Laboratory Measurement of the Absorption Spectra of Water Vapor and Carbon Dioxide Relevant to the ARM Program

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Introduction

Important new concerns have arisen recently during the process of applying the currently available molecular spectroscopic data bases such as HITRAN (HIgh-Resolution TRANmission; Rothman et al. 1996) and GEISA (Gestion et Etude des Informations Spectroscopiques Atmospheriques; Jacquinet-Husson et al. 1999). These range from a) the lack of accurate data on the spectral lines of CO_2 in the hot bands and in the ν_2-fundamental band in the 15-μm region, the spectral lines of water vapor in the ν_2-fundamental band at 6.3 μm and in the thermal infrared (8 μm to 12 μm) region; b) the spectral lines in all of the shortwave (500 nm to 1100 nm) bands of water vapor; to c) the difference, if any, in the absorption characteristics of water vapor near saturation, especially in the shortwave region. The concerns b) and c) arose on account of the recently identified enhanced absorption of solar radiation by the atmosphere. Our laboratory has been addressing the concerns b) and c) in collaboration with the National Aeronautics and Space Administration's (NASA's) Ames Research Center (ARC) and Science and Engineering Services Inc (SESI), respectively. The task a) was performed at Stony Brook. Nemtchinov, currently at NASA's JPL, was involved in measuring and analyzing some of the data obtained in task b) at ARC. The data presented as a poster at the 1999 Atmospheric Radiation Measurement (ARM) Program Science Team Meeting were preliminary. Since then we have performed

additional measurements that we are in the process of interpreting and analyzing. As an important addendum to that poster presentation represented by this extended abstract, we include here a brief discussion of some significant errors that we have discovered in the spectral line intensities in the shortwave bands of water vapor listed in the HITRAN and GEISA data bases, which incidentally contain the same data sets.

The Thermal Infrared Spectra of CO_2 and H_2O

The spectra were obtained using a high-resolution Bruker IFS-120 HR Fourier-transform spectrometer (FTS) and cryogenically cooled absorption cells. The absolute intensities and self- and air-broadened half-widths of lines were derived from measured spectral transmittance data using a non-linear least-squares fitting routine developed in our laboratory. This routine fits multiple independent spectra taken at each temperature simultaneously and yields results as a consistent set of line parameters. We reported the intensities and self-broadening coefficients at 296 K of several lines between 717 cm^{-1} and 721 cm^{-1} in the Q-branch and between 722 cm^{-1} and 750 cm^{-1} in the R-branch of the hot band of CO_2. We also determined the intensities and N_2- and air-broadening parameters (half-widths and lineshapes) of the strong lines of the fundamental band that overlap the lines of the hot band. The aim was to examine the shapes of the troughs between the strong lines of the fundamental band and their effect on the lines of the hot band. These data are now being extended to lower temperatures and to other lines in the bands. We reported preliminary measurements at 296 K of the intensities, self-broadened linewidths, and self-induced lineshifts of 181 lines of water vapor in the 950 cm^{-1} to 1315 cm^{-1} region. We compared our data on the intensities and linewidths with the entries in the HITRAN data base. We also reported similar data determined at 284 K and 296 K in the ν_2-fundamental band at 6.3 μm. We compared our results with the entries given in the HITRAN database. Our intensity data agree with HITRAN data within 15%. However, the discrepancies in the self-broadened linewidths listed in the data base and measured fall within ± 30%.

Shortwave Absorption Bands of Water Vapor

We reported preliminary data obtained in the 980-nm to 1037-nm region at ARC using a 25-m base path White cell with effective optical path of 1.307 km and a Bomem DA8 high-resolution FTS. Several lines missing in the HITRAN data base were identified. Our intensity data were, on the average, about 20% to 30 % higher than those listed in the database. Our comments on HITRAN apply to GEISA as well, since the latter is essentially a duplication of the former as far as the data on this molecule are concerned. We found our data to be generally compatible with the intensity data reported by Chevillard et al (1989). This particular comparison applies to the weak lines in the 979-nm to 994-nm region. This seemed odd, since the measured data of Chevillard et al. were acknowledged to be the source of the databases for these spectral lines. We therefore selected over 50 of the "best-measured" lines from the tables of Chevillard et al. (1989) to compare with HITRAN. About half of these lines were previously measured by Giver et al. (1982). Each of the 1982 line intensity values agreed with the corresponding data of Chevillard et al. (1989) within 6%, which was within the experimental error. After making this comparison, we made a similar comparison with four other published articles reporting original experimental data (Mandin et al. 1986, 1988; Camy-Peyret et al. 1986; Toth 1994), which were also adapted by the two data bases. All the measurements reported by the French team and Toth were

performed using the same FTS and the 6-m base path White cell at the Kitt Peak Solar Observatory. All of the articles by the French team report intensities in the units of cm^{-2} atm^{-1} at 300 K while Toth reported at 297 K. HITRAN lists intensity data at 296 K in units of cm^{-1}/(molecule^{-1} cm^{-2}) and provides software for easy conversion to any temperature T. Therefore, we converted the HITRAN entries to values at 300 K for comparison with all the data obtained by the French group and to values at 297 K for comparison with Toth. Then the ratio of the measured intensities and those in HITRAN should simply be the conversion {from (cm^{-2} atm^{-1})$_T$ to (cm^{-1}/molecule cm^{-2})$_T$} factor $n_L(T_0/T)$, where $T_0 = 273.16$ K and n_L is the Loschmidt number. The conversion factors for the 300 K and 297 K data sets should, therefore, be 2.446E19 and 2.471E19, respectively. What we found, however, is rather complex and intriguing. We show the ratios for all the five reported spectral regions in Figure 1. The five spectral regions are as follows: 8036 cm^{-1} to 9482 cm^{-1} (Mandin et al. 1988), 9603 cm^{-1} to 11500 cm^{-1} (Chevillard et al. 1989), 11610 cm^{-1} to 12861 cm^{-1} (Toth 1994), 13200 cm^{-1} to 16500 cm^{-1} (Mandin et al. 1986), and 16500 cm^{-1} to 25250 cm^{-1} (Camy-Peyret et al. 1986). In addition, we show one set (open
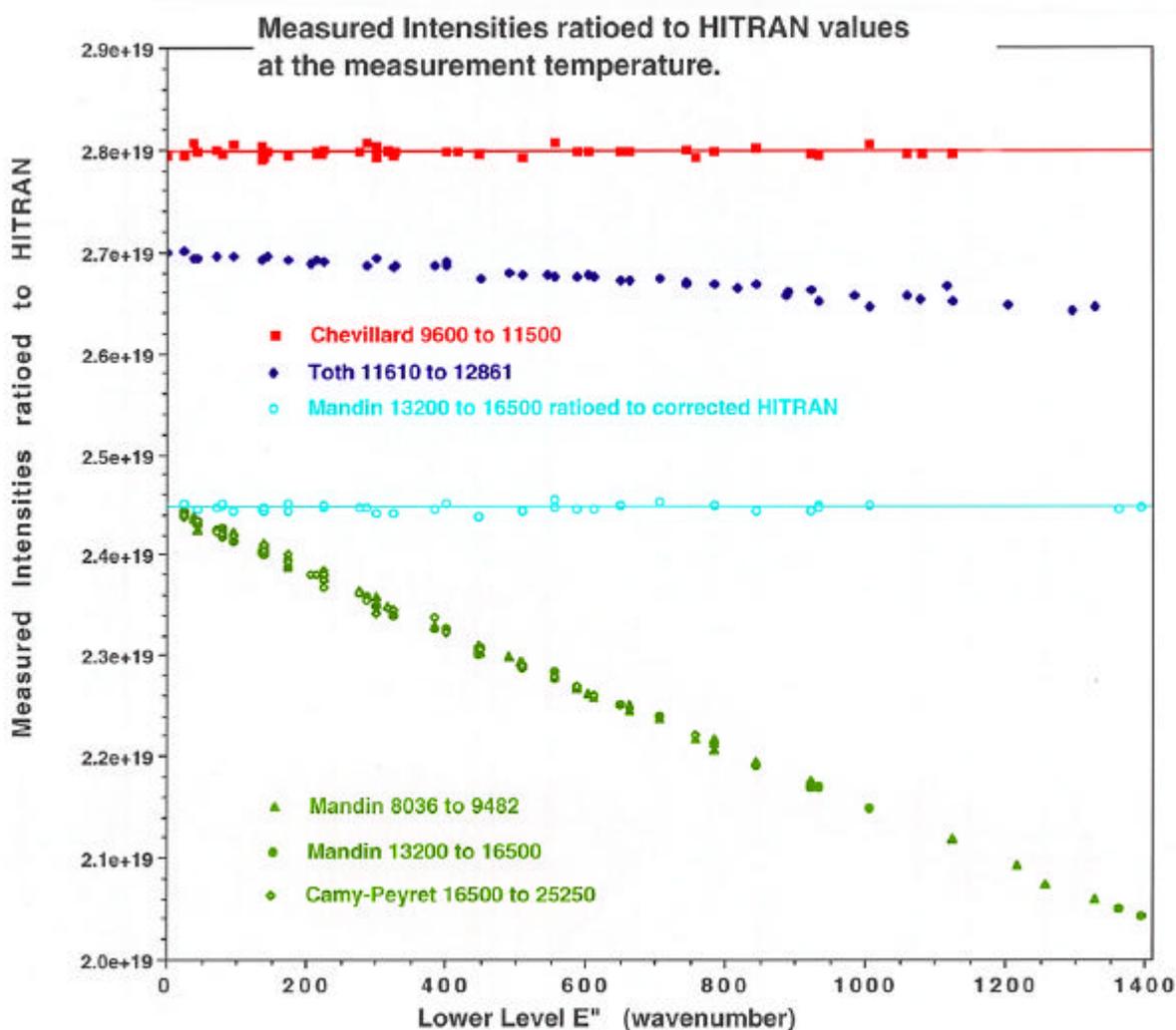
Figure 1. Measured intensities ratioed to HITRAN values at the measurement temperature.

circles) that was ratioed to "corrected" HITRAN data. In the 8036 to 9482, 13200 to 16500, and 16500 to 25250 cm^{-1} spectral intervals, we noted substantial dependence upon E'', the energy of the lower quantum level. A fit to these points yields 2.447E19 at $E'' = 0$, which is the only place on the graph where the ratio has the expected value. On the other hand, the 9600 cm^{-1} to 11500 cm^{-1} data set shows no such dependence upon E'', which is as it should be. But the average value of the ratio is 2.798E19 instead of 2.446E19. It would seem that all the HITRAN entries should be increased by 14.4% in this spectral region. The ratios in the 11610 cm^{-1} to 12861 cm^{-1} region exhibit a small dependence on E'' when ratioed to HITRAN data after conversion to 297 K, but none when ratioed with HITRAN data at 296 K. This suggests that the 1 K difference was neglected when Toth's measured data were converted into HITRAN units, which is unimportant since 1 K is the estimated uncertainty in the temperature of the measurements. However, the ration then is exactly the Loschmidt number 2.687×10^{19} instead of $n_L(273.16/297)$. Thus, this oversight makes it necessary to increase the HITRAN data in this spectral region by 8.7%. For the data in the three spectral intervals shown in Figure 1, which exhibit significant dependence upon E'', it would seem that the HITRAN entries were converted without using the negative sign in the Boltzmann factors $\exp(-hcE''/T)$ evaluated at 296 K and 300 K. To test this, we multiplied the HITRAN data by the correction factor $\exp[-2(hcE''/k)\{(1/296) -(1/300)\}]$, thereby eliminating the dependence upon E''. This is shown in Figure 1 by the open circles, which correspond to an average ratio of 2.447E19. All of the intensities in the two data bases should be decreased by the above stated exponential factor for all the three spectral regions mentioned.

Measurement of the Absorption Characteristics of Water Vapor Near Saturation

As we have run out of space here, we refer the reader to Report DOE/ER-0738, the *Proceedings of the Eighth ARM Science Team Meeting* held in 1998, in which we described our apparatus, the special design of the absorption cell, and the photo-acoustic laser-spectroscopic procedure. We showed some preliminary data at this Science Team meeting and have since followed up with more definitive measurements, which are however still preliminary. They will be reported at the next meeting.

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