RADIANCE SIMULATIONS OF SELECTED ATMOSPHERIC SPECIES AT DIFFERENT OBSERVER ALTITUDES FOR GROUND-BASED FTIR SPECTROSCOPY: IMPLICATIONS FOR AEROSOL POLLUTED SITES IN WEST AFRICA

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Abstract

The pure air and clear sky conditions necessary for continuous Fourier Transform Infra-Red (FTIR) measurements of trace gases are issues of concern for West African sites. This is due to possible severe interruption by Sahara dust outbreak, which leaves trails throughout the year. Using data simulated by means of an atmospheric radiative transfer code, it is strengthened that the lower strengths observed for selected trace gas absorption spectra for higher observation altitudes may imply that increasing measurement altitudes or initiating balloon measurements to avoid aerosols and its associated haze conditions would be at the risk of managing reduced FTIR signatures. Continuous FTIR measurements in aerosol-polluted regions on the other hand can be a novel method for establishing more links between mineral aerosols and trace gas mixing ratios and or heterogeneous chemistry.

Key words*: Trace gases, FTIR, spectroscopy, aerosols, and atmospheric pollution.*

Introduction:

Interest in the monitoring and measurements of atmospheric trace-gases and aerosols has increased in recent times because of their contribution to changes associated with the earths climate. Trace-gases play significant roles in atmospheric chemistry as observed with ozone in the stratosphere and troposphere. Aerosols on the other hand impact climate through their radiative properties, (IPCC, 2001).

Aerosols affect several processes connected with trace gases in the atmosphere. For instance the absorption coefficient of trace species, which is a function of temperature, pressure, and gas volume mixing ratios (Kuntz, 2000), can be affected by aerosols in heavily polluted sites. Aerosols can modify ambient temperatures through direct radiative forcing. They may also add to the effective air mass, which affect retrieved concentrations since synthetic spectra used for retrievals are generated based on knowledge of air mass distributions (Hase & Hopfner, 2000; Meir et al, 2004). Similarly, the perturbation and

redistribution of energy by aerosols may influence atmospheric stratification, turbulent mixing and atmosphere-surface interaction

The roles of aerosols in heterogeneous chemistry of atmospheric species are of considerable interest. Aerosols and clouds provide the condensed phase in which heterogeneous chemistry take place within the atmosphere. In the background troposphere for example, nitric acid formation is known to be enhanced by the deposition of N_2O_5 on wetted aerosols and droplets (Crutzen, 1994). The increased concentration of nitric acid is of course a major course for the springtime ozone hole in the Antarctic stratosphere (Crutzen and Arnold, 1986). Aerosols action is also implicated as a possible cause of ozone decrease at mid-latitudes and the sub-tropics where higher solar fluxes and temperatures compared to the polar regions imply that sulphate or carbon aerosols may act as is the case with polar stratospheric clouds that initiate winter time polar ozone depletion (Schneider, 2002). Optical changes by aerosols which arise through their

modification of the solar radiation available to reacting atmospheric species is equally important when considering the chemistry of trace gases. The modification of the concentration of solar ultraviolet (UV) radiation by aerosols is reported to as affect photolysis rates in heterogeneous reactions; especially those connected with ozone formation (Martin et al. 2003). Atmospheric chemistry is substantially influenced by a wide range of chemical processes. which are driven by the action of solar UV radiation (<400nm:UV-B) on ozone (O_3) and water vapor (Crutzen. 1994: Crutzen and Zimmermann. 1991). Another chemical relevance of aerosol optical depths is associated with temperature dependence of bimolecular reactions (Cox and plane. 1996). Chemical action of sulphur aerosols as atmospheric sinks for ammonia has been considered by Noonan et al (2004).

Measurements of trace gases in West Africa are important for a number of reasons: One is that West Africa is considered to be the world's largest biomass burning region (Marticorena and Cairo, 2006). Biomass burning. natural gas and automobile emissions are important sources of C_2H_6, C_2H_2, CO and many other gases (Zhao et al, 2002); these could be particularly high in countries such as Nigeria due to petroleum exploration, increasing population and urbanisation. At the moment measurements of trace gases in the region are mostly undertaken within the African Monsoon Multidisciplinary Analysis (AMMA) project (http://www.ofps.ucar.edu/amma). These measurements are often intermittent and for only a few species. Continuous ground-based Fourier Transform Infra-Red (FTIR) spectroscopy is a method for studying temporal distributions of a larger number of species and would be useful for obtaining information regarding sources. sinks and transport. The method has not yet commenced in West African sites.

In Nigeria the center for Remote Sensing is at Jos a high altitude station ~1159 meters above sea level. This site just like other areas in West Africa may not present very clear skies needed for trace gas monitoring during the harmattarn season owing to the influence of Sahara dust conditions. This often results in high aerosol optical depths ($\hat{o}_{500nm} > 2.2$) (Nwofor, 2006). with dust trails left throughout the year. Avoiding aerosol-associated particle pollution and haze during ground-based FTIR spectroscopy may imply elevating measurement platforms by several kilometers or launching

balloons above the aerosol height. Both options involve increasing observer altitudes. In this study, we investigate the possible effects of increasing observer altitudes- on retrieved trace gas radiances using the FTIR spectroscopic technique.

Method

The work involves the analysis of simulations of trace gas absorption spectra for some selected species for different observer elevations using the Karlsruhe Optimized and Precise Radiative Transfer Algorithm (KOPRA) developed at the Institut Fur Meteorologie und Klimarforschung (IMK) Forschungszentrum Karlsruhe (FZKA) Germany. (Stiller et al. 1998: Stiller. 2000). The species examined were $ClNO_3$. H_2O. CO_2. O_3. and C_2H_2. These species play significant roles in atmospheric chemistry (Crutzen. 1994: Kley, 1994; Zhao et al 2002). From data obtained from ground-based FTIR sites operated by the IMK-FZKA at Izana Observatory on the Island of Tenerife (28° north, 2.37 km above sea level-a.s.l) and at Kiruna in the north of Sweden (65.50°north, 0.42km a.s.l) it was found that CO_2 is homogenous. H_2O decreases sharply in the troposphere while O3, C_2H_2 and $ClNO_3$ have higher concentrations in the stratosphere. (Schneider, 2002).

These simulations were made for both sites to test the effects of altitude on trace gas absorption line strengths by modifying the observer elevation impute in the radiative transfer algorithm (KOPRA) and plotting the resulting absorption strengths. The data from Izana were from measurements made for given species on the same days so that the only variable in the KOPRA impute model was the observer height. At Kiruna however, measurements made at different periods of the year are used to infer the possible effects of the seasons.

Background Theory

Ground-based FTIR spectroscopy allows for the detection of wide variety of atmospheric constituents simultaneously using specially designed spectrometers. At IMK, the BRUKER IFS, 120M or alternatively the BRUKER AFS 120 HR spectrometers with apodised spectral resolutions of 0.0035cm^{-1} and 0.0025cm^{-1} respectively are commonly used (Blumenstock et al, 1997). The spectrometers are essentially a Michelson interferometer which produces and

recombines two wave trains of monochromatic radiance with relative phase difference that depend on mirror displacement (http://www-imk.fzk.de/asf/boden/bruker.htm). If the mirror displacement is x for instance. these interfere constructively to yield a maximum detector signal-interferogram if the optical path difference is an exact multiple of the wavelength
i.e.

$$2x = n\lambda \ (n = 0. 1. 2. 3…) \qquad (1)$$

The interferogram $I(x)$ is converted to a spectrum S (k) by Fourier transformation i.e.

$$S(k) = \int_{k=-\infty}^{\infty} I(x)\cos(2\pi kx)dk \qquad (2)$$

where $k = 2\pi/\lambda$ is the wave number (Riley et al 1998)

For radiation originating at z and observed at z_0, neglecting the terrestrial atmosphere as a radiation source (intensity at mid IR range relative to the corresponding sun intensity ~ 1 %); in the absence of scattering which is unimportant in the IR region and under assumptions of local thermodynamic equilibrium. the radiative transfer equation (Chandrasekhar, 1960) is

$$S(\nu, z_0) = \beta(\nu, T_{sun})e^{-\tau(\nu, z_0, \infty)} \qquad (3)$$

where $\beta(\nu, T)$ is the source function for a black body at frequency and temperature T given by

$$\beta(\nu. T) = \frac{2h\nu^3}{c^2}\frac{1}{\exp(\frac{h\nu}{k_\beta T} - 1)} \qquad (4)$$

and $c = \nu\lambda$ is the speed of light. Hence the spectral radiance $S(\nu. z_0)$ is a function of the observer position since the atmospheric optical depth $\lambda(\nu. z_0, \infty)$ depends on the observer altitude. (Cox and Plane. 1996)

i.e.

$$\tau(\nu. z_0. \infty) = \int_{z_0}^{\infty}\sigma dz \qquad (5)$$

where σ = absorption cross section of a molecule and dz is a vertical height
From the point of view of statistical mechanics. the absorption coefficient k_{nm} of a molecule with energy levels E_n and E_m for radiation with frequency v_{nm} is given by (Chandrasekhar, 1960)

$$\kappa_{nm} = \frac{8\pi^2 ng_n}{3hcQ}\nu_{nm}\langle\mu_{nm}\rangle^2\left[\exp\left(-\frac{E_m}{k_BT}\right) - \exp\left(-\frac{E_n}{k_BT}\right)\right] \qquad (6)$$

Where g_n = the total degeneracy of state at energy level E_n, Q = total internal partition function, n = total number density of molecule regardless of state and μ_{nm} = electrical dipole matrix element for transitions between E_n and E_m. Spectral absorption therefore increases with number density $n \sim m_r$ (m_r = air mass) and hence reduces with observation altitude assuming uniform mixing. The effect of changing Solar Zenith Angle (SZA) hence seasons (Bracher et al. 2004) can be derived from the equation relating the air mass with SZA (Kasten. 1966)

given by

$$m_r = \left[\cos\delta + 0.15(93.885 - \delta)^{-1.253}\right]^{-1} \qquad (7)$$

$m_t = 1$ when the sun is directly overhead otherwise $m_t \sim \sec\delta$. $\delta = SZA$.

Results

Figures 1(a-e) and 2(a-e) are derived from KOPRA forward model simulations of the variations in the absorption spectra of CO_2, $ClNO_3$, O_3, H_2O, and C_2H_2 with observer elevation for Izana and Kiruna measurements respectively. The observations are shown with the dates of the observations indicated in the legend in year/month/day (yymmdd). The absorptions are derived from spectral intensity plots (on the vertical axis) which are in units of absolute radiance ($nW/(cm^2$ sterad $cm^{-1})$) versus wave number (cm^{-1}). Hence absorptions are lower for higher absolute radiance.

Figure 1 shows that absorptions are generally weaker for all the species if observations are made at altitudes above 2.37km. In figure 2. where the Kiruna data is shown measurements made at different days are included in the plots to show the effects of seasonal changes i.e. changing SZA on absorption. The dates of the observations are indicated in the legend in year/month/day (yymmdd).

In Fig.2 just like Fig.1, absorptions are lower for increasing observer elevations. In addition, absorption is found to be more for measurements made during the summer months at Kiruna. The results also give indication of vertical distribution and mixing with the more troposphere-mixed specie such as CO_2 (Schneider, 2002) having greater observer elevation effect at the altitudes considered.
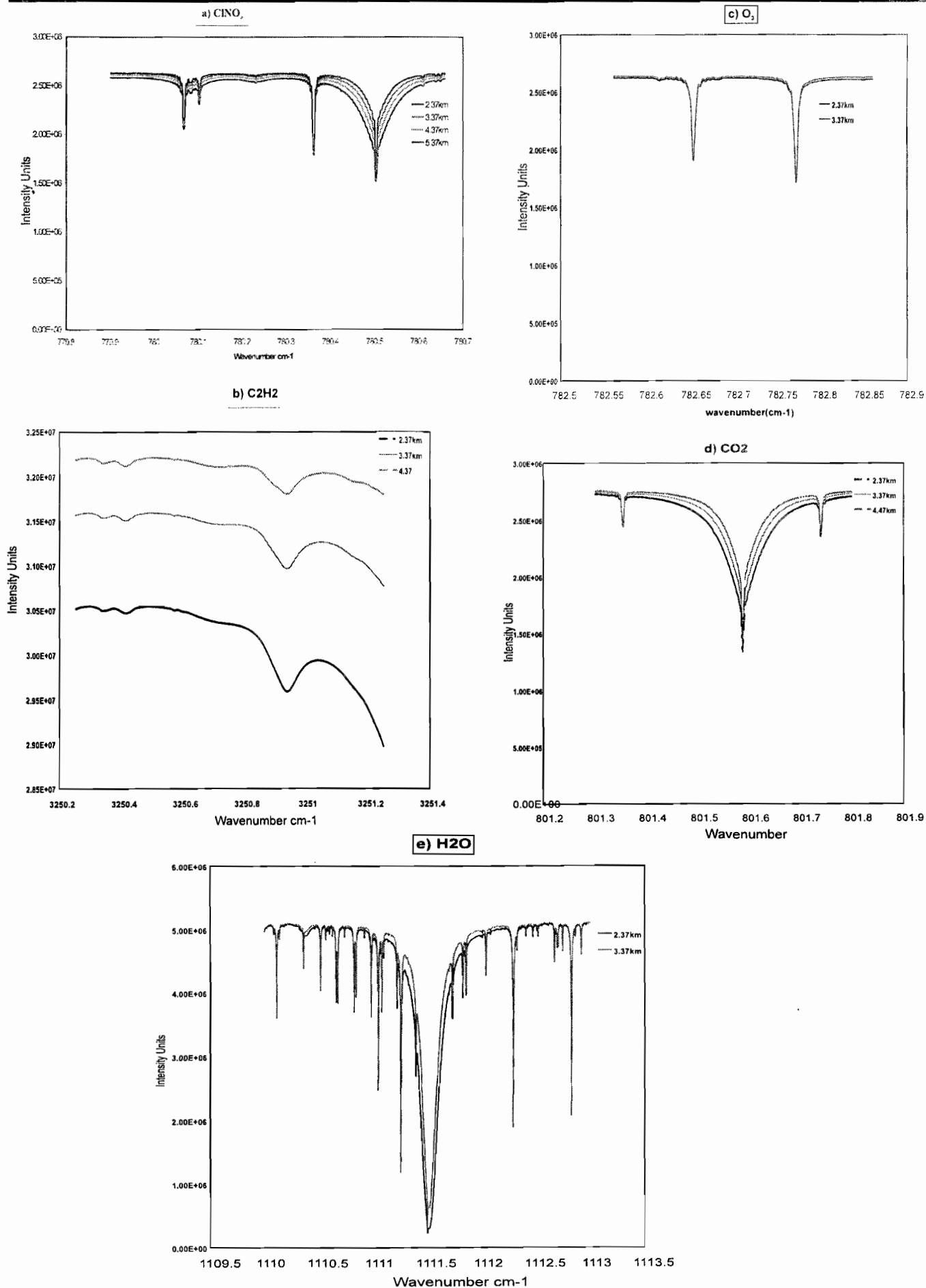
Figure 1(a-e): KOPRA simulations of (a) $CINO_3$, (b) C_2H_2, (c) O_3, (d) CO_2, and (e) H_2O spectra for Izana
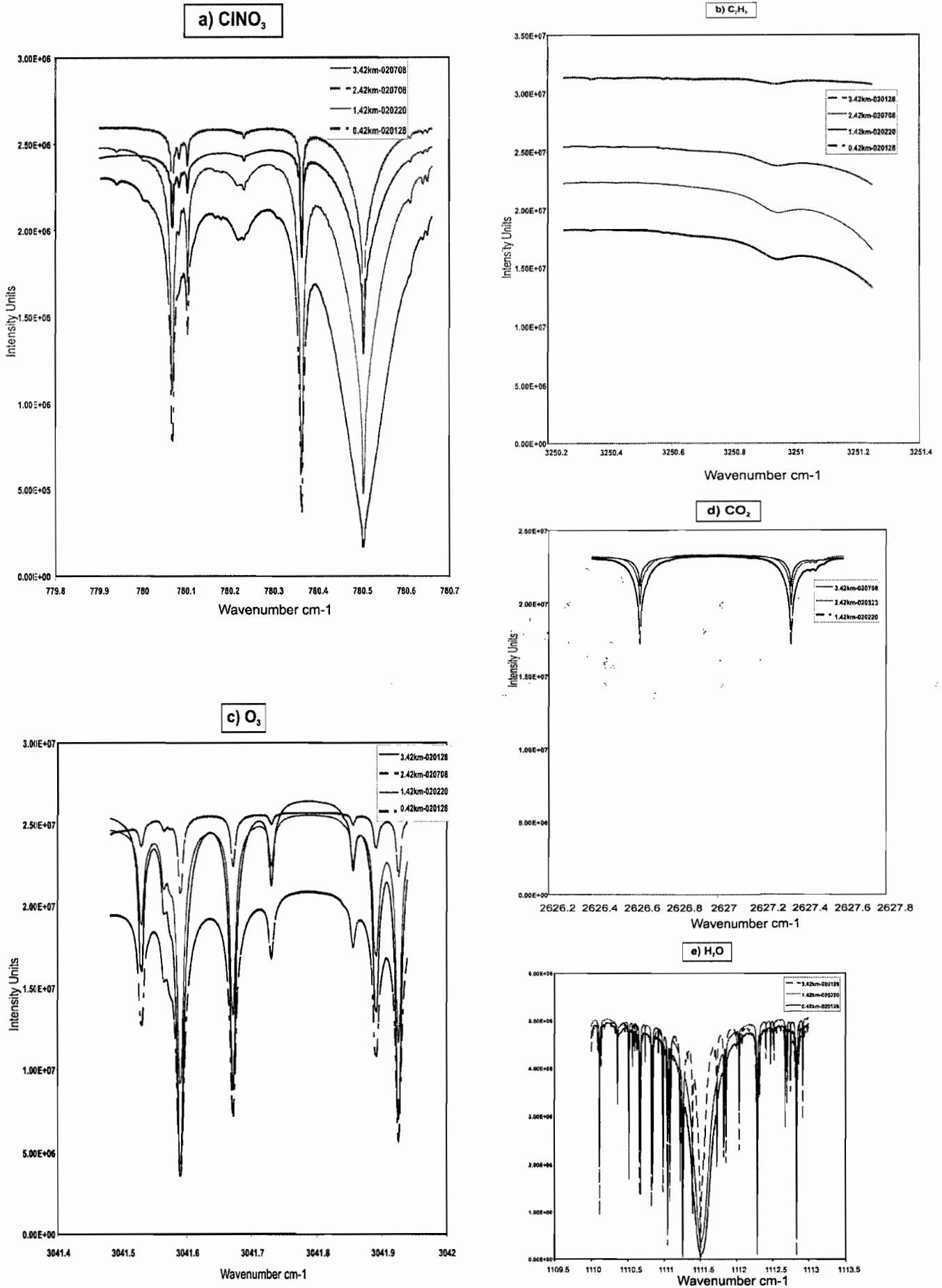
Fig. 2(a-e): KOPRA simulations of (a) $ClNO_3$, (b) C_2H_2, (c) O_3, (d) CO_2, and (e) H_2O spectra for Kiruna

Implications and Recommendations

The results in this work show that absorptions generally decreased with observation altitude for all the species considered at both the sub-tropical and high latitude sites. These results tend to suggest that the height criterion for ground-based FTIR Remote Sensing of trace gases may be more justified in regions that are far from pollution sources such as Kiruna and Izana Tenerife: But for areas under heavy aerosol pollution such as in West Africa. the height criterion may not be enough as line strengths that tend to decrease with altitude may be worsened at such sites. Since FTIR Remote Sensing facilities are located at places that are elevated to the solar transparency and away from pollution sources. the effort to elevate Remote Sensing platforms at aerosol polluted sites in West Africa may be at the risk of managing reduced tropospheric gas line strengths. These issues may be of serious relevance for FTIR measurements at sites such as Jos and others in West Africa. The results call for establishment of more FTIR trace gas campaigns in West Africa. The present trends of going for elevated regions of the world for trace gas measurements should therefore be accompanied with measurements at aerosol polluted regions especially when higher platforms may hamper FTIR resolution as was shown in the various simulated spectra presented in this paper. This is very useful considering the growing interest in atmospheric chemistry of the tropics as a whole and West Africa in particular. First, the low zenith angles in the tropics and the accompanying increase in solar UV flux results in highest concentrations of the oxidizing OH radical which play a central role in ozone chemistry (Crutzen 1994). The influence of pollution and anthropogenic production of ozone precursors such as $NO_{,}$ and CO. and large-scale production of ozone enhancing species in the troposphere are linked to biomass burning during the dry season. Also transport of air containing direct precursors of ozone destroying species from the polar vortex to the mid-latitudes are thought to be strongly initiated in the tropics from where majority of source gases enter the stratosphere (Schneider, 2002). The West African region in particular is identified as one of the most sensitive regions to climate variability and trends in the world. The Sahara region is considered as one of the most important sources of mineral aerosols to most parts of the globe including Europe and the Americas (Kaufman et al, 2004. This emanates from the yearly *Harmattan* dust outbreak. It is

therefore important to take deliberate steps towards a multi-faceted evaluation of concentrations of trace gas species under the varying aerosol conditions in the West African region. Continuous measurements by ground-based FTIR spectroscopy as are presently carried out at the Kiruna and Izana sites by IMK, FZKA could be employed to search for aerosol fingerprints in aerosol-correlated retrieved concentrations time series. The inverse method of inferring trace gas concentrations from aerosol optical characteristics is presently useful (Paton-Wash et al. 2004)

Acknowledgements

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