such remaining errors will be mostly systematic, with limited impact on the surface flux estimates in that those are derived from atmospheric CO_2 gradients rather than absolute levels.

G. Atmospheric Water Vapor

The CO_2 flux inversion methods, which may use satellite estimates of CO_2 concentration, are based on the dry-air volume mixing ratio. For a given dry-air volume mixing ratio, water vapor in the atmosphere increases the total air mass and therefore decreases the concentration of CO_2 . Atmospheric water-vapor content and its uncertainty are very much a function of latitude and season (linked to the temperature through the atmospheric capacity). In midlatitude, a typical H_2O content is 10 kg m^{-2} or 1‰ of the total atmospheric mass. By use of fields from NWP models, the uncertainty can be reduced to a fraction of this value. In the tropics the total water-vapor content can rise to 100 kg m^{-2} , and a typical uncertainty is 10 kg m^{-2} or 1‰ of the total atmospheric mass. Therefore a typical error on the conversion between the CO_2 volume mixing ratio and the dry-air CO_2 volume mixing ratio is between 0.1 and 1‰. This error may decrease in the future with the constant improvement of weather models and the associated assimilation procedures of satellite data.

6. Conclusions

In this paper we discuss the accuracy of CO_2 column spaceborne estimates from spectroscopic measurements at high resolution in the 1.6- and 2- μm absorption bands by using the differential absorption technique. The accuracy required to improve our knowledge of the carbon budget is on the order of 1% or 3.6 ppm. Because of this stringent requirement, many sources of error have to be considered that are neglected when a similar technique is used for other gases.

The error budget (Table 3) indicates that the objective is difficult to attain on individual shots. Several sources of error amount to between 1 and 2 ppm.

The weighting function of the 2.0- μm channel increases with pressure, which makes it more sensitive

Table 3. Estimate of the Various Error Sources Identified and Quantified in this Paper for the Retrieval of CO₂-Weighted-Column Concentration from Space

Error Source	Assumed Uncertainty	Error (ppm) 2.0 μm	Error (ppm) 1.6 μm	Comment
Radiometric noise	SNR = 200	0.9	1	Random
Temperature profile	Current ECMWF error at 50° latitude	1.7	0.4	Can be improved to 0.2 ppm by using coincident measurement in both channels
Surface pressure	Ocean: <1 hPa	0.6	0.3	Random. May decrease with new Digital Elevation Model
	Land: 5 hPa	3.6	1.8	Can be corrected by addition of an O ₂ band
Water vapor	H ₂ O column: 1–10 kg m ⁻²	0.03–0.3	0.03–0.3	Random. May improve with NWP models
Atmospheric scattering	Thin cirrus optical thickness 0.02	4	4	Can be corrected by addition of an O ₂ band
	Aerosol optical thickness 0.05	1.5	1.5	
Absorption coefficient	4%	15	15	Bias. Will decrease to better than 0.5% with laboratory measurements

to the boundary layer, where the concentration gradients are expected to be the largest and the easiest to relate to surface fluxes. This makes it better suited to the science objectives than the 1.6- μm channel. On the other hand, the 1.6- μm channel is less sensitive to several sources of uncertainties, in particular, the temperature profile and the surface pressure.

There are two major sources of error that need to be resolved for a useful measurement of the CO₂ from space by using the method described in this paper. One is the spectroscopic parameters. This can be resolved relatively easily from additional Sun photometry measurements from surface-based instruments during the development of the space mission. The other one is the impact of atmospheric scattering resulting from aerosol and undetected clouds. This error can be rather large and may lead to spatial biases as the distribution of atmospheric scatterers is not uniform. Additional studies are needed to properly evaluate this source of uncertainty and the accuracy of a correction algorithm that uses an oxygen absorption band.

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