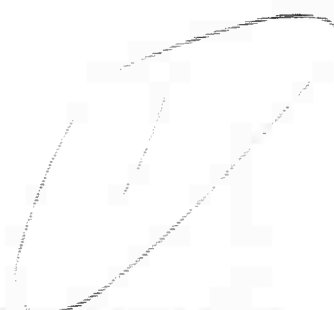


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## SPECTRAL EMISSIVITIES AND INTEGRATED INTENSITIES OF THE 6.3- $\mu$ FUNDAMENTAL BAND OF H<sub>2</sub>O\*

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**Abstract**—Spectral emissivities of the  $\nu_2$ -fundamental band of water have been measured between 550° and 2200°K. The hot water vapor samples were produced in a small supersonic burner using H<sub>2</sub> and O<sub>2</sub> gases. The variation of the spectral emissivities of H<sub>2</sub>O as a function of temperature has been obtained for a constant amount of H<sub>2</sub>O in the optical path. An estimate of the integrated intensity of the 6.3- $\mu$  fundamental band has been made from the high temperature emission spectra. The observed integrated intensity of the 6.3- $\mu$  H<sub>2</sub>O band was  $300 \pm 20$  per cent ( $\text{cm}^{-2}\text{-atm}^{-1}$ ) at 273°K and is independent of the temperature.

### INTRODUCTION

THE INFRARED spectral absorptivities of water at room temperature have been extensively studied.<sup>(1-9)</sup> More recently, emission and absorption measurements were made also at higher temperatures, using various experimental techniques.<sup>(10-15)</sup> However, these measurements become increasingly difficult as the temperature and pressure are raised. The lack of high temperature window materials for hot cells which transmit beyond 4  $\mu$  has been the major limitation. Thus, measurements of spectral emissivities of hot water vapor have been limited to the spectral region below 4  $\mu$  for temperatures  $> 1000^\circ\text{K}$  and to temperatures  $\leq 1000^\circ\text{K}$  for the spectral region above 4  $\mu$ . The supersonic burner technique which was used in this laboratory to generate hot gases in previous spectroscopic measurements of CO<sub>2</sub> and H<sub>2</sub>O,<sup>(14-17)</sup> lends itself to high temperature measurements of the spectral emissivities in the spectral region above 4  $\mu$  since no windows are necessary. However, the total pressure of the hot gas is limited to 1 atm in this technique.

It is the purpose of this report to describe the measurements of the spectral emissivities of water between 4 and 12  $\mu$  for temperatures ranging from 550° to 2200°K. The measurements were made at a total pressure of 1 atm with a nearly constant amount of H<sub>2</sub>O in the path. From the spectral emissivities obtained at the higher temperatures, the integrated intensity of the 6.3- $\mu$   $\nu_2$ -H<sub>2</sub>O band has been determined.

### EXPERIMENTAL PROCEDURE

The experimental apparatus (burner and optical system) has been described previously.<sup>(14,17)</sup> In the present study the calcium fluoride prism was replaced by a sodium

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chloride prism. Various monochromator slit widths (from 0.25 mm to 1.5 mm) were used in this investigation, depending upon the energy level emitted from the gas. Line-reversal temperature measurements with high spatial resolution were made<sup>(18)</sup> in the exit jet of the burner used in this present study. In these measurements, RP-1 (in which sodium butoxide was dissolved) was used as fuel. The temperature variation across the exhaust jet (except the boundary layer) was determined to be not more than  $\pm 1.5$  per cent. The boundary layer was estimated to be very small ( $\sim 3$  per cent of the total geometrical path).<sup>(17)</sup>

The gas temperature at different mixing ratios was determined by the standard transmission-emission technique,<sup>(19)</sup> and the results were given previously.<sup>(15)</sup> In addition to the double impingement injector used in most of the previous and present experiments, a specially designed injector was used for the very lean mixture ratios to obtain temperatures of  $\sim 500^\circ\text{K}$ . The gas temperature versus mixing ratios for this injector are given in Fig. 1. The measurements were made in various spectral regions in the 2.7- and 6.3- $\mu$   $\text{H}_2\text{O}$  bands. No systematic difference between the temperatures measured in the two spectral regions was observed.

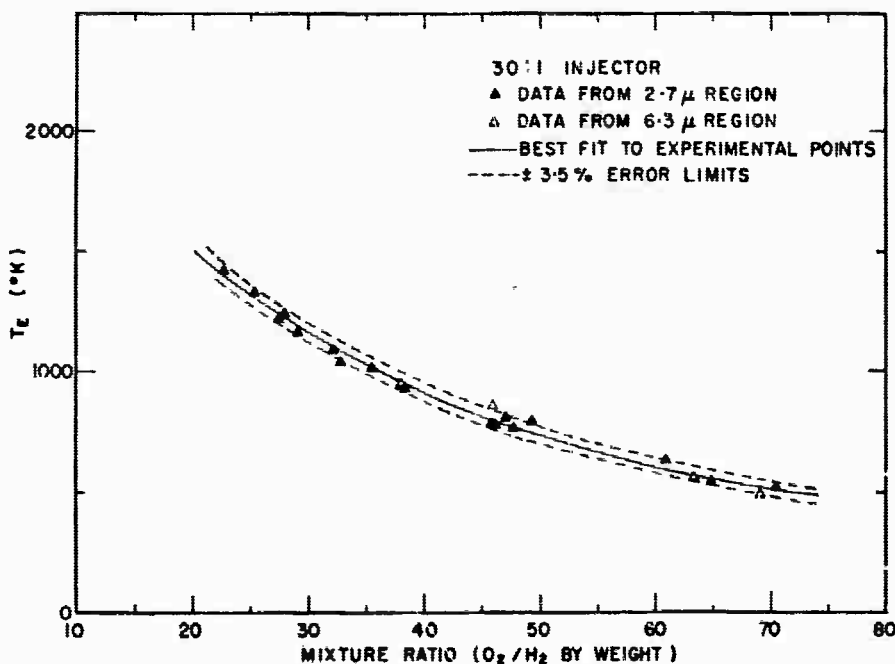


FIG. 1. Measured exit temperatures vs. mixture ratio ( $\text{O}_2/\text{H}_2$  by weight) of the 30 : 1 injector. Combustion chamber pressure  $\sim 30$  atm, area ratio = 1 : 5.25. (Data were taken at different spectral locations in the 2.7- and 6.3- $\mu$  water bands.)

From the temperature vs. mixture ratio plot, the gas composition was calculated by a computer program by means of a "shifting changing to frozen equilibrium expansion model" as described previously.<sup>(17)</sup> The resulting optical depth  $pl$  (cm·atm) versus temperature is given in Fig. 2. The uncertainty in the determination of the temperature and partial pressure of  $\text{H}_2\text{O}$  was about  $\pm 3.5$  per cent. The pathlength  $l$  of 31 mm was known to within  $\pm 1.5$  per cent so that the total error in optical depth was about  $\pm 5$  per cent.

The optical depth was normalized to STP density by  $u = l p_{\text{H}_2\text{O}} T_0 / T$  (cm·atm)<sub>STP</sub>, where  $p_{\text{H}_2\text{O}}$  = partial pressure of the emitting species in atm,  $T_0 = 273^\circ\text{K}$ ,  $l$  = geometrical pathlength, and  $T$  = sample gas temperature. The normalized optical depth is also given in Fig. 2. It is seen that the value is nearly constant for the temperature range

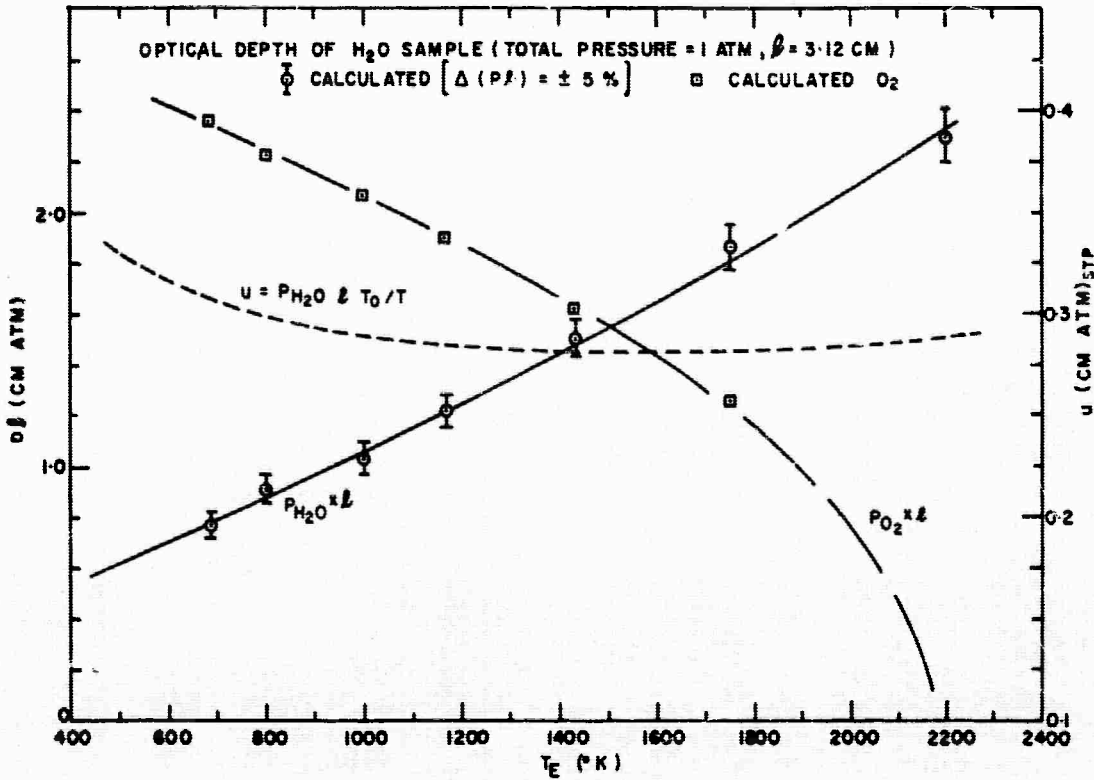


FIG. 2. Optical depth of H<sub>2</sub>O in the gas sample as calculated by the "shifting changing to frozen equilibrium expansion model". Values are given for  $p_{\text{H}_2\text{O}} \times l$  and  $u = p_{\text{H}_2\text{O}} l T_0 / T$ . The uncertainty is  $\pm 5$  per cent.

investigated. To obtain the optical path in pr cm,  $u$  must be multiplied by  $\rho^0 = 8.042 \times 10^{-4}$  g/cm<sup>3</sup>. In Fig. 2 the optical depth O<sub>2</sub> which is present in the sample is also given.

The emissivity measurements were made by determining the spectral energy emitted from the gas and dividing by the blackbody energy for the particular wavenumber and gas temperature. The emitted energy was obtained on an absolute basis by relating the instrument deflection to the standard blackbody source:

$$\epsilon(\nu, T) = \frac{G(\nu) N^0(\nu, T_B)}{B(\nu) N^0(\nu, T)} \quad (1)$$

where  $\epsilon$  = emissivity,  $\nu$  = wavenumber (cm<sup>-1</sup>),  $G(\nu)$  = pen deflection of gas emission ( $\mu\text{V}$ ),  $B(\nu)$  = pen deflection of standard blackbody source ( $\mu\text{V}$ ),  $N^0(\nu, T_B)$  = blackbody energy of standard blackbody source, whose temperature  $T_B$  was determined by a platinum-rhodium thermocouple, and  $N^0(\nu, T)$  = blackbody energy at gas temperature  $T$ .

Readings from the traces (burner and blackbody emission) were made at constant micrometer drum readings of the spectrometer and served as input to a computer data reduction program.

The use of a double pass monochromator with the internal chopper and the NaCl prism gave rise to "false radiation" in the monochromator resulting in a zero-shift which was larger than indicated by the manufacturer (about  $0.05 \mu\text{V}$  at  $7 \mu$ ). We believe the reason for this was the high temperature ( $80^{\circ}$ – $85^{\circ}\text{C}$ ) of the instrument. The higher temperature was necessary because the instrument is located near the ocean in the open air and only protected by an insulating box. The higher temperature probably resulted in larger temperature gradients in the instrument, giving rise to the "false radiation". It was therefore necessary to determine the zero level at every wavelength of the instrument.

Checks were also made for stray light. Different cut-off filters were placed in front of the entrance slit of the monochromator, and neither energy emitted from the supersonic burner or the globar source indicated the presence of stray light. The wavenumber calibration of the two prisms was made from known absorption spectra of atmospheric water and carbon dioxide, ammonia at 25–100 mmHg partial pressure and an open dish of methanol.<sup>(20)</sup>

This calibration was checked frequently between the actual data taking runs of the burner. The maximum deviation encountered was 2 drum divisions, resulting in a shift of  $5 \text{ cm}^{-1}$  at  $6 \mu$ , which was then corrected by the data reduction program.

The uncertainty in the spectral emissivity values was estimated to be about  $\pm 15$  per cent for runs at  $T > 1000^{\circ}\text{K}$  and about  $\pm 25$  per cent for runs at  $T < 1000^{\circ}\text{K}$ .

## RESULTS AND DISCUSSION

### *Spectral emissivities*

Representative spectra of the  $6.3\text{-}\mu$  band at a total pressure of 1 atm are shown in Figs. 3 through 7 for temperatures  $540^{\circ}$ ,  $1030^{\circ}$ ,  $1535^{\circ}$ ,  $1850^{\circ}$ , and  $2200^{\circ}\text{K}$ , respectively. The spectrum at  $540^{\circ}\text{K}$  was made with a spectral slit width of  $75 \text{ cm}^{-1}$  at  $6 \mu$ , because the emitted energy was very low. This relatively large slit width did not permit partial resolution of the spectrum but rather only gives the band contour. The spectrum at  $1070^{\circ}\text{K}$  and all following spectra were made with the smaller spectral slit width of  $24 \text{ cm}^{-1}$  which resulted in some fine structure. The spectrum at  $1535^{\circ}\text{K}$  (Fig. 5) shows a marked increase in area under the curve. Many higher order transitions become excited, which reduce the self-absorption. At the longer wavelength, the band is overlapped by the rotational band. The averaged emissivities of the rotational band are indicated by a dotted line. The extension of the dotted line into the  $6.3\text{-}\mu$  band was obtained in the following way. In Fig. 8, the spectral emissivities between  $3000 \text{ cm}^{-1}$  and  $500 \text{ cm}^{-1}$  are given in a semi-logarithmic plot. The spectral region includes the long wavelength wing of the  $2.7\text{-}\mu$  fundamental band, the entire  $6.3\text{-}\mu$  band and the short wavelength wing of the pure rotational band. As has been noted previously,<sup>(15)</sup> part of the wing contours appear on this semilog plot as straight lines, and, assuming that we can continue the straight lines into the overlap region, we can separate overlapping bands in this approximate fashion. Transferring the straight line wing contour back onto the emissivity plots, (Figs. 5–7), one obtains an estimate of the contribution of the overlap of the different bands.

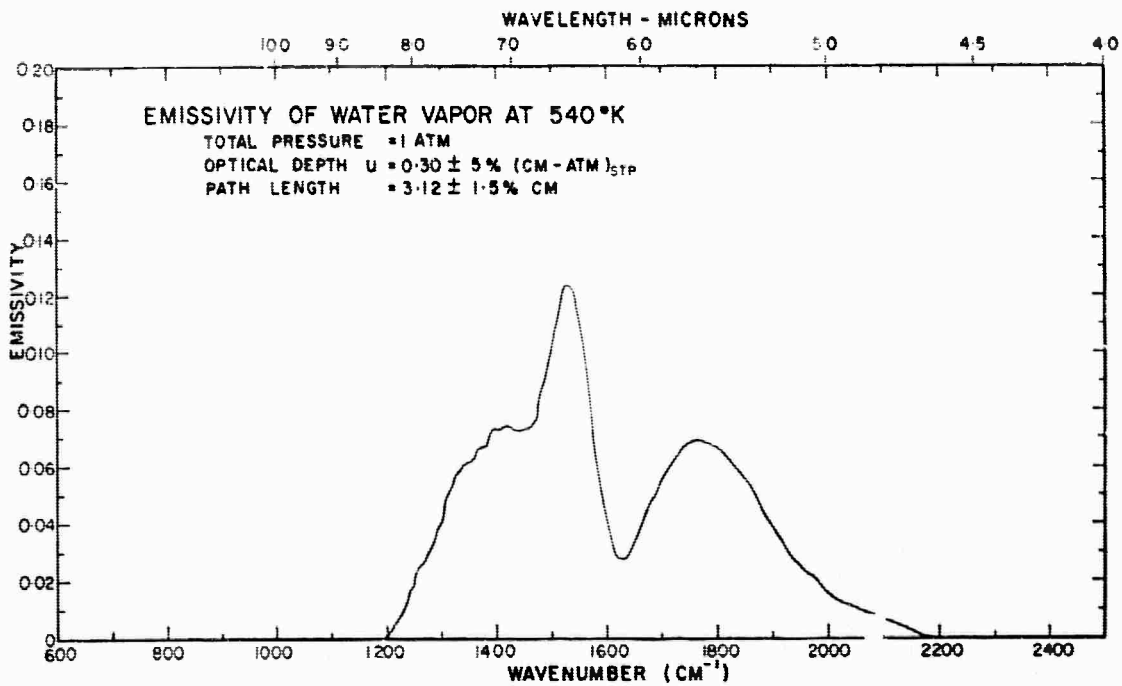


FIG. 3. Spectral emissivity of H<sub>2</sub>O at 540°K, taken with a KBr prism. Average spectral slit width = 70 cm<sup>-1</sup>.

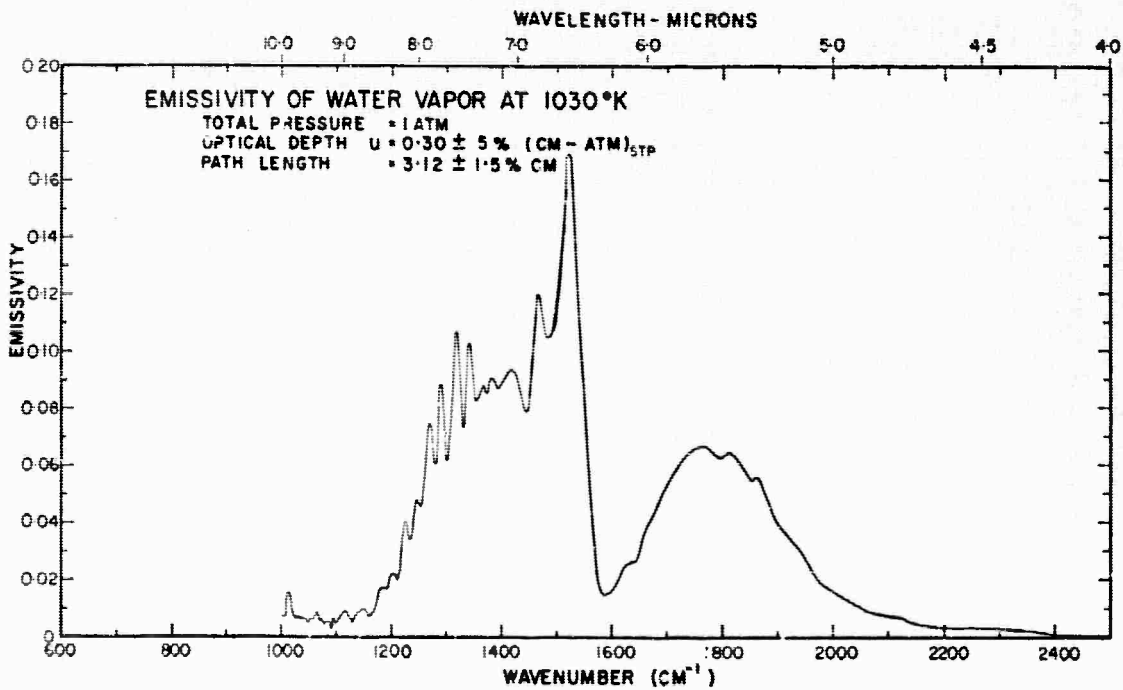


FIG. 4. Spectral emissivity of H<sub>2</sub>O at 1030°K, taken with a NaCl prism. Average spectral slit width = 25 cm<sup>-1</sup>.

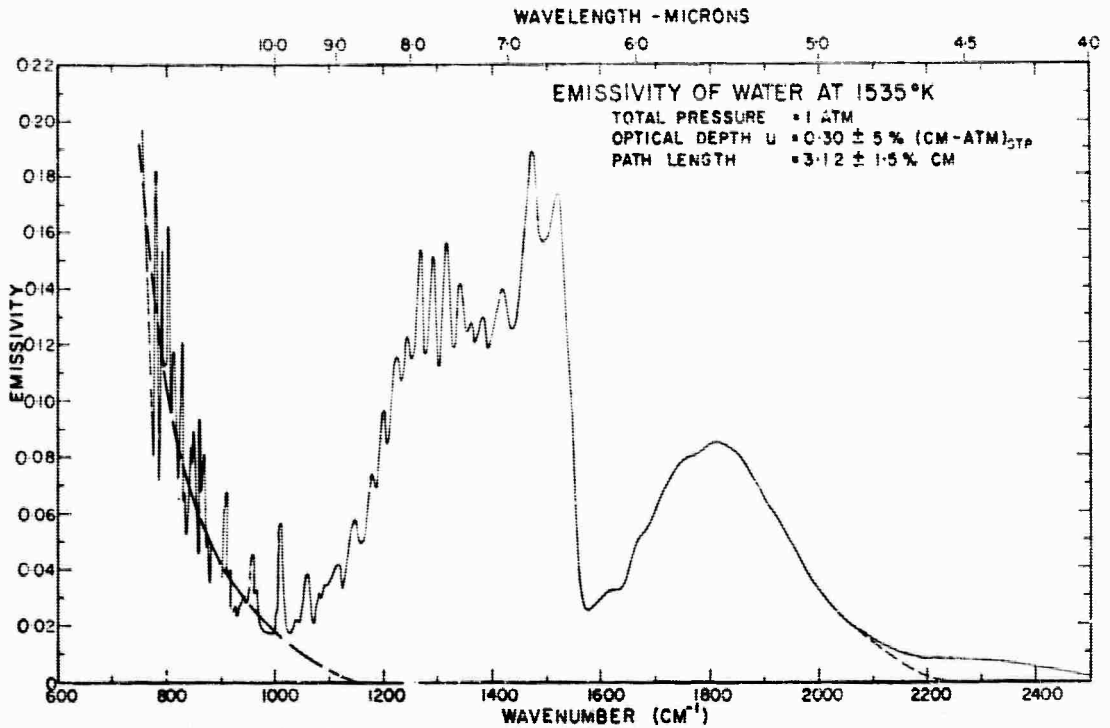


FIG. 5. Spectral emissivities of H<sub>2</sub>O at 1535°K, taken with a NaCl prism. Average spectral slit width = 25 cm<sup>-1</sup>. The contour of the rotational band is indicated by a dotted line.

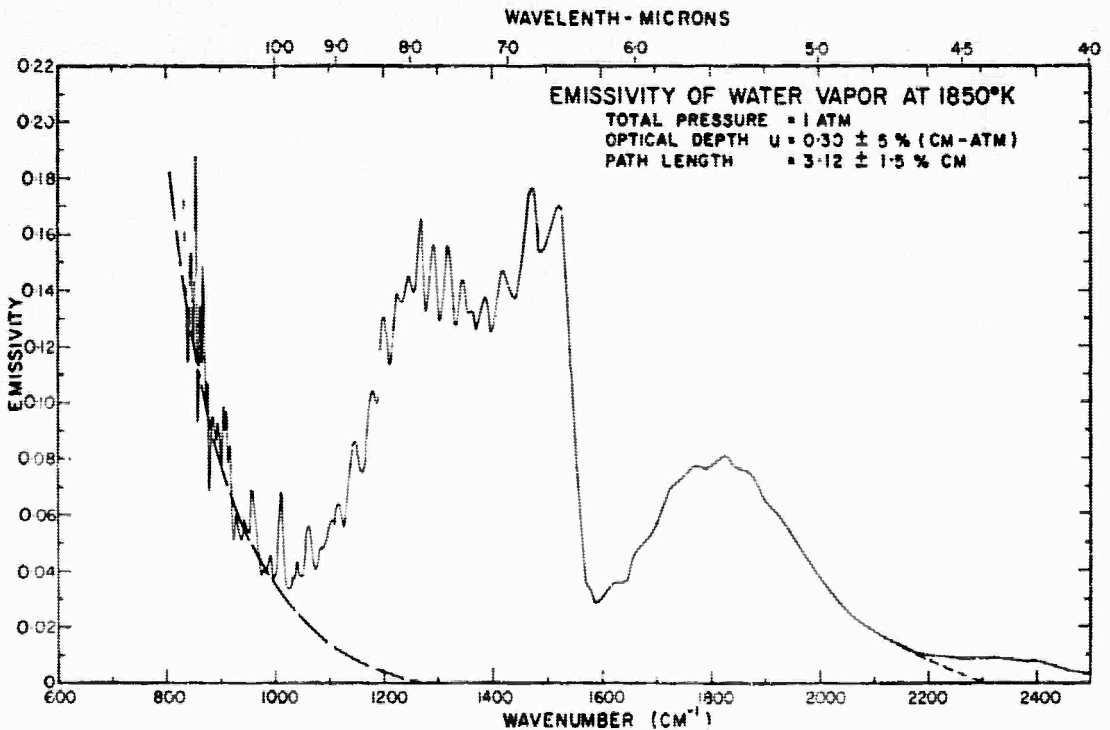


FIG. 6. Spectral emissivities of H<sub>2</sub>O at 1850°K, taken with a NaCl prism. Average spectral slit width = 25 cm<sup>-1</sup>. The contour of the rotational band is indicated by a dotted line.

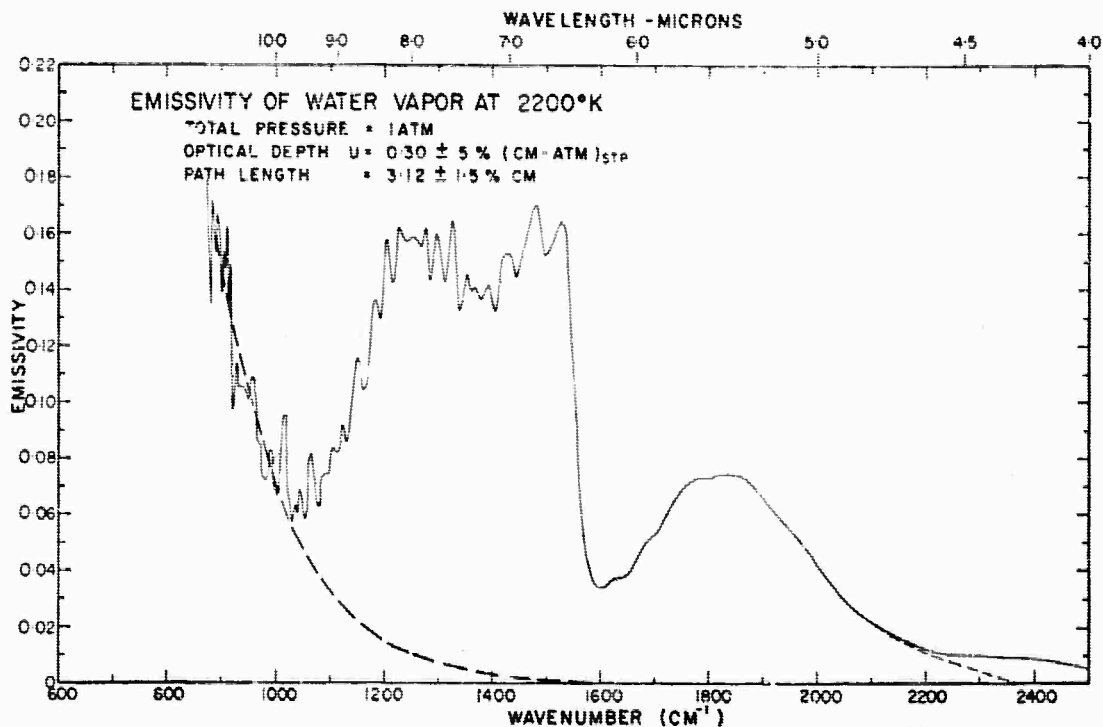


FIG. 7. Spectral emissivities of H<sub>2</sub>O at 2200°K, taken with a NaCl prism. Average spectral slit width  $\approx 25$  cm<sup>-1</sup>. The contour of the rotational band is indicated by a dotted line.

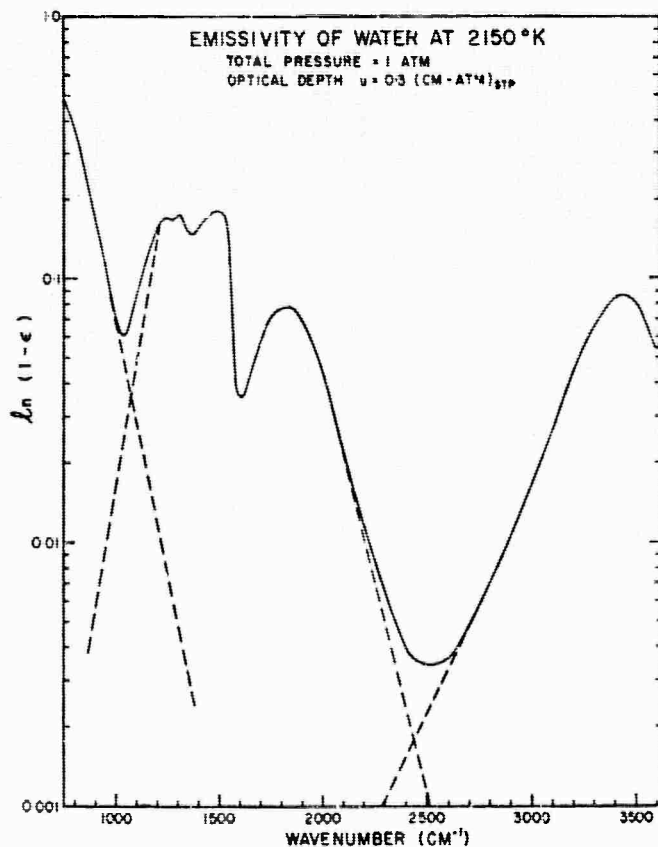


FIG. 8. The log of spectral emissivities of H<sub>2</sub>O at 2150°K between 3400 cm<sup>-1</sup> and 500 cm<sup>-1</sup>, with extrapolation (dotted line) of the band wings into the overlap regions.

The spectral emissivities at 1850° and 2200°K indicate further growths of the 6.3- $\mu$  band as well as the pure rotational band. There is also some overlapping with the 2.7- $\mu$  fundamental band on the short wavelength end of the band. The dotted line is obtained again by extrapolating the wing contour back on the semilog (Fig. 8). However, it should be noted that a small amount of emission from the strong 4.3- $\mu$  fundamental band of CO<sub>2</sub> is present. This is due to contaminants in the H<sub>2</sub> and O<sub>2</sub> gas supplies. An impurity level of only 0.1% CO<sub>2</sub> results in an emissivity of  $\epsilon \sim 2 \times 3.12 \times 0.001 = 0.006$  at 2300 cm<sup>-1</sup> and 2200°K, where  $k = 2 \text{ atm}^{-1} \cdot \text{cm}^{-1}$  was taken from reference 18, with  $l = 3.11 \text{ cm}$  and  $p_{\text{CO}_2} = 0.001 \text{ atm}$ .

In Fig. 9, a comparison is made between two spectra taken with slit widths of 0.5 mm and 0.25 mm, respectively. Except for the more pronounced maxima and minima, no appreciable difference is observed in the average contours.

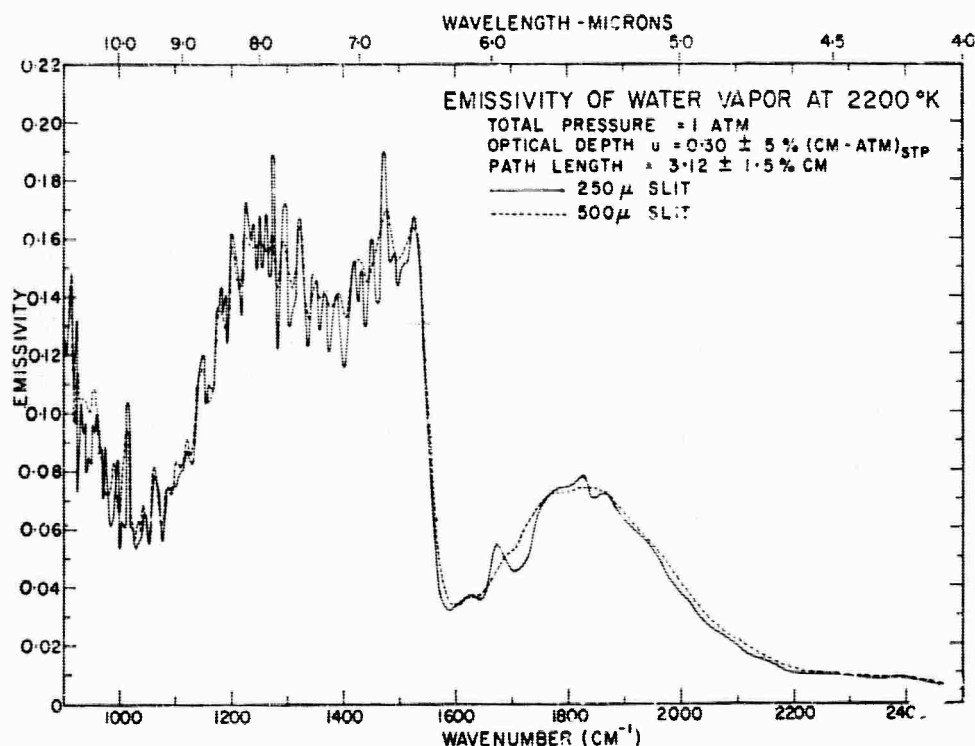


FIG. 9. Spectral emissivity of H<sub>2</sub>O at 2200°K, taken with a NaCl prism. Average spectral slit width = 13 cm<sup>-1</sup> (solid line) and 25 cm<sup>-1</sup> (dotted line).

### Integrated intensity

The integrated intensity of a vibration-rotation band  $\alpha(T)$ , (cm<sup>-2</sup>·atm<sup>-1</sup>) normalized to STP conditions, is given by

$$\alpha(T) = \int_{\text{band}} k(\nu, T) d\nu = \left( \lim_{u \rightarrow 0} \frac{1}{u} \right) \int_{\text{band}} \ln \left[ \frac{1}{1 - \epsilon(\nu, T)} \right] d\nu \quad (2)$$

where  $k(\nu, T)$  is the spectral absorption coefficient,  $u = p_{\text{H}_2\text{O}} l T^\circ / T$ ,  $T^\circ = 273.2^\circ\text{K}$  and

$T$  = gas temperature. In the present experiments, an extrapolation to zero pathlength was not possible (neither  $p$  total,  $p_{\text{H}_2\text{O}}$ , nor  $l$  could be varied). Therefore,  $\alpha(T)$  can only be determined by integrating the spectral emissivities, if sufficient temperature smearing was present.

A temperature smearing effect is obtained at the higher temperatures.<sup>(21)</sup> Higher rotational levels are then populated and the resulting lines fill the space between the strong lines appearing at lower temperatures. With the assumption that the integrated intensity of fundamental vibration-rotation bands is temperature independent (which has been verified up to  $\sim 2200^\circ\text{K}$  for H<sub>2</sub>O<sup>14</sup> and to  $2400^\circ\text{K}$  for CO<sub>2</sub><sup>17</sup> and NO<sup>22</sup>), an estimate of  $\alpha$  can be obtained if we find a constant maximum value of  $\alpha$  within the temperature range investigated. In Fig 10, the integrated intensity of the 6.3- $\mu$  fundamental band of

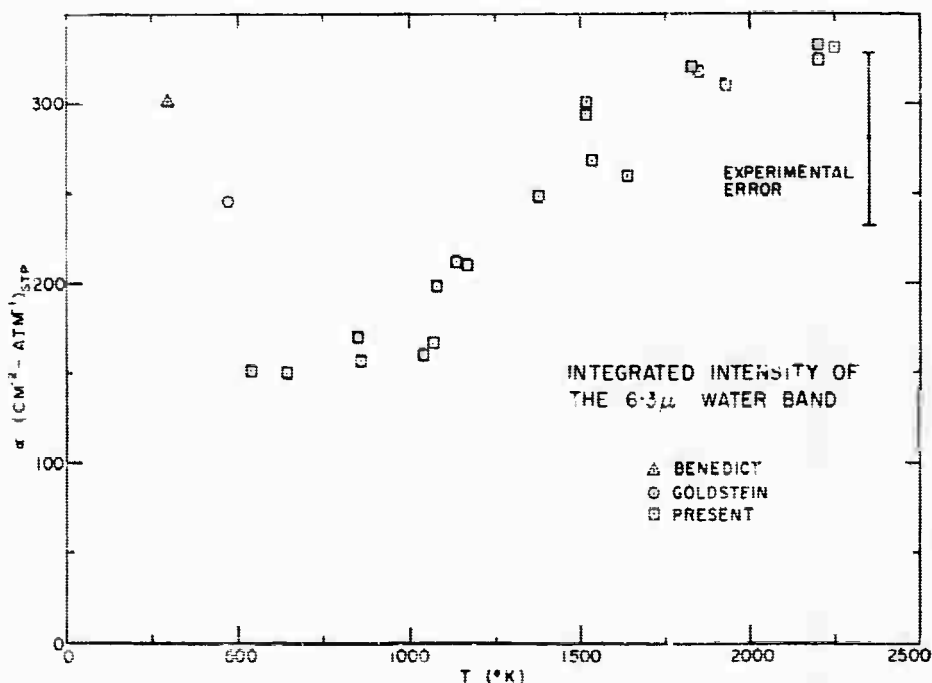


FIG. 10. Integrated intensity of the 6.3- $\mu$  fundamental band of H<sub>2</sub>O between 300°K and 2200°K.

20 spectra is plotted between 550° and 2200°K. The integration was performed with a planimeter, using the dotted line from the rotational band as the baseline at the long wavelength wing. At about 1800°K,  $\alpha$  reaches a constant level of about 300 ( $\text{cm}^{-2}\cdot\text{atm}^{-1}$ )<sub>STP</sub>, which compares well with the room temperature value of BENEDICT and PLYLER.<sup>(23)</sup> The point at 473°K obtained by GOLDSTEIN<sup>(11)</sup> is in agreement with the present results when we consider the experimental errors. It was assumed that our values are uncertain by about  $\pm 20$  per cent due to the experimental error in the temperature determination, the uncertainty of the separation process of neighboring bands, and the assumption that the band was sufficiently smeared.