The effect of variations of half-widths upon outgoing radiation in a small water vapor spectral interval

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ABSTRACT

Recent high resolution laser spectroscopy, applied to the vibration-rotation spectrum of water vapor, indicates that half-widths involving high values of the rotational quantum numbers are in disagreement with corresponding half-widths determined theoretically. The present calculation compares atsmospheric transmission results and outgoing intensity obtained from theoretically determined values with those obtained using the recently available laser spectroscopy data. For a zenith angle of zero degrees, the atmospheric transmission and outgoing intensity are found to be 8.35 % and 10.25 ergs cm^{-2} sec^{-1} $ster^{-1}$, respectively, for the theoretically determined values, while the laser spectroscopy values increase the transmission and outgoing intensity to 10.0 % and 10.74 ergs cm^2 sec^{-1} $ster^{-1}$. The preseent calculations are restricted to a narrow spectral region extending from 1 877.15 cm^{-1} to 1 880.00 cm^{-1} in the neighborhood of the experimental spectroscopy measurements.

Introduction

Recent high resolution laser spectroscopy (Blum et al., 1972; Patel, 1972) applied to the vibration-rotation spectrum of water vapor indicates that half-widths involving high values of the rotational quantum numbers (J) are in disagreement with corresponding half-widths determined theoretically. The divergence between measured and calculated half-widths is observed to increase as J increases. Blum et al. state that the observed line widths for high J values are two to four times narrower than the generally accepted widths calculated by Benedict & Calfee (1967). However, measurement of the corresponding line intensities and line positions are found to be in reasonable agreement with those values determined theoretically. Line intensities and line positions are therefore accepted as calculated since the relative error in neglecting these variations is expected to be small when compared to the large discrepancies between measured and calculated half-widths.

In view of the large half-width discrepancies, Blum et al. imply that large errors in calculated atmospheric transmission may result. The present calculation compares atmospheric transmission results and outgoing intensities using the recently available laser spectroscopy data with results obtained using the theoretically determined values by Benedict and Calfee.

Theory and computational details

Presently the spectroscopy measurements of Blum et al. cover only a very narrow spectral region in the neighborhood of 1 879 cm^{-1}. For this reason, the present calculations are restricted to the spectral region extending from 1 877.15 cm^{-1} to 1 880.00 cm^{-1}. This spectral interval contains 10 lines including the 4 lines investigated by Blum et al.

The Lorentz line shape is assumed, and pressure broadening and temperature corrections are included for the half-widths according to classical kinetic theory. The outgoing intensity and atmospheric transmission is calculated at the reference height of 20 km which is, for all practical purposes, equal to the top of the atmosphere of this spectral region. Contributions to transmission above 20 km are very small so that Doppler broadening effects can be safely disregarded.

For a small spectral interval of width $\Delta\nu$, the mean transmission is given by

$$\bar{T}r = \frac{1}{\Delta\nu}\int_{\Delta\nu} \exp\left(-\int \sum_{i=1}^{N} \frac{S_i(\theta)\,\alpha_i(P,\theta)\,\varrho_v\,dz}{\pi[(\nu-\nu_{i0})^2+\alpha_i^2(P,\theta)]}\right)d\nu \quad (1)$$

where the summation index i refers to all spectral lines centered at wave-number ν_{i0} within the interval $\Delta\nu$ as well as the line wings of lines outside this interval. P is pressure, θ is temperature, ϱ_v water vapor density and z is height. The line intensity S is temperature dependent while the half-width α is pressure and temperature dependent. In terms of the kinetic theory of gases, the half-width is expressed as

$$\alpha_i(P,\theta) = \alpha_i(P_0,\theta_0)\,\frac{P}{P_0}\left(\frac{\theta_0}{\theta}\right)^{1/2} \quad (2)$$

No spectral model is assumed. The frequency integration is carried out pointwise in steps of approximately one-tenth of the smallest occurring half-width at normal temperature and pressure, and convergence is checked.

The line intensities at reference temperature θ_0 are tabulated by Benedict & Calfee. Quantum theoretical relationships give the temperature dependency of the line intensities. The $S_i(\theta)$'s are expressed in terms of the tabulated line intensities at reference temperature θ_0 as given by

$$S(\theta) = S(\theta_0)\left(\frac{\theta_0}{\theta}\right)^{3/2} \exp\left[-1.4388\,\nu''\left(\frac{1}{\theta}-\frac{1}{\theta_0}\right)\right] \times \left[\frac{1-\exp(-1.4388\,\nu_0/\theta)}{1-\exp(-1.4388\,\nu_0/\theta_0)}\right] \quad (3)$$

where the lower energy values ν'' are also taken from Benedict & Calfee. The assumed pressure and temperature distribution is the U.S. Standard Atmosphere. Corresponding moisture data are obtained from the *Handbook of Geophysics and Space Environments.*

Integration along the path is performed in one kilometer increments starting at the reference level at 20 km. The very reliable Curtis-Godson approximation is used in order to simplify the calculations. This approximation replaces the half-width α_i occurring in the denominator of the exponent of equation (1) by a weighted value α_i as given by

$$\tilde{\alpha}_i = \frac{\int S_i(\theta)\,\alpha_i(\theta_0,P_0)\,\frac{P}{P_0}\,\varrho_v\,dz}{\int S_i(\theta)\,\varrho_v\,dz} \quad (4)$$

This approximation gives exact agreement of the weak line limit of the transmission function.

In addition to the ten lines contained within the arbitrarily chosen wave-number interval, the contributions of twelve relatively strong lines outside the interval are also included. Test computations indicate that the contribution from numerous neighboring weak outside lines is negligible.

Results and conclusion

Transmission and outgoing intensities as a function of zenith angle are calculated for three cases. The first set of calculations (Case I) uses the standard theoretical half-widths and line intensities as given by Benedict & Calfee. The second set of calculations (Case II) assumes half-widths for J less or equal to 8 do not require correction as implied by measurements of Fridovich (1969). A linear scaling is then used for half-widths with J values greater than 8 in order to approximate the measured values. If α_0 is the theoretical half-width, then the corrected half-width α is approximated by

$$\alpha = \alpha_0\,(1-0.0957(J-8)) \text{ for } J>8$$

$$\alpha = \alpha_0 \qquad \text{for } J \leq 8$$

This seems to be the best fit based on the sparse experimental data now available. Finally, the third set of calculations (Case III) assumes that all theoretical half-widths are too large by a factor of three. This non-realistic case represents the maximum possible error in transmisssion of a given spectral region.

The total atmospheric transmission (Tr) and intensity of outgoing radiation (I) versus zenith angle (θ) is shown in Table 1. For a zenith angle of 0 degrees, the transmission and outgoing intensity for Case I are found to be 8.35% and 10.25 ergs $cm^{-2}\,sec^{-1}\,ster^{-1}$, respectively, while scaling (Case II) increases the transmission and outgoing intensity to 10.0% and 10.74 ergs $cm^{-2}\,sec^{-1}\,ster^{-1}$. Case III gives the maximum possible deviation from the

Table 1. *Transmissivity Tr and intensity I of outgoing radiation as a function of zenith angle θ for each of the three cases*

Zenith angle (deg.)	Case I (theoretical)		Case II (predicted)		Case III (extreme)	
θ	Tr (%)	I (erg cm^{-2} sec^{-1} $ster^{-1}$)	Tr (%)	I (erg cm^{-2} sec^{-1} $ster^{-1}$)	Tr (%)	I (erg cm^{-2} sec^{-1} $ster^{-1}$)
0	8.35	10.25	10.02	10.74	31.01	13.10
25	6.86	9.94	8.32	10.42	28.72	12.87
50	2.95	8.92	3.77	9.35	20.99	11.97
75	0.044	6.50	0.075	6.80	Not Calculated	

theoretical results (Case I) and represents an extreme situation for this spectral region.

Radiative cooling, which is proportional to the radiative flux divergence is not calculated in the present study. This quantity has very little meteorological significance due to the narrowness of the spectral interval.

If these calculations are indicative of other spectral regions, the relative error in the total transmission can be expected to be of the order of 15–25%. However, the relative error in the intensity of outgoing radiation can be expected to be less than 5%. It will be important to extend these calculations to other parts of the spectrum as more experimental data becomes available.

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ВЛИЯНИЕ ВАРИАЦИЙ ПОЛУШИРИН УХОДЯЩУЮ РАДИАЦИЮ В УЗКОМ СПЕКТРАЛЬНОМ ИНТЕРВАЛЕ ВОДЯНОГО ПАРА

Современная лазерная спектроскопия с высоким разрешением в применении к колебательно-вращательному спектру водяного пара показывает, что полуширины спектральных линий, соответствующих высоким значениям вращательных квантовых чисел, расходятся с соответствующими полуширинами, определенными теоретически. В данных расчетах результаты по пропусканию атмосферы и интенсивности уходящей радиации, полученные с помощью теоретически определенных полуширин, сравниваются с результатами, полученными с помощью имеющихся данных лазерной спектроскопии. Для зенитного угла, равного нулю градусов, атмосферное пропускание и уходящая радиация найдены равными 8,35 % эрг $см^{-2}$ $сек^{-1}$ $стер^{-1}$, соответственно, для теоретически определенных величин, в то время как данные лазерной спектроскопии увеличивают пропускание и уходящую радиацию до 10,0 % и 10,74 эрг $см^{-2}$ $сек^{-1}$ $стер^{-1}$. Настоящие расчеты ограничены узкой спектральной областью, простирающейся от 1 877,15 $см^{-1}$ до 1 880,00 $см^{-1}$, в окрестности экспериментальных спектроскопических измерений.