

Atmospheric water vapor complexes and the continuum

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Received 23 October 2003; revised 9 January 2004; accepted 20 February 2004; published 24 March 2004.

[1] Estimates of absorption optical depths for the bound complexes $\text{H}_2\text{O}-\text{H}_2\text{O}$ and the sum of $\text{H}_2\text{O}-\text{N}_2$, $\text{H}_2\text{O}-\text{O}_2$, and $\text{H}_2\text{O}-\text{Ar}$ at visible and near-infrared wavelengths are compared to the same quantities calculated from a frequently used water continuum parameterization (MT_CKD) and from a theoretical far wing water vapor lineshape theory. The temperature dependences of some of these optical depths are also compared. The comparisons suggest qualitatively that water complexes may contribute to the continuum at these wavelengths, and show that the temperature dependence of the continuum might provide insight into the role of the complexes in the atmosphere. Because of the dearth of laboratory measurements of the continuum at these wavelengths, and because the current estimates for the equilibrium constants of these water vapor complexes remain highly uncertain, more observations are needed before the importance of water complexes can be accurately quantified. *INDEX TERMS:* 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 3359 Meteorology and Atmospheric Dynamics: Radiative processes. *Citation:* Daniel, J. S., S. Solomon, H. G. Kjaergaard, and D. P. Schofield (2004), Atmospheric water vapor complexes and the continuum, *Geophys. Res. Lett.*, *31*, L06118, doi:10.1029/2003GL018914.

1. Introduction

[2] The water vapor continuum was observed more than half a century ago by *Elsasser* [1938], who noted inconsistencies between his theoretical calculations of water vapor absorption and measurements discussed in *Hettner* [1918], particularly around 1000 cm^{-1} . Since then numerous continuum observations have been reported in microwave and infrared wavelength regions. More details concerning the history of the continuum are available elsewhere [*Tipping and Ma*, 1995, and references therein]. The physical mechanism or mechanisms giving rise to the continuum have long been debated. Observations show that the continuum is dependent upon pressure, and that both water-water ('self-broadening') and water-x ('foreign-broadening', where 'x' can be any other atmospheric gas) interactions must be considered to fully describe the pressure dependence of the absorption features. It is possible that more than one mechanism could contribute, and that different mechanisms could operate in different wavelength regions. For example, the pure rotational

transitions at far-infrared wavelengths could be dependent upon different physical interactions than the ro-vibrational transitions found in the near-infrared.

[3] It has been suggested that the continuum may be caused by the far wings of allowed transitions of the water vapor monomer. The theory used to estimate the line shapes further from line centers is often referred to as 'far wing theory' and has been shown to describe the observed far wing self-and foreign-continuum accurately from $300\text{--}1000\text{ cm}^{-1}$ [*Cormier et al.*, 2002; *Davies et al.*, 1982; *Ma and Tipping*, 2000; *Ma and Tipping*, 2002; *Rosenkranz*, 1985]. Another proposed cause of the water vapor continuum is the presence of bound water complexes. There has been particular interest in the temperature dependence of the observed absorption near $1,200\text{ cm}^{-1}$, which is consistent with water dimer absorption at temperatures below around 350 K and with collision broadening dominating above about 400 K [*Loper et al.*, 1983; *Montgomery and Paul*, 1978; *Varanasi*, 1988]. A third potential contributor to the continuum is metastable complexes, molecular interactions that can affect absorption properties but do not result in the formation of bound complexes. It is thought that the number of these interactions may be large at atmospheric conditions [*Epifanov and Viganin*, 1997] with the band width being affected by the duration of the molecular interaction. This third process will not be considered further in this work due to uncertainties in the absorption cross sections.

[4] Because of the uncertainty in the cause of the continuum, the semi-empirical Clough-Kneizys-Davies (CKD) continuum model [*Clough et al.*, 1989] is implemented by the majority of atmospheric radiative transfer calculations that account for the water vapor continuum [*Soden et al.*, 2000]. The most recent version, and the one used in the comparisons here, is referred to as the MT_CKD continuum; it differs from previous versions in that it includes an empirical collision-induced component in addition to a line shape component [*Mlawer et al.*, 2004]. Because only a few continuum observations have been made in the visible and near-infrared, semiempirical models at these wavelengths have generally relied upon extrapolations from longer wavelengths where more data is available. By comparing to narrowband radiometer observations of a narrowband radiometer used in the Atmospheric Radiation Measurement Enhanced Shortwave Experiment (ARESE), *Vogelmann et al.* [1998] found that the CKD continuum (version 2.2) is likely too large in the 950 nm region. This is consistent with the results of *Sierk et al.* [2004], in which spectral atmospheric continuum estimates from direct sun observations were used to conclude that the MT_CKD continuum exhibits a similar spectral shape but a larger magnitude by

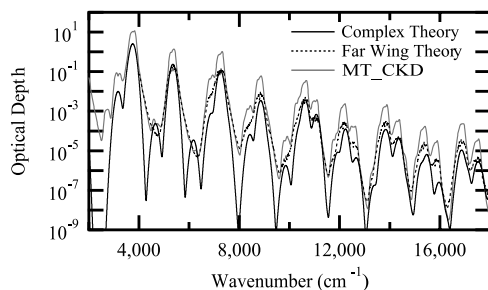


Figure 1. Comparison of optical depths from MT_CKD (gray curve) and the theoretical far wing (dashed curve) foreign water vapor continua with those of H₂O-O₂, H₂O-N₂, and H₂O-Ar (black curve).

about 50% in this wavelength region (about 100% for CKD version 2.4.1). *Sierk et al.* [2004] also found that the MT_CKD parameterization underestimates the continuum absorption in the 720 nm band by about 40%, while CKD version 2.4.1 demonstrates good agreement. Furthermore, it has been suggested that water dimer absorption may be implicitly included in the CKD continuum model based on laboratory observations between 5,000 and 5,600 cm⁻¹ [Ptashnik et al., 2004].

[5] There is thus a need to consider information that may help to identify the mechanisms and processes that could contribute to the continuum, particularly in the visible and near-infrared regions where the greatest uncertainty in the magnitude of the continuum is likely to be found. In this work, by comparing estimates of the absorption optical depths of H₂O-H₂O, H₂O-N₂, H₂O-O₂, and H₂O-Ar both to far wing theory and to MT_CKD estimates of the foreign and self water vapor continua, we probe the potential importance of these complexes. Uncertainties in abundance estimates and in knowledge of the vibrational band shapes [Kjaergaard et al., 2003] are currently very large, so that a fully quantitative analysis is not possible at present. However, using current information to estimate water complex absorption optical depths we will show that these species should be considered possible contributors to the water vapor continuum at visible and near-infrared wavelengths, meriting further laboratory and field measurements.

2. Water Complex Absorption

[6] The existence of water complexes is well established. Indeed, several have been directly observed at microwave and infrared wavelengths in molecular beam and cold matrix experiments [Cohen and Saykally, 1993; Leung et al., 1989; Perchard, 2001; Peterson and Klemperer, 1984; Schofield and Kjaergaard, 2003 and references therein]. Hence, the outstanding issues involve quantifying the number of the complexes found in the atmosphere and how strongly those complexes absorb across a range of wavelengths from the visible to the millimeter-wave regime.

[7] With regard to the abundance of complexes, we estimate equilibrium constants employing an equilibrium statistical mechanics approach. The approach to the calculations and comparisons to other reported values can be found in Kjaergaard et al. [2003]. As an example, the equilibrium constants calculated for the water dimer at 296 K and 260 K are 0.011 atm⁻¹ and 0.024 atm⁻¹,

respectively. Spectral absorption is also estimated here from theoretical considerations. In particular, vibrational band frequencies are calculated for the OH-stretching and HOH-bending fundamental and overtone regions, as explained in Kjaergaard et al. [1994] and Schofield and Kjaergaard [2003]. Both transition strengths and positions are calculated using a harmonically coupled anharmonic oscillator local mode model with necessary parameters obtained from *ab initio* methods.

[8] Even using the most complete information concerning the water complexes, large uncertainties remain in estimates of their atmospheric importance, due to uncertainties in absorption cross section lineshapes [Kjaergaard et al., 2003] and in the the previously mentioned abundance calculations [see also Schenter et al., 2002]. The uncertainties in the calculated positions and integrated oscillator strengths of the water complex transitions are thought to be less significant in light of their favorable comparisons to observations [Low and Kjaergaard, 1999; Pfeilsticker et al., 2003; Schofield and Kjaergaard, 2003]. Some past attempts to measure the absorption due to the water dimer in the visible and near-infrared have been unsuccessful [Daniel et al., 1999; Hill and Jones, 2000], but the positions and strengths of the dimer transitions considered in these studies may have been inaccurate [Low and Kjaergaard, 1999]. More recently, using long-path spectroscopic measurements Pfeilsticker et al. [2003] believe they have positively identified a water dimer absorption feature at about 749.5 nm, which is in broad agreement with the combination of a the measured equilibrium constant of Curtiss et al. [1979] and theoretical absorption predictions [Low and Kjaergaard, 1999; Schofield and Kjaergaard, 2003].

3. Comparisons

[9] In Figure 1, we compare absorption optical depth estimates for H₂O-O₂, H₂O-N₂, and H₂O-Ar complexes calculated using the techniques described in section 2 from both the semi-empirical MT_CKD foreign continuum and the far wing line shape theory for H₂O-N₂ interactions [Ma and Tipping, 2000]. Optical depth estimates for H₂O-H₂O are compared to the MT_CKD and far wing theory [Ma and Tipping, 2002] self continuum estimates in Figure 2. The temperature for these comparisons is assumed to be 296K, the water vapor volume mixing ratio is 0.01, the total pressure is 1000 mb, and the path length is 1 km. We make no statement about the weak absorption between bands because of the uncertainties in the absorption band shapes of the complexes. Rather, we emphasize the broadband behavior of the integrated cross section of the bands.

[10] The similarity in the spectral shapes of the foreign continua and the water complexes is apparent in Figure 1 for an assumed Gaussian band shape with a full-width-half-maximum (FWHM) of 200 cm⁻¹ applied to the transitions of the complexes. The complexes H₂O-N₂ and H₂O-O₂ both contribute significantly to the total estimated water complex absorption, with H₂O-Ar estimated to play a lesser role, contributing between 5–10% of the total. The optical depths of the complexes are less than those of the MT_CKD parameterization and are similar in magnitude and shape to those of the far wing line shape theory but fall off slightly faster with increasing energy. However, the far wing theory

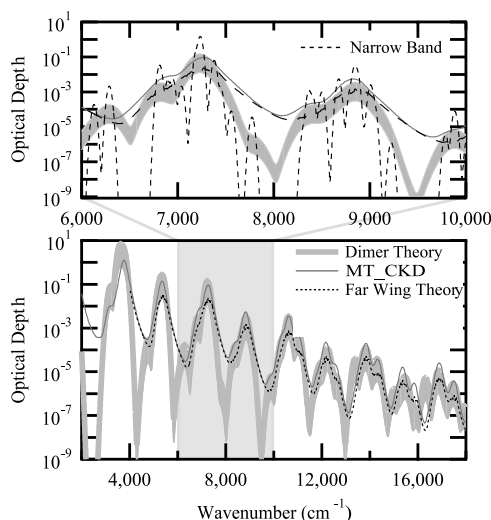


Figure 2. Same as Figure 1 but for the self continua and H₂O-H₂O optical depths. The shaded region represents a range of equilibrium constants from 0.01 to 0.12 atm⁻¹. Top panel expands the 6,000 to 10,000 cm⁻¹ region and includes dimer calculations assuming a narrower, 40 cm⁻¹ FWHM.

was developed to explain the far wings of the water monomer lines and is not expected to be as accurate near band centers. Table 1 quantifies the comparison between the integrated optical depths of the water complexes and the MT_CKD continuum in nine energy regions between 2,600 to 18,000 cm⁻¹. The absorption optical depths of the water complexes are estimated to be between 4% and 20% of the MT_CKD continuum with better agreement generally occurring at lower energies.

[11] In the lower panel of Figure 2, the broad agreement among the self continua and water dimer calculations is again apparent. However, there are a few dimer features not associated with water monomer bands, and thus not associated with any far wing continuum features. Three of these features have been suggested as possible locations to observe the dimer [Schofield and Kjaergaard, 2003], and indeed the feature at 13,401 cm⁻¹ (mistakenly written as the 13,810 cm⁻¹ transition in the text of Schofield and Kjaergaard [2003]) is the one believed to have been observed in the atmosphere [Pfeilsticker et al., 2003]. In

Table 1. Integrated Optical Depths Calculated From Water Complex Theory Divided by Those From the MT_CKD Parameterization

Energy Region (cm ⁻¹)	Water Dimer Strength Divided by Self Component	Water Complex ^a Strength Divided by Foreign Component
2,600–4,900	0.57	0.20
4,900–5,900	0.17	0.16
5,900–7,900	0.11	0.10
7,900–9,500	0.05	0.06
9,500–11,500	0.08	0.11
11,500–13,000	0.05	0.05
13,000–14,900	0.07	0.07
14,900–16,300	0.05	0.04
16,300–18,000	0.05	0.05

^aIncluding H₂O-N₂, H₂O-O₂, and H₂O-Ar.

the upper panel of Figure 2, an additional curve (dashed line) shows the dimer optical depths expanded between 6,000 and 10,000 cm⁻¹ when a Gaussian band shape with a FWHM of 40 cm⁻¹ is applied. This clearly shows that the band width does have important implications to both the detection of and absorption by the complexes.

[12] The peak cross section values for the dimer represent about 5% to 57% of the MT_CKD continuum with better agreement at lower energies, as shown in Table 1, and is nearly independent of the Gaussian width chosen. If the higher equilibrium constants of Goldman et al. [2001] are used, our dimer calculations imply integrated optical depths 60% to 660% of the MT_CKD continuum. The dimer observation of Pfeilsticker et al. [2003] combined with the calculated cross sections of Low and Kjaergaard [1999] suggests that our calculated equilibrium constants are too low and that those calculated by Goldman et al. [2001] are too large; hence, the most appropriate optical depths would fall somewhere in between. This finding is supported by the observations of Ptashnik et al. [2004].

[13] Next we compare the temperature dependence of the water dimer with other continua optical depths. The ratio of the water dimer optical depths at 296 K relative to 260 K is compared to the same quantities for the MT_CKD self continuum and the far wing self continuum in Figure 3. For both temperature cases, the pressure, H₂O volume mixing ratio, and pathlength are assumed to be 1000 mb, 0.002, and 1 km, respectively. While the dimer exhibits a significant temperature dependence, this is due to the changing equilibrium constant with temperature, and so the optical depths notably demonstrate none of the spectral variation found in the MT_CKD and far wing continua. This spectral invariance arises from our assumption, made because of the lack of better knowledge, that the dimer vibrational band shape and width are temperature independent. For both the self and foreign continua, we are aware of no observations yet made in the visible/near-infrared wavelength regions that can quantify the nature of the temperature dependence. When such observations are available, comparisons such as these could help identify a preferred theory. We do not show temperature dependences for the other complexes because the spectral changes are not independent of the highly uncertain band shape.

4. Conclusions

[14] We have made comparisons of the calculated absorption optical depths due to water complexes with

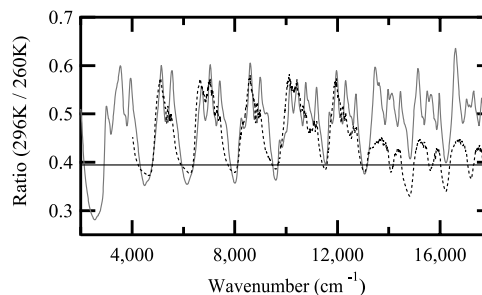


Figure 3. Ratio of optical depths at 296 K to 260 K for the MT_CKD (gray curve) and theoretical far wing (dashed curve) self continua and the water dimer theory (black curve).

current estimates of the self and foreign continua at visible and near-infrared wavelengths. The comparisons are largely qualitative rather than quantitative due to the large uncertainty in the complexes' equilibrium constants and the dearth of laboratory and atmospheric observations confirming the magnitude and shape of the continuum. However, the results of this study suggest that the water dimer and other water complexes cannot be discounted as playing a role in the observed water continuum at these wavelengths. The comparisons also suggest that due to differences among the complex/continua estimates, temperature dependence and its spectral character would be a useful place to focus laboratory observations aimed at discriminating among possible theories.

[15] **Acknowledgments.** We are grateful to R. H. Tipping, T. W. Robinson and D. L. Howard for helpful discussions. We are grateful to the National Oceanic and Atmospheric Administration, the Marsden Fund, administered by the Royal Society of New Zealand, and the University of Otago for financial support. JSD would like to thank the Department of Chemistry at the University of Otago for its kind hospitality during this work.

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