

# Final Report

## Project Title: Discrete and Continuum Absorption Parameters for Water Vapor in the Midinfrared

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## I. Research Objectives

This two-year project consisted of three principal objectives: (i) the measurement of the mid-infrared water-vapor continuum absorption using long-pathlength Fourier-transform infrared spectroscopy (FTIR); (ii) the measurement of the mid-infrared continuum absorption of H<sub>2</sub>O vapor using linear absorption spectroscopy and cavity-ringdown spectroscopy in the region between 9  $\mu$ m and 11  $\mu$ m; and (iii) the determination of the pressure and temperature dependent lineshape and lineshift parameters of H<sub>2</sub>O vapor.

The present effort addresses the needs of the AIRS project for an accurate model of the water-vapor continuum to ensure reliable sea-surface temperature retrievals by this nadir viewing instrument, particularly at tropical latitudes, where the high relative humidity leads to significant contribution of the water-vapor continuum to the measured radiances in the 10  $\mu$ m to 12  $\mu$ m atmospheric window.

The infrared absorption coefficient of water vapor has two contributions resulting from both a structureless continuum (background) and resonant (local) water lines. The total absorption may be expressed as  $k = k_c + k_r$ , where  $k_c$  and  $k_r$  are the continuum and resonant water-vapor absorbances, respectively. The first term,  $k_c$ , is given by the following expression: [1]

$$k_c(v, T) = (N_0/P_{ref})(T_{ref}/T)[C_s(v, T)*P_{H2O}^2 + C_f(v, T)*P_{H2O}P_f], \quad (1)$$

where  $N_0$  is the number density under standard conditions of  $P_{ref} = 1$  atm or 101.325 kPa and  $T_{ref} = 296$  K,  $P_{H2O}$  is the partial pressure of water vapor, and  $P_f$  is the partial pressure of the foreign gas.  $C_s(v, T)$  and  $C_f(v, T)$  are the self- and foreign-gas-broadening continuum absorption coefficients, respectively ( $\text{molecules}^{-1}\text{cm}^2\text{atm}^{-1}$ ).

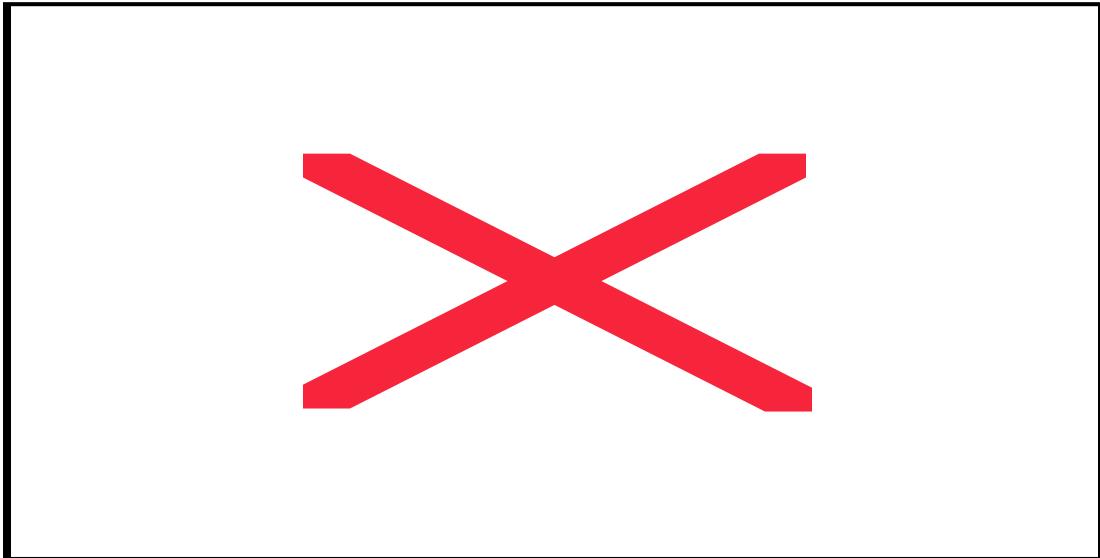
## II. Summary of Progress and Results

### *Mid-infrared cavity ringdown measurements of the water vapor continuum*

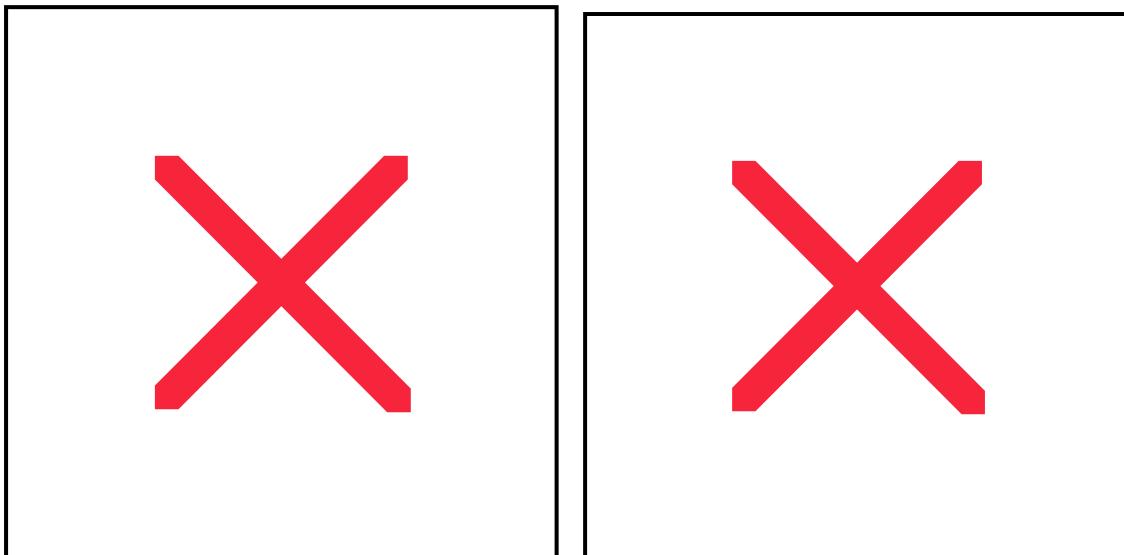
The water vapor continuum in the mid-infrared has been reported by a number of investigators.[2-5] The value of  $k_c(v,T)$  at a water vapor pressure of 10 Torr is approximately  $10^{-6} \text{ cm}^{-1}$ . The measurement of such weak absorption is only possible with instruments equipped with long optical pathlength cells. The bulk of the reported data was obtained using White cells. In this report, we have measured the continuum absorption coefficients of water vapor using cavity ringdown (CRD) spectroscopy at an effective pathlength of approximately of 200 m. The cavity is excited by less than 1 mW of infrared power from a tunable microwave sideband offset from a 5 W to 10 W CO<sub>2</sub> laser line. The full description of the apparatus is given in detail elsewhere.[6]

Unlike most previous studies, the present measurements were performed in pure water vapor eliminating the uncertainty introduced by the second term,  $C_f(v,T)$ , in Eq.[1] for H<sub>2</sub>O-N<sub>2</sub> mixtures. This approach was taken because  $C_s$  dominates over  $C_f$  and because it eliminates the uncertainty from the gas composition and homogeneity of the mixing. The CRD measurements were performed at room temperature (296 K), with water vapor pressures between a few mTorr and 16 Torr. Measurements were performed over the wavenumber number range from  $930 \text{ cm}^{-1}$  to  $970 \text{ cm}^{-1}$ , as indicated with arrows in Fig. 1 above the simulated HITRAN spectrum. In some cases, resonant absorption from nearby water line(s) makes significant contributions to the measured absorption rate. The resonant part was calculated at the actual pressures and temperatures used and subtracted from the data prior to obtaining the continuum absorption coefficient from a least-squares analysis.

Two basic types of measurements were performed: i) during a slow linear increase of the water vapor pressure in the cell and ii) after incremental increases and decreases of water vapor pressure from an equilibrium condition. Both methods provided the same values for the absorption coefficients. Typical data obtained as a function of water vapor pressure is shown in the left panel of Fig. 2. In a single 10 min experiment,  $\approx 1000$  data points were acquired. Each data point was obtained from a non-linear least squares fit of the average of 500 ringdown events. The small volume of the cell (2 liters) makes such experiments possible. The absorption coefficients follow the expected quadratic dependence on pressure given by Eq. (1). The data in the right panel are presented in a linear form by plotting the absorbance against the product of the water-vapor pressure and number density to determine the absorption coefficient ( $\text{cm}^{-1} \text{ atm molecules/cm}^3$ ) from the fitted slope.



**Fig. 1.** Simulated spectrum of resonant water vapor at 10 Torr and with a 200 meter pathlength calculated from the HITRAN database using the graphical user interface program described elsewhere.[7] Each arrow is related to either the lower or upper microwave side band of various CO<sub>2</sub> laser lines ( $\Delta_{CO_2} \pm 0.469 \text{ cm}^{-1}$ ). The horizontal line indicates the expected continuum absorbance.



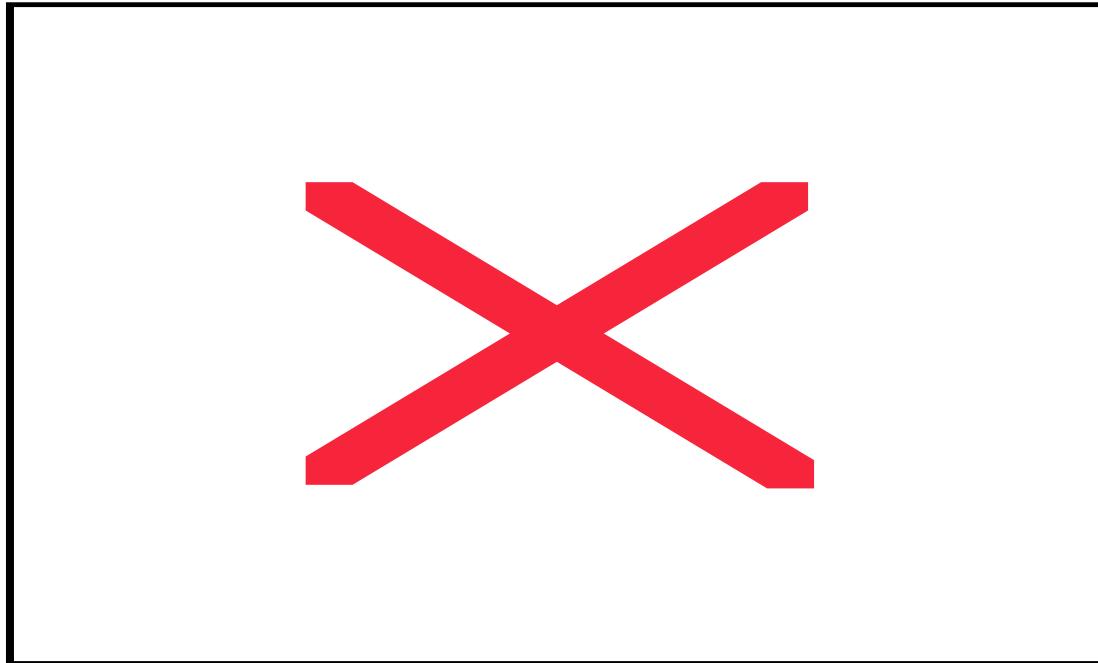
**Fig. 2.** Left panel: Absorbance of pure water vapor near the 10P(8) CO<sub>2</sub> laser line (lower side band,  $\nu = 954.076 \text{ cm}^{-1}$ ) versus pressure. Right panel: same data presented versus the product of pressure and number density. The slope of fitted line is the continuum absorption coefficient. The small resonant absorption contribution has been subtracted in both cases. Note the expected zero intercept at zero pressure-density product.

### ***Midinfrared Fourier-transform study of the water-vapor continuum***

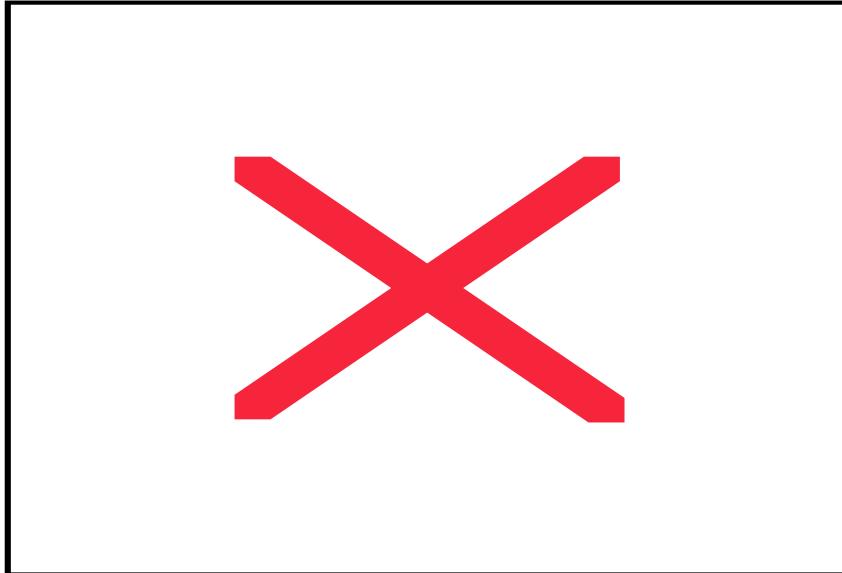
Fourier-Transform Infrared (FTIR) spectra of the water-vapor continuum have also been measured. The absorption measurements were obtained using a 116.2 m absorption cell over the spectral region from  $850\text{ cm}^{-1}$  to  $1250\text{ cm}^{-1}$ .[8] The FTIR method has the obvious advantage of having broad spectral coverage. The disadvantages of this technique include i) the large cell volume necessary to support the multipass cell ( $\approx 130$  liters) and ii) the long measurement time (2 hrs to 12 hrs depending on spectral resolution). The white cell was stabilized at a temperature of 328.1 K, thus permitting measurements at water vapor pressures between 25 and 67 Torr. The measured absorption coefficients were converted to the reference temperature of  $T = 296$  K for comparison with other published data using the expression [2],

$$C_s(v,T) = C_s(v,296) \exp[T_{\text{char}}(1/T - 1/296)], \quad (2)$$

where  $T_{\text{char}} = 1800$  K. The absorption spectra for three different pressures are presented in Fig. 3. As seen from the sloping base line, the smooth drop in absorption correctly reflects the known frequency trend of the continuum absorption. The absorption coefficients were obtained from the fit of the base line between the strong resonant water lines. The far-wing resonant absorption is negligible in these gap regions for the pressure range used in these studies. An expanded portion of this data near where some of the ringdown measurements were performed is shown in Fig. 4.



**Fig. 3.** Experimental water vapor absorption spectra at  $T = 328.1$  K and pressures of 25.2 Torr, 48.6 Torr, and 67 Torr, from bottom to top, respectively. The pathlength is 116.2 m for all spectra.

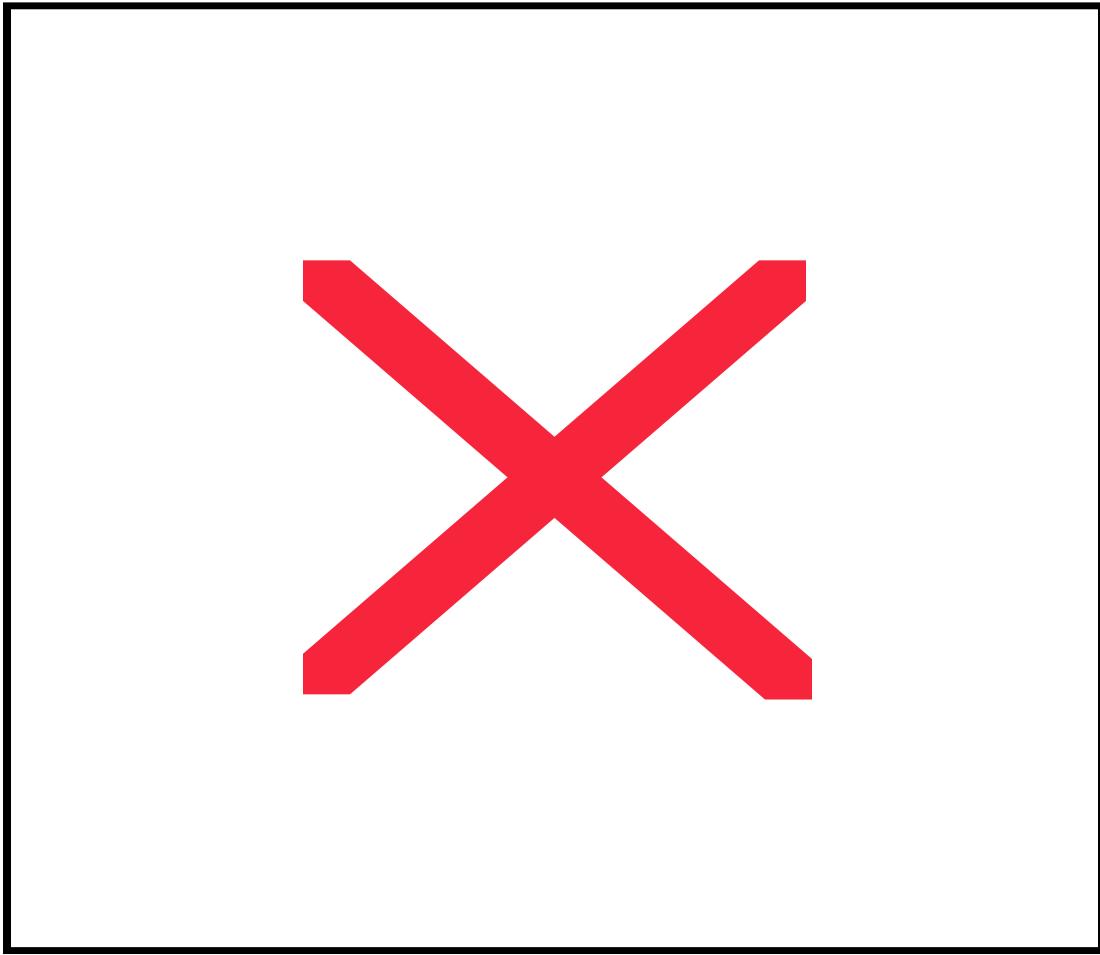


**Fig. 4.** Absorption spectrum of water vapor at 48.6 Torr and T = 328.1 K in the wavenumber range from 945 cm<sup>-1</sup> to 955 cm<sup>-1</sup>. The solid line is the linear fit of the base line within the trace noise limits. This line represents the water-vapor continuum absorbance.

### ***Comparisons of measurement techniques***

A principal objective of our investigation was to present independent measurements of the water-vapor continuum absorption in the mid-infrared using different methods, to provide an assessment of the accuracy and consistency of different approaches. In Fig. 5, we summarize the present results with the reference data reported from previous studies. As seen from the theoretical ([5], solid curve) and experimental ([2, 3], open and closed triangles) reference data, there is significant scatter of about 20 % in the reported numbers. Our ringdown measurements indicated with “x” symbols in Fig. 5 also exhibit comparable scatter consistent with the reference data. Each of the three experimental data points is the average of 10 to 12 independent measurements. We have also calculated the value of the absorption coefficient from our ringdown data assuming the data scatter represents the statistical error in our measurements. For pure water vapor at T = 296 K, the resulting continuum absorption coefficient is  $1.98(15) \times 10^{-22}$  molecules<sup>-1</sup> cm<sup>2</sup> atm<sup>-1</sup> at 949 cm<sup>-1</sup>.

The upper dashed line in Fig. 5 is the best fit to our FTIR data indicated with “+” symbols. The data show small scatter and parallel the frequency trend of the reference data. However, the absolute value of the continuum absorption coefficient is about 30 % higher. Possible sources of error include poor signal-to-noise ratio and baseline drift such as from condensation on the White cell mirrors of water or oil vapor from the pumping system. We note that the mirrors in the ringdown cell were heated above ambient to prevent condensation while the mirrors for the FTIR cell were not heated. Using the data from the ringdown measurements as calibration data for the FTIR baseline brings our FTIR data into good agreement with the reference data.



**Fig. 5.** Water vapor continuum absorption coefficients in the CO<sub>2</sub> laser line region. The diamonds and triangles represent the data from Ref. [2] and [3], respectively. The “+” and “x” are our data from the ringdown measurements and White cell, respectively. The solid curve represents theoretical prediction [5], and the dashed line is the fit to our FTIR data only.

### ***Continuing studies***

The recent progress we have made using cavity rindown spectroscopy is largely attributed to improving the thermal stability of the CO<sub>2</sub> laser. Given the improved operating performance of the CRD spectrometer and the success of the current studies, we are currently extending continuum absorption measurements to other CO<sub>2</sub> laser lines.[9] We also plan to exploit the tunability of the ringdown instrument to obtain accurate lineshape parameters of a few strong water lines in the mid-IR, similar to our recent studies in the THz region. [10]

### **III. Data management/archival strategy/accomplishments**

As an important part of the experimental investigation of the continuum absorption of H<sub>2</sub>O, we have developed an interactive Windows program for direct comparison of experimental data with the latest HITRAN database information. The program includes features to vary partial, total air pressure and temperature for various molecules listed in the HITRAN database using trackbars. Changes to simulated spectra (absorbance or transmission) are therefore updated in real time. These features are extremely useful for modeling spectra and for comparison with experimental data under various laboratory conditions. Although the interface to HITRAN is a fairly recent addition, descriptions of other features of this software are given at

<http://physics.nist.gov/Divisions/Div44/facilities/uvs/jb95userguide.htm>

We also plan to provide the continuum coefficients in cross section form and discrete lineshape parameters of water vapor to the HITRAN database as they become available.

### ***Conclusion***

The present cavity ringdown measurements provide results consistent with the independent measurements of Roberts *et al.* and Cormier *et al.* We find a value for the continuum absorption coefficient of  $1.98(15) \times 10^{-22}$  molecules<sup>-1</sup> cm<sup>2</sup> atm<sup>-1</sup> at 949 cm<sup>-1</sup>, in good agreement with the value of  $2.20(13) \times 10^{-22}$  molecules<sup>-1</sup> cm<sup>2</sup> atm<sup>-1</sup> obtained by Cormier *et al.* at 944 cm<sup>-1</sup>. We thus agree with the finding of Cormier *et al.* that “empirical models of the water vapor continuum which are commonly used in atmospheric radiative transfer calculations overestimate the continuum absorption by 10 % - 15 %.” The findings of Cormier *et al.* and the present study validate the concern of the ARIS team that the accepted value for the water-vapor continuum absorption in the 10 μm to 12 μm region is too large. [11] We, thus, further recommend use of the data from Roberts *et al.* and Cormier *et al.* or the present results for the extraction of sea-surface temperature (SST) profiles from the AIRS measurements.

#### IV. References

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