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A correlated-k distribution scheme for overlapping gases suitable for retrieval of atmospheric constituents from moderate resolution radiance measurements in the visible/near-infrared spectral region

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Abstract. An accurate and fast radiative transfer scheme for the simulation of the spectral radiance measurements of a new generation of multichannel moderate resolution satellite spectrometers, such as GOME/ERS-2 (240-790 nm) and SCIAMACHY/ENVISAT-1 (240-2385 nm), has been developed. Representative absorption cross sections of the individual molecular line-absorbers CH_4, CO, CO_2, H_2O, N_2O, and O_2 for relatively narrow spectral intervals ($\leq$ 0.2 nm) have been determined using a combined correlated-k (c-k) distribution and exponential sum fitting of transmittances (ESFT) scheme. The speed of the c-k calculations mainly depends on the channel-dependent spectral resolution of the instruments. For the measurements to be made by SCIAMACHY, this may be up to 800 times faster than line-by-line calculations. The agreement between c-k radiances and line-by-line reference radiances is in the range 1-2%. The dominant error ($\sim$1%) is attributed to the correlation assumption made when applying the k distribution method to inhomogeneous atmospheres. As the commonly used c-k methods for overlapping gases are shown to result in large radiance errors at SCIAMACHY spectral resolution or do not permit individual representative absorption cross sections to be defined for each absorber separately, a new and novel method for the accurate simulation of overlapping absorption has been developed, verified, and validated. This technique enables overlapping line absorption to be considered for arbitrary spectral correlation of the monochromatic absorption cross sections of the individual gases. The new c-k scheme is based on a linear mixing of two radiance terms determined assuming correlation and anticorrelation of the monochromatic absorption cross sections of the overlapping gases.

1. Introduction

The ultraviolet, visible, and near-infrared spectral regions are increasingly being exploited for the remote sounding of the Earth's atmosphere and surface. An essential part of most inversion algorithms, used to retrieve atmospheric parameters from remote sensing measurements, is an accurate forward model. The latter computes the measured quantities, i.e., the radiances, by using a model, that describes the radiative transfer through an atmosphere having a given composition. SCIATRAN is such a radiative transfer (RT) forward model developed for the retrieval of atmospheric constituents from measurements of the upwelling terrestrial (nadir) radiance and extraterrestrial solar irradiance in the ultraviolet to near-infrared (UV-NIR) spectral region.

SCIATRAN has been optimized for use in the inversion of the radiance measurements made by the new generation of multichannel moderate resolution diode array satellite spectrometers such as the scanning imaging absorption spectrometer for atmospheric chartography (SCIAMACHY) instrument (240-2385 nm) [*Burrows et al.*, 1995; *Bovensmann et al.*, 1999] and its smaller-scale version, the Global Ozone Monitoring Experiment (GOME) (240-790 nm) [*Burrows et al.*, 1999; *European Space Agency (ESA)*, 1995]. GOME was launched aboard the ESA ERS-2 satellite in April 1995 and has now made nearly 5 years of successful measurements. ERS-2 flies in a Sun-synchronous orbit having a local equator crossing time of 1030 LT. SCIAMACHY is planned to be launched aboard the ESA ENVISAT-1 satellite in mid-2001 (Sun-synchronized orbit with 98.55° inclination, equator crossing 1000 LT).

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Table 1. Approximate Spectral Range, Spectral Resolution, and Dispersion per Detector Pixel (Pixel Resolution) of the Eight SCIAMACHY Channels

Channel	Spectral Range (nm)	Spectral Resolution FWHM (nm)	Pixel Resolution (nm)	$\Delta\lambda^{c-k}$ (nm)[a]
1	240 - 314	0.24	0.12	-
2	309 - 405	0.26	0.13	-
3	394 - 620	0.44	0.22	0.050
4	604 - 805	0.48	0.24	0.050
5	785 - 1050	0.56	0.27	0.050
6	1000 - 1750	1.60	0.74	0.200
7	1940 - 2040	0.22	0.11	0.025
8	2260 - 2385	0.24	0.12	0.025

[a]Interval $\Delta\lambda^{c-k}$ denotes the width of the corresponding c-k spectral averaging intervals as described in section 4.

SCIAMACHY measures scattered, reflected, and transmitted light in nadir, limb, and solar and lunar occultation viewing geometries. The instrument comprises eight spectral channels, each having 1024 detector diodes. In this manner the spectral regions 240-1750 nm, 1940-2040 nm, and 2260-2385 nm (see Table 1) are observed simultaneously. In comparison, GOME is limited to nadir viewing and has only four channels. Spectrally, these are nearly identical with the first four shortwave channels of SCIAMACHY. The absolute radiometric accuracy of the SCIAMACHY level 1 data product is predicted to be about 3-4% for the Sun-normalized radiance. The relative radiometric accuracy is, however, estimated to be much better than 1%. Dependent on the retrieval algorithm and on the information to be extracted, the RT forward model to be used for retrieval has similarly high requirements. From the SCIAMACHY measurements the total columns and vertical profiles of many important trace gases are to be derived (for example, O_3, NO_2, BrO, SO_2, HCHO, and the trace gases discussed in this paper). In addition, information on pressure, temperature, aerosols, clouds, and the surface spectral reflectance can be retrieved. The near-simultaneous limb and nadir observations of the same air mass enable the atmospheric column of constituents in the lower troposphere to be determined. The scientific objectives of SCIAMACHY are related to tropospheric, stratospheric, and mesospheric chemistry and dynamics. For more information on the data products and the scientific objectives of both SCIAMACHY and GOME, the reader is referred to *Bovensmann et al.* [1999] and *Burrows et al.* [1999], and the references given therein.

For trace gas retrieval, molecular absorption has to be accurately simulated. The monochromatic absorption cross sections of so-called line absorbers, gases exhibiting highly structured electronic-vibrational-rotational or vibrational-rotational absorption bands, may be calculated from spectroscopic databases, describing the line parameters such as line position, line intensity, and lower state energy. Their cross sections strongly depend on wavelength, pressure, and temperature. In contrast, the absorption cross sections of UV-visible "continuum absorbers," such as ozone, exhibit a smooth wavelength dependence (compared to the SCIAMACHY resolution) and rather weakly depend on pressure and temperature (i.e., altitude) as compared to absorbers with a resolved line spectrum. This study focuses on the fast and accurate simulation of SCIAMACHY nadir radiance measurements in spectral regions dominated by line absorption. A fast RT model is essential, even if a look-up table scheme is to be used in routine retrieval, because the development and optimization of retrieval algorithms generally requires a large amount of RT simulations [e.g., *Buchwitz et al.*, 2000].

A classical method to model line absorption is the time-consuming monochromatic line-by-line (LBL) approach. However, if individual absorption lines are not resolved, spectrally averaged radiances rather than monochromatic radiances are needed to simulate the measurements. The method of choice for the fast computation of spectrally averaged radiances is the correlated-k (c-k) distribution method, because this approach is compatible with the monochromatic structure of the multiple-scattering RT equation. This method was first described about 10 years ago [*Goody and Yung*, 1989; *Goody et al.*, 1989; *Lacis and Oinas*, 1991; *Fu and Liou*, 1992]. Recently, several studies using this technique have been published [*Hollweg*, 1993; *Kratz*, 1995; *Mlawer et al.*, 1997; *Kratz et al.*, 1998; *Firsov et al.*, 1998; *Cusack et al.*, 1999; *Sun and Rikus*, 1999]. They have focused on aspects such as how to significantly reduce the number of terms or quadrature points (and therefore computer time) and how to deal with inhomogeneous atmospheres and overlapping line absorption for a specific application.

As the emphasis of most of these studies has been climate research they focused on wavenumber intervals being typically orders of magnitude larger (≈ 100 cm^{-1}, containing several 100 or 1000 individual lines) than the small spectral intervals to be considered in our applications (0.05-5 cm^{-1}, with only a few lines). *Fischer and Grassl* [1991] used the c-k/ESFT method for multiple-scattering radiance simulations in the 755-770 nm spectral region (O_2 A band) at 1 nm resolution (~ 17 cm^{-1}) to determine cloud parameters from space. However, they did not provide details about the accuracy of their method in comparison to LBL calculations.

The present study is the first detailed investigation of the c-k method addressing its appropriateness for subnanometer resolution covering nearly the entire solar spectral region. The statistical assumptions usually adopted for overlapping line absorption, for example, the assumed multiplication property of band transmittances, are shown in this investigation to result in large radiance errors at the spectral resolution required

for our applications. Similarly, the popular alternative "single complex gas" approach is also not appropriate for our retrieval applications, because this method is based on the assignment of a single representative absorption cross section or coefficient to several line absorbers.

To solve the important problem of overlapping gases, a new method has been developed. This novel approach is not based on statistical assumptions and enables individual cross sections for each absorber to be defined and used.

The structure of this manuscript is as follows: Section 2 describes briefly the radiative transfer model SCIATRAN. Section 3 introduces the c-k method and the new scheme for the simulation of overlapping line absorption. Section 4 describes how the effective absorption cross sections, representative for finite spectral intervals, are determined. A comparison of c-k radiances with LBL reference radiances follows in section 5. The residual c-k radiance error is analyzed in section 6, and the improvement in computer time relative to LBL calculations is reported in section 7.

2. Radiative Transfer Model

The radiative transfer model SCIATRAN solves the monochromatic RT equation for a plane-parallel vertically inhomogeneous atmosphere using the finite difference method [*Barkstrom*, 1976] taking into account multiple scattering. The sphericity of the Earth is treated in a pseudospherical manner, i.e., the solar source function (the number of solar photons reaching a given altitude before being scattered for the first time) is evaluated taking the sphericity of the Earth and refraction fully into account.

SCIATRAN is an extension of the UV/visible GOMETRAN RT model [*Rozanov et al.*, 1997]. The capability of accurately simulating molecular line absorption from the atmospheric gases CH_4, CO, CO_2, H_2O, N_2O, and O_2 in the 440-2400 nm spectral region has been added. Both a line-by-line reference scheme and a significantly faster correlated-k distribution scheme have been developed and implemented in SCIATRAN.

The numerical solution of the RT equation is the Sun-normalized radiance (usually the radiance for a constant solar flux of π), which is also call intensity in this study. This intensity is obtained at all altitude levels and directions simultaneously, since all intensities are coupled due to multiple scattering. In the following, intensity refers to the top-of-atmosphere radiance, if not stated otherwise, since this is the quantity measured by the satellite instruments.

In addition to molecular line absorption, "broadband absorption" due to ozone, NO_2, BrO, and other trace gases absorbing in the ultraviolet and visible spectral regions and Rayleigh scattering by air molecules is considered. Parameterization schemes for scattering and absorption by clouds [*Kurosu et al.*, 1997] and aerosols [*Hoogen*, 1995; *Kauss*, 1998] and the MODTRAN aerosol model based on *Shettle and Fenn* [1979] are included, covering the entire 240-2400 nm spectral region. Rotational Raman scattering by air molecules can also be modeled [*Vountas et al.*, 1998]. This inelastic scattering scheme is compatible with the line-by-line mode of SCIATRAN but not appropriate for use with the c-k scheme because of the spectral averaging performed in c-k mode.

3. A Novel Approach to Solve the Problem of Overlapping Gases

The quantity measured by SCIAMACHY, GOME, and similar passive remote sensing spectrometers is the spectrally averaged radiance $\bar{I}_{\Delta\lambda}(\lambda_j)$, defined as the monochromatic radiance I_λ convolved with the (typically bell-shaped) instrument slit function f^{inst}:

$$\begin{aligned}\bar{I}_{\Delta\lambda}(\lambda_j) &= \int_{\lambda_j-\Delta\lambda/2}^{\lambda_j+\Delta\lambda/2} f^{\text{inst}}_{\lambda,\lambda_j} I_\lambda \, d\lambda \\ &\approx \sum_{i=1}^{N} w_i \, f^{\text{inst}}_{\lambda_i} I_{\lambda_i}(\{k_{\lambda_i}\}). \qquad (1)\end{aligned}$$

Here λ_j denotes the center wavelength of detector pixel number j, the w_i are the quadrature coefficients, and N is the number of discrete spectral points needed to accurately approximate the integral by a finite sum. The symbol $\{k_{\lambda_i}\}$ represents all absorption cross sections of one or more line absorbers needed to numerically determine the radiance at a given spectral point λ_i. The interval $\Delta\lambda$ is typically several times larger than the full width at half maximum (FWHM) of the instrument slit function f^{inst}. To evaluate this integral numerically, I_λ needs to be determined in the interval $[\lambda_j - \Delta\lambda/2, \lambda_j + \Delta\lambda/2]$ on a wavelength grid λ_i sufficiently fine to assure an accurate integration. For line absorption the required sampling frequency is usually high (several hundred points per SCIAMACHY detector pixel), resulting in unacceptably large computation time. It is therefore important to develop alternative schemes, which enable equation (1) to be evaluated more rapidly.

The c-k method is the method of choice to solve this problem. A detailed description can be found elsewhere [e.g., *Lacis and Oinas*, 1991]. For the reasons explained in section 4 the following brief discussion of this technique is restricted to a slit function assumed to have a constant value inside $\Delta\lambda$ but zero outside. This corresponds to setting f^{inst} equal $1/\Delta\lambda$ in equation (1). Subsequently, spectral averaging intervals $\Delta\lambda^{c-k}$, which are much smaller than the $\Delta\lambda$, are selected to cope with problems related to slit function changes and wavelength interpolation.

3.1. General Description of the c-k Method

The c-k method, as applied to vertically inhomogeneous atmospheres, is an extension of the k-distribution method, which is restricted to homogeneous

atmospheres. The latter was proposed by *Ambartzumian* [1936] for the simulation of the radiative transfer in stellar atmospheres. Initially, the case of a homogeneous atmosphere containing a single line absorber is considered.

The monochromatic absorption cross section of a given line absorber in a given spectral interval $\Delta\lambda$ (containing several absorption lines) is a rapidly varying function of wavelength having several maxima and minima. As a result, specific values of the cross section occur many times. If the line absorber cross section is the only optical parameter within interval $\Delta\lambda$ that varies (significantly) with wavelength, the monochromatic radiance is (nearly) identical at those wavelengths where the cross sections are identical. To determine the mean radiance it would therefore be sufficient to calculate the monochromatic radiance only at wavelengths where the cross sections are (significantly) different. The mean radiance can be computed as a weighted average of these monochromatic radiances. The weights being the fraction of $\Delta\lambda$ covered by a given constant cross section, or, more precisely, by cross sections of a given magnitude range. This is the basis of the k-distribution method. A small set of M representative absorption cross sections k_i are defined, each k_i representing a given magnitude range of monochromatic cross sections appearing in the spectral interval. Instead of using N quadrature points, coupled with the corresponding monochromatic cross sections k_{λ_i}, the monochromatic RT equation only has to be solved M times using the representative absorption cross sections k_i. The number M is usually much smaller than N, provided a good set of representative cross sections has been found:

$$\bar{I}_{\Delta\lambda} \approx I^{c-k}_{\Delta\lambda} := \sum_{i=1}^{M} \omega_i \, I_i\,(k_i)\,. \tag{2}$$

The symbol $\{k_{\lambda_i}\}$, used in equation (1), has been replaced by k_i, as only one line absorber, pressure, and temperature is considered. The weights ω_i are normalized such that $\sum_i \omega_i = 1$. Weight ω_i can be understood as the fraction of the spectral interval $\Delta\lambda$ covered by absorption cross section k_i.

The solution of the multiple-scattering RT equation requires a large range of (optical) path lengths and corresponding line absorber transmittances to be considered simultaneously. The mean transmittance $\bar{T}_{\Delta\lambda}$ for a homogeneous path and a given line absorber is approximated by a finite sum of pseudomonochromatic (Beer-Lambert law) transmittances:

$$\begin{aligned}\bar{T}_{\Delta\lambda}(m) &:= \frac{1}{\Delta\lambda}\int_{\Delta\lambda} \exp(-k_\lambda\, m)\, d\lambda \\ &= \int_0^1 \exp(-k_g\, m)\, dg \\ &\approx \sum_{i=1}^{M} \Delta g_i \, \exp(-k_i\, m) \\ &= \sum_{i=1}^{M} \omega_i \, \exp(-k_i\, m). \end{aligned} \tag{3}$$

The symbol m denotes the absorber amount in number of molecules per unit area. For a homogeneous atmosphere, m is equal to ρ times l, where ρ is the number of molecules per unit volume of the line absorber, and l is the geometrical path length. The interval dg describes the fraction of the wavelength interval $\Delta\lambda$ which is covered by absorption cross sections between k and $k + dk$. This implies that $dg = f(k)dk$, where $f(k)$ is the cross section distribution function, and $g(k)$ is the corresponding cumulative probability, i.e., $g(k)$ is the fraction of interval $\Delta\lambda$ with absorption cross sections less than k. The cumulative probability $g(k)$ can be inverted to obtain $k(g)$ ($\equiv k_g$). Using a regularly sampled wavelength grid λ_i, k_g can simply be obtained by sorting k_{λ_i} by magnitude and normalizing the new "wavelength" axis g to the interval $[0, 1]$. The sorted cross section k_g is, in contrast to k_λ, a fairly smooth curve. This enables the integral over the monochromatic transmittance to be approximated by a finite sum having a significantly smaller number of terms (here M) than would be required for the highly structured k_λ (see Figures 1a and 1b).

To determine appropriate k_i values, the pseudowavelength axis g is divided into M pseudowavelength subintervals Δg_i. One representative cross section k_i and weight ω_i is assigned to each subinterval, as will be described in more detail below.

The extension of the k-distribution method to inhomogeneous atmospheres is described in detail elsewhere [*Goody and Yung*, 1989; *Goody et al.*, 1989; *Lacis and Oinas*, 1991; *Fu and Liou*, 1992]. The main assumption in this case is that the line absorber cross sections are sufficiently wavelength-correlated for different pressures and temperatures, resulting in transformations $\lambda \rightarrow g$ being similar at all altitudes. However, this is only exactly true for specific conditions [*Goody et al.*, 1989; *Fu and Liou*, 1992; *West et al.*, 1990]. The validity of this correlation assumption has to be carefully checked for each given application. The error introduced by applying the k-distribution method to inhomogeneous atmospheres (correlated-k distribution method) needs to be quantified by comparison with LBL calculations (see section 5).

3.2. Overlapping Line Absorption

To extend the c-k method to overlapping line absorption, two fundamentally different methods are generally utilized.

The first approach is based on combining two or more overlapping line absorbers to generate a "single complex gas" [*Goody et al.*, 1989; *Fu and Liou*, 1992; *Mlawer et al.*, 1997; *Sun and Rikus*, 1999]. This approach is not appropriate for our applications, as this method is based on assigning a single representative absorption

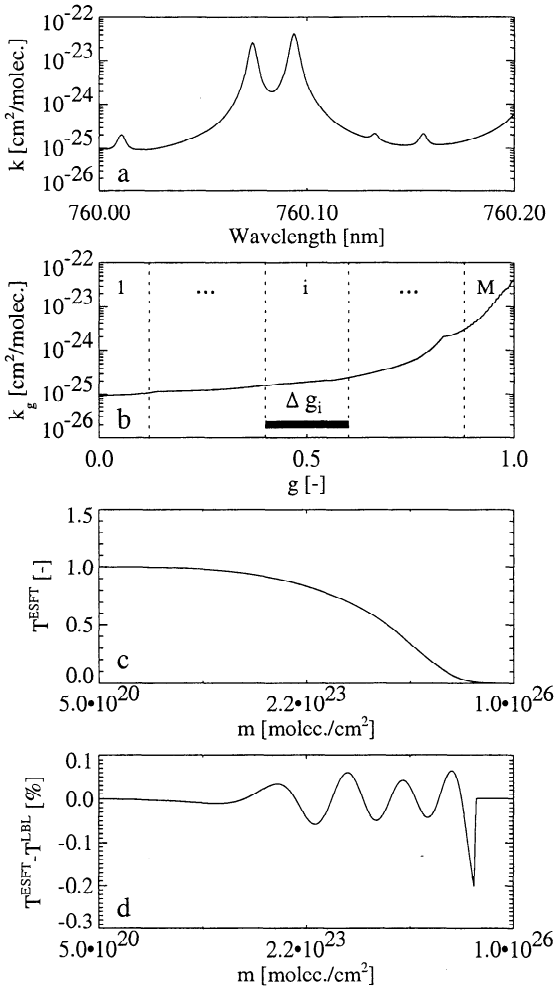

Figure 1. (a) Monochromatic O_2 absorption cross section k_λ at 500 hPa and 250 K in a spectral interval corresponding to a single detector pixel of channel 4. (b) The corresponding k-distribution (sorted cross section). The dashed vertical lines indicate g subintervals Δg_i. (c) Exponential sum fitting transmittance (ESFT) (equation (7)), and (d) relative difference between ESFT and reference mean line-by-line (LBL) transmittance. Note that the error has been set to zero for absolute transmittances below 0.01. The rms deviation between the ESFT and the mean LBL transmittance is 0.035% (M=10). Using less than 10 coefficients results in rms errors of 0.24% for M=8, and 2.7% for M=5.

cross section to several line absorbers. Furthermore, the single complex gas "absorption cross section" cannot be regarded as an absorption cross section in the usual sense, because of its dependence on the relative amounts of each gas. Our retrieval applications, however, require individual cross sections for each gas to be defined separately. They need be defined without any specific constraints or limitations from overlapping gases. Otherwise it is not possible to utilize an important SCIATRAN capability, namely the fast calculation weighting functions [*Rozanov et al.*, 1998]. These weighting functions are the derivatives of the radiance with respect to atmospheric and surface parameters to be retrieved. They are determined quasi-analytically by solving the linearized RT equation and are required in least squares minimization schemes, which often form part of the retrieval algorithm. This quasi-analytical weighting function scheme enables time-consuming numerical perturbation methods to be entirely avoided.

The second widely adopted approach combines k_i parameters determined individually for each line absorber by assuming a certain spectral correlation between the cross sections of the individual gases [*Isaacs et al.*, 1987; *Lacis and Oinas*, 1991; *Fu and Liou*, 1992; *Firsov et al.*, 1998]. To simplify the notation, only two overlapping line absorbers are considered in the following equations and related discussion.

Provided that each line absorber l individually is characterized by the pseudo-cross-section and weight combinations $\{k_i^{(l)}, \omega_i^{(l)}\}_{i=1,\ldots,M}$ (at each altitude level), then two overlapping line absorbers can be characterized by $\{k_i^{(1)}, k_j^{(2)}, \Omega_{ij}\}_{i,j=1,\ldots,M}$. The weights Ω_{ij} can be interpreted as the fraction of the wavelength interval $\Delta\lambda$ covered by cross sections represented by the combination $\{k_i^{(1)}, k_j^{(2)}\}$. For two overlapping absorbers the RT equation has to be solved M^2 times, if all combinations $\{k_i^{(1)}, k_j^{(2)}\}$ are included. The individual (pseudomonochromatic) radiances finally have to be added with weighting factors Ω_{ij} to obtain the desired mean radiance for the entire wavelength interval $\Delta\lambda$.

The most common statistical approach used to combine the individual c-k coefficients $k_i^{(l)}$ assumes that the monochromatic transmittances or cross sections of the overlapping line absorbers are completely uncorrelated within the wavelength interval of interest [*Lacis and Oinas*, 1991; *Fu and Liou*, 1992]. To a good approximation this would be the case if the individual absorption lines were quasi-randomly distributed with respect to their spectral position. In this case the mean transmittance can be calculated as the product of the mean transmittances of the individual absorbers, resulting in $\Omega_{ij} = \omega_i^{(1)} \times \omega_j^{(2)}$ (product of the individual weights). Here the RT equation also has to be solved M^2 times.

If the cross sections of the line absorbers are perfectly *correlated* [*Isaacs et al.*, 1987], i.e., provided that the wavelength dependence of each absorber cross section is similar, only coefficients with the same index need to be combined. In this case, $\Omega_{ij} = \omega_i \delta_{ij}$, where δ_{ij} denotes the Kronecker symbol. The advantage of this approach is that only M radiative transfer simulations are necessary. This correlation assumption, however, is considered to be quite unrealistic and in most cases results in a significant systematic overestimation of the transmittance [*Firsov et al.*, 1998] and the radiance.

As will be shown in detail below, none of these (rather extreme) statistical assumptions is appropriate for our applications, mainly due to the narrow spectral intervals used here. Recently, *Firsov et al.* [1998] have pre-

sented a scheme that enables partial correlation to be taken into account. Their scheme, however, only applies to a homogeneous path, although the authors indicated that it might be extended to inhomogeneous atmospheres.

To solve the problem of partial or arbitrary correlation, a new method, based on a linear combination of two radiances calculated separately assuming positive and negative correlation (anticorrelation) of the individual monochromatic absorption cross sections, has been developed. In the following $I^{+\text{corr}}$ denotes the radiance calculated assuming positive cross section correlation and $I^{-\text{corr}}$ denotes the radiance determined assuming anticorrelation. Note that because of the small number of lines per spectral interval in our application the terms "correlation" or "correlated spectra" used in this study do not precisely refer to the exact mathematical (statistical) definition of correlation. Here (positive) correlation refers to cross sections with similar wavelength dependence. Anticorrelation refers to spectra where, for example, the maxima of the cross sections of the first gas coincide with the minima of the second gas. In this sense, the degree of correlation of transmittances is assumed to be similar to the degree of correlation of the corresponding absorption cross sections (within a given wavelength interval). The radiance $I^{+\text{corr}}$ ($:= \sum_i \omega_i I_i^{+\text{corr}}$) is calculated using c-k coefficient and weight combinations $\{k_i^{(1)}, k_i^{(2)}, \omega_i\}$; that is, the pseudo-cross-section of absorber (1) representing the smallest cross sections (i.e., $k_1^{(1)}$) is combined with the pseudo-cross-section of absorber (2) also representing the smallest cross sections (i.e, $k_1^{(2)}$), etc. The radiance $I^{-\text{corr}}$ is calculated using the combinations $\{k_i^{(1)}, k_{M+1-i}^{(2)}, \omega_i\}$; that is, the smallest pseudo-cross-section of the first absorber (i.e., $k_1^{(1)}$) is combined with the largest pseudo-cross-section of the second absorber (i.e., $k_M^{(2)}$), and so on (at each altitude). Note that this requires $\omega_i = \omega_{M+1-i}$ and the same M for both absorbers. The mean radiance for each c-k spectral interval $\Delta\lambda$ is now determined by $2M$ radiative transfer calculations according to

$$I_{\Delta\lambda}^{c-k} = \alpha I^{+\text{corr}} + (1-\alpha) I^{-\text{corr}} = \sum_{i=1}^{M} \left[\alpha \omega_i I_i^{+\text{corr}} + (1-\alpha)\omega_i I_i^{-\text{corr}}\right]. \quad (4)$$

The mixing parameter α is determined, for each c-k interval $\Delta\lambda$ individually, by adjusting the c-k radiance exactly to the mean reference radiance $I_{\Delta\lambda}^{\text{LBL}}$, obtained from line-by-line simulations, of a reference scenario (i.e., for a selected atmosphere, solar zenith angle (SZA), albedo, viewing geometry, and observer altitude):

$$\alpha := \frac{I_{\Delta\lambda}^{\text{LBL}} - I^{-\text{corr}}}{I^{+\text{corr}} - I^{-\text{corr}}}. \quad (5)$$

This approach leads to negligible radiance errors provided the actual scenario is similar to the reference scenario defined for the determination of α. As, however, α can be expected to be mainly determined by the degree of correlation of the monochromatic cross sections, the scenario dependence of α is predicted to be rather weak. Parameter α should be close to 1 for positively correlated cross sections (i.e., similar wavelength dependence), close to zero for anticorrelation of the individual cross sections, and between zero and 1 for arbitrary correlation. To ensure that α is restricted to the interval $[0, 1]$, α is set to zero or 1 if equation (5) results in values less than zero or larger than 1, respectively. If the denominator $(I^{+\text{corr}} - I^{-\text{corr}})$ is close to zero, α is set to 0.5. The implications of the scenario dependence of α will be discussed in more detail in section 5, where it will be demonstrated that a single arbitrary reference scenario is sufficient to determine an α spectrum that is applicable to a wide range of conditions.

4. Determination of Representative Absorption Cross Sections k_i

4.1. Instrument Resolution and Sampling Considerations

Spectrometers have unique instrument slit functions f^{inst} which may change as a function of time, for example, due to thermal effects. To avoid the generation of new representative cross sections k_i for each slit function type or slit function change, a flexible approach is required.

This problem can be overcome by selecting spectral averaging intervals $\Delta\lambda^{c-k}$ being significantly smaller (about 1/8) than the FWHM characterizing the instrument resolution in a given channel (see Table 1). This means that the corresponding spectral resolution of the c-k radiance is significantly higher than the instrument resolution. The c-k radiances can then be convolved with an appropriate function f^{c-k} to consider the instrument resolution. If the selected $\Delta\lambda^{c-k}$ is sufficiently narrow compared to the instrument resolution, $f^{c-k} = f^{\text{inst}}$ is a good approximation. The latter approximation has been adopted here.

This approach implies that the wavelength grid of the simulation is significantly finer than the measurement grid (about four points per detector pixel). Therefore it also helps to significantly reduce wavelength interpolation errors, which are unavoidable if the c-k database wavelength grid is not identical with the measurement grid.

4.2. Generation of c-k Databases

For each c-k spectral interval $\Delta\lambda^{c-k}$, each line absorber, pressure, and temperature, one set of M c-k coefficients k_i is determined by minimizing the following expression:

$$\sum_{n=1}^{N_m} \left[\bar{T}_{\Delta\lambda^{c-k}}(m_n) - T^{\mathrm{ESFT}}_{\Delta\lambda^{c-k}}(m_n, M, \vec{k}, \vec{\omega})\right]^2. \quad (6)$$

The ith components of vectors $\vec{k}$ and $\vec{\omega}$ are k_i and ω_i, respectively. The ESFT transmittance $T^{\mathrm{ESFT}}_{\Delta\lambda^{c-k}}$ is given by

$$T^{\mathrm{ESFT}}_{\Delta\lambda^{c-k}}(m_n, M, \vec{k}, \vec{\omega}) = \sum_{i=1}^{M} \omega_i \exp(-k_i m_n). \quad (7)$$

The reference mean transmittance $\bar{T}_{\Delta\lambda^{c-k}}$ is derived from high-resolution LBL transmittance calculations (see equation (3)). It has been calculated for a range of column amounts m_n, with $n = 1, ..., N_m$, in molecules/cm^2. The column amounts have been selected such that a large range of values is covered, from a small fraction of a typical vertically integrated concentration profile to several times a typical vertical column. The latter are for photon paths nearly parallel to the Earth's surface. The multiply scattered solar photons travel along many different paths. These paths are defined in the RT model by discrete angles and the altitude grid. Therefore the k_i values have to be appropriate to reproduce the mean transmittance for a large range of optical path lengths simultaneously. This is achieved by minimizing the difference between the ESFT and the mean LBL transmittance for a large number of different column amounts simultaneously (see Figure 1). The minimization procedure is based on a nonlinear least squares (NLLS) method that permits constraints to be placed on all fit parameters to ensure positive k_i values (quadratic programming (QP) method) [*Gill et al.*, 1981].

The number of terms M and the weights ω_i ($= \Delta g_i$) are preselected as they need to be identical for all transmittance fits corresponding to a given spectral interval $\Delta\lambda^{c-k}$ (i.e., for all pressure and temperature combinations). The M pseudo-cross-sections k_i are free fit parameters, apart from the constraint that avoids negative values. The weights ω_i are preselected Gaussian quadrature weights [*Press et al.*, 1992] in the interval $[0, 1]$. The optimum M, which should be as small as possible, has been derived by comparing the c-k radiances with LBL radiances (see section 6).

The monochromatic absorption cross sections k_λ used in this study are taken from the HITRAN 96 database of spectroscopic line parameters [*Rothman et al.*, 1998], assuming a Voigt line shape. The Voigt routine of *Humlicek* [1982] has been used for the line shape calculations.

Solving equation (6) is usually referred to as "exponential sum fitting of transmittance functions", or ESFT. Therefore the parameters k_i are in the following also referred to as ESFT coefficients. *Wiscombe and Evans* [1977] have solved the ESFT problem by taking care of avoiding ill-conditioning and related problems. The scheme of Wiscombe and Evans, however, cannot be used here, since our application requires the number of terms M and the weights ω_i in a given spectral interval $\Delta\lambda^{c-k}$ to be preselected.

The iterative minimization process benefits from a good first guess. The first guess ESFT coefficients k_i° are obtained by solving a linear least squares problem for each Δg_i interval separately, thereby ensuring that the subinterval transmittance is well approximated by a single exponential function, for all absorber amounts m_n simultaneously:

$$\begin{aligned} \bar{T}_{\Delta g_i}(m_n) &:= \frac{1}{\omega_i}\int_{\Delta g_i} \exp(-k_g m_n) dg \\ &\approx \exp(-k_i^\circ m_n). \end{aligned} \quad (8)$$

The first-guess coefficients can strictly be interpreted as being representative for the cross sections that have been mapped into the corresponding Δg_i interval. The transmittance corresponding to the entire physical wavelength interval $\Delta\lambda^{c-k}$ can, however, in general be better approximated by using the described NLLS fitting procedure, as this method permits all coefficients to be varied simultaneously. It should be noted that the NLLS fit is not explicitly constrained to maintain the ranking of the ESFT coefficients. Thus $k_i > k_{i+1}$ for certain i is possible. Using the final NLLS coefficients, however, not only improves the transmittance fit but, more importantly, also results in better agreement of c-k and LBL radiances. For instance, in the 760 nm O_2 A band region the difference is reduced to $\sim$ 1-2% rather than $\sim$ 4% when using the first-guess coefficients.

A statistical analysis of the root-mean-square (rms) and maximum ESFT transmittance fit errors for all line absorbers, spectral intervals, pressures, and temperatures (in total about 3×10^6 cases) shows that the rms errors are less than 1% in about 90% and less than 3% in about 98% of all cases (M=5, $\Delta\lambda^{c-k} \approx$ FWHM/8). The maximum errors are less than 3% in about 90% of all cases. However, these errors cannot easily be related to radiance errors as they are not systematic (i.e., they scatter around zero at different pressures, temperatures, and optical path lengths) and are expected to cancel to a large extent when the radiance is calculated (see section 6). If the individual transmittances are averaged to consider the instrument resolution, the rms and the maximum errors are reduced to being generally less than 1%.

A summary of the ESFT databases, including spectral range, corresponding line absorbers, and number of terms M, is given in Table 2. The ESFT coefficients have been determined for 10 pressures (0.01, 1, 10, 100, 300, 500, 700, 900, 1000, 1050 hPa) and 6 temperatures (160, 210, 250, 275, 300, 330 K). As will be discussed in more detail below, a value of M=5 has been selected for strong line absorbers and M=1 for weak line ab-

Table 2. Overview of the ESFT Database

Number	Line Absorber	Spectral Range (nm)	$\Delta\lambda^{c-k}$ (nm)	M
1	CH_4	1630 - 1720	0.200	5
2	CH_4	1720 - 1800	0.200	1
3	CH_4	2230 - 2400	0.025	5
4	CO	2300 - 2400	0.025	1
5	CO_2	1420 - 1460	0.200	5
6	CO_2	1560 - 1630	0.200	5
7	CO_2	1630 - 1680	0.200	1
8	CO_2	1920 - 2060	0.025	5
9	H_2O	440 - 450	0.050	5
10	H_2O	464 - 476	0.050	5
11	H_2O	480 - 515	0.050	5
12	H_2O	520 - 610	0.050	5
13	H_2O	620 - 675	0.050	5
14	H_2O	685 - 760	0.050	5
15	H_2O	770 - 1070	0.050	5
16	H_2O	1070 - 1560	0.200	5
17	H_2O	1560 - 1670	0.200	1
18	H_2O	1670 - 1800	0.200	5
19	H_2O	1920 - 2060	0.025	5
20	H_2O	2230 - 2300	0.025	1
21	H_2O	2300 - 2400	0.025	5
22	N_2O	2230 - 2325	0.025	1
23	O_2	625 - 640	0.050	5
24	O_2	685 - 702	0.050	5
25	O_2	755 - 775	0.050	5
26	O_2	1230 - 1310	0.200	5

sorbers (note that for a given absorber to be classified as weak or strong depends on the spectral position). Using larger M values results in a significant increase in computer time but only in a small improvement in accuracy (see section 6). On the other hand, it might be possible for certain spectral regions to further optimize the selection of the M values by using smaller values, especially in regions where the absorption is only moderate or small.

5. Comparison With Line-by-Line Radiances

The c-k scheme described above has been implemented in the RT model GOMETRAN. The extended model is called SCIATRAN. The coefficients k_i for a given pressure and temperature, i.e., altitude, are derived in SCIATRAN from tabulated coefficients using a bilinear interpolation scheme. The α spectra are also precalculated.

All wavelength-dependent optical parameters that do not correspond to line absorption (i.e., the ozone absorption cross section, the Rayleigh-scattering cross section, the aerosol and cloud scattering and absorption coefficients, the scattering phase functions, and the surface albedo) are only calculated at the center wavelength of a given $\Delta\lambda^{c-k}$ interval. The water vapor continuum absorption is not yet implemented.

To validate the new c-k scheme, the c-k radiances were compared with convolved line-by-line reference radiances (see left-hand side of equation (1)). This necessitated the implementation of a line-by-line scheme in SCIATRAN. In line-by-line mode the monochromatic absorption cross sections of each line absorber, at each wavelength, and each altitude are calculated utilizing the HITRAN 96 database of line parameters assuming Voigt line shapes all altitudes. It has been carefully checked by several means that the HITRAN data are correctly processed. Details concerning the line-by-line model can be found in the work of *Buchwitz et al.* [1998].

To make sure that the SCIATRAN c-k and LBL implementations do not contain any common and self-canceling errors, SCIATRAN was also compared with the independent radiative transfer model MODTRAN 3.7 V1.0 [*Kneizys et al.*, 1996], which uses DISORT for the multiple-scattering calculations [*Stamnes et al.*, 1988]. Agreement within a few percent was found in the 700-800 nm region (O_2 and H_2O), where the spectral resolution of both models is similar [*Buchwitz et al.*, 1998]. The observed differences are probably best explained by the fact that multiple-scattering problems can be treated in a more appropriate way by the c-k method than by a band model approach [e.g., *Goody and Yung*, 1989] as used in MODTRAN 3. Excluding spectral intervals dominated by strong line absorption, the agreement between the models is within 1%. The new MODTRAN 4 will be based on the c-k method but has not yet been available for comparison.

5.1. Nonoverlapping Line Absorption

In the spectral region between 240 and 1200 nm, overlap of line absorption is negligible as the O_2 and H_2O bands are mostly well separated. Overlap of line absorption is only of significance for the SCIAMACHY channels 6, 7, and 8. Figure 2 shows a typical comparison of c-k and LBL radiances in a spectral region dominated by one strong line absorber. As can be seen, the agreement between the convolved radiances is within 1-2%.

Similar results have been obtained for other spectral regions, for other solar zenith angles (covering the range of about 20°-92° relevant for our applications), and for different atmospheric scenarios and surface albedos. For spectral regions with weak line absorption the errors are much smaller. For example, the radiance error is less than 0.06% around 500 nm (weak H_2O absorption).

The spectral region between 685 and 710 nm has been used by *Noël et al.* [1999] to retrieve water vapor total column amounts from GOME observations. In that study, the c-k mode of SCIATRAN has been used to derive appropriate parameters for the transmittance model used in the fitting process. This spectral region contains in addition to H_2O absorption the O_2 B band, which was used for air mass corrections. The de-

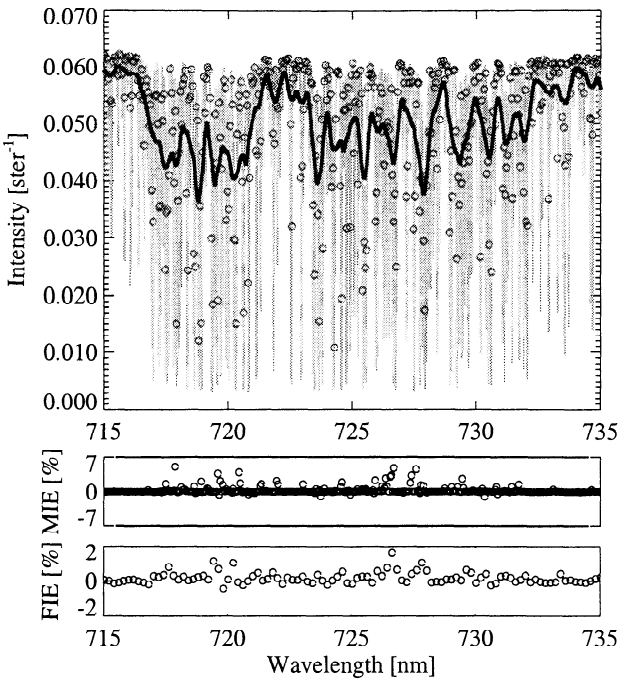

Figure 2. (top) Top-of-atmosphere intensities (Sun-normalized radiances) for nadir-viewing geometry in the 720 nm spectral region, which is dominated by strong H_2O line absorption. LBL intensities (thin grey lines), c-k intensities for c-k intervals of 0.05 nm (circles), and convolved LBL and c-k intensities (slit function full width at half maximum (FWHM) 0.35 nm) shown as black solid lines (not distinguishable on this scale). (middle) Relative difference (MIE = mean intensity error) between c-k and LBL mean intensities for each 0.05 nm c-k interval (without slit function convolution). (bottom) c-k intensity error after slit function convolution (FIE = final intensity error). Scenario: U.S. standard atmosphere, SZA 60°, albedo 0.1, tropospheric maritime and stratospheric background aerosol.

rived water vapor columns show good agreement with independent Special Sensor Microwave Imager (SSM/I) satellite measurements. GOME water vapor retrieval reported by *Noël et al.* [1999] represents the first application of our c-k model.

5.2. Overlapping Line Absorption: α-Mixing Scheme

The most significant overlap in the 1000-1750 nm spectral region (SCIAMACHY channel 6) is due to strong H_2O and CO_2 absorption bands near 1435 nm. ESFT coefficients for both absorbers have been generated using M=5 and $\Delta\lambda^{c-k}$= 0.2 nm ($\approx$ FWHM/8). The agreement with LBL calculations is within 1-2% for the convolved radiance if only one absorber is present in the model atmosphere.

To model both absorbers simultaneously in SCIATRAN, the commonly adopted statistical assumptions concerning the degree of correlation between the individual absorption cross sections (section 3.2) have been tested.

The assumption of uncorrelated spectra or random line positions [*Lacis and Oinas*, 1991; *Fu and Liou*, 1992], corresponding to the c-k coefficient and weight combinations $\{k_i^{(H_2O)}, k_j^{(CO_2)}, \omega_i \times \omega_j\}$, result in radiance errors of up to ± 10% in the 1435 nm region. This is mainly due to the fact that the average distance between CO_2 lines is about 0.4 nm, i.e., one line (if any) per 0.2 nm ESFT interval.

Ackermann [1979] has investigated the multiplication property assumption for overlapping H_2O and CO_2 absorption bands in the thermal spectral region around 15 μm. He concluded that the error introduced by this assumption is less than 1% at 5 cm^{-1} resolution; 5 cm^{-1} corresponds to about 1 nm resolution at 1435 nm. We have also determined the difference between the convolved product of the monochromatic transmittances and the product of the convolved transmittances (see also *Fu and Liou* [1992], particularly their equations (5.1) and (5.2)) but in the 1435 nm spectral region. For a homogeneous path (800 hPa, 275 K) and absorber column amounts according to the U.S. standard atmosphere, differences of up to 25% at 1 nm (or 5 cm^{-1}) resolution were obtained. This error reduces to about ± 10% for the 1.6 nm SCIAMACHY resolution. In comparison with the results obtained by *Ackermann* [1979] this shows that the magnitude of the transmittance error can be significantly different in different spectral regions and cannot be extrapolated from one region to another.

The assumption of perfect correlation (similar wavelength dependence) [*Isaacs et al.*, 1987], corresponding to the combinations $\{k_i^{(H_2O)}, k_i^{(CO_2)}, \omega_i\}$, results in radiance errors of up to +20% (systematic overestimation) in the same 1435 nm region.

Thus neither of the commonly adopted statistical assumptions is appropriate for our applications. The anti-correlation assumption (not used in the literature), corresponding to the combinations $\{k_i^{(H_2O)}, k_{M+1-i}^{(CO_2)}, \omega_i\}$, has also been investigated and a systematic underestimation of up to -30% was found.

The results obtained with the new α-mixing scheme, described in section 3.2, will be presented and discussed in detail in the following. The scenario dependence of the α scheme has been investigated by defining four significantly different scenarios S1, S2, S3, and S4, as summarized in Table 3. The pressure, temperature, and ab-

Table 3. Definition of Four Scenarios Used to Test the Scenario Dependence of the α-mixing Scheme Around 1435 nm

ID	Atmosphere	SZA	Viewing Geometry
S1	U.S. standard	50°	nadir view from satellite
S2	U.S. standard	88°	nadir view from satellite
S3	U.S. standard	50°	zenith view from surface
S4	tropical	20°	nadir view from satellite

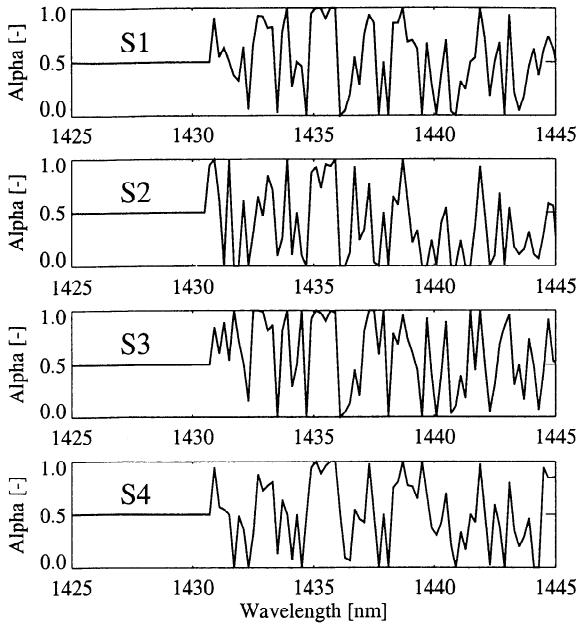

Figure 3. Mixing parameter α for scenarios S1 to S4.

sorber volume mixing ratio profiles are extracted from MODTRAN 3 [*Kneizys et al.*, 1996; *McClatchey et al.*, 1972]. Each scenario differs from the selected reference scenario S1, namely with respect to solar zenith angle (S2), observer altitude (S3) (here the radiance has been determined at the Earth's surface), and atmospheric composition (S4). Figure 3 shows that α spectra of the scenarios S1 to S4 correlate quite well.

Each c-k radiance spectrum (S1-S4) has been compared with the corresponding LBL spectrum. In this comparison, only a single α-spectrum determined from scenario S1 has been used. Figure 4 shows the results of the α-mixing method. As can be seen from Figures 4c, 4d, and 4e, the c-k and LBL radiances agree to within 1-2% for scenarios S2, S3, and S4, respectively. This shows that the scenario dependence of the mixing parameter α is not significant. As expected, α is mainly determined by the degree of correlation of the individual monochromatic absorption cross sections. These results indicate that the calculation of one α-spectrum for an arbitrary reference scenario suffices for the accurate simulation of the radiance for all other scenarios. This has also been confirmed for other relevant spectral regions, as discussed in the following.

The α-mixing method has also been applied to other spectral regions of channel 6 and to the channels 7 and 8. Channel 6 covers two other regions with significant overlap: 1230-1310 nm (H_2O and O_2) and 1670-1720 nm (H_2O and CH_4). These regions contain one strong absorber overlapping with another moderate absorber. In this case it turned out to be sufficient to use a constant α of 0.5 to achieve agreement with LBL results at the 1% level.

The spectral resolution of the SCIAMACHY measurements in channels 7 and 8 is rather high (0.35 cm^{-1}, $\lambda/\Delta\lambda^{FWHM} \approx 10{,}000$). In addition, there is significant overlap of H_2O, CO_2, CH_4, N_2O, and CO absorption bands. Both the high resolution and the strong overlap represent a worst case for the application of the c-k method, with respect to computational speed.

Channel 7 contains strong overlapping CO_2 and H_2O bands covering the entire channel. M=5 has been selected for both absorbers, and a single α-spectrum has been generated covering the entire channel. The c-k and the LBL radiances in channel 7 turned out to agree within about 1-2%.

Channel 8 contains a mixture of strong and weak bands of H_2O (strong above 2300), CH_4 (strong), N_2O (weak), and CO (weak). To consider the overlapping H_2O and CH_4 absorption bands (M=5 each), a channel 8 α spectrum has been generated starting at 2300 nm. Weak absorption in this context implies that the selection of M=1 yields sufficient accuracy. The number of overlapping strong line absorbers is limited to two for the present α-mixing scheme. The number of (additional) weak line absorbers, however, is not limited, since they can be handled as continuum absorbers.

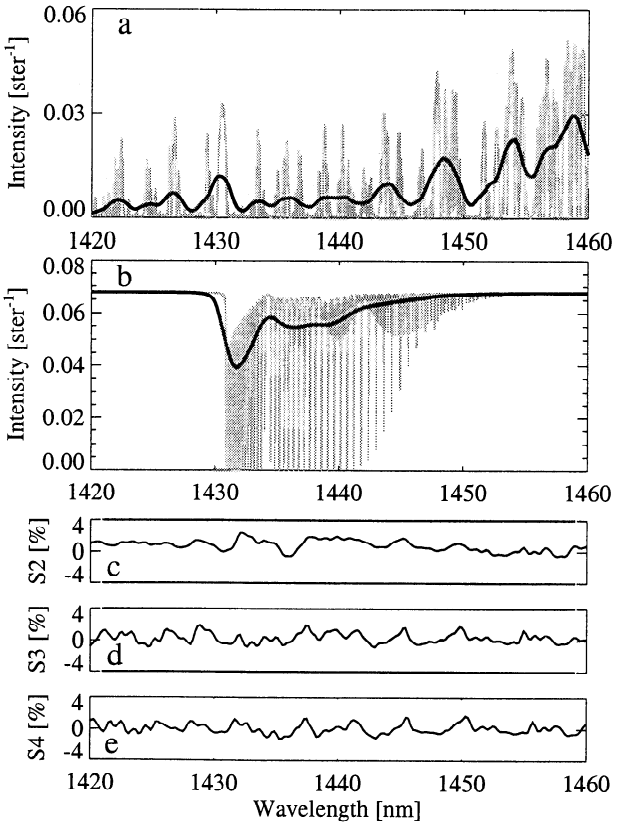

Figure 4. (a) Monochromatic LBL top-of-atmosphere intensity (thin grey line) and convolved LBL intensity (thick dark line, FWHM 1.6 nm) for scenario S1 in the 1435 nm spectral region, which is dominated by strong overlapping H_2O and CO_2 absorption. (b) As Figure 4a but for CO_2 absorption only. (c-e) Relative difference between c-k and the LBL intensities for scenarios S2, S3, and S4 using mixing parameter α from scenario S1.

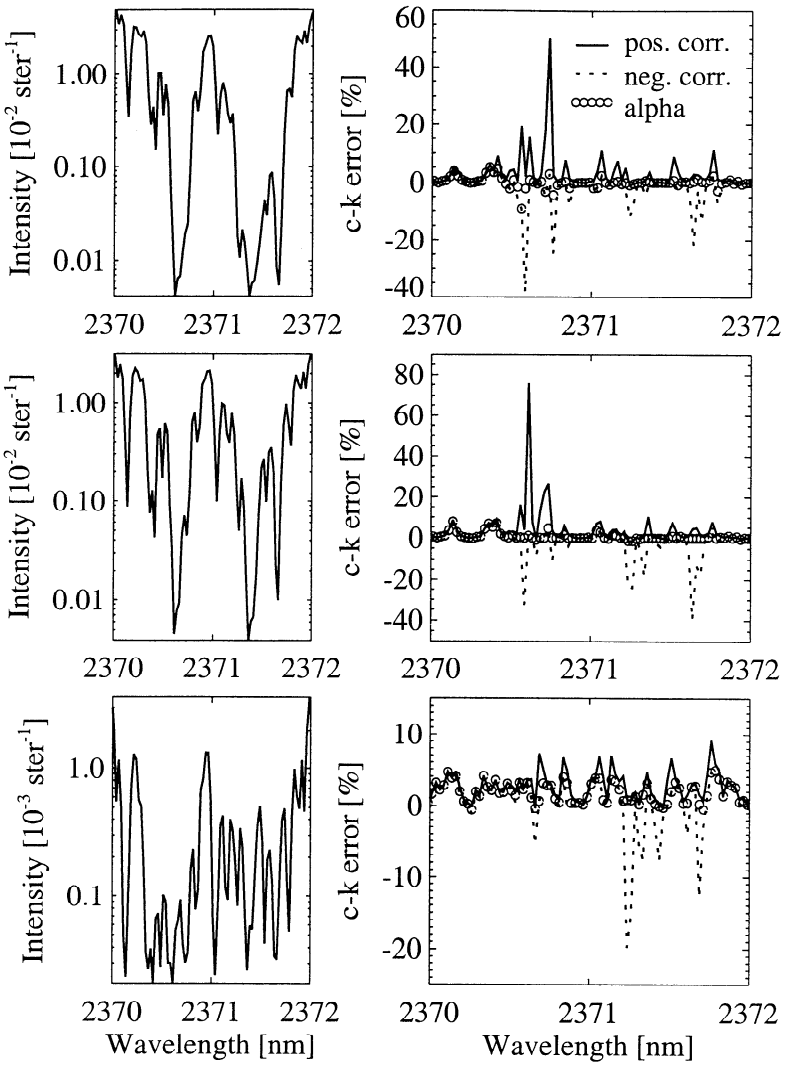

Figure 5. Comparison of c-k with mean LBL intensities before slit function convolution for individual c-k averaging intervals $\Delta\lambda^{c-k}$ of 0.025 nm (center wavelengths denoted by circles on the right-hand side panels) for three different scenarios. (top) Tropical atmosphere, SZA 30°. (middle) U.S. standard atmosphere, SZA 60°. (bottom) Subarctic winter atmosphere, SZA 85°. The LBL intensity spectra are shown to the left and percentage c-k - LBL differences are shown to the right for c-k intensity $I^{+\text{corr}}$ (solid line), $I^{-\text{corr}}$ (dotted line), and both intensities combined (circles) using mixing parameter α from the second scenario (U.S., 60°).

One important spectral region observed by SCIAMACHY contains the relatively weak CO overtone band centered at 2347 nm in channel 8. Note that in this spectral region the radiance $I_i^{+\text{corr}}$ is calculated using c-k coefficients and weight combination $\{k_i^{(\text{H}_2\text{O})}, k_i^{(\text{CH}_4)}, k_1^{(\text{CO})}, \omega_i\}$. Radiance $I_i^{-\text{corr}}$ is determined using combination $\{k_i^{(\text{H}_2\text{O})}, k_{M+1-i}^{(\text{CH}_4)}, k_1^{(\text{CO})}, \omega_i\}$. Figure 5 shows a 2 nm spectral interval in channel 8 to demonstrate how the α-mixing scheme works in this spectral region; c-k radiances calculated assuming correlated and anticorrelated cross sections (i.e., $I^{+\text{corr}}$ and $I^{-\text{corr}}$, respectively) deviate by up to 70% from the LBL results, whereas α mixing of these radiances according to equation (4) reduces this deviation to a few percent. Note that α has been determined from a reference scenario only (here: U.S. standard atmosphere and SZA 60°). The remaining deviation is further reduced by instrument slit function convolution. The agreement between the convolved c-k and the convolved high-resolution LBL radiance is better than 1% as shown by the top panel in Figure 6. Note that the scenario selected for this figure (tropical atmosphere and SZA 30°) significantly differs from the reference scenario used in the α-spectrum calculation.

Accurate modeling of the small spectral CO absorption structures is essential for CO total column retrieval from SCIAMACHY channel-8 observations. The effect of CO absorption on the radiance is of the order of 2-4% at SCIAMACHY resolution. This means that the estab-

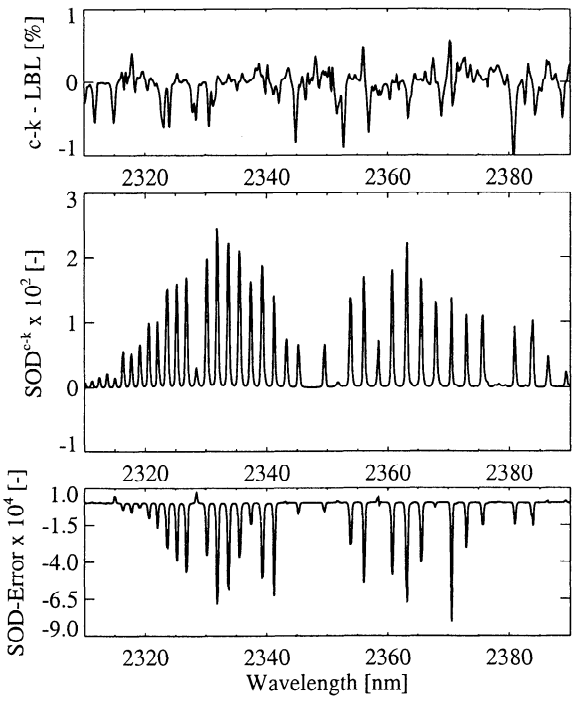

Figure 6. (top) Percentage difference between c-k and line-by-line intensities after convolution (tropical atmosphere, SZA 30°). (middle) CO slant optical depth (SOD) scaled by 100. Since $\ln((I+\Delta)/I) \approx \Delta/I$ for small Δ, the numbers on the y axis express the intensity chance due to a 100% CO concentration change at all altitudes. (bottom) Absolute difference between SOD spectra obtained from c-k and LBL intensities scaled by 10,000.

lished c-k radiance error of 1% in channel 8 corresponds to 25-50% of the depth of a typical CO absorption line. If the wavelength dependence of the c-k radiance error were perfectly correlated with the CO absorption lines (worst-case situation), it would lead to a CO total column error of up to 25-50%, which is unacceptably large.

The CO absorption structure may be defined as $\ln(I^{\text{-CO}}/I^{\text{+CO}})$, termed "slant optical depth" (SOD). Here $I^{\text{-CO}}$ is the radiance calculated without CO present in the atmosphere, and $I^{\text{+CO}}$ is calculated with CO present. This quantity is used, for example, by the GOME Differential Optical Absorption Spectroscopy (DOAS) ozone total column retrieval algorithm [*Burrows et al.*, 1999]. Carbon monoxide SOD-spectra have been calculated in c-k and in line-by-line mode. As shown in Figure 6, the depth of the CO absorption lines calculated in c-k mode agree with line-by-line calculations to within 2% (2% underestimation of CO absorption). The wavelength dependence and the magnitude of this error is nearly independent of the selected scenario (not shown), which indicates that the error spectrum (bottom panel) might be used to correct the c-k SOD-spectra. From this we conclude that the c-k forward modeling error on CO retrieval may be reduced to less than 1%. These results show that small absorption structures can be modeled quite accurately using SCIATRAN in its c-k mode.

6. Error Analysis of c-k Radiances

From detailed investigations performed to further improve the accuracy of our c-k scheme we conclude that it seems not to be possible to substantially reduce the residual c-k radiance error below the 1-2% level without a significant increase in computer time. Several sources contribute to this error: (1) ESFT transmittance fit errors, (2) errors resulting from the convolution of the c-k radiance with the same (SCIAMACHY) slit function as the LBL radiance, which is convenient, but may not be the optimum, (3) c-k coefficient pressure and temperature interpolation errors, and (4) errors due to the correlation assumption inherent in the c-k method (described in section 3). As demonstrated by the previous discussion, there are basically no additional errors resulting from a strong overlapping line absorption. The relevant error sources are quantified by the following:

6.1. ESFT Fit Error

The influence of ESFT fit errors on the radiance has been investigated by further improving the accuracy of the ESFT fits. This has been achieved by performing a series of NLLS fits, each starting with quasi-randomly modified first-guess coefficients, resulting in fit errors significantly smaller than the errors obtained using the default procedure described in section 4. By using this more accurate but slower procedure, the number of fits with rms errors between 2 and 4% was reduced by a factor of about 5-10, and errors larger than 4% have been nearly eliminated. Using this improved database of c-k coefficients, however, did not result in a significant reduction of the radiance error (for example, in the O_2 A band region the maximum deviation is only reduced from 1.5% to 1.2%). Similar results have been found by increasing M, which also significantly reduces the transmittance fit error without a corresponding significant reduction of the radiance error. For example, in the O_2 A band region the rms transmittance errors are less than 2% in 94% of all cases for M=5. For M=10, the errors are less than 0.1% in 94% of all cases, which is a significant improvement of the transmittance fits. The overall radiance error, however, is only reduced from a maximum value of 1.5% for M=5 to 1.0% for M=10. This is not considered a significant improvement, taking into account that this doubles the radiative transfer computation time. This surprising result is best explained by the fact that the ESFT fit errors, which are not systematic, largely cancel in the final radiance calculations, as each single radiance value is determined by a large number of transmittances at different pressures, temperatures, path lengths, and ($\Delta\lambda^{c-k}$ center) wavelengths. It is therefore concluded that the transmittance fit errors do not significantly contribute to the 1-2% overall radiance error.

6.2. Convolution Error

The convolution error is less than about 0.5%. This was established by comparing c-k radiances with high-resolution LBL radiances, which were first averaged over $\Delta\lambda^{c-k}$ intervals before being convolved and sampled according to the c-k wavelength grid.

6.3. Interpolation Error

The error due to pressure and temperature interpolation of the c-k coefficients was estimated by employing a significantly finer pressure and temperature grid. The interpolation error was found to be less than $\sim$ 0.2%.

6.4. c-k Correlation Assumption Error

The error introduced by the correlation assumption applied to the k-distribution method in inhomogeneous atmospheres was estimated by using homogeneous atmospheres, with constant pressures and temperatures (identical to database values to avoid interpolation errors), and using constant absorber concentrations. The radiance error could be reduced to well below 1%. In addition, improving the transmittance fits as described in section 6.1 resulted in a corresponding reduction of the radiance error. Similar results were not observed in inhomogeneous atmospheres. In conclusion, the overall 1-2% radiance error seems to be mainly determined by the error introduced by the correlation assumption. We estimate this c-k correlation error to $\sim$ 1%.

7. Improvements in Computational Speed

The c-k calculations are significantly faster than the LBL calculations for two reasons.

First, the RT (matrix) equation needs to be solved less frequently in c-k mode than in LBL mode. For example, in the 400-800 nm spectral region (channels 3 and 4) the RT equation has to be solved 5 times (for M=5) in each 0.05 nm c-k interval and about 100 times in LBL mode employing spectral sampling intervals of 0.0005 nm. Therefore the c-k mode is 20 times faster in this spectral region. In the spectral region 1000-1750 nm (channel 6) the c-k calculations are a factor of 80 faster (single line absorber case) since the spectral resolution is 4 times lower than in channels 3 and 4. In channels 7 and 8 the speed can only be improved by a factor of 5 (still assuming 0.0005 nm LBL sampling, which corresponds to about four points per Doppler halfwidth in channel 8). Note that these numbers do not depend on the speed of the LBL reference model.

Second, the LBL mode requires time-consuming absorption cross section calculations (Voigt line shape), whereas the corresponding ESFT coefficients in the c-k mode (including the α spectra) are already precalculated. In principle, it is also possible to precalculate the monochromatic absorption cross sections needed in the LBL calculations, but this would require an excessively large storage space. This might, however, be an appropriate solution for small spectral windows.

In summary, the c-k scheme, developed in this study and implemented in SCIATRAN, is about 60 times faster than the LBL mode in the 720 nm spectral region (H_2O), about 25 times faster in the O_2 A band region around 760 nm, about 800 times faster in the 1000-1750 nm region (SCIAMACHY channel 6) for a single line absorber, and about 400 times faster for two overlapping gases. In channels 7 and 8 the gain in computer time is about a factor of 20.

8. Conclusions

A line-by-line (LBL) method, developed mainly for reference purposes, and a significantly faster advanced correlated-k distribution (c-k) scheme have been described and introduced. They are proposed for use in the radiative transfer modeling of molecular line absorption in the Earth's atmosphere from gases such as CH_4, CO, CO_2, H_2O, N_2O, and O_2 in the 440-2400 nm spectral region. Both schemes were implemented in the radiative transfer model SCIATRAN. A comparison of their speed and accuracy has been undertaken and is reported. The c-k parameters or representative absorption cross sections at $\leq$ 0.2 nm resolution were determined using an appropriate nonlinear least squares (NLLS) exponential sum fitting of transmittances (ESFT) approach. The c-k scheme has been optimized for the retrieval of atmospheric parameters from SCIAMACHY/ENVISAT-1 and GOME/ERS-2 Sun-normalized radiances taking into account the channel-dependent spectral resolution of these spectrometers.

A novel method, which adapts the correlated-k approach making it applicable for spectral regions containing two strong overlapping line absorbers and arbitrary additional minor or continuum absorbers, has also been developed and validated within this investigation. This α-mixing scheme combines individual representative absorption cross sections determined separately for each line absorber. Since the α-mixing scheme enables overlapping gases to be treated in a radiative transfer model as any other absorber and because this method is applicable to any degree of correlation of the monochromatic absorption cross sections of the individual line absorbers, it is considered to be more flexible than any previous c-k method developed to consider overlapping line absorption. By comparison of its accuracy with that of the c-k scheme for a single line absorber, it has been shown that no additional errors are introduced by the new α-mixing scheme. The computer time is only a factor of 2 larger compared to single-absorber c-k calculations.

The c-k radiances agree with line-by-line reference radiances within approximately 1-2%. This 1-2% error is mainly due to the correlation assumption made

when applying the k distribution method to inhomogeneous atmospheres. For weak absorption bands the agreement is much better ($\sim 0.1\%$). Agreement within a few percent has been found when comparing the convolved c-k and line-by-line SCIATRAN radiances with radiances computed with the MODTRAN/DISORT radiative transfer model. The agreement is better than 1% in spectral regions where line absorption is small.

The c-k calculations are a factor of 20-800 faster than the LBL calculations. The c-k scheme is much faster because of the reduction in spectral sampling compared to line-by-line simulations (up to a factor of 80 in our case). In addition, time-consuming Voigt line shape calculations are avoided since the representative absorption cross sections are precalculated. The gain in computer time depends almost linearly on the required spectral resolution, i.e., the larger the FWHM, the faster the c-k simulation. The error analysis also showed that a significant improvement of the accuracy requires a substantial increase in computer time.

SCIATRAN in its c-k mode has been successfully applied to water vapor total column retrieval from GOME observations by *Noël et al.* [1999]. SCIATRAN is currently being extended to better account for the sphericity of the Earth in order to accurately simulate the limb radiance measurements of SCIAMACHY [*Rozanov et al.*, 1999; *Kaiser et al.*, 1999]. Although the c-k scheme presented here has not yet been validated by comparison with line-by-line radiances for limb-viewing geometries, the accuracy is expected to be similar to that established in this study for the calculation of nadir radiances.

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