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Line Shape and the Water Vapor Continuum

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ABSTRACT

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A formulation is developed in which the contribution of the far wings of collisionally broadened spectral lines to the water vapor continuum absorption is established. The effects of deviations from the impact (Lorentz) line shape due to duration of collision effects are treated semi-empirically to provide agreement with experimental results for the continuum absorption and its temperature-dependence. The continua due to both water–water molecular broadening (self-broadening) and water–air molecular broadening (foreign broadening) are discussed. Several atmospheric validations of the present approach are presented.

RESUME

On développe une formulation dans laquelle on établit la contribution des ailes éloignées des raies élargies par collision au continuum d'absorption de la vapeur d'eau. Les effets des déviations de la forme de raie d'impact (Lorentz) sont traités de façon semi-empirique pour fournir un accord avec les résultats expérimentaux concernant le continuum d'absorption et sa dépendence en température. Les continua dûs à l'effet d'élargissement moléculaire eau–eau (self broadening) et air–eau (foreign broadening) sont discutés. Plusieurs validations atmosphériques de cette approche sont présentées.

INTRODUCTION

The continuum absorption due to water vapor has posed a complex problem for researchers concerned with atmospheric radiative problems. In fact, a universally accepted definition of continuum absorption has not been established making more difficult the discussion of the effect. The regions of the atmos-

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pheric spectrum in the microwave and the infrared with the greatest transparency, the windows, are strongly dependent on the water vapor continuum. These spectral regions are at 0 cm^{-1}, 800–1200 cm^{-1} and 2000–3000 cm^{-1}. Laboratory measurements of the water vapor continuum are made difficult by the long path lengths required with conventional spectroscopic techniques or by the complexities encountered with methods of high sensitivity such as spectrophone detection. Atmospheric measurements are adversely affected by the difficulty in adequately characterizing the path, aerosol attenuation, turbulence, scintillation and instrument calibration. From a theoretical point of view, the continuum has posed a comparably complex problem and still lacks a completely satisfactory explanation. The issue of whether the absorption represents an excess or deficiency is fundamentally dependent on the line shape formulation chosen as reference as well as on the frequency regime of interest. A theoretical understanding of this problem entails a satisfactory description of the line shape and its temperature-dependence from line center to the far line wing requiring a proper treatment of the physical processes occurring in the time associated with the duration of collision. Further, an adequate model must also address the issue of collision-induced spectra as well as the possibility of dimer absorption.

LINE SHAPE FORMULATION

In our consideration of the continuum, we start with a line shape formulation for the absorption coefficient $k(\nu)$ (cm^2/molec.), that is applicable from the microwave to the infrared (Clough et al., 1983):

$$k(\nu)=R(\nu)\langle\phi(\nu)+\phi(-\nu)\rangle \tag{1}$$

with:

$$R(\nu)=\nu\frac{1-e^{-\beta\nu}}{1+e^{-\beta\nu}} \tag{2}$$

$$=\nu\tanh(\beta\nu/2) \tag{3}$$

where ν is the wavenumber value, $R(\nu)$ (cm^{-1}) is a radiation field term at temperature T with $\beta=hc/kT$ (cm), and $\langle\phi(\nu)+\phi(-\nu)\rangle$ is the symmetrized power spectral density function (Van Vleck and Huber, 1977). The term $R(\nu)$ includes the effect of stimulated emission. This formulation has a number of attractive properties: its appropriateness to all spectral domains and the fact that the symmetrized power spectral density function satisfies an important intensity sum rule, the Nyquist theorem. For the application of this formalism to the computation of spectra in terms of line transition data, we obtain:

$$k(\nu)=\nu\tanh(\beta\nu/2) \times\sum_i \tilde{S}_i(T)\frac{1}{\pi}\left[\frac{\alpha_i}{(\nu-\nu_i)^2+\alpha_i^2}\chi(\nu_i-\nu)+\frac{\alpha_i}{(\nu+\nu_i)^2+\alpha_i^2}\chi(\nu+\nu_i)\right] \tag{4}$$

where $\tilde{S}_i$ ($\mathrm{cm^2/molec.}$) is the intensity of the transition at wavenumber value ν_i ($\mathrm{cm^{-1}}$) and halfwidth α_i ($\mathrm{cm^{-1}}$). The Lorentz function, $f(\nu-\nu_i)$ (cm):

$$f(\nu-\nu_i)=\frac{1}{\pi}\frac{\alpha_i}{(\nu-\nu_i)^2+\alpha_i^2} \tag{5}$$

is the line shape function appropriate to the impact approximation for which the collision time is assumed to be instantaneous. The χ function is a semi-empirical function applied to the impact result to correct for duration of collision effects and to attain agreement between calculated and measured spectra. With $\chi=1$, this line shape reduces to the Lorentz shape in the infrared, since $R(\nu)\to\nu_i$ for $|\nu-\nu_i|\ll\nu$, and to the Van Vleck-Weisskopf shape in the microwave, since $R(\nu)\to\beta\nu^2/2$. We adopt a notation in which a tilde over a quantity indicates that the radiation term, $R(\nu)$, has been excluded from that quantity.

At this stage we define a continuum absorption by excluding from the power spectral density function fast spectral components associated with the line center. The continuum, $\tilde{C}(\nu)$, is given by:

$$\tilde{C}(\nu)=\langle\phi(\nu)+\phi(-\nu)\rangle_{\mathrm{c}} \tag{6}$$

$$=\sum_i \tilde{S}_i[f_{\mathrm{c}}(\nu-\nu_i)\chi(\nu-\nu_i)+f_{\mathrm{c}}(\nu+\nu_i)\chi(\nu+\nu_i)] \tag{7}$$

where f_{c} is a line shape with the strong central component excluded (Clough et al., 1980). We systematically define f_{c} $(\nu\mp\nu_i)$ in the following way:

$$f_{\mathrm{c}}(\nu\mp\nu_i)=\begin{cases}\dfrac{1}{\pi}\dfrac{\alpha_i}{25^2+\alpha_i^2} & |\nu\mp\nu_i|\leqslant 25\ \mathrm{cm^{-1}}\\[2ex] \dfrac{1}{\pi}\dfrac{\alpha_i}{(\nu\mp\nu_i)^2+\alpha_i^2} & |\nu\mp\nu_i|\geqslant 25\ \mathrm{cm^{-1}}\end{cases} \tag{8}$$

The function f_{c} is indicated schematically in Fig. 1 by the solid curve. Another function that has been used by Burch in some of his work is indicated by the dashed line in Fig. 1. The lack of agreement among researchers on the line shape formulation and on the definition of the function f_{c} has inhibited the intercomparison and validation of continua. It must be emphasized that the continuum and the details of the line-by-line calculation are inextricably related. The present formulation for the continuum is consistent with the FASCODE line-by-line model (Clough et al., 1986). Similarly, it is important to recognize that band models developed to describe molecular absorption, must also be derived in the context of a consistent treatment of the continuum. To

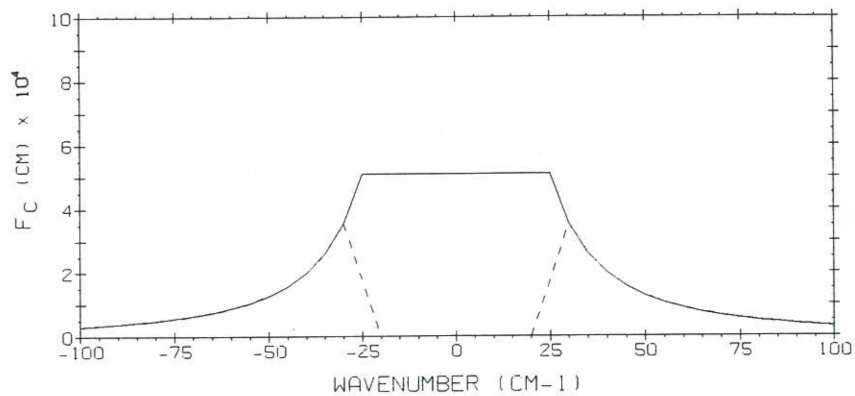

Fig. 1. The line shape function, $f_c(\nu)$, used to develop the continuum (solid curve). The dashed curve represents the function used by Burch.

be more explicit, if a band model is to be used in conjunction with a continuum, then the absorption effects included in the continuum must be excluded from the band model. We should note that the continuum functions have been developed in such a way as to obey Beer's law.

It is an important consideration that the continuum coefficient, $\tilde{\tilde{C}}(\nu)$, is proportional to collider density, ρ. Since the collision frequency which is proportional to density determines the broadening, density is more appropriate as the dependent variable than pressure. At constant temperature the distinction is not relevant. The values for the self broadened halfwidths, α_i^0, referred to atmospheric density, ρ_0, are of the order of 0.1 cm^{-1} (0.5 cm^{-1} for self-broadened water vapor). With the halfwidth density-dependence given by:

$$\alpha_i = \alpha_i^0 (\rho/\rho_0) \tag{9}$$

the α_i^2 terms in eq. 8 may be dropped and the continuum shape function becomes:

$$f_c(\nu \mp \nu_i) = \begin{cases} \dfrac{1}{\pi} \dfrac{\alpha_i^0 (\rho/\rho_0)}{25^2} & |\nu \mp \nu_i| \leqslant 25\ \mathrm{cm}^{-1} \\[2ex] \dfrac{1}{\pi} \dfrac{\alpha_i^0 (\rho/\rho_0)}{(\nu \mp \nu_i)^2} & |\nu \mp \nu_i| \geqslant 25\ \mathrm{cm}^{-1} \end{cases} \tag{10}$$

The density scaling of the continuum is established as:

$$\tilde{C}(\nu) = \tilde{C}^\circ(\nu)\ (\rho/\rho_0) \tag{11}$$

since f_c is proportional to (ρ/ρ_0) for all values of ν.

The temperature-dependence of the absorption is dependent on the radiation term, $R(\nu)$ in eq. 2, the strength $\tilde{S}_i$, the halfwidth α_i^0, and on the line shape factor χ. The dependence is known theoretically for $R(\nu)$ and for $\tilde{S}_i$ and is satisfactorily described through an empirical exponent, m, determined from measurements for α_i where:

$$\alpha_i(\rho,T) = \alpha_i^0 (T/T_0)^m (\rho/\rho_0)$$

For the line shape factor χ the situation is more complicated. Near line center, $|\nu \pm \nu_i| < 5\ \mathrm{cm}^{-1}$, χ is essentially unity for all temperatures. However far from line center the temperature-dependence for χ must be inferred from the temperature of the absorption resulting from many overlapping lines.

WATER VAPOR

We are now in a position to apply the formulation we have developed to water vapor absorption. Performing a line-by-line calculation using the entire set of water vapor lines from 0 cm^{-1} to 10,000 cm^{-1}, we obtain the power spectral density function for self-broadened water vapor shown in Fig. 2. The dotted curve is attained by utilizing the continuum line shape function, f_c, thus excluding from the power spectral density function the contribution of the line centers, and providing a spectrum of low spectral content designated as the continuum. The well known water vapor bands associated with pure rotation (0 cm^{-1}), ν_2 (1600 cm^{-1}), ν_1 of HDO (2720 cm^{-1}), $2\nu_2$ (3100 cm^{-1}), ν_1 (3660 cm^{-1}) and ν_3 (3760 cm^{-1}) are evident in Fig. 2. In Fig. 3 we indicate two

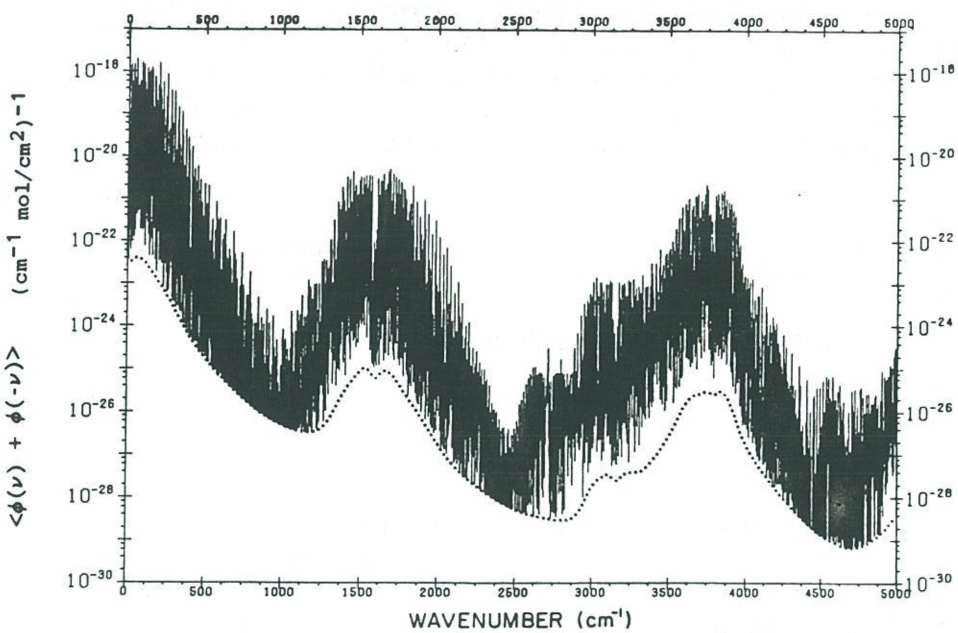

Fig. 2. The symmetrized power spectral density function for self-broadened water vapor at 26.7 mb. and 296 K (solid curve). The continuum is indicated by the dotted curve.

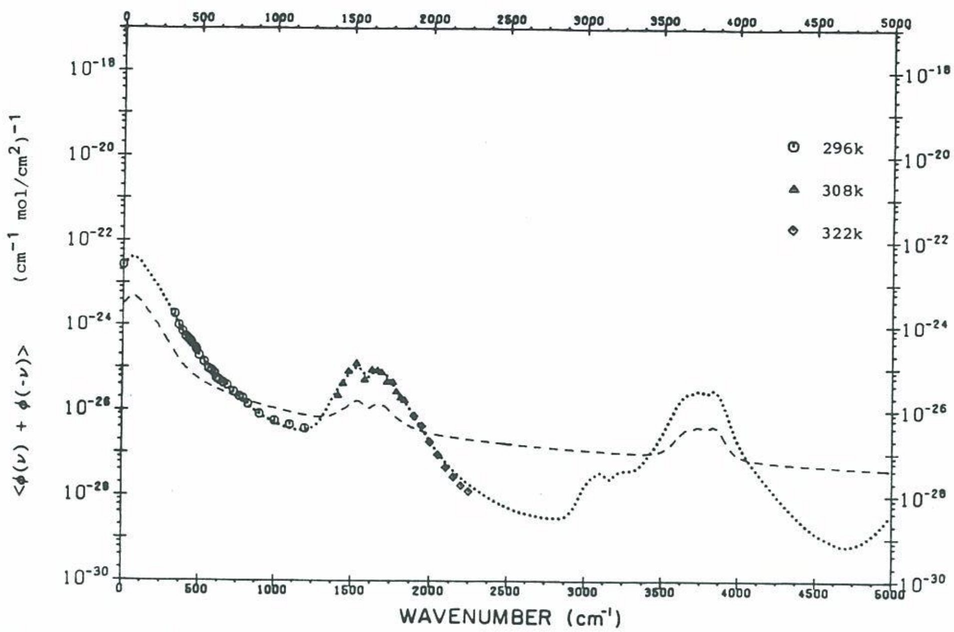

Fig. 3. The continuum for self-broadened water vapor. The dashed line is the impact result and the dotted curve is with the χ function adjusted to fit the experimental data of Burch, 1981. The broadening pressure is 1013 mb.

continua, one obtained using the impact line shape ($\chi = 1$), and the other with a function obtained by adjusting the parameters in an empirical χ-function to attain agreement with the indicated spectral results (Burch, 1981; Burch and Alt, 1984; Burch, 1985).

Note that in Fig. 3 the continuum coefficient for self-broadened water vapor, $\tilde{C}_s^0$, exhibits an excess absorption with respect to the reference impact continuum ($\chi = 1$) in the center of the bands at 0–500 cm^{-1} and 1400–1800 cm^{-1} and a deficiency between central band absorption regions, 800–1200 cm^{-1} and 1800–3300 cm^{-1}. This result is consistent with theoretical requirements and is a direct consequence of the formulation. The χ function associated with the line shape for self-broadened water vapor, designated χ_s, is shown by the solid curve in Fig. 4. The functional form of χ is given by:

$$\chi = \begin{cases} 1 - (1 - \chi') \dfrac{(\nu \mp \nu_i)^2}{25^2} & |\nu \mp \nu_i| \leqslant 25 \text{ cm}^{-1} \\ \chi' & |\nu \mp \nu_i| \geqslant 25 \text{ cm}^{-1} \end{cases} \qquad (12)$$

where for self-broadening χ_s is obtained by setting $\chi' = \chi_s'$ with:

$$\chi_s' = 8.63 \exp(-z_1^2) + (0.83 z_2^2 + 0.033 z_2^4) \exp(-|z_2|) \qquad (13)$$

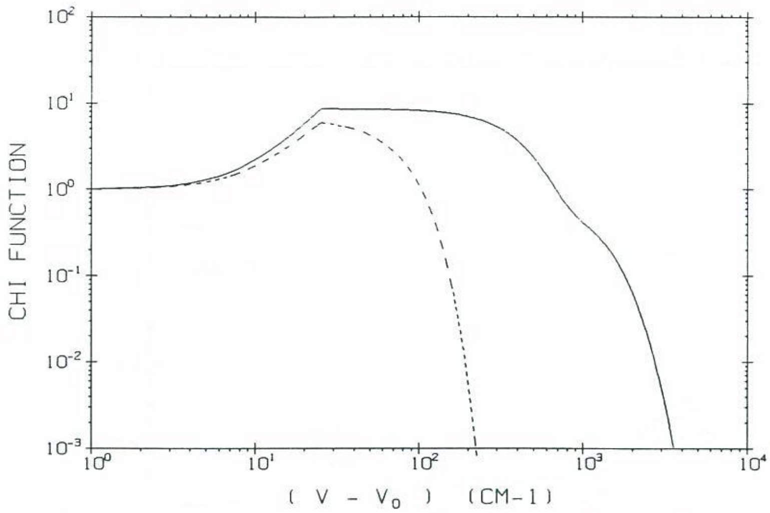

Fig. 4. The χ function for water at 296 K. The solid curve is for self-broadening; the dashed curve is for foreign-broadening.

where $z_1 = (\nu \mp \nu_i)/400$ and $z_2 = (\nu \pm \nu_i)/250$ at 296 K. From eq. 12 and Fig. 4 we note that χ is continuous at 25 cm^{-1}, but that the first derivative is discontinuous. This is a direct consequence of the choice of f_c (eq. 8) but causes no particular problems in the formulation.

The self-continuum for water vapor demonstrates a rather strong temperature-dependence, particularly in the 1000 cm^{-1} window. It is an important shortcoming of the current state of line shape theory for molecular collisions, that the temperature-dependence of the far wings, or alternatively of the continuum in the window regions, is not explained. Rosenkranz (1985, 1987), in two particularly interesting papers, has proposed an alternative formulation to eqs. 1 and 3, which leads to a strong temperature-dependence consistent with observations in the far-wing regions. This proposed formulation warrants additional scrutiny. The dimer has often been postulated as a source of the continuum absorption primarily as a consequence of its simple and attractive temperature-dependence. However, the absence of spectral structure, difficulties in explaining spectral pressure-dependence and the fact that the absorption in the windows as developed in this paper represents an excess with respect to the impact line shape are in direct contradiction with the dimer theory. On the other hand, dimers should be formed under atmospheric conditions so that the central issue becomes the question of dimer lifetime (Suck et al., 1979).

For pragmatic purposes the temperature-dependence of the continuum has been treated as follows: the parameters in an analytical χ function are obtained by least-squares fitting the calculated continuum to the data of Burch at 296 K and 338 K. These parameters for 296 K and 338 K are then extrapolated to

260 K and a continuum for that temperature is calculated. This is potentially a source of error; however, validations for atmospheric measurements have provided remarkably good results. Continua for 338 K, 296 K and 260 K are shown in Fig. 5.

An analogous treatment is performed for air-broadening of water vapor, referred to as foreign broadening. Fig. 6 shows the empirical continuum, $\tilde{C}_f^0$, fit to the data of Burch as well as the continuum for the impact approximation. For the foreign-broadened case, the line wings decay much more rapidly as a function of wavenumber difference from line center than for the self-broadened case. This is reflected in the foreign chi-function, χ_f shown by the dashed curve in Fig. 4. For the foreign continuum χ_f is obtained by setting $\chi' = \chi_f'$ in eq. 12 with:

$$\chi_f' = 6.65 \exp(-z_1^2) \tag{14}$$

where $z_1 = (\nu \pm \nu_i)/75$. For the window regions of the foreign continuum, 1000 cm^{-1} and 2500 cm^{-1} in Fig. 6, an absorption coefficient has been added to the continuum resulting from the present formalism in order to attain agreement with atmospheric measurements (Roberts et al., 1976). The contribution of the foreign continuum is very small in these spectral regions making the measurements particularly difficult. The observed effect may be due to collision

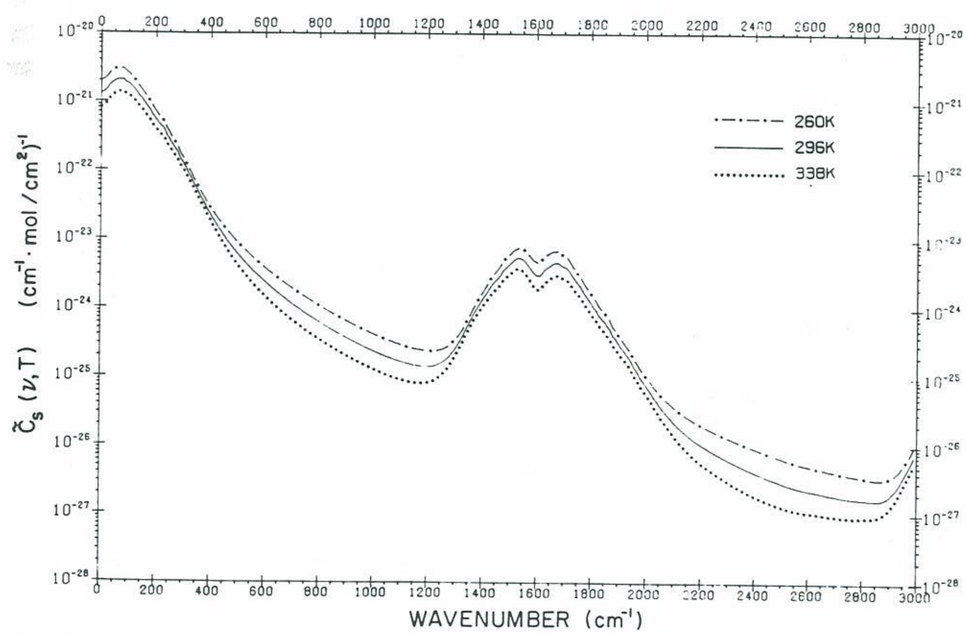

Fig. 5. The self-broadened water vapor continuum at 338 K, 296 K and 260 K. The continua at 338 K and 296 K have been fit to data and the 260 K continua have been extrapolated.

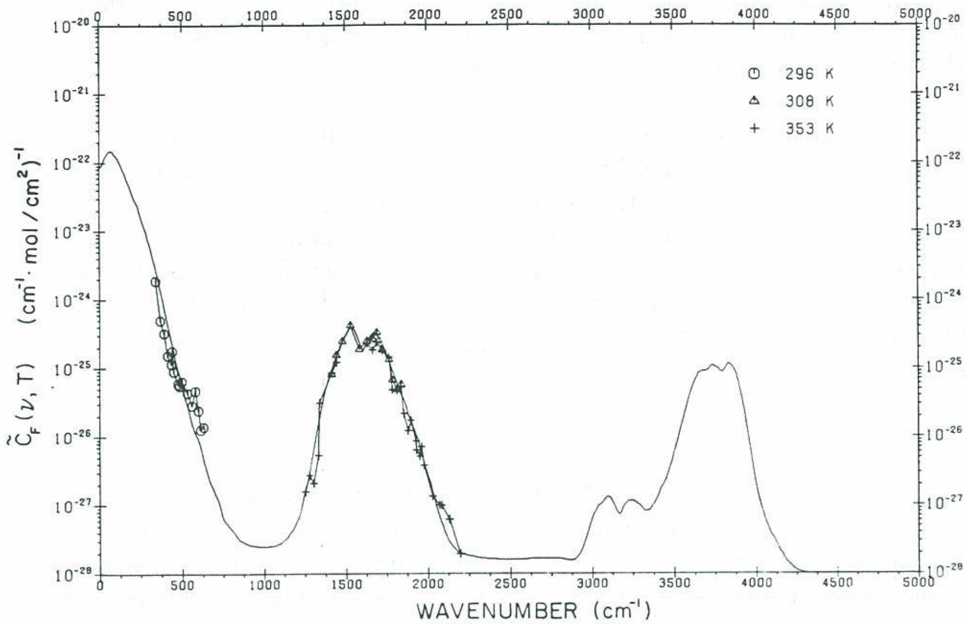

Fig. 6. The continuum for foreign-broadened water vapor. The solid curve is the calculated continuum with the χ function adjusted to fit the experimental data of Burch, 1981. The broadening pressure is 1013 mb.

induced spectra or humidity-dependent aerosols. No significant temperature-dependence has been observed for the foreign continuum.

The total absorption coefficient due to self- and foreign-water-vapor continuum, $k_c(\nu)$, is given by the relation:

$$k_c(\nu) = \nu \tanh(\beta\nu/2)\ [\tilde{C}_s^0(\rho_s/\rho_0) + \tilde{C}_f^0(\rho_f/\rho_0)] \tag{15}$$

It is an important point that for atmospheric conditions, the foreign continuum is dominant for in-band absorption and the self continuum is dominant for the out-of-band absorption, the window regions of water vapor spectrum.

ATMOSPHERIC VALIDATION

The most important element in the development of an atmospheric transmittance/radiance model is validation with atmospheric data. Since the atmospheric window at 1000 cm^{-1} (10 μm) is of such importance, we consider that spectral region in more detail. The continuum currently being used in FASCOD2 has been adjusted to fit the more recent measurements at 1000 cm^{-1} of Burch and Alt, 1984 (Fig. 7). In Fig. 8 we show a plot of the optical depth for a 1-km path at 990 cm^{-1} as a function of water vapor density from LOWTRAN7 (Kneizys et al., 1988) which incorporates this continuum de-

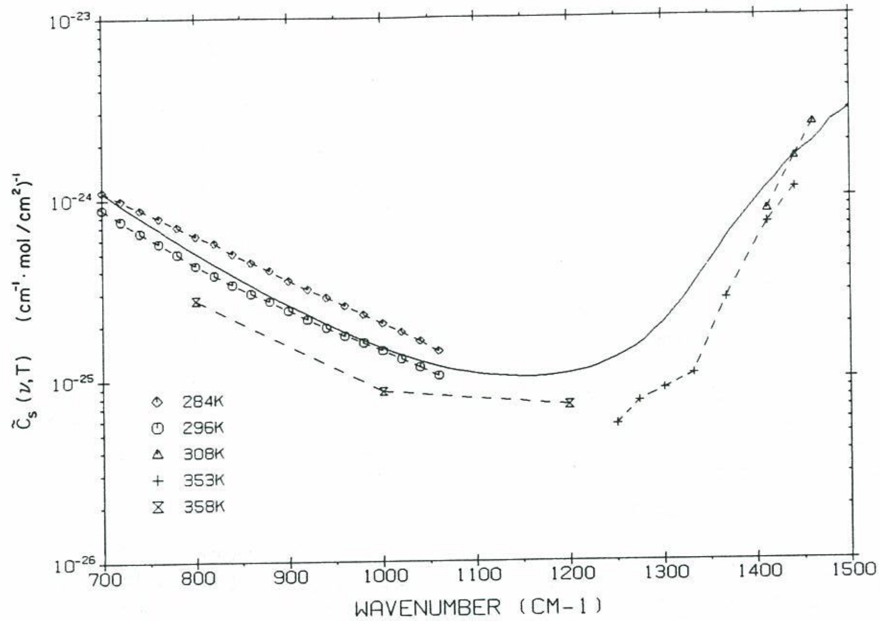

Fig. 7. Details of the self-broadened continuum at 1000 cm^{-1}. The solid line is the calculated continuum at 296 K. The data for 284 K and 296 K are from Burch and Alt (1984); the other data are from Burch (1981).

velopment. We consider two sets of atmospheric measurements: one from the Air Force Wright Aeronautical Laboratories (AFWAL) taken over an 8-km path and for a range of visibilities (Kneizys et al., 1984) and the other from the Technion Institute in Israel over an 8.6-km path (Oppenheim and Lipson, 1986). Both of these sets of measurements were taken with circular variable filter (CVF) spectrometers. Since the atmospheric measurements include extinction due to aerosol effects, the calculated optical depths, which do not include aerosol contributions, are less than those for the atmospheric measurements. The calculations do take into effect the contribution from other molecules (intercept) and from the local water vapor lines. Spectral validation of the continuum model with the Technion measurements for the 8–12 micron window is shown in Fig. 9 and for the 3–5 micron window in Fig. 10. Of particular note is the excellent agreement between calculation and observation obtained at 4.75 μm and 3.2 μm. These two regions demonstrate the predictive capability of the current formulation since there has been no adjustment with data in these spectral regions. With respect to the continua beyond 5000 cm^{-1}, it should be emphasized that the calculations are essentially qualitative and unvalidated. This is particularly the case for the self-broadened continuum, important between the bands.

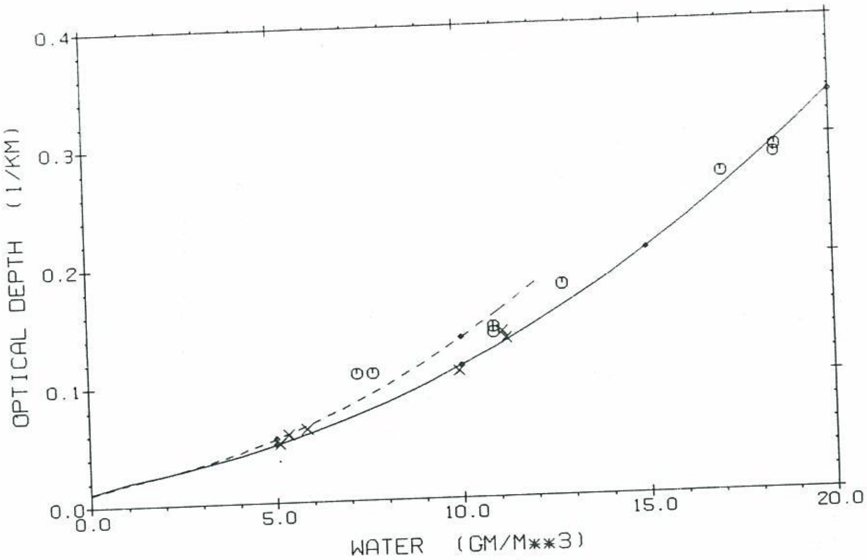

Fig. 8. The optical depth for a 1-km path at 990 cm^{-1} as a function of water vapor density. The calculations are from LOWTRAN with the self-continuum of Fig. 7. The solid curve is for 296 K and the dashed curve is for 284 K. The data are from Kneizys et al., 1984. The ×-symbols are for cases with visibilities > 15 km.

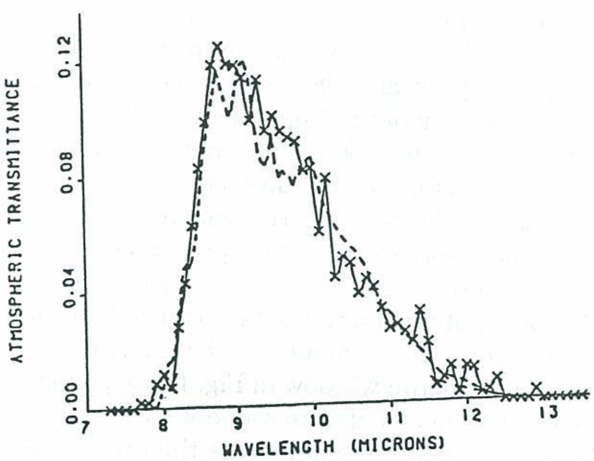

Fig. 9. Spectral comparison between a CVF measurement in the 8–12 micron window over a 8.637-km path by Technion (Oppenheim and Lipson, 1985) and a LOWTRAN calculation with the FASCOD2 continuum (dotted curve). The measurement conditions: $T=297.5$ K, $P=1008$ mb., $RH=85\%$, and visibility = 15 km.

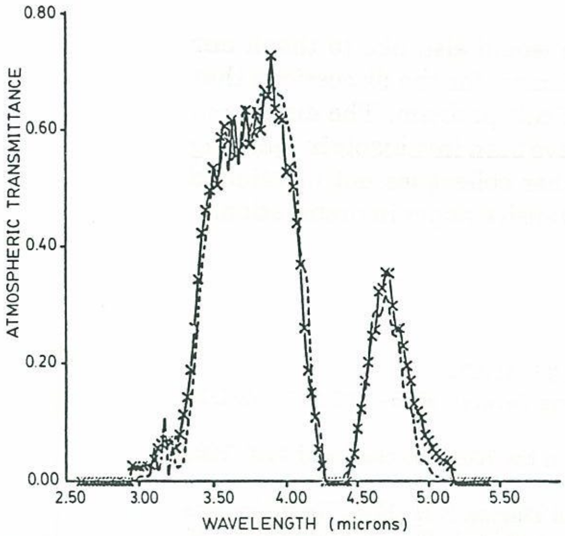

Fig. 10. Spectral comparison between a CVF measurement in the 3–5 micron window over a 10.37-km path by Technion (Oppenheim and Lipson, 1985) and a LOWTRAN6 calculation (dotted curve). The measurement conditions: $T=283$ K, $P=899$ mb., $RH=68\%$ and visibility $=40$ km.

SUMMARY

The present discussion is not intended as a comprehensive review of the water vapor continuum problem. It is rather a description of a specific approach that is consistent with the physics of the problem and that has been constrained to provide results consistent with experimental measurements. The choice of measurements used for this discussion has been highly selective. This is related to a need for internal consistency of the observations, our estimation of the accuracy of the measurements and a treatment of the data that is in the context of the current development. The present status should be regarded as useful if not definitive. In order to meet current objectives in atmospheric remote sensing and related phenomena, more observations of high accuracy both in the laboratory and in the atmosphere are required, and significant advances in the theoretical treatment of the effects of collision on molecular line shape need to be achieved. A floppy disk containing a program to calculate continuum absorption coefficients as described here and consistent with FASCOD2 and LOWTRAN7 is available from the authors.

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