Reports

Tunable Infrared Laser Spectroscopy of Atmospheric Water Vapor

Abstract. *Absorption lines in the ν_2 band of water vapor at 6.3 micrometers have been fully resolved by using a tunable semiconductor laser. Three atmospheric water vapor lines near 5.32 micrometers were studied in detail and found to have line widths two to four times narrower than the width calculated by Benedict and Kaplan.*

Water vapor plays a prominent role in determining the infrared properties of the atmosphere. Its absorption spectrum contains a large number of strong lines in the infrared around 3 and 6 μm and above 10 μm (*1*). These absorption lines directly, and often predominantly, affect the transmission of radiation through the atmosphere (*2*). Atmospheric transmission in the infrared is important in laser applications that require passage of the beam through the atmosphere. Furthermore, the infrared absorption and emission by water vapor in these bands is a significant factor in determining the heat balance of the lower atmosphere, as well as of the earth itself (*3*). The transmission (or absorption) of the atmosphere near a water vapor line depends on the strength and width of that line. We have fully resolved (resolving power approximately 5×10^7) for the first time several lines in the 6.3-μm ν_2 band of water vapor and, thereby, accurately determined their strengths and widths. Also, we have studied in detail three atmospheric water vapor lines near 5.32 μm by using a tunable PbSSe semiconductor laser. While the observed line strengths are in good agreement with the calculated strengths (*4*), the observed line widths are two to four times narrower than the generally accepted widths (*4*) calculated by Benedict and Kaplan (*5*).

The semiconductor diode laser used in these experiments was fabricated from a single crystal of $PbS_{0.6}Se_{0.4}$ (*6*) and emitted radiation near 5.3 μm. The laser was mounted on the cold finger of a liquid helium Dewar at 10° to 15°K and operated with a d-c bias current of several hundred milliamperes. The power output occurred in several laser modes separated by $\lesssim 1$ cm^{-1}, with $\geqq 10$ μw in the stronger modes which were used in these experiments. With a power output of more than 10 μw the modes are estimated to have line widths of less than 1 Mhz (3×10^{-5} cm^{-1}) and are capable of completely resolving typical Doppler-broadened molecular absorption lines (*6*). Fine tuning of the laser modes was accomplished by varying the d-c bias current. A relative frequency calibration of the tuned laser mode used in these experiments was obtained by measuring the mode frequency as a function of current with a grating spectrometer (resolution approximately 0.2 cm^{-1}) (*6*). In this manner we measured the average tuning rate of 510 Mhz/ma over a 75-ma current range (1.25 cm^{-1}). The tuning rate (and therefore the relative frequency of the laser mode) obtained in this manner is estimated to be constant and accurate to within ± 10 percent. Spectra were obtained by measuring the amplitude of the laser radiation transmitted through a laboratory ambient air path. The laser radiation was mechanically chopped, passed through a grating spectrometer for line identification and tuning rate calibration, and detected with a Ge:Cu photoconductor cooled by liquid helium.

Table 1. Properties of observed (Obs.) water vapor lines near 1879 cm^{-1} (5.32 μm). The calculated (Calc.) values are from Benedict and Calfee (*4*); $J(K_a,K_c)$, quantum numbers of rotational energy levels; ν, wave number; full width, full width at half absorption coefficient maximum.

Rotational transition $J(K_a,K_c)$	Calc. ν (cm^{-1})	$\Delta\nu$ (cm^{-1})		Full width (cm^{-1})		Intensity (cm^{-2}/atm)	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
16 (1,16) ← 15 (0,15) 16 (0,16) ← 15 (1,15)	1879.01	− 0.26*	− 0.33	0.015	0.064	0.0014	0.0013
13 (1,12) ← 12 (2,11)	1879.34	0†,‡	0‡	0.031	0.068	0.0089	0.0099
13 (2,12) ← 12 (1,11)	1879.60	0.28§	0.26	0.029	0.068	0.0024	0.0032

* Line A. † Line B. ‡ Assumed zero for reference. § Line C.

The spectra of three atmospheric water vapor absorption lines near 5.32 μm are shown in Fig. 1. Since only the relative frequency tuning of the laser is accurately known, the frequency relative to the position of the center line is given on the abscissa. Note that the resolution of approximately 3×10^{-5} cm^{-1} indicated by the vertical bar in Fig. 1 yields fully resolved absorption spectra. The data were taken with a $PbS_{0.6}Se_{0.4}$ laser transmitting over a 7.4-m path of laboratory air at 295°K. The ambient relative humidity was 18 percent, yielding water vapor partial pressure of 3.6 torr in the air. The three lines labeled A, B, and C are identified as members of the $\nu_2[(010) \leftarrow (000)]$, 6.3-$\mu$m fundamental vibration-rotation band of H_2O by using the grating spectrometer and the published water vapor line positions (*4*). The rotational transitions involved and their calculated wave numbers are given in Table 1 with the quantum numbers of the rotational energy levels in the form $J(K_a,K_c)$. Note that line A is twofold degenerate. The identification of these lines is supported by (i) the agreement between the measured and calculated line parameters discussed below, (ii) the absence of any calculated lines of similar strength within a 5-cm^{-1} span about 1879 cm^{-1}, and (iii) the appearance of a broad unresolved absorption in the region 1879 to 1880 cm^{-1} in the water vapor absorption spectra observed by Ben Aryeh (*7*) and Benedict *et al.* (*8*). Since the laser output amplitude is changing slowly with wave number (diode current), one can estimate the background signal level (dashed line of Fig. 1) at the absorption line centers and, thus, determine the absorption coefficient as a function of wave number (ν). The line widths (full width at half absorption coefficient maximum) and intensities deduced in this manner are summarized in Table 1. The calculated values from Benedict and Calfee (*4*) are also given for comparison. The measured line separations, $\Delta\nu$, and the line widths have the accuracy of the measured tuning rate (± 10 percent). The line intensities are estimated to have an accuracy of ± 15 percent.

A comparison of the measured and calculated entries of Table 1 shows good agreement except for the line width. The line separations agree, the error being determined by the inaccuracy of ± 0.05 cm^{-1} for the calculated line positions (*4*). The line intensities agree to within 25 percent. Note that theory predicts a 3/1 ratio of the intensity of line B to that of line C, in reasonable agreement with experiment. However, the observed line widths are two to four times narrower than the calculated widths. For line A, the absorption coefficient measured at the line center is four times larger than that expected from the Benedict and Kaplan line-width calculations (*5*). Similar arguments apply to lines B and C. These molecular absorptions are produced by transitions between levels with high rotational energy ($J \geqq 12$) of the H_2O molecule, and collision broadening due to N_2 and O_2 is expected to be relatively small (*5, 9*). However, line A is surprisingly narrow, having a width only three times larger than the limiting low-pressure Doppler width of 0.0055 cm^{-1}. The widths calculated by Benedict and Kaplan for the three lines are nearly equal to the value (0.064 cm^{-1}) determined from a minimum cross section chosen to correspond closely with that expected from kinetic theory (*5*). In the model used, it was assumed that the collision cross section for line broadening cannot fall below the minimum cross section. This minimum cross section was found from an assumed minimum impact parameter of 3.2 Å, a value slightly larger than the kinetic theory diameter (3.14 Å) derived from studies of the pressure-volume-temperature relationships of mixtures of H_2O and N_2 (*10*). Our results show that the collision cross section for line broadening can fall well below that predicted by kinetic theory. Small values of the line-broadening cross section for high rotational energies are not unreasonable, since for high rotational states collisions are less effective in altering either the molecular rotational energy or the orientation of the angular momentum.

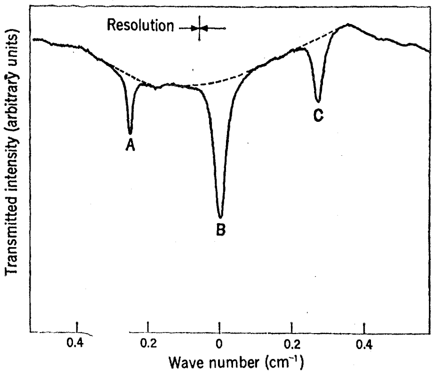

Fig. 1. Relative intensity of laser radiation transmitted over a 7.4-m air path, as a function of wave number (near 5.32 μm).

Patel (*11*) has measured the full width of the $11(3,9) \leftarrow 10(2,8)$ line at 1885.24 cm^{-1} to be 0.087 cm^{-1} (accuracy unstated) by using an InSb spin-flip Raman laser. The calculated (*4*) width is 0.1088 cm^{-1}. The discrepancy in widths is not as great as those we have observed for transitions involving higher *J* values, which indicates that the divergence between observed and calculated widths increases as *J* increases.

In conclusion, we have fully resolved several absorption lines of the atmosphere in the ν_2 water vapor band by using a tunable semiconductor laser. The observed line widths are two to four times narrower than calculated widths. Thus, the absorption coefficients at the line centers are correspondingly larger than indicated by the calculated parameters. The discrepancies in the relative positions of lines A and C (Table 1) are 0.07 and 0.02 cm^{-1}, larger than the observed line widths. These discrepancies have important implications concerning the infrared transparency of the atmosphere, particularly for monochromatic sources. For wavelengths near lines such as the ones we have studied, large errors in the calculated transmission of the atmosphere are introduced by the uncertainty in the absorption line widths and line positions. Hence, numerical calculations (*12*), which were made by using the line parameters given by Benedict and Calfee (*4*), have limited accuracy in wavelength regions where transitions involving high *J* values are important. (These are often regions of relatively high transmission, or "atmospheric windows.") More extensive measurements of the type reported here, carried out for a larger number of lines and involving methods for absolute calibration, are needed to accurately establish atmospheric transmission in these regions.

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