Contribution of water vapor dimers to clear sky absorption of solar radiation

By PETR CHÝLEK*, Q. FU, H. C. W. TSO and D. J. W. GELDART, *Atmospheric Science Program, Departments of Physics and Oceanography, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada*

ABSTRACT

Using recently derived-values of the water vapor dimer spectral absorption cross section we calculate the water vapor dimer contribution to the clear sky absorption of solar radiation. We consider the water dimer concentrations deduced from local equilibrium thermodynamics, and we account for the overlap of water vapor dimer and monomer absorption bands. We estimate that water vapor dimer contribution to the clear sky broad band column absorption of solar radiation is around 3 and 6 W/m^2 for the cases of midlatitude summer and tropical atmosphere, respectively, at the solar zenith angle of 30°. For the cases of midlatitude winter, the US standard atmosphere and subarctic winter atmosphere, the dimer contribution to the absorption of solar radiation is less than 1 W/m^2. Due to an uncertainty of the dimer's concentration within clouds, we are not able to deduce, at this time, the dimer absorption in a cloudy atmosphere.

1. Introduction

Several recent studies suggest that the observed atmospheric solar absorption may exceed model calculations (Kiehl and Trenberth, 1997). Currently, it is not clear whether this discrepancy is caused by inaccuracy of experimental observations (Stephens, 1996), by excess absorption limited to cloudy sky (Cess et al., 1995; Ramanathan et al., 1995; Pilewskie and Valero, 1995) or by excess absorption which occurs in clear atmosphere as well (Arking, 1996; Charlock and Alberta, 1996). Some observations indicate that the excess absorption may be higher in the tropics and decrease with increasing latitude (Li et al., 1995; Li and Moreau, 1996).

Association of water molecules due to hydrogen bonding has been considered for a long time to be a possible source of a water vapor continuum absorption observed within atmospheric window

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* Corresponding author.
E-mail: chylek@fizz.phys.dal.ca

(Varanasi et al., 1968). Recent experimental (Armbruster et al., 1981) and theoretical (Masella and Flament, 1997; Tso et al., 1998) studies of water vapor dimer make it plausible that the hydrogen bonded water molecules may contribute to the absorption of solar radiation as well. Till now, dimers have not been included in radiative transfer models. The purpose of this paper is to estimate the absorption of solar radiation in a clear sky atmosphere due to water vapor dimers using a recent calculation of the water vapor dimer spectral absorption cross section (Tso et al., 1998).

The first estimate of the atmospheric absorption of solar radiation by water vapor dimers was obtained (Chylek and Geldart, 1997) using a perturbed quantum mechanical harmonic oscillator model and the assumption that the total strength of the intramolecular vibrational-rotational bands of the dimer was approximately equal to twice that of the monomer (an approximate sum rule).

In this work, we use the results of a more extensive and detailed quantum mechanical calculation of the water vapor dimer absorption cross

section (Tso et al., 1998) that includes absorption due to fundamental, combination and overtone bands. We discuss the dimer atmospheric concentration, the overlap of dimer absorption bands with water vapor monomer bands, and estimate the effect of dimers on the broad band absorption of solar radiation in a clear sky atmosphere.

2. Absorption cross-section

A water vapor dimer is formed by two water vapor molecules bound by a weak interaction potential (hydrogen bonding). An equilibrium configuration of molecules of a dimer was calculated by several authors using ab initio quantum chemistry and semi-empirical methods (Coker and Watts, 1987; Kim et al., 1992). We have calculated the absorption cross-section of water vapor dimers (Tso et al., 1998) in local thermal equilibrium at temperatures typical of the lower troposphere using the quantum mechanical coupled nonlinear Heisenberg equations of motions. Approximations based on the hierarchy of energy scales in the dynamics of the hydrogen-bonded dimer allowed us to calculate the dimer absorption spectrum from the far IR wavelengths up to 0.5 μm, including the contributions of overtone and combination transitions. The Horner's method (Horner, 1972) is employed to account for nonlinearity of the governing equations and a semi-classical approach is adopted to treat the rotational spectrum.

The molecular interaction produces an intermolecular absorption bands in a low frequency range (0 to about $800 \, cm^{-1}$) and introduces a shift in central frequencies of the water vapor intramolecular vibrational bands. The intermolecular vibrations and the dimer's slow rotations combine with the intramolecular fundamental, overtone and combination bands to form broad dimer absorption bands. The details of the quantum mechanical theoretical calculations and numerical solution of nonlinear equations of motion have been presented elsewhere (Tso et al., 1998). Only the results are summarized here.

Fig. 1 shows the structure of the fundamental intramolecular stretching modes and their first and the second harmonics. There is a clear correspondence between water vapor monomer rotational-vibrational bands and broad band dimer structure. Fig. 2 shows the dimer absorption cross
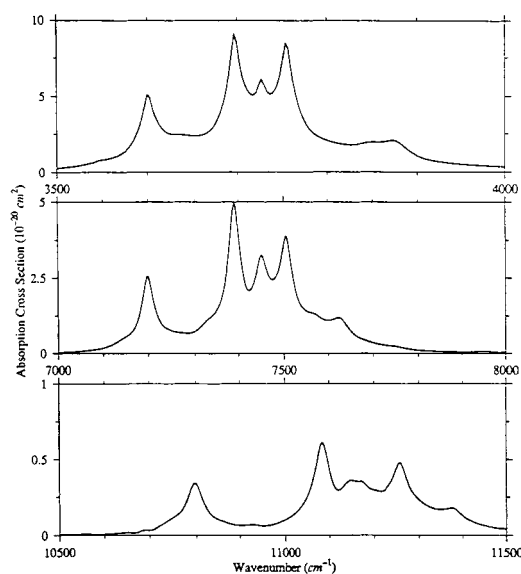

Fig. 1. The structure of the water vapor dimer fundamental stretching modes band (top panel) and their first (middle panel) and the second harmonics (bottom panel). The spectral resolution of numerical calculation is $3 \, cm^{-1}$.
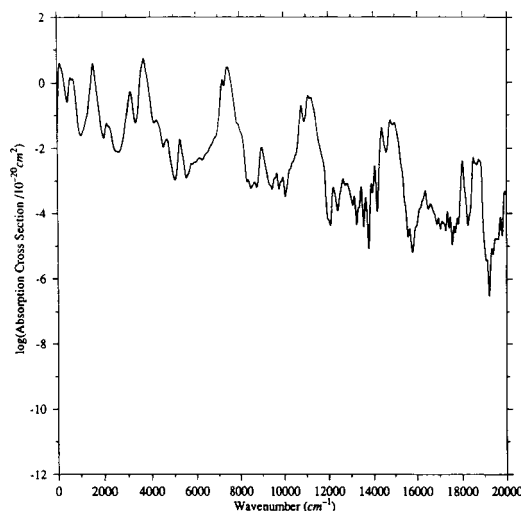

Fig. 2. The water vapor dimer absorption cross section in the 0 to $20{,}000 \, cm^{-1}$ frequency range.

section up to $20{,}000 \, cm^{-1}$. The dimer absorption cross section decreases with the frequency at much slower rate than the water vapor monomer cross section.

The dimer absorption cross sections averaged over the bands of 3500 cm^{-1} width (Fig. 3) are in a reasonable agreement with a previous estimate using the approximate sum rule (Chylek and Geldart, 1997)

To calculate the effect of water vapor dimers on the absorption of solar radiation in the atmosphere using broad band radiation models, the overlap of absorption bands of water vapor monomer and dimer has to be taken into the account. A comparison of the column absorption calculated using a narrow band and a broad band model of Fu and Liou (1992) suggests that the calculated averaged absorption cross sections should be reduced by a factor, given in the fourth column of the Table 1. The dimer effective absorption cross section, which takes into the account the overlap between the

Fig. 3. The dimer absorption cross section (σ_D) averaged over the 3500 cm^{-1} wide bands compared with the cross section σ_o deduced using the sum rules (Chylek and Geldart, 1997). The "effective" cross section, σ_{eff}, includes the correction for the overlap of dimer and monomer absorption bands.

dimer and monomer absorption bands, is defined as $\sigma_{eff} = \sigma_d/\alpha$ (shown as a dashed line in Fig. 3). The effective cross section characterizes the additional absorption of solar radiation due to dimers in broad band radiation models. To obtain the effective cross section, we assumed that, for given spectral interval, the transmission (weighted by solar irradiance) of the atmosphere containing both the monomer and the dimer is equal to the transmission of the monomer only atmosphere multiplied by the dimer transmission calculated using the dimer effective absorption cross section.

Our previous estimate of the dimer absorption (Chylek and Geldart, 1997) had no information on the frequency distribution of the dimer absorption cross-section within bands of 3500 cm^{-1} width. Consequently, the overlap between the dimer and monomer absorption bands was not taken into the account and the resulting dimer absorption was overestimated (an approximate upper bound).

3. Atmospheric concentrations

Dimer concentration depends on the dimer internal parameters (rotational constants, binding energy and frequencies of absorption bands as is apparent from eq. (1)) and on the external parameters, like the atmospheric temperature and the water vapor concentration. There is a considerable uncertainty in theoretically calculated dimer mass mixing ratio due to uncertainty of dimer parameters needed in calculations. In general, dimer concentrations deduced from experimental observations and from calculations using experimental values of equilibrium constants are higher than those deduced by purely theoretical models. In the following we present 4 different expressions for dimer mass mixing ratio.

Using the equilibrium thermodynamics, Suck et al. (1982) derived the expression for the water vapor dimer mass mixing ratio

$$\frac{m_2}{m_1} = \frac{h^6 e}{64\pi^5 (2m)^{3/2} k^4 T^4} \sqrt{\frac{I_2^a I_2^b I_2^c}{(I_1^a I_1^b I_1^c)^2}}$$

$$\times \exp(\varepsilon_B/kT) \prod_{i=1}^{6} \frac{1}{\sinh(h\nu_i/2kT)}, \qquad (1)$$

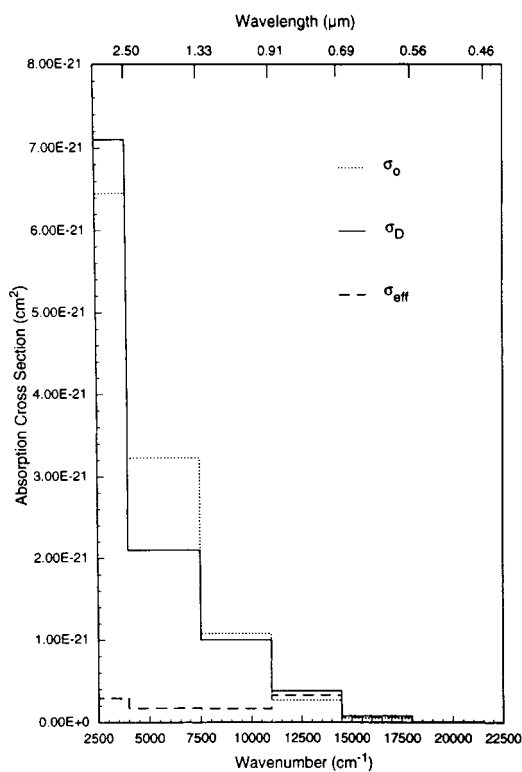where m_2 and m_1 is the total mass of the water vapor dimer and monomer, respectively, e is water

Table 1. *Water vapor dimer absorption cross section averaged over the listed spectral bands*

Wavenumber (cm^{-1})	σ_{o} (cm^2)	σ_{D} (cm^2)	α	σ_{eff} (cm^2)
500–4000	64.5×10^{-22}	71.0×10^{-22}	37	1.9×10^{-22}
4000–7500	32.3	21.0	19	1.1
7500–11000	10.8	10.0	2.9	3.4
11000–14500	2.7	3.8	1.35	2.8
14500–18000	0.5	0.8	1.15	0.7
18000–21500	0.1	0.08	1.15	0.07

σ_{o} is the dimer absorption cross section deduced using the approximate sum rule (Chylek and Geldart, 1997), σ_{D} is the dimer absorption cross section obtained by averaging the spectral calculations (Tso et al. 1998) shown in Fig. 2. σ_{eff} is the "effective" absorption cross section obtained by dividing the σ_{D} by the factor account for the overlap of the dimer and the monomer absorption bands. The overlap factor in the first band applies only to the frequencies within the solar spectral range (above 2000 cm^{-1}).

vapor pressure, T the temperature (K), h is the Planck constant, k is the Boltzmann constant, I_2^j and I_1^j (with $j = a, b, c$) are the three principal moments of inertia of the dimer and the monomer, ε_{B} is the dimer binding energy (defined to be positive), and v_i are the frequencies of the 6 dimer intermolecular bands.

To estimate the dimer concentration at saturation water vapor in the atmosphere we use eq. (1), the dimer binding energy of 5.5 kcal/mol (Curtiss et al., 1979) and the dimer's intermolecular frequency bands as obtained theoretically by Munoz-Caro and Nino (1997). To facilitate an easy use of the results in atmospheric applications, we parameterize the obtained dimer mass mixing ratio at saturation water vapor pressure as a function of the atmospheric temperature (between 273 and 313 K) in the form

$$C_1 = 144 \exp(-3535/T). \qquad (2)$$

The mass mixing ratio, C_1, provides a lower dimer concentration (by a factor of two to four) than expressions based on experimental laboratory results (Braun and Leidecker, 1974; Mhin et al., 1993), experimental measurements of the $H_2O + H_2O = (H_2O)_2$ equilibrium constant (Slanina, 1988), or on laboratory measurement of water vapor dimer fundamental frequencies.

A similar expression, leading to about two times higher dimers' concentration, was deduced from the laboratory measurements (Braun and Leidecker, 1974; Mhin et al., 1993)

$$C_2 = 811 \exp(-3800/T). \qquad (3)$$

Slanina (1988) calculated the dimer concentration using the experimental values of water mon-

omer to dimer equilibrium reaction constants. We use his values obtained at 273.15 and 298.15 K and fit them to the form

$$C_3 = 337 \exp(-3418/T). \qquad (4)$$

Slanina's data parameterized in a quadratic form were used previously by Chylek and Geldart (1997).

The frequencies of intermolecular fundamental bands calculated by Munoz-Caro and Nino (1997) are considerably higher than some of the experimentally observed dimer frequencies. For this reason, we have scaled theoretical frequencies of intermolecular fundamental bands by a common factor to obtain a better agreement with the experimentally observed frequencies. The numerical results using the scaled intermolecular frequencies and eq. (1) for dimer concentration are parameterized as

$$C_4 = 395 \exp(-3422/T). \qquad (5)$$

The atmospheric profiles of the dimer mass mixing ratio (using the four above listed estimates) for several typical atmospheric situations are shown in Fig. 4. For our numerical estimate of the broad band absorption of solar radiation in clear sky atmosphere due to dimers, we use the theoretically derived dimer concentration, C_1, and remember that, according to other authors, atmospheric concentration can be up to a factor of four higher. For graphical representation of the absorption, we consider all listed concentrations, C_1 to C_4, to demonstrate a possible range of results. There is great need to obtain high resolution theoretical absorption cross-sections and to use real atmosphere measurements to determine
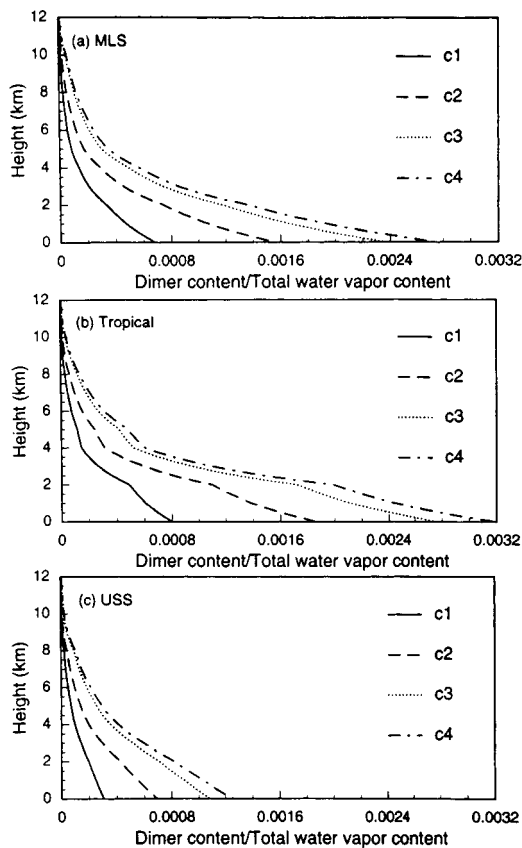
Fig. 4. Dimer concentrations using the four different estimates (C_1, C_2, C_3 and C_4) of the dimer mass mixing ratio in the midlatitude summer (MLS), tropical and US standard (USS) atmospheres.

experimentally the atmospheric dimer concentration. Until then, our results provide only an order of magnitude estimate of the possible dimer effect.

4. Absorption in clear sky atmosphere

The dimer absorption optical thickness, at wavenumber v, can be written in the form (Chylek and Geldart, 1997)

$$\tau_0(v) = (\mathrm{RH})WN_A\,C\sigma_D(v)/2M, \qquad (6)$$

where W is the water vapor column amount (g/cm^2), RH is the relative humidity, N_A is the Avogadro number, M the molecular weight of water, C the fraction of water molecules that are

in the form of dimer at 100% relative humidity and $\sigma_D(v)$ is the dimer absorption cross section and frequency v.

To calculate the absorption of solar radiation in the atmosphere, a radiation model developed by Fu and Liou (1992) was used. The radiative transfer scheme used is the delta-four-stream approximation which is applied to nonhomogeneous atmospheres. The gaseous absorption due to H_2O, CO_2, O_3, CH_4, and N_2O is parameterized using the correlated k-distribution approach. Surface albedo is taken to be 0.05. Atmospheric profiles of midlatitude summer, midlatitude winter, subarctic winter, tropical, and US standard atmospheres were used.

The optical depths of model midlatitude summer (MLS) and tropical atmospheres are shown in Fig. 5 for the cases when the atmospheres contain water vapor monomer only (a solid line), monomer and a dimer with the mass mixing ratio C_1 (a dotted line) and monomer and dimer with the mass mixing ratio C_4 (a dashed line). The optical depths of the US standard (USS) and subarctic winter (SAW) atmospheres are shown in Fig. 6. The integrated water vapor contents used are 2.94 cm for the MLS, 4.10 cm for the tropical, 1.42 cm for the USS and 0.42 cm for the SAW atmosphere. The dimer contribution to the atmospheric optical thickness is significant only in between major water vapor monomer absorption bands in the near infrared and visible part of the spectrum.

Fig. 7 shows the column broad band absorption of solar radiation under clear sky conditions as a function of the cosine of the solar zenith angle for the cases of selected models of the atmosphere using the discussed four estimates of the dimer concentrations. Considering the dimer concentration C_1 (eq. (2)), the effect of the water vapor dimer on atmospheric column absorption of solar radiation in clear sky atmosphere at high solar zenith angles is around 3 and 6 W/m^2 for the case of midlatitude summer and the tropical atmospheres. The dimer contribution is less than 1 W/m^2 for the cases of midlatitude winter, subarctic winter and US standard atmospheres.

The consideration of other dimer concentrations appearing in the published literature (C_2, C_3) and the concentration C_4 can increase the dimer absorption up to a factor of four. These higher clear sky dimer concentrations, however, lead to the absorption values that are not supported by
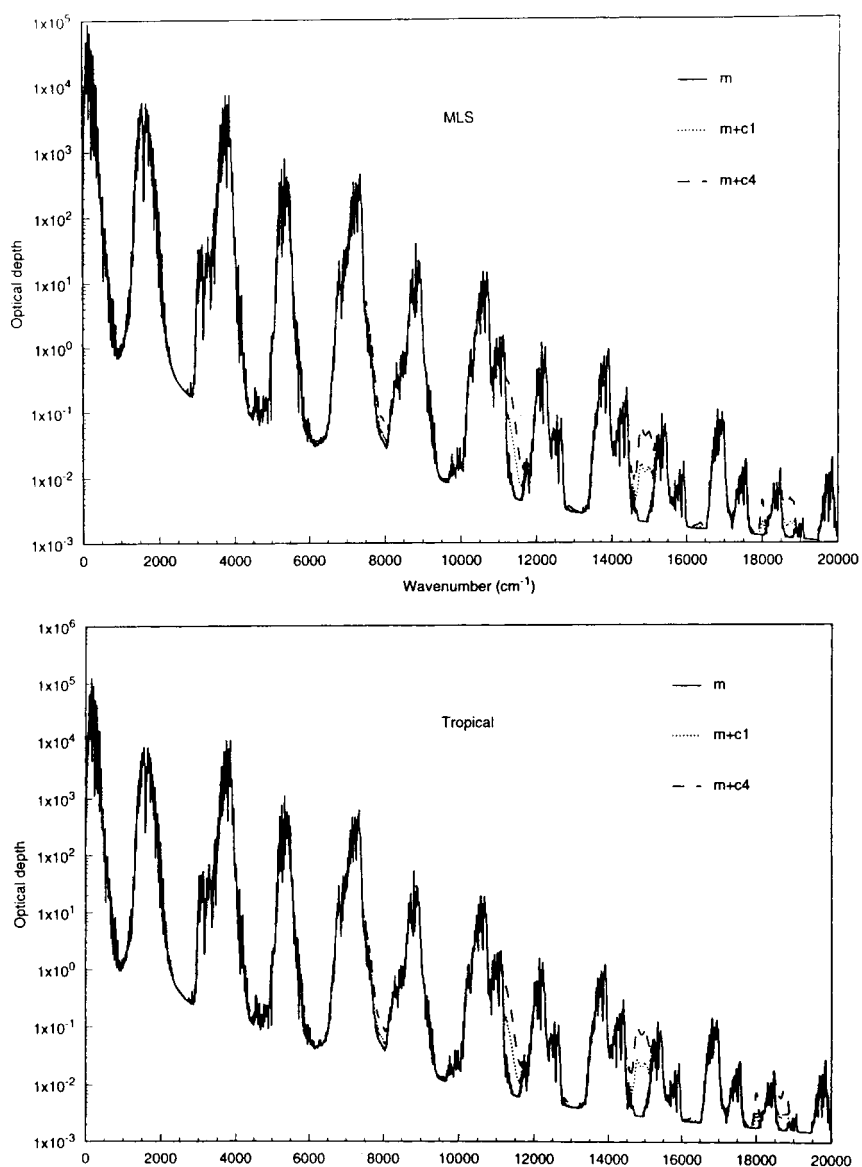
Fig. 5. Optical thickness of the clear sky atmosphere with and without water vapor dimer contribution for midlatitude summer (MLS) and the tropical atmospheres.

current atmospheric radiation measurements (Fu et al., 1998).

5. Summary and discussion

Using the first theoretical calculation of the water vapor dimer absorption cross-section (Tso et al., 1998) and an estimate of the dimer atmospheric concentration based on equilibrium thermodynamics, we conclude that the water vapor dimer contribution to the broad band column absorption of solar radiation in clear sky atmosphere is relatively modest, reaching about 3 and 6 W/m² for midlatitude summer and tropical atmosphere at the solar zenith angle of 30°. The
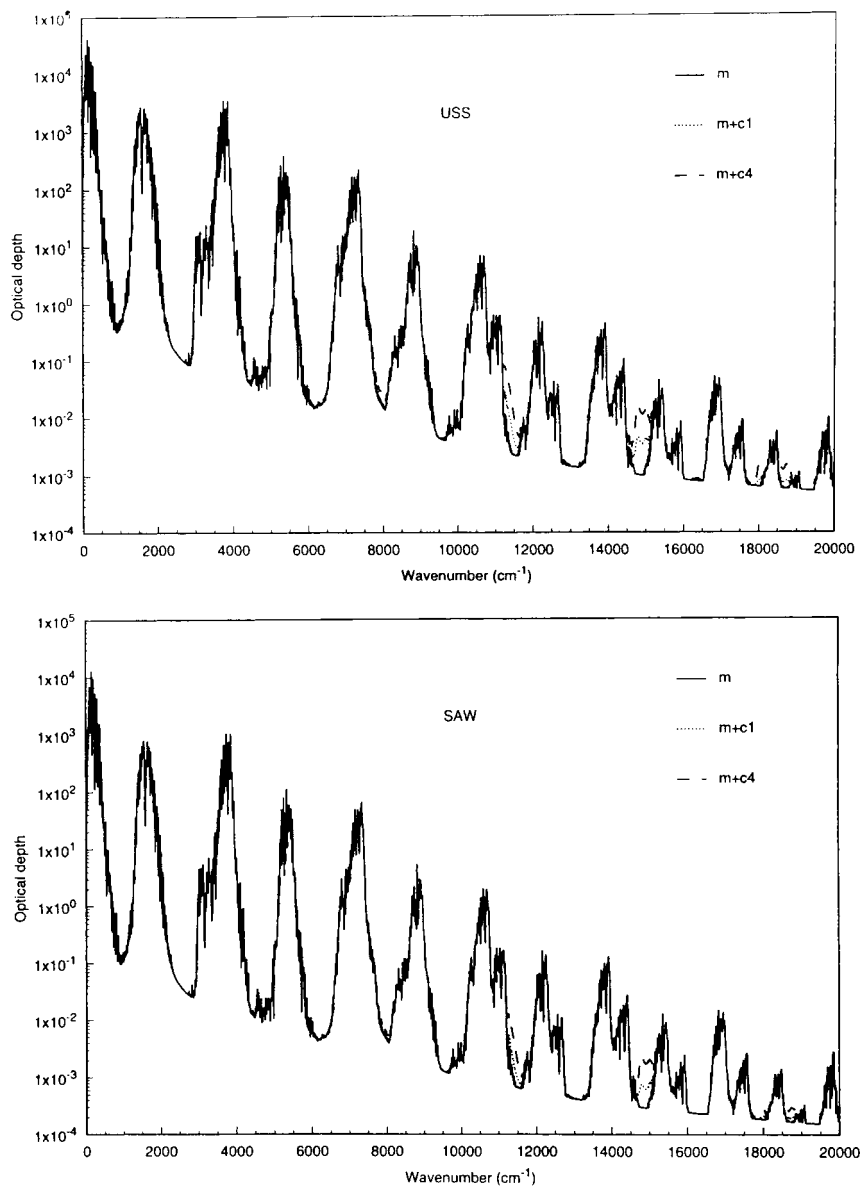
Fig. 6. Optical thickness of the clear sky atmosphere with and without water vapor dimer contribution for the US standard (USS) and subarctic winter (SAW) atmospheres.

dimer absorption is less than 1 W/m² in midlatitude winter, subarctic winter and the US standard atmospheres. This absorption is considerably lower than previous upper bound estimate (Chylek and Geldart, 1997) that did not take into the account the overlap between the water vapor dimer and monomer absorption bands.

The dimer is not the only water vapor cluster that is expected to exist in the atmosphere. Ab initio quantum chemistry study of small water vapor clusters (Xantheas, 1995) suggests that the binding energy of a water molecule within a trimer and tetramer may be two or three times as large as within a dimer. This would considerably
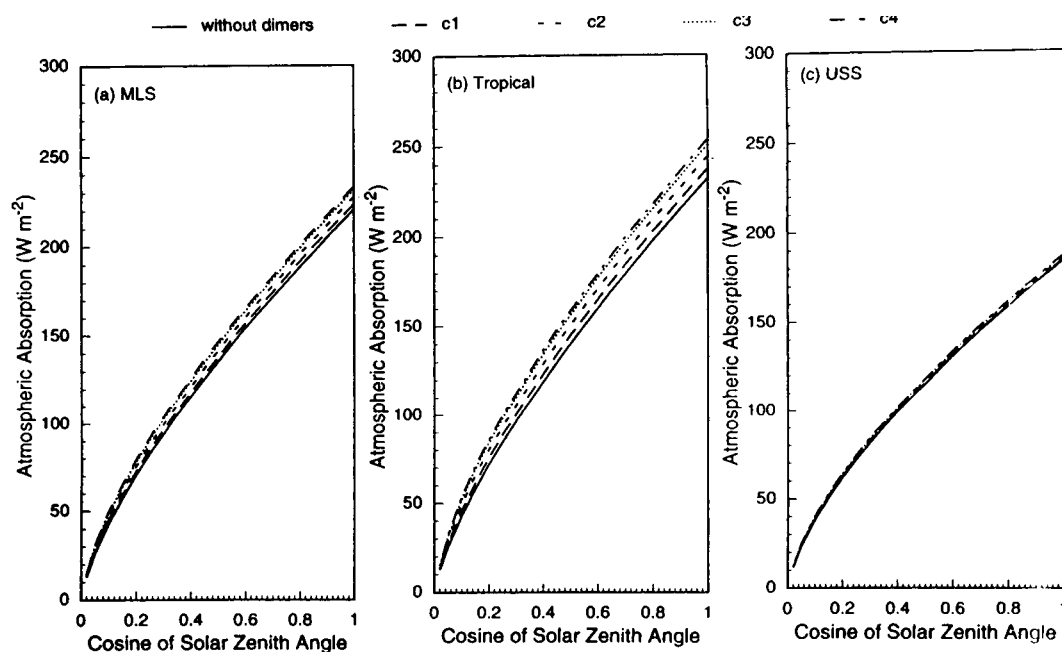
Fig. 7. Atmospheric absorption of solar radiation with and without water vapor dimers in midlatitude summer (MLS), tropical and US standard (USS) atmospheres as a function of cosine of the solar zenith angle. Numerical results were obtained using the Fu and Liou (1992) radiation code.

enhance their atmospheric concentrations. In some laboratory experiments (Paul et al., 1977) the observed concentrations of trimers and tetramers were higher than that of dimers. In addition a regular dodecahedral cluster structure (20 water molecules), or dodecahedral structure with an additional molecule trapped inside the cage (21 water molecules) were suggested to be relatively stable cluster configurations. Thus we expect these larger clusters to be present in the atmosphere as well with their absorption spectrum superimposed upon that of a dimer.

Theoretical calculations of Xantheas (1995) suggest that the fundamental bands corresponding to the water vapor bending modes and to the free O–H modes in clusters are shifted by less then $100 \, cm^{-1}$ with respect to monomer positions. On the other hand, the fundamental absorption stretching bands participating in the hydrogen bonding are redshifted by a larger amount. For the fundamental bands of trimer the red shift is between 300 and $400 \, cm^{-1}$; for the tetramer the shifts are between 400 and $600 \, cm^{-1}$. In higher

overtone bands these red shifts will be multiplied by the order of higher harmonics present. When we reach the spectral region of the fourth harmonic, around $18,000 \, cm^{-1}$, the shifts of bands of individual small clusters will spread the absorption over more than $2000 \, cm^{-1}$. Consequently a hierarchy of clusters in the atmosphere will produce a broad pseudo-continuum without any sharp spectral features that is not easy to observe. The infrared cavity ringdown laser absorption spectroscopy measurements (Paul et al., 1997) demonstrated that an ensemble of clusters of various sizes can produce a continuum absorption spectrum resembling that of liquid water or amorphous ice.

The current parameterization of water vapor absorption lines is done in a way to account for any absorption at solar and terrestrial wavelengths that may be produced by clusters. Consequently the cluster effect is already partially built in, in the form of absorption by wings of far away spectral lines. The current parameterization of the line wings accounts for both, the collisional line

broadening and cluster absorption. It is a pragmatic solution that, however, may not be based on real physics.

The concentration of water vapor dimers within water and ice clouds can be higher that the predictions of the equilibrium thermodynamics (eq. (1)) due to cluster formation during the evaporation and sublimation of small cloud droplets and ice crystals (Murad and Bochsler, 1987) and due to ice fragmentation processes (Crifo, 1990). These processes which can enhance the concentration of dimers and larger water vapor clusters (Carlon 1979, 1984) within the clouds are not currently well understood.

Other atmospheric dimers like $H_2O \cdot O_2$, $H_2O \cdot N_2$, $H_2O \cdot O_3$, $O_2 \cdot O_2$, $O_2 \cdot N_2$ and $H_2O \cdot NO_x$ will also contribute to the absorption of solar radiation in the atmosphere. The magnitude of most of these contributions is not currently known. The recent estimate (Solomon et al., 1998) of solar clear sky absorption by collision pairs of $O_2 \cdot O_2$ and $O_2 \cdot N_2$ is between 2 and 3 W/m². The existence of dimers ($H_2O \cdot H_2O$, $CO_2 \cdot CO_2$ and $H_2 \cdot N_2$) was also suggested to explain the observed spectral features in atmospheres of other planets (Fox and Kim, 1988) and comets (Crifo, 1990).

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