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Radiative effects of tropospheric ionisation

K. L. Aplin

Rutherford Appleton Laboratory, Space Science and Technology Department, Chilton, Didcot, Oxon OX11 0QX, UK

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Correspondence to: K. L. Aplin (k.l.aplin@rl.ac.uk)

Abstract

Despite the increasing evidence that cosmic ray variations may influence clouds and climate, there has been little discussion of the direct radiative effects of atmospheric ionisation. Laboratory experiments show that hydrated molecular cluster-ions, formed in the atmosphere by cosmic rays, absorb in the infra-red continuum at wavelengths of 9–12 μm. The tropospheric magnitude of this effect is estimated: transmittance anomalies from clear sky ion concentrations peak at ~2% at 10 km in the mid-latitudes. A simple isothermal clear sky atmospheric model suggests the integrated effect of the absorption is ~2 $\mathrm{Wm^{-2}}$. The effect appears detectable in existing surface data sets; surface micrometeorological data shows a significant anticorrelation between downwelling infra-red radiation and atmospheric cosmic ray ionisation. This is consistent with the infra-red attenuation observed in laboratory studies of cluster-ion absorption. If atmospheric ionisation from cosmic rays has universally direct radiative effects, then reinterpretation of satellite cloud data may be necessary.

1. Introduction

Atmospheric aerosol electrification in non-thunderstorm conditions arises from hydrated cluster ions formed by radiolysis, primarily from cosmic rays. Possible connections between atmospheric electricity and climate have long been a source of speculation (e.g. Ney, 1959) but have a new urgency following establishment of the positive correlation between cosmic rays and satellite-derived cloud cover (Svensmark and Friis-Christensen, 1997). Quantifying the atmospheric radiative balance is fundamental to understanding natural and anthropogenic climate variability, and it is important to identify factors that may modulate it.

Several plausible physical mechanisms exist connecting ionisation to clouds and the planetary radiation balance (e.g. Yu and Turco, 2001; Harrison and Aplin, 2001; Tripathi and Harrison, 2002). These mechanisms are indirect and involve several (sometimes highly contentious) steps. Investigation of the *direct* rôle of charged particles in radiative transfer processes has hitherto been very limited, yet there is increasing evidence that ionisation influences clouds and climate (Carslaw et al., 2002). Theoretical calculations show that the radiative absorption of charged water drops is negligible, but sub-micron charged water clusters or droplets are more likely to absorb electromagnetic radiation (Geldart and Chylek, 2001). The simplicity of atmospheric cluster-ions directly absorbing solar radiation and modifying the radiative balance, summarised with the existing cloud mechanisms in Fig. 1, is a strong motivation. In this paper, the evidence for ion clusters directly absorbing infra-red radiation is discussed, and the magnitude of the atmospheric effect estimated.

2. The infra-red continuum problem

The near infra-red (IR) atmospheric radiative properties of the water molecule are well-known, and result from rotational and vibrational transitions of its hydrogen bonds (e.g. Peixoto and Oort, 1992). There also exists a weak broad-band (8–50 μm) IR absorption, unattributed to any well-known atmospheric species, with pressure and temperature dependency greater than any known water vapour absorption. This anomaly between accepted theory and observations is referred to as the IR continuum problem. The possible presence of atmospheric water dimers is a long-established explanation (Bignell, 1970). Recent theoretical work implies that atmospheric water vapour clusters, particularly dimers and trimers, do exist in sufficient concentrations to account for the continuum (Goldman et al., 2001; Evans and Vaida, 2000). However, oligomers of water have apparently never been measured in the atmosphere (Headrick and Vaida, 2001) and their molecular structure and associated radiative properties are poorly understood.

Continuum absorption effects are highly relevant for climate studies, as much of the present cloud climatology is based on IR satellite data. For example, the International Satellite Cloud Climatology Project (ISCCP) data set is a composite global satellite cloud data set, frequently used in climate studies, derived from measurements in the IR and visible (Rossow, 1991). 60% of the satellites contributing IR measurements to the ISCCP data set measure in the IR continuum absorption range. A further motivation to understand the IR continuum is the need to quantify atmospheric water vapour absorption and its variability, currently thought to be in the range 1–6 $\mathrm{W m^{-2}}$ (Chylek et al., 1999; Vaida et al., 2000). Radiative absorption of water vapour needs to be better understood to improve parameterizations for cloud models and calculate the water vapour contribution to greenhouse forcing (e.g. Brindley and Harries, 1998; Geldart and Chylek, 2001). The need for accurate climate change predictions clearly necessitates investigation of any physical processes that may be relevant for the IR continuum problem.

3. The role of molecular water clusters

Atmospheric small ions are clusters of water molecules around a charged centre, typically represented by chemical formula $X^+(H_2O)_n$ or $Y^-(H_2O)_n$, where n is the number of water molecules in the cluster ($n < 10$) and X^+ and Y^- are charged atmospheric species. Typical tropospheric ion concentrations are $10^3 - 10^4\ \mathrm{cm^{-3}}$ (MacGorman and Rust, 1998). The charged water cluster $H_3O^+(H_2O)_n$ is a common tropospheric positive ion species (Keesee and Castleman, 1985; Nagato et al., 1999). Atmospheric small ions of different chemical composition are also hydrated to a similar extent and may result in comparable radiative absorption properties to neutral water clusters such as dimers and trimers. Carlon and Harden (1980) and Carlon (1982a, b) found that the IR absorption properties of both neutral and charged molecular water clusters matched the pressure and temperature dependencies of the continuum absorption extremely well. This provoked their laboratory investigation of the IR absorption properties of charged water clusters, which is extended to the interactions of tropospheric ions and water vapour in this paper.

Carlon (1981a) showed that the positive molecular cluster ion species $H_3O^+(H_2O)_n$

can exist in equilibrium with larger neutral clusters. After perturbations to the charged-neutral cluster equilibrium, recovery takes place over a timescale of minutes to hours; the chemical changes during this return to equilibrium are thought to lead to the broadband IR absorption properties of the water vapour (Carlon, 1981b). Carlon found that the positively charged cluster concentration is proportional to the calculated number of neutral clusters, and the IR absorption of water vapour varied as its positive ion concentration. Although the water cluster population is not known, (Headrick and Vaida, 2001) the positive ion concentration N_+ can be measured via the positive air conductivity σ_+ by (1), where μ is the electrical mobility (e.g. Carlon, 1982b; Moore and Vonnegut, 1988)

$$\sigma_+ \approx N_+ e \mu. \tag{1}$$

In the closed, saturated system of Carlon's laboratory experiments, with ionisation enhanced by a radioactive source, the maximum concentration of charged water clusters was $\sim 10^7\ \mathrm{cm}^{-3}$. Even these concentrations, which greatly exceed typical ion concentrations in the unsaturated free troposphere, are insufficient to explain the atmospheric IR continuum absorption. The interaction between charged and neutral clusters leads to the absorption signal of the charged clusters, but a larger concentration of neutral clusters is required to account for the atmospheric IR continuum absorption. Carlon (1981a) estimated neutral cluster concentrations in saturated air to be $10^{10}-10^{15}\ \mathrm{cm}^{-3}$, which is similar to the atmospheric dimer concentrations of $10^{10} - 10^{14}\ \mathrm{cm}^{-3}$ thought to be responsible for the IR continuum absorption (Vaida et al., 2000). A weak IR absorption from these neutral-charged cluster interactions may therefore occur in the cloud-free atmosphere, proportional to the positive molecular cluster-ion population.

4. Atmospheric evidence for IR absorption of atmospheric ions

IR radiation reaching the Earth is emitted from clouds and atmospheric molecular species. In the cloud-free sky, the longwave radiation reaching the surface is therefore determined by the integrated radiative properties of atmospheric species in the column of air above. If atmospheric ions do absorb significant quantities of IR radiation, this effect may be observable in the downwelling longwave radiation. The laboratory experiments discussed above show a greater ion concentration could lead to greater absorption of IR, with an anticorrelation between the ion concentration and downwelling longwave radiation. Synchronous atmospheric ion and radiative flux measurements do not yet exist, but in the free troposphere, where aerosol concentrations are low, the ionisation rate is a good proxy for the ion concentration. Data from surface neutron counters is readily available to indicate the tropospheric ionisation rate from cosmic rays (CR). Low and high-energy CR can penetrate to the surface at high geomagnetic latitudes, but only high-energy CR are detected by neutron counters at equatorial latitudes (e.g. Wolfendale, 1963). In this section, measurements of the surface radiation balance are analysed and compared to neutron counter data as a proxy for ionisation.

Downwelling longwave radiation L_d is one component of the net radiative flux density R_n

$$R_n = S_g + S_d + (L_d - L_u), \tag{2}$$

where S_g is the global solar irradiance, S_d the reflected irradiance, L_d the downwards long-wave flux and L_u the upwards long-wave flux. R_n, S_g and S_d are routinely measured. L_u can be estimated for the earth's surface by assuming it is a black body radiating at a temperature T_a. Because of the limited spectral response of instruments used to measure R_n, only the fraction of the radiation in the wavelength window of the instrument is read. Using the Planck spectrum and the Stefan-Boltzmann law, (Houghton, 2002), L_d can therefore be calculated from (3):

$$L_u = \frac{\int\limits_{\lambda_1}^{\lambda_2} \frac{8\pi hc\lambda^{-5}d\lambda}{\exp\{hc/(k\lambda T_a)-1\}}}{\int\limits_{0}^{\infty} \frac{8\pi hc\lambda^{-5}d\lambda}{\exp\{hc/(k\lambda T_a)-1\}}} \sigma T_a^4. \tag{3}$$

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(2) permits L_d to be found as the residual, given values of L_u, R_n, S_g and S_d.

The HAPEX-Sahel micrometerological experiment in 1992 measured 10 min average surface fluxes in the Sahel region of Africa, near Niamey, Niger (13°30′ N, 2°5′ E) (Gash et al., 1997). This data set was chosen because it was a summer experiment with many clear days, and the tropical latitude maximised flux values compared to the expected signal. S_g and S_d were measured to ±3% using Kipp and Zonen CM5 solarimeters, and R_n to ±5% with a Middleton net radiometer. Emitted IR radiation in the 8–14 μm range was measured indirectly using a surface viewing Heimann KT15 IR thermometer (±0.1°C). This gives the radiative temperature of the surface, which can be used to calculate the upwelling longwave radiation from (3) for $\lambda_1 = 8\,\mu$m and $\lambda_2 = 14\,\mu$m. Coincident daily average values of neutron count rates were obtained from the University of Oulu/Sodankyla Geophysical Observatory, Finland (67°22′ N, 26°38′ E) . This high-latitude station covers a broader CR spectral range than is measured in the tropics; daily moving averages were calculated in order to extract the global daily CR fluctuations. Daily (144 point) centred moving averages of L_d were also calculated; averages containing less than 130 data points because of instrument problems were excluded.

As cloud emits longwave radiation, cloud-free days provide the simplest conditions for a CR-L_d comparison. Weather conditions at Niamey were generally fine with scattered cumulus clouds; there were 6 clear days over the measurement period, and 26 days out of 40 on which the integrated solar radiation exceeded 80% of the maximum possible for the time of year, here called “sunny days”. Sunny periods were more persistent than totally clear days, and the daily averaged effects of scattered cumulus cloud are probably unlikely to contribute significantly to L_d emission. The two periods of six consecutive sunny days when L_d and CR data were available were selected for further analysis, using anomalies from a linear trend over the duration of the experiment. During a period of enhanced cosmic ionisation, year days 227–232 (14–19 August 1992), the correlation between the L_d and neutron counter anomalies was -0.752 with $N = 721$ pairs of measurements, Fig. 2. Persistence in the L_d measurements reduced this to a statistical significance of 97.6%.

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The error in the calculated upwelling longwave radiation derived from the IR thermometer measurements was determined empirically as ±2%. Propagation of errors from the quantities measured in (2) gives the overall uncertainty in the derived L_d as ±7%. Series of random errors within this range were generated and added to L_d; the correlation with CRs remained statistically significant. The anticorrelation therefore persists even when conservative experimental error is considered. Correlations with other radiative quantities for the same period were also calculated for comparison, Table 1. The insignificance of these correlations indicates the physical mechanism causing the anticorrelation acts uniquely between L_d and CRs. This supports the laboratory evidence that ion species present in the atmosphere absorb IR radiation.

5. Estimation of tropospheric ion absorption profile

The detailed mechanism of ions absorbing IR radiation as they interact with neutral clusters is clearly very complex. The magnitude of this effect throughout the troposphere is estimated below. Simplified representations of the positive ion concentration, absorption cross-section and pressure variation with height are included. Water vapour absorption is excluded, and the positive ion composition is assumed to be entirely composed of water ion clusters $H_3O^+(H_2O)_n$.

Carlon (1982a) measured absorption cross-section α and N_+ in the 8–13 μm band, and found a positive linear relationship between α and N_+ outside the condensation régime. The IR continuum wavelengths of 9.3 and 11.78 μm are selected for further analysis here because the experimental ion concentrations were closest to those found in the troposphere. Linear regression is used to estimate α as a function of N_+; the linear correlation coefficient between α and N_+ was 0.932 at 9.3 μm and 0.711 at 11.78 μm. Although the absorption of water vapour, and other species, is almost negligible at these wavelengths (e.g. Peixoto and Oort, 1992; Cormier et al., 2002), there are several weak vacuum absorption lines near these wavelengths in the HITRAN spectroscopic database (Rothman et al., 1998). The limitations of Carlon's experiments at atmospheric pressure and the vacuum lines in HITRAN prevent detailed comparisons, but there is evidence that water vapour absorption may be responsible for the slight positive offsets in the $\alpha - N_+$ regression. The intensity of water vapour absorption in Carlon's experiment at 11.78 μm can be calculated from the offset of 0.1909 gcm^{-2} to be 4.85×10^{-21} cm^{2}molecule^{-1}. The intensity of the vacuum absorption at 11.77 μm is 2.11×10^{-20} cm^{2}molecule^{-1}, which is comparable. α can therefore be expressed (in gcm^{-2}) as

$$\alpha = aN_+ + b, \tag{4}$$

where a is the dependency on ion concentration (of order 10^{-6}) and b is a constant offset resulting from weak background water vapour absorption. Exclusion of measured background water vapour absorption in order to estimate the effect solely from ions gives

$$\alpha = aN_+. \tag{5}$$

The atmospheric ion concentration varies with height z because of the variation of penetration in CRs throughout the atmosphere. This accounts for the maximum ion concentration of about 6000 cm^{-3} at 15 km. Vertical tropospheric positive ion concentration measurements are reported in MacGorman and Rust (1998); the profile is well-approximated by a quadratic in z.

The Beer-Lambert law for transmission of light of wavelength λ through a medium of thickness S is

$$\frac{I}{I_0}(\lambda) = \exp[-\rho\alpha(\lambda)S] \tag{6}$$

(e.g. Peixoto and Oort, 1992) where I/I_0 is the ratio of received to initial intensity (the transmittance), and ρ is the density. Absorption by atmospheric ions varies with height z, as both ρ and α are functions of z. The transmittance profile can therefore be estimated at 11.78 and 9.3 μm from

$$\frac{I}{I_0}(z, \lambda) = \exp[-\rho(z)\alpha(z, \lambda)z] \tag{7}$$

by combining (5) and (6), and using a standard exponential atmosphere assumption for $\rho(z)$ (e.g. Seinfeld and Pandis, 1998). Calculations using (7) are presented in Fig. 3.

Estimated transmittance anomalies (Fig. 3) are negligible close to the ground, as expected from the relatively low atmospheric ion concentrations and short path length. The transmittance drops sharply as N_+ increases and ρ decreases, to a minimum at ~10 km of 97.4% at 9.3 μm and 98.6% at 11.78 μm (±0.5%). The minimum in transmittance at ~10 km corresponds to a balance between the increasing ion concentration and decreasing atmospheric density, at comparable heights to high cloud. The increased penetration of CRs then causes the ionisation and cross section to rise less steeply up to 25 km where the anomaly is ~0.5%.

The radiative effect of integrated ion absorption can be estimated by assuming a simple cloud-free one-layer isothermal atmosphere, perfectly absorbing in the IR, and perfectly transparent in the solar spectrum with albedo of 0.3 and atmospheric IR emissivity of 0.9 (e.g. Houghton, 2002). This gives a mean surface temperature T_s of 296 K, and an atmospheric temperature T_a of 249 K. The contribution of the 9–12 μm band to the total Planck black-body spectrum was calculated at T_a. If the integrated ionic absorption of ions is estimated to be 5% across the 9–12 μm region, the radiative effect at T_a can then be estimated from the Stefan-Boltzmann law as ~2 Wm^{-2}. Neglecting the radiative properties of hydrated cluster-ions could therefore represent an error of up to 0.5°C in temperatures derived from IR measurements.

6. Discussion

Carlon's laboratory experiments show strong evidence for the IR absorption properties of hydrated cluster-ions in the 9–12 μm range. This is backed up by suggestive atmospheric observations showing that downwelling IR fluxes in the 8–14 μm wavelength band in almost clear sky were significantly attenuated during a six-day period of increased CR ionisation. This has implications for satellite observations of meteorological parameters, such as cloud, retrieved from IR measurements. The well-known correlation between cosmic rays and clouds (Svensmark and Friis-Christensen, 1997) appears to only exist in IR satellite data sets (Sun and Bradley, 2002; Kristjánsson et al., 2002). Its estimated magnitude is 1–2 $\mathrm{Wm^{-2}}$, close to the predicted size of ionic absorption estimated above. These factors indicate that hydrated cluster-ions absorbing IR as they interact with neutral clusters could be an observable and significant atmospheric effect.

This presents substantial evidence for the clear sky IR absorption properties of atmospheric ions. The predicted clear sky tropospheric IR absorption profile by protonated water cluster ions was estimated at 9.3 μm and 11.78 μm, and transmittance was reduced by up to (2.6±0.5)%. The sign of the observed effects is consistent with that expected from theory. Now that sufficiently sophisticated ion counters are available (Aplin and Harrison, 2001), further measurements of both ions and longwave radiation are desirable. Vertical soundings would be of value in testing the predictions above in more detail, but further IR spectroscopy measurements would be required to determine the detailed spectral response.

It is important to quantify the IR absorption of atmospheric ions. If the effect is detectable, there are implications for satellite observations of meteorological parameters retrieved from IR measurements. An unparameterised absorption process such as the IR response of water cluster ions could cause spurious signals in satellite data.

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Table 1. Correlations of daily averaged net radiation R_n, longwave up L_u and longwave down L_d in Niger with cosmic rays for days 227–232 1992

Quantity	Correlation with cosmic rays for days 227–232 1992	Statistical significance?
R_n	−0.117	No
L_u	−0.453	No
L_d	−0.752	Yes

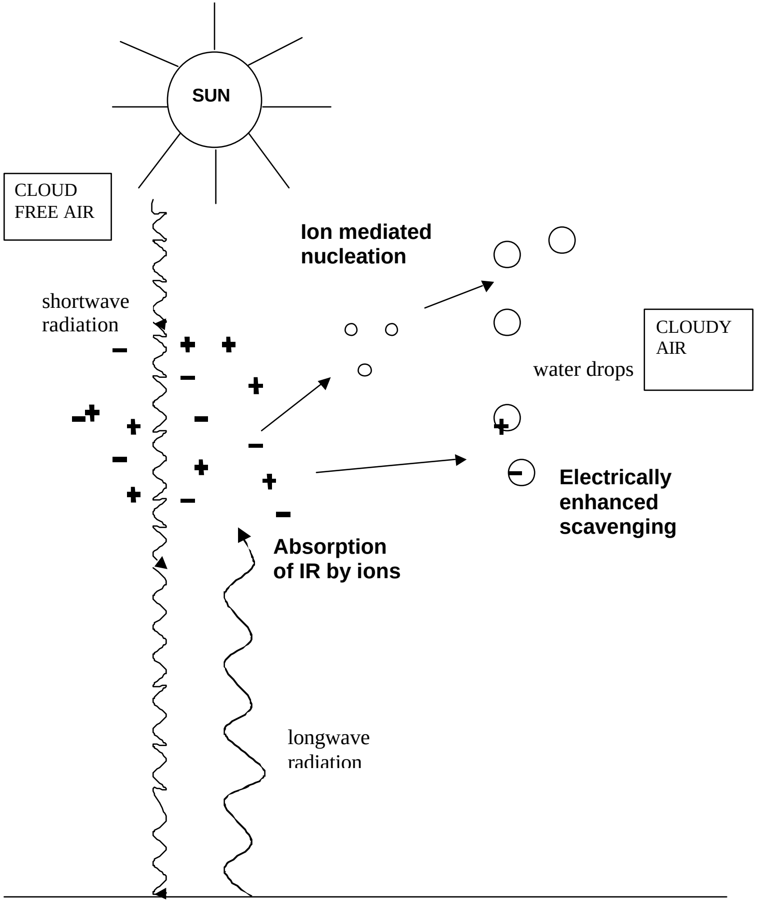

Fig. 1. Possible mechanisms by which ionisation in the atmosphere may influence the radiative balance.

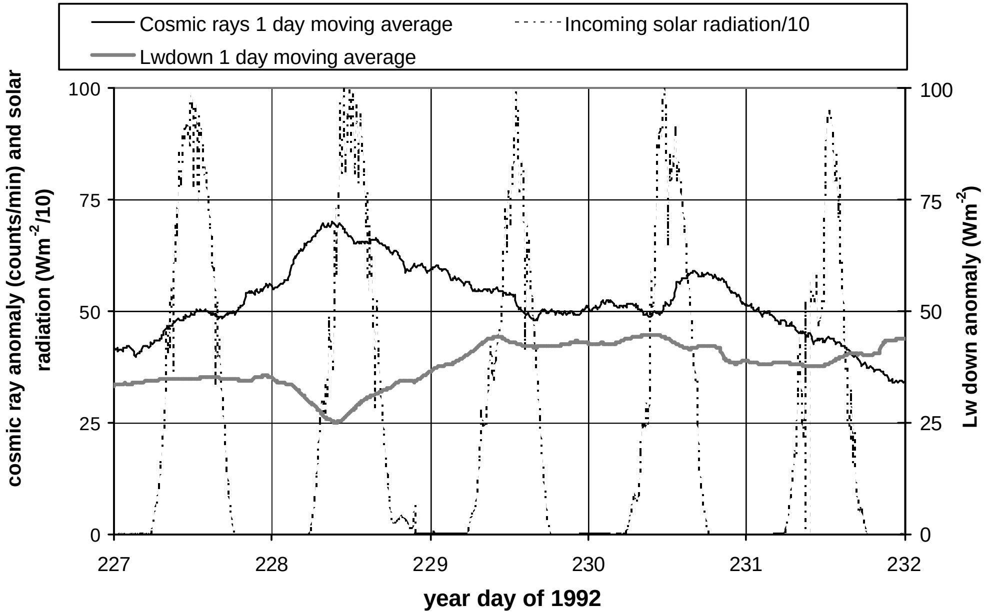

Fig. 2. Longwave down and cosmic ray daily average anomalies on year days 227–232 1992. (r = −0.752, P = 97.6%). Global solar irradiance is also shown; this was a prolonged period of sunshine with scattered Cu clouds.

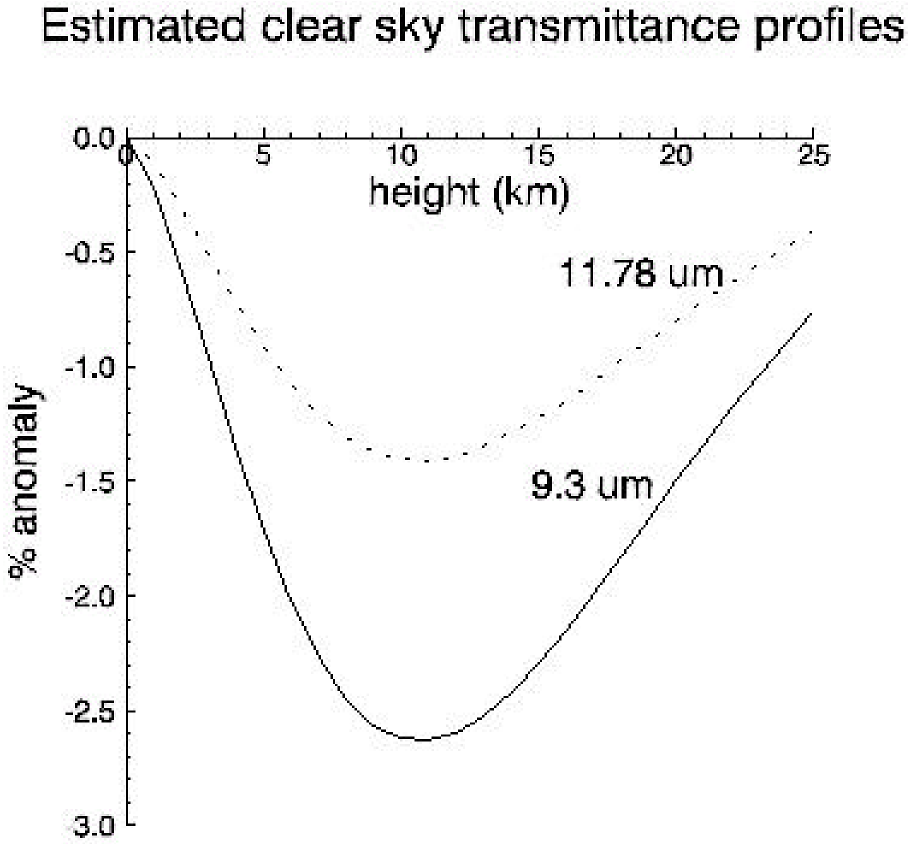

Fig. 3. Estimated tropospheric transmittance anomalies at 11.78 and 9.3 μm from molecular water cluster ions, where 0 is the transmittance from an ion-free atmosphere. The maximum errors occur at the maximum anomaly and are estimated as ±25% at 9.3 μm and ±37% at 11.78 μm.