Collision-Induced Effects and the Water Vapor Continuum

E. J. Mlawer, S. A. Clough, and P. D. Brown
Atmospheric and Environmental Research, Inc.
Cambridge, Massachusetts

D. C. Tobin
University of Wisconsin
Madison, Wisconsin

Introduction

Continuum absorption by water vapor in the longwave spectral region plays a key role in the radiation balance of the earth. In the past, there has been debate concerning the form of water vapor responsible for this absorption. This debate was resolved in the 1980s with the development of the CKD continuum model (Clough et al. 1989), which was based upon a water vapor monomer lineshape formalism applied to all spectral regions from the microwave to the shortwave. This continuum model has since been validated and improved (Brown et al. 1998) using a large number of high-resolution spectral observations associated with a wide range of atmospheric conditions, most notably those measurements taken with the atmospheric emitted radiance interferometer (AERI; Revercomb et al. 1997) at the Southern Great Plains (SGP) site of the Atmospheric Radiation Measurement (ARM) Program. The ability of the CKD model to accurately account for these numerous spectral observations indicates that it has the correct scaling with respect to water vapor abundance, pressure, and temperature, and has effectively ended speculation that there is significant longwave continuum absorption due to water vapor dimers or multimers.

The revisions that have been made to the CKD model improved selected spectral regions of the model's foreign- and self-broadened water vapor continua but did not alter its basic formalism. In this formalism, the two continua are defined as a sum over all water vapor lines using a semi-empirically determined lineshape (minus the contribution from the Lorentz lineshape close to the line center). A consequence of the semi-empirical nature of these lineshapes, in which the coefficients were determined by a least-squares procedure using laboratory data, is that certain properties of the lineshape are not consistent with a proper physical model. This represents a clear shortcoming in the CKD continuum model. In addition, new measurements, both from the laboratory (Tobin et al. 1996) and the field (Tobin et al. 1998), have surpassed the older measurements in resolution and spectral coverage and have indicated that the continuum has spectral features heretofore unseen. It is not possible to revise the CKD model using a lineshape formalism in a way that suitably fits these new features. For these reasons, coupled with new requirements placed on water vapor continuum modeling by current remote sensing needs, a revised formulation for the water vapor continuum has been developed.

This paper presents preliminary results from a revised formulation for the foreign continuum. Even though the formulation presented is not derived from first physical principles, there is a clear physical interpretation for each component of the revised continuum. The continuum obtained from this modified formulation provides substantially better agreement with the Tobin laboratory and field data than previous versions of the CKD model.

The CKD Continuum Formulation

The definition of the water vapor continuum used for this work is any observed absorption not attributable to the local line contribution. (The local lineshape is defined as the Lorentz lineshape within 25 cm^{-1} of the line center, minus the value of the Lorentz lineshape at 25 cm^{-1}, and is equal to zero elsewhere.)

The CKD continuum followed the development of the Van Vleck-Huber lineshape formalism (Van Vleck and Huber 1977)

$$k(\upsilon) = \upsilon \tanh(h\upsilon/2kT) \left\langle \phi(\upsilon) + \phi(-\upsilon) \right\rangle, \qquad (1)$$

where $\left\langle \phi(\upsilon) + \phi(-\upsilon) \right\rangle$, the symmetrized power spectral density function, is equal to the Fourier transform of the autocorrelation function of the dipole moment operator, and υ is the frequency. This lineshape has the important properties that it is applicable to all spectral domains and that, in thermal equilibrium, absorption, and emission are equal for an arbitrary spectral interval.

If the unphysical assumption is made that the broadening collision occurs instantaneously (at t=0), which is referred to as the impact approximation, then the symmetrized power spectral density function becomes

$$\langle \phi(\upsilon) + \phi(-\upsilon) \rangle = \sum_i \frac{\tilde{S}_i}{\pi} \left[\frac{\alpha_i}{(\upsilon - \upsilon_i)^2 + \alpha_i^2} + \frac{\alpha_i}{(\upsilon + \upsilon_i)^2 + \alpha_i^2} \right] \qquad (2)$$

where $\tilde{S}_i$ is the line intensity, υ_i is the line center, α_i is the halfwidth, and the sum is over all water vapor lines. A comparison between the water vapor continuum resulting from the impact approximation and the laboratory data of Burch and collaborators (Burch 1981; Burch and Alt 1984; Burch 1985) indicates that the impact approximation continuum is too weak in regions near the band center and too strong in between bands. Even without this poor agreement with data, the highly unphysical impact approximation, which leads to discontinuities at t=0 in all derivatives of the autocorrelation function of the dipole moment operator, would make a poor candidate for a theoretical basis on which to base the continuum.

The discontinuities at t=0 in the autocorrelation function can be avoided if the far wings decay at least exponentially. If the impact approximation autocorrelation function is modified as in Anderson and Weiss (1953) to account for noninstantaneous collisions, then the symmetrized power spectral density function becomes

$$\langle \phi(\upsilon) + \phi(-\upsilon) \rangle = \sum_i \frac{\tilde{S}_i}{\pi} \left[\frac{\alpha_i}{(\upsilon - \upsilon_i)^2 + \alpha_i^2} \chi(\upsilon - \upsilon_i) + \frac{\alpha_i}{(\upsilon + \upsilon_i)^2 + \alpha_i^2} \chi(\upsilon + \upsilon_i) \right] \qquad (3)$$

where the χ-function is given by

$$\chi(\upsilon - \upsilon_i) = A \exp\left[-t_d^2 (\upsilon - \upsilon_i)^2 \right] \qquad (4)$$

where t_d represents a small duration of collision. In Eq. (4), A is a constant trivially greater than unity, chosen to leave the integral of the lineshape unchanged from the value obtained using the Lorentz lineshape. It is possible to choose a value of t_d that gives agreement in between water vapor bands between the continuum associated with Eqs. (3) and (4) and the Burch data, a result of satisfying the need for the lineshape to have appropriate sub-Lorentzian behavior in the far wings. However, employing this more physical lineshape does nothing to increase the in-band absorption of the continuum, as required by the laboratory data.

This issue was addressed in the development of the initial version of the CKD continuum model, CKD_0, by treating the χ-function as semi-empirical: constrained to have Gaussian decay in the far wings with its other properties determined by minimizing the error of the continuum relative to the Burch data. The result of this least-squares procedure for the foreign water vapor continuum was

$$\tilde{C}(\upsilon) = \sum_i \tilde{S}_i \left[f_c(\upsilon - \upsilon_i) \chi'(\upsilon - \upsilon_i) + f_c(\upsilon + \upsilon_i) \chi'(\upsilon + \upsilon_i) \right], \qquad (5)$$

where $f_c(\upsilon\text{-}\upsilon_i)$ is the Lorentz lineshape with the local lineshape removed and

$$\chi'(\upsilon - \upsilon_i) = A \exp\left[-\left(\frac{\upsilon - \upsilon_i}{75 \text{ cm}^{-1}} \right)^2 \right] \qquad (6)$$

with A = 6.65. (The χ'-function obtained for the self-continuum has a slightly more complicated form.) The resulting lineshape is super-Lorentzian within 100 cm^{-1} of line center, and sub-Lorentzian further away, causing a net increase in the integrated absorption coefficient for an arbitrary line of ~0.3%, a small, but non-trivial amount. The continuum defined by Eqs. (5) and (6) is shown by the dashed curve in Figure 1 for the longwave spectral region. Also shown are the laboratory data due to Burch.

The continuum resulting from Eqs. (5) and (6) is often inappropriately referred to as a far-wing continuum. However, both the intermediate and far wings of the lineshape contribute non-negligibly to the continuum, with the region within 25 cm^{-1} of line center for a given line responsible for approximately two-thirds of its integrated continuum absorption coefficient.

The general agreement between the model and available data, including subsequent validations with field data (Brown et al. 1998) for a variety of conditions, has conclusively established that the observed continuous absorption features due to water vapor are attributable to the water vapor monomer. To improve the agreement with field observations, empirical adjustments in limited spectral regions have been made to the continuum generated by

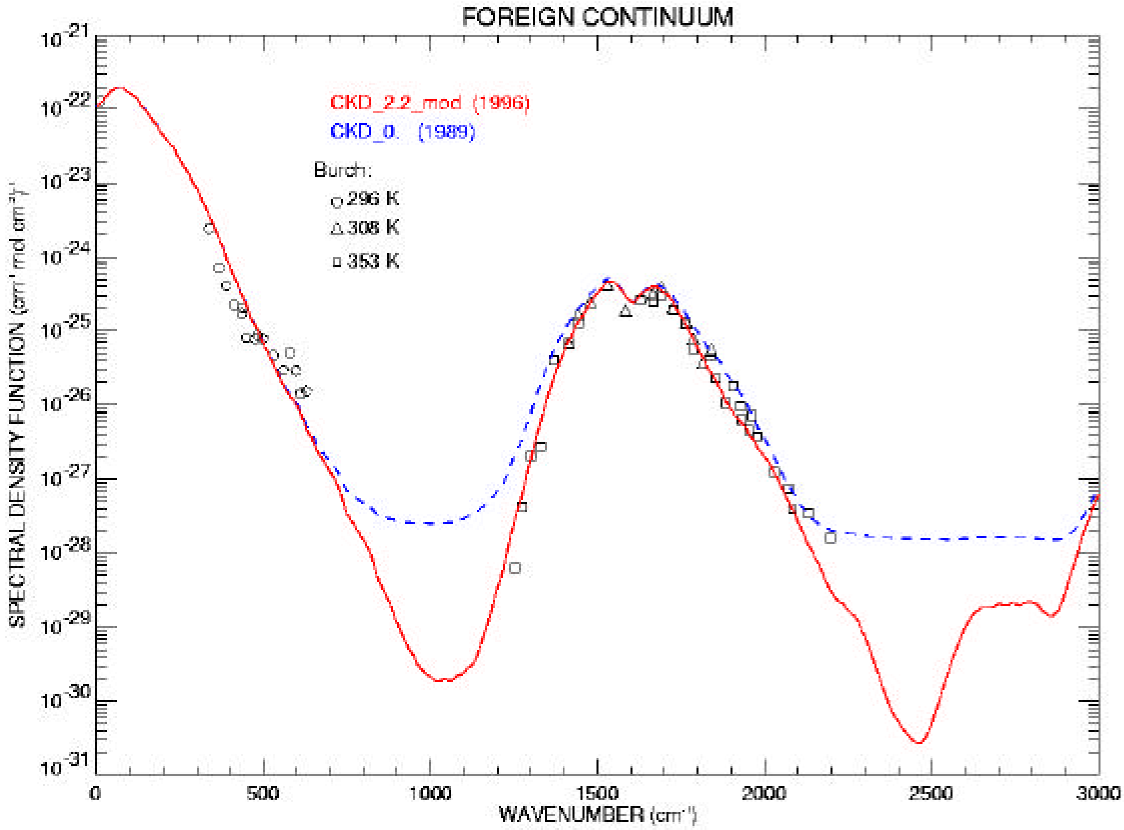

Figure 1. The CKD_0 (dashed) and CKD_2.2_mod (solid) foreign water vapor continuum models for the longwave spectral region. Also shown are the laboratory measurements due to Burch. (For a color version of this figure, please see *http://www.arm.gov/docs/documents/technical/conf_9803/mlawer-98.pdf*.)

Eqs. (5) and (6) (and the corresponding self-continuum), as indicated by the solid curve in Figure 1. However, a proper formulation that takes into account this field data has not been developed for the continuum until the present work.

New Data

Using a Fourier transform spectrometer, Tobin et al. (1996) performed measurements of the foreign- and self-broadened continua within the υ_2 band of water vapor (~1300 cm^{-1} to 2050 cm^{-1}). Because their spectra were recorded at a higher resolution (0.040 cm^{-1}) than used by Burch, in addition to verifying the accuracy of Burch's data at the original frequencies, the Tobin measurements were able to probe in narrower microwindows between the lines in the band than had been done before. For the repeated spectral elements, there was general agreement between the two sets of measurements. However, the Tobin measurements in narrower microwindows indicated that the foreign- and self-continua had greater spectral content than had been observed formerly. These higher-frequency spectral features, located in proximity to water vapor line centers, provide evidence that there is significantly greater absorption near line center than had been believed previously.

In addition to this laboratory data, Tobin et al. (1998) have obtained values for water vapor continuum coefficients as a result of measurements taken with an extended spectral range AERI at the Surface Heat Budget of the Arctic Ocean (SHEBA) ice station (Moritz et al. 1993). Most importantly, these measurements indicate that the CKD foreign continuum is too great from 380 cm^{-1} to 500 cm^{-1}. An additional implication of these observations is that the foreign continuum has little or no temperature dependence, in agreement with the CKD formulation.

The Modified Continuum Formulation

For a continuum formulation to provide agreement with all available observations and have a sound physical basis, it must possess

- a component of a form similar to Eqs. (5) and (6), but with A=1, to account for the intermediate and far wings of allowed transitions.
- a high-frequency component near line center to provide agreement with the data from Tobin et al. (1996).
- a low-frequency component to provide agreement at the centers of the pure rotation and υ_2 bands, where few spectral lines exist.

It is important to note that these three components must be added together in this formulation, in contrast to the multiplicative approach used previously [as indicated in Eq. (5)]. Although the physical source of the third term is unclear, its scaling with collider density and its slowly varying spectral behavior with an absence of features resembling rotational transitions are suggestive of a short-lived complex of water vapor and a colliding molecule. Constraining the lineshape components to have these properties and employing a least-squares technique with the data mentioned above [microwave measurements were also used (Rosenkranz 1998)], the following continuum formulation was attained:

$$\tilde{C}(\upsilon) = \tilde{C}_0(\upsilon) + \tilde{C}_1(\upsilon) + \tilde{C}_2(\upsilon) \quad (7)$$

$$\tilde{C}_0(\upsilon) = \sum \tilde{S}_i \; f_c(\upsilon - \upsilon_i) \exp\left[-\left(\frac{\upsilon - \upsilon_i}{b}\right)^2\right] + (\upsilon \to -\upsilon) \quad (8)$$

$$\tilde{C}_1(\upsilon) = \sum_i \gamma_1(\upsilon_i - \upsilon_{i,band}) \tilde{S}_i \frac{\alpha_1}{(\upsilon - \upsilon_i)^2 + \alpha_1^2} \exp\left[-\left(\frac{\upsilon - \upsilon_i}{b_1}\right)^2\right] + (\upsilon \to -\upsilon) \quad (9)$$

$$\tilde{C}_2(\upsilon) = \sum_i \gamma_2(\upsilon_i - \upsilon_{i,band}) \tilde{S}_i \frac{\alpha_2}{(\upsilon - \upsilon_i)^2 + \alpha_2^2} \exp\left[-\left(\frac{\upsilon - \upsilon_i}{b_2}\right)^2\right] + (\upsilon \to -\upsilon) \quad (10)$$

where the Lorentz halfwidths, α_1 and α_2, have values of 0.6 cm^{-1} and 45 cm^{-1}, respectively, and the Gaussian decay widths b, b_1, and b_2 are given by 110 cm^{-1}, 450 cm^{-1}, and 70 cm^{-1}, respectively. In Eqs. (9) and (10), the functions $\gamma_1(\upsilon_i\text{-}\upsilon_{i,band})$ and $\gamma_2(\upsilon_i\text{-}\upsilon_{i,band})$ are given by

$$\gamma_1(\upsilon_i - \upsilon_{i,band}) = 0.03 \exp\left[-\left(\frac{\upsilon_i - \upsilon_{i,band}}{270\ \mathrm{cm}^{-1}}\right)^2\right] \quad (11)$$

$$\gamma_2(\upsilon_i - \upsilon_{i,band}) = 0.02 \exp\left[-\left(\frac{\upsilon_i - \upsilon_{i,band}}{150\ \mathrm{cm}^{-1}}\right)^2\right], \quad (12)$$

where $\upsilon_{i,band}$ is the center of the vibrational band containing the line centered at υ_i. The presence of the terms γ_1 and γ_2, which are essential in attaining agreement with the data, causes the collision-induced terms to be stronger near the center of the vibrational band. This is suggestive of a "hindered rotor" effect, in which the interaction between the water vapor molecule and the colliding molecule is more effective in causing a transition when the radiating molecule is in a lower rotational state.

Figure 2 shows the Tobin laboratory data, the fitted foreign continuum given by Eqs. (7) through (12), and its three functional components for the υ_2 band of water vapor. This figure clearly demonstrates the high-frequency nature of the continuum measurements and the effectiveness of the fit in reproducing this behavior. Figure 3 shows the data, the revised continuum, and a recent version of the CKD continuum for a 250 cm^{-1} segment of the center of this band. For the entire υ_2 band, the error relative to the laboratory data is a factor of 5 lower with the modified formulation. Figure 4 shows the revised model applied in the pure rotation band of water vapor, and shows the improved agreement with data compared with CKD_0. It is important to note that, due to the consistency of the data from the microwave, pure rotation band, and υ_2 band used in the fitting procedure, the equations defining the revised continuum are able to provide agreement with this data in a natural and straightforward way.

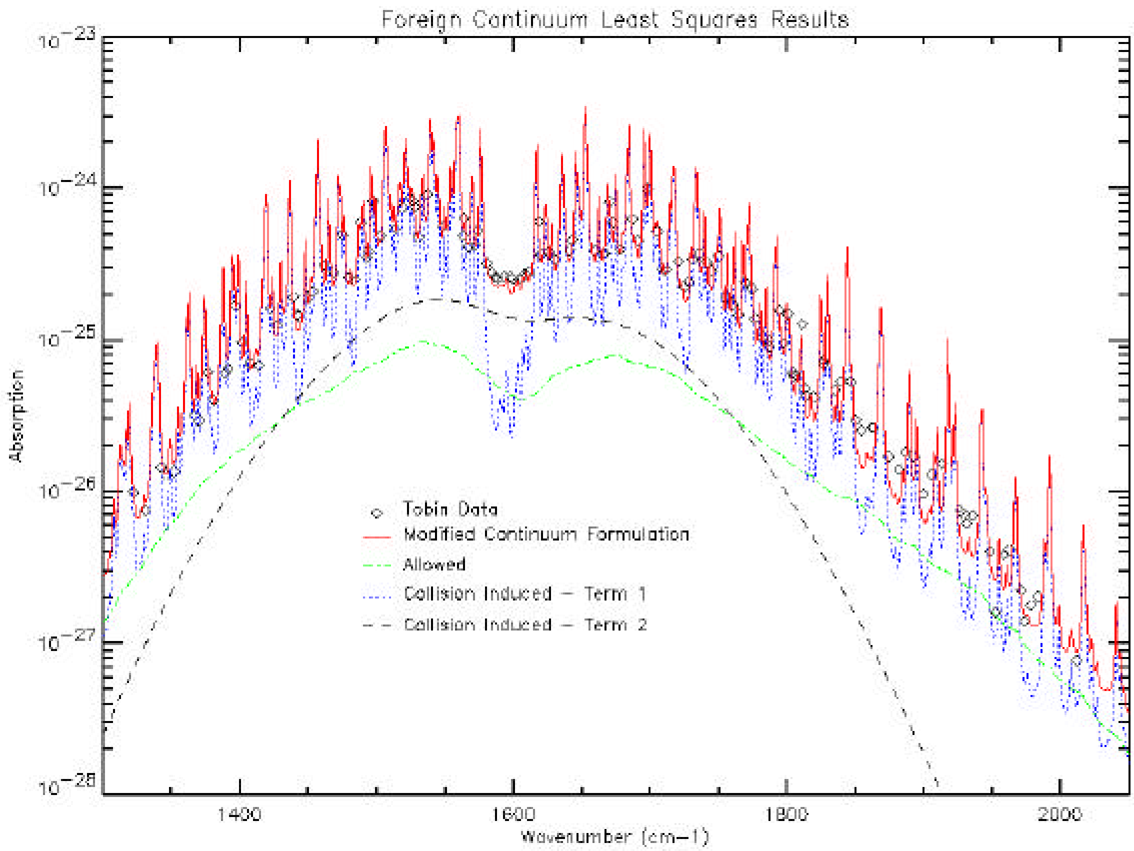

Figure 2. The modified foreign water vapor continuum formulation defined by Eqs. (7) through (12) (solid) and its three functional components for the υ_2 fundamental band: allowed transitions [Eq. (8), dashed-dotted], high-frequency collision induced transitions [Eq. (9), dotted], and low-frequency collision-induced transitions [Eq. (10), dashed]. Also shown are the laboratory measurements due to Tobin et al. (1996). (For a color version of this figure, please see *http://www.arm.gov/docs/documents/technical/conf_9803/mlawer-98.pdf*.)

Figure 5 presents the effect of using the revised continuum (designated CKD_2.3), once incorporated into the rapid radiation transfer model (RRTM) (Mlawer et al. 1997), to compute the fluxes and cooling rates for the midlatitude summer atmosphere. The computed ~1 W/m^2 difference in OLR is seen for all atmospheric profiles examined. The cooling rate differences between the modified and original formulations are substantial, with increased cooling in the lower troposphere and a decrease in the upper troposphere due to the weaker continuum absorption in the pure rotation band. The differences in outgoing radiation implied by the revised continuum will also have important implications for retrievals of atmospheric properties from satellites. Figure 6 presents the brightness temperature as a function of wavenumber for two calculations of upwelling radiance by the line-by-line radiative transfer model (LBLRTM), one using the standard water vapor continuum (CKD_2.2) and the other using the revised formulation (CKD_2.3). As can be seen in this figure, the differences between the two calculations can be large, as great as 4K.

It is important to emphasize that, although a major source of the water vapor continuum is absorption by short-lived collisional complexes of water vapor with another molecule (for the self continuum, also water vapor), the continuum is related to the water vapor monomer and not the dimer. This is evident in the clearly causal relationship between the water vapor monomer line absorption spectrum and the collision-induced absorption spectrum given by Eqs. (9) and (10). This validates a main conclusion expressed in Clough et al. (1980) and Clough et al. (1989). However, the present work presents a clear departure from the CKD formulation, in which the wings of allowed monomer transitions are responsible for the water vapor continuum. It was this

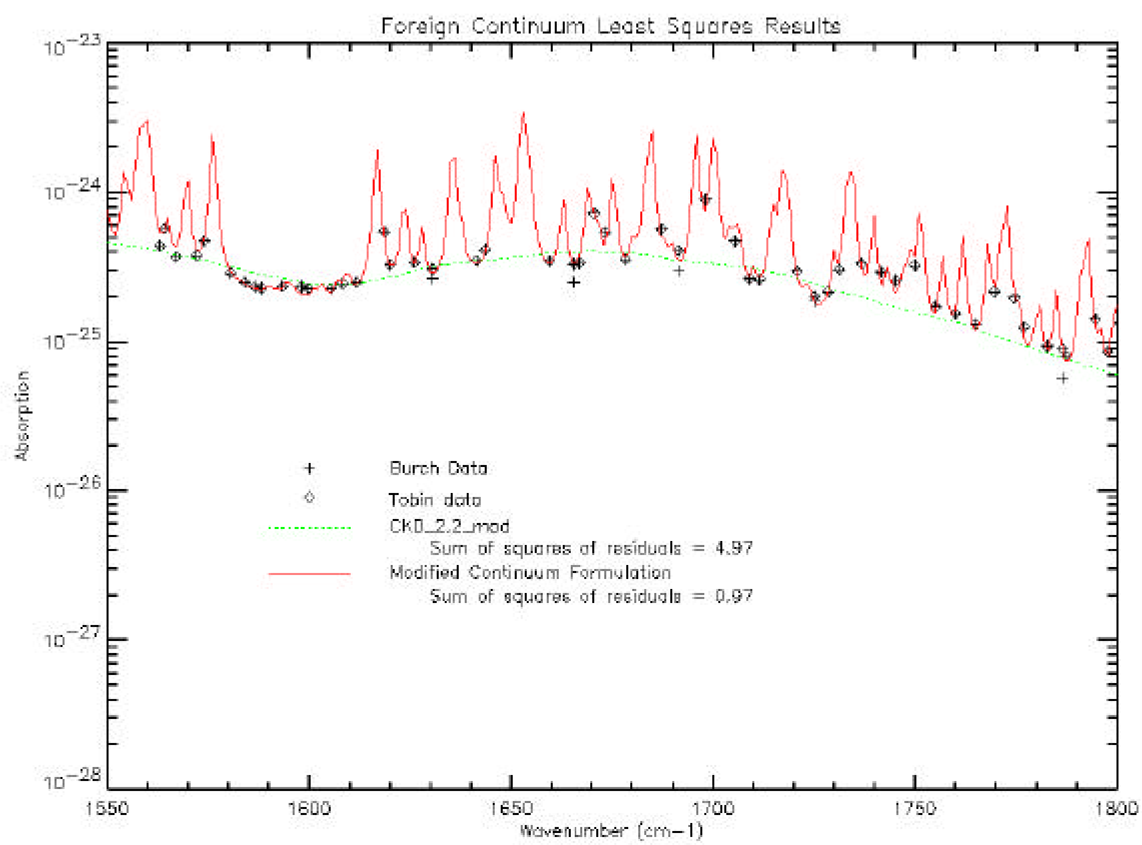

Figure 3. The modified foreign water vapor continuum formulation (upper curve) and the CKD_2.2_mod foreign continuum (lower, smooth curve) for the 1550 cm^{-1} to 1800 cm^{-1} spectral interval. Also shown are the laboratory measurements due to Tobin et al. (1996) and Burch (1981). (For a color version of this figure, please see *http://www.arm.gov/docs/documents/technical/conf_9803/mlawer-98.pdf*.)

conclusion that led to the multiplicative lineshape formulation [Eq. (5)] employed in CKD_0, now replaced by the use of three spectral components [Eqs. (7) through (10)] in an additive formulation necessitated by the multiple quantum mechanical sources of the continuum.

Future Work

Much work remains to be done in this research effort. First, the final form of the foreign continuum formulation must be determined and then validated against high-resolution observations such as those from AERI. Second, this procedure developed for the foreign continuum must be adapted to the self continuum. Third, these continua must be extended into the near infrared and visible spectral regions, and validated against appropriate observations.

It is anticipated that this formulation will lead to a better understanding of water vapor lineshapes and, in particular, establish the cause of the "hindered rotor" property of the collision-induced transitions. This would be an important step in achieving the ultimate objective of this research effort, an explanation from first principles of the water vapor continuum.

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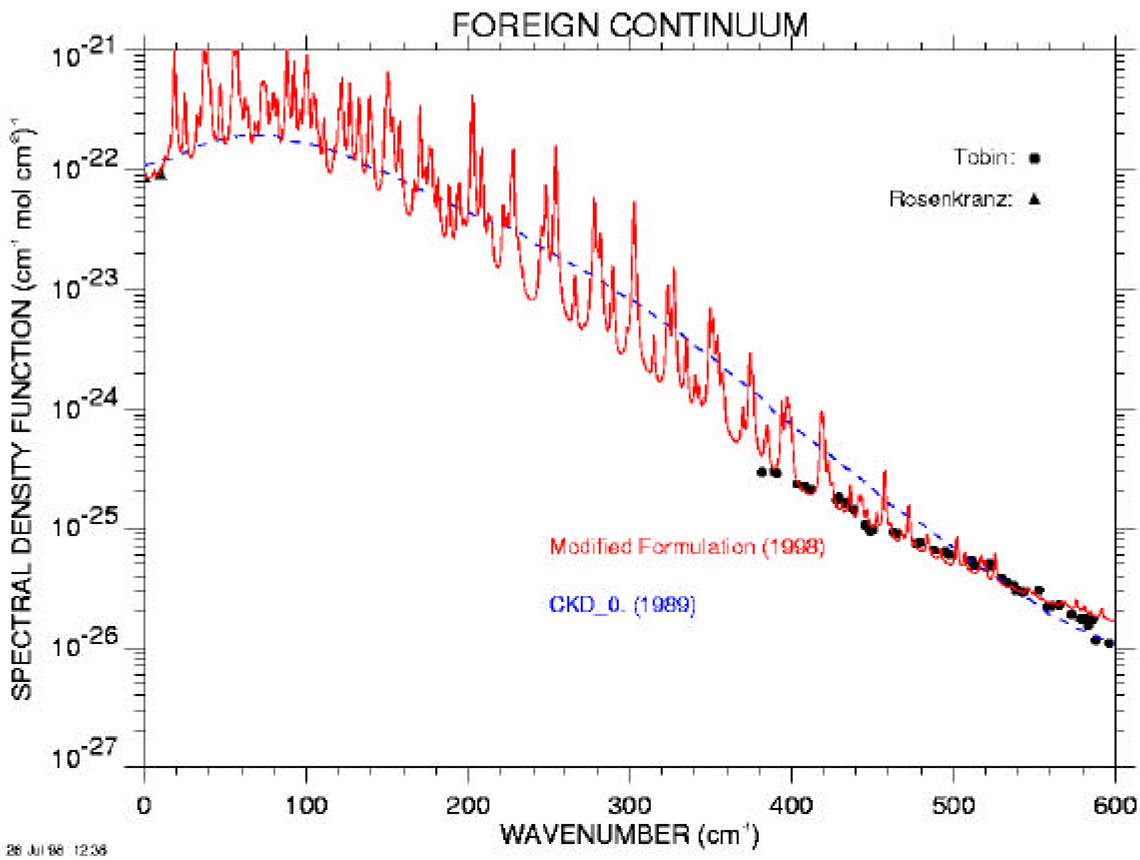

Figure 4. The modified foreign water vapor continuum formulation (solid) and the CKD_0 foreign continuum (dashed) for the rotation band. Also shown are the measurements due to Tobin et al. (1998) and Rosenkranz (1999). (For a color version of this figure, please see *http://www.arm.gov/docs/documents/technical/conf_9803/mlawer-98.pdf*.)

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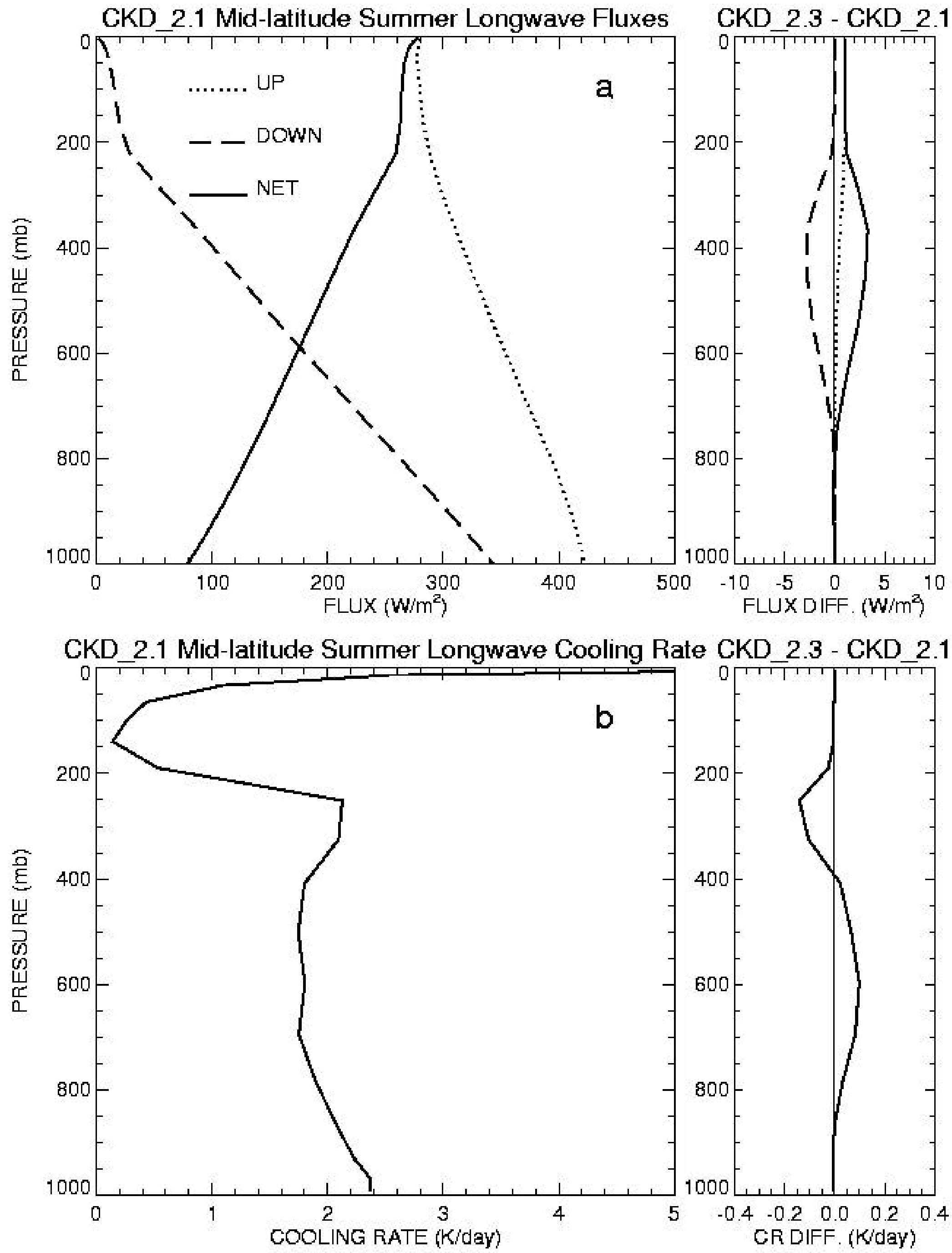

Figure 5. (a) The net, up, and down longwave fluxes for the midlatitude summer atmosphere calculated by a version of RRTM using the CKD_2.1 continuum (left panel), and the differences for these quantities between RRTM using the modified continuum formulation (CKD_2.3) and RRTM using CKD_2.1 (right panel). (b) Same as (a), except for longwave cooling rates.

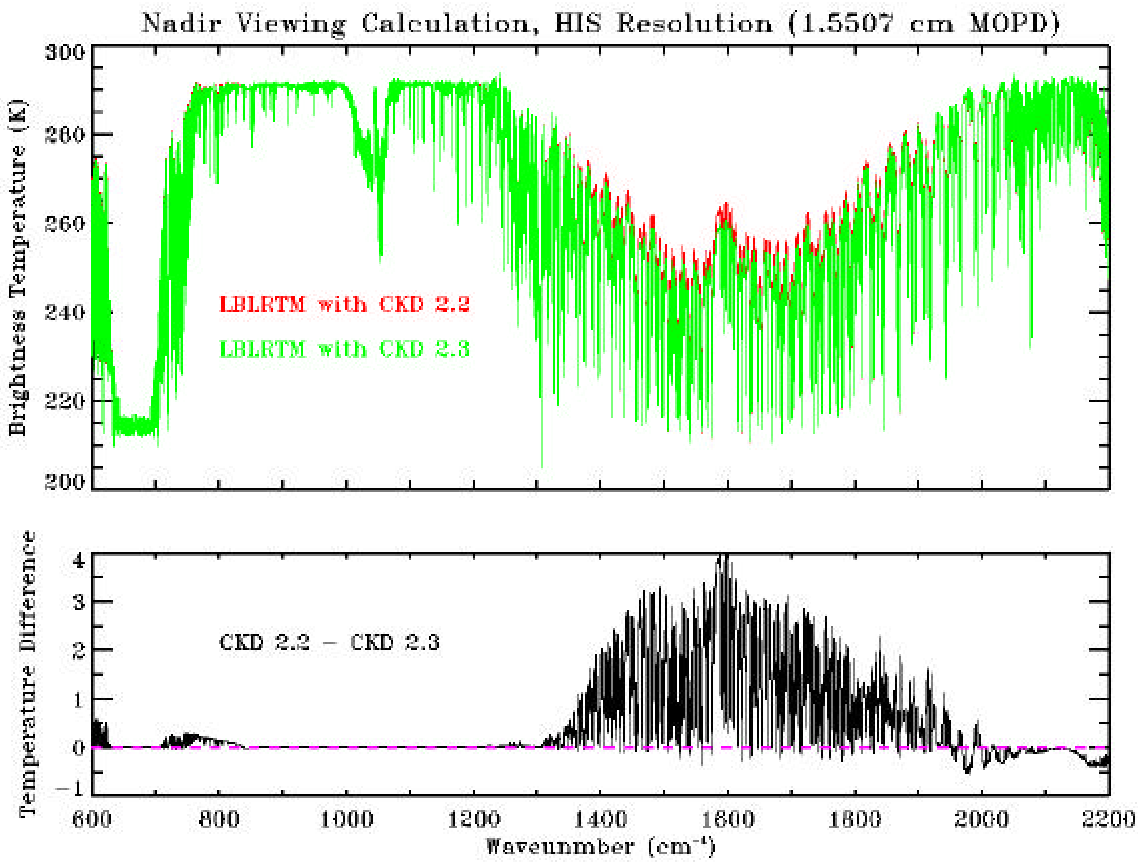

Figure 6. (upper panel) The brightness temperature as a function of wavenumber for two calculations of upwelling radiance by the LBLRTM, one using the standard water vapor continuum (red curve; CKD_2.2) and the other using the revised formulation (green curve; CKD_2.3). (lower panel) The difference in brightness temperature for the two calculations shown in the upper panel. (For a color version of this figure, please see *http://www.arm.gov/docs/documents/technical/conf_9803/mlawer-98.pdf*.)

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