

the $5d^2$ state after one cycle is $\chi/(1+\chi)$. The results of the experiment show that

$$1 - (\chi/1 + \chi) = 0.6 \text{ or } \chi = 0.67.$$

The oscillator strength of the $6p5d-5d^2$ transition is quickly found, given the strength of the $6p5d-6s^2$ transition

$$\frac{A(6p5d-5d^2)}{A(6p5d-6s^2)} = \frac{\chi}{1} = 0.67 = \frac{g_{5d^2} f_{5d^2} \lambda_{6s^2}^2}{g_{6s^2} f_{6s^2} \lambda_{5d^2}^2}.$$

Therefore $f_{5d^2} = 0.67/5 \times 0.14 \times (18207/3501)^2 \approx 0.51$. In the above calculation the value $f_{6s^2} = 0.14$ has been used. This is in agreement with the value of Brecht, Kowalski, Lido, Ma, and ZuPutlitz,⁴ and with that of Penkin,⁵ Dickie and Kelly⁶ quote a value $f_{6s^2} = 0.10$, whereas Miles and Wiese⁷ give $f_{6s^2} = 0.16$.

It is remarkable that the oscillator strength is this high. In the previous paper it was shown that the oscillator strength of the closely related $6s6p-6s5d$ transition was $f \sim 0.0034$. Both transitions involve a $6p-5d$ single electron transition and the wavelengths are nearly the same (1.6 vs 1.5 μ). In spite of their apparent similarity, the strengths are different by over two orders of magnitude. On the other hand, both numbers

depend on previous measurements of the strengths of the $6s6p-6s^2$ and $6p5d-6s^2$ transitions. Part of the disparity may be accounted for by error in the latter measurements, though no errors are apparent. It can be hoped that computer calculations, such as those of McCalvert and Trefftz on other barium transitions,⁸ will shed some light on the subject.

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[†]Also Fannie and John Hertz Fellow at the University of California, Davis-Livermore, California.

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Raman-scattering cross sections for water vapor

C. M. Penney and M. Lapp

General Electric Corporate Research and Development, Schenectady, New York 12301

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We present cross sections for Raman scattering from water vapor excited at the four argon-laser wavelengths 476.5, 488.0, 496.5, and 514.5 nm. These cross sections, for the strong vibrational band centered at a shift near 3654 cm^{-1} , are approximately 2.5 times larger than the corresponding N_2 Q -branch cross sections, and follow closely the expected $(1/\lambda_R)^4$ dependence, where λ_R is the Raman scattering wavelength. We also report observations of the room-temperature depolarization and spectral profile of the band, and the overall spectral distribution of the scattering from 470 to 630 nm, for incident light at 488 nm. The latter observation indicates the absence of any other strong vibrational Raman-active modes.

In addition to basic physical and chemical information, Raman scattering (RS) from water vapor provides a basis for remote probing of vapor concentration. For example, Melfi *et al.*¹ and Cooney² have used this process to measure atmospheric humidity as a function of altitude. Likewise, it offers promise as a spatially resolved probe of water-vapor density for combustion systems.³ However, published information about the absolute magnitude, depolarization, and detailed spectral distribution of water-vapor RS is incomplete.

The observed water-vapor vibrational Raman band is centered at a shift of approximately 3654 cm^{-1} . With respect to the absolute intensity of this band, Cooney⁴ has calculated its ratio to that for the corresponding nitrogen vibrational RS-band intensity per molecule for incident light at 347.1 nm. This calculation was based on data from remote atmospheric-humidity measurements in a field experiment. Cooney obtained a ratio of $5.1 \pm 75\%$. Using a similar analysis of field data, Melfi¹ obtained $3.8 \pm 25\%$ for this ratio for 694.3 nm excitation. In a previous paper,⁵ we reported a ratio of $2.5 \pm 10\%$ for excitation at 514.5 nm. These results

lead to absolute RS cross sections for water vapor because the corresponding cross sections for N_2 have been well determined.⁵⁻⁸ However, the resulting water-vapor cross sections do not follow the expected $(1/\lambda_R)^4$ dependence.⁹ (Here λ_R is the Raman-scattering wavelength that corresponds to each incident wavelength.) Additional results and the existence of some weak water-vapor transitions in the visible have led to speculation¹⁰ about possible departures from this fourth-power dependence. Thus precise measurements over a range of incident wavelengths are needed to test the existence and magnitude of any such departures.

With respect to the overall spectral distribution of water vapor RS, Johnston and Walker¹¹ reported in 1932 the possibility of a second vibrational band at a shift of 1648 cm^{-1} . Although a band near 1648 cm^{-1} has been seen in liquid water¹² it was not seen in the vapor, in independent observations by Rank *et al.*¹³ It is of interest to determine the existence and strength of this band and other possible significant bands because, on the one hand, they might be useful as additional measures of water vapor, and on the other hand, they might

interfere with RS measurements of trace constituents with nearby lines. Finally, to augment confidence in RS measurements of water-vapor density in different environments it is desirable to know the band profile and depolarization of this scattering under various well-determined conditions.

Our work pertaining to these questions was first described at the Joint Conference on Sensing of Environmental Pollutants (1971).¹⁴ This paper reports an expansion of that work. We present here room-temperature (24 °C) measurements of the water-vapor RS cross section for the band centered at 3654 cm⁻¹. The measurements were obtained using incident light at four argon-ion-laser wavelengths: 476.5, 488.0, 496.5 and 514.5 nm. In addition, we report observations of the depolarization and profile of this band, and the overall frequency distribution of the RS under excitation at 488 nm.

EXPERIMENTAL ARRANGEMENT

The equipment used for this study included a $\frac{3}{4}$ m double monochromator with linear wavelength drive, an argon-ion laser, a thermopile power meter, and a Pyrex and Teflon scattering cell mounted in an oven capable of controlling the cell temperature to values between 24 and 200 °C. Attached to the cell was a cold finger that extended outside the oven. This appendage was heated separately and was temperature-controlled to within ± 0.1 °C to determine the water-vapor pressure. Further details of the optical and signal-processing apparatus have been described elsewhere.^{3,14-16}

OVERALL SPECTRAL DISTRIBUTION

The experimental arrangement described in the preceding section was used initially to observe the overall spectral distribution of the Raman scattering from 470 to 630 nm. The water-vapor pressure was main-

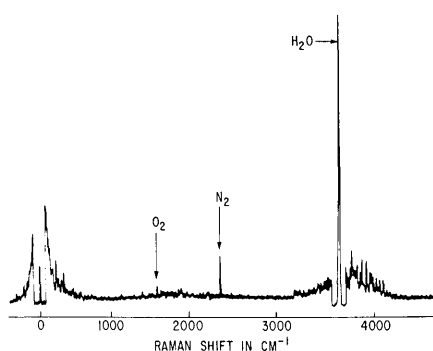


FIG. 1. Spectral distribution of Raman scattering from water vapor and a trace of air. The peak height of the exciting line, which results from spectrally unshifted scattering of the incident beam by water vapor and cell walls, is attenuated by a factor of approximately 10^5 . The peak height of the H₂O vibrational band is attenuated by a factor of $10 \pm 20\%$. The slit function for this measurement is triangular with approximately 8 cm⁻¹ full width at half-maximum. The vapor was maintained at 150 °C in a cell surrounded by an oven, with a cold finger temperature of 98 °C.

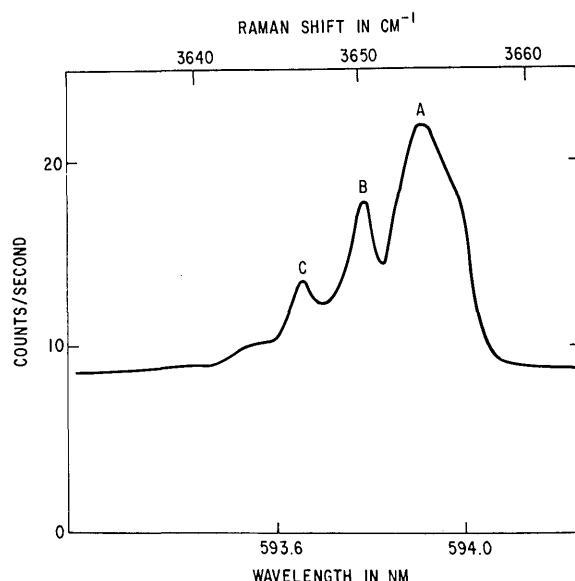


FIG. 2. Band profile of water-vapor Raman scattering at 24 °C, excited by the 488 nm line of an argon laser. The slit function for this computer-processed data is triangular with a full width at half-maximum of 1.8 cm⁻¹. The three peaks marked A, B, and C are at Raman shifts of 3653.8, 3650.1, and 3646.4 cm⁻¹. These shifts were determined by calibration against a neon 594.483 nm reference line. However, observed short-range variations in our spectrometer wavelength drive contribute an absolute uncertainty of 0.5 cm⁻¹, and relative uncertainties of about 0.25 cm⁻¹ in their positions.

tained near 1 atm at a cell temperature of 150 °C and the light beam in the scattering region was about 1.2 W in the single line at 488 nm. The resulting spectral distribution of the Raman scattering is shown in Fig. 1. In addition to the expected strong water-vapor vibrational band, two sharp bands are observed from the background air in the cell. The pure rotational scattering near the excitation line is extremely weak, relative to its intensity from pure nitrogen. There is a barely discernible broad band centered between the O₂ and N₂ bands. This band might be water-vapor scattering or fluorescence from the cell windows. It reaches a peak intensity less than a few tenths of a percent of the strong water-vapor band.

BAND PROFILE

In Fig. 2 we show the detailed shape of the 3654 cm⁻¹ band in the cell at 24 °C (with the cold finger at 22 °C). The background level and absence of background structure was determined by traces taken with the water vapor frozen out by dry ice and the cell back-filled to atmospheric pressure with argon. This procedure verified that there is no apparent structure introduced by argon-laser plasma lines.

The band has appreciable intensity near room temperature over a spectral width of approximately 20 cm⁻¹. The three peaks marked A, B, and C are reproducible, having been observed in numerous traces from water vapor in the cell and in the open atmosphere. We note that Rank *et al.*¹³ described this band as a

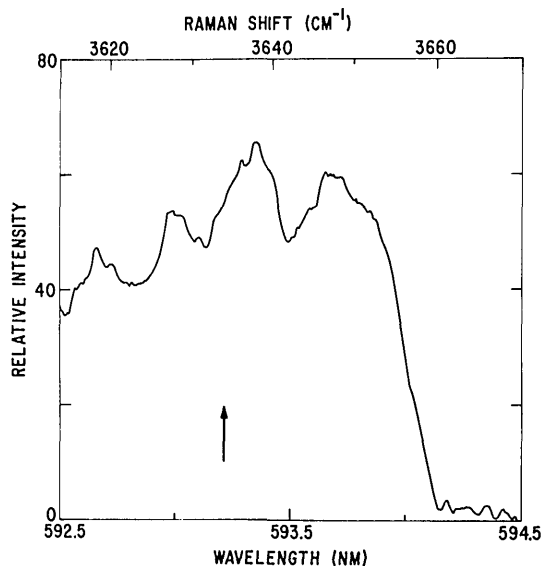


FIG. 3. Part of the band profile of water-vapor Raman scattering from an $\text{H}_2\text{--O}_2$ flame at approximately 1500°K. This band has an appreciable intensity over a spectral interval of at least 3 nm. The slit function for this measurement was triangular with 4.6 cm^{-1} full width at half-maximum. Further experimental details are given in the second paper listed in Ref. 3.

doublet with shifts of 3653.9 and 3646.1 cm^{-1} , close to the A and C peaks in Fig. 2, and that Benedict¹⁷ has given the ν_1 vibrational frequency for the band origin as 3657.05 cm^{-1} . A detailed theoretical analysis of the band shape as a function of temperature up to about 350 °C has been developed recently by Bribes *et al.*¹⁸

We have also observed water-vapor RS at higher temperatures.³ A typical band shape in an $\text{H}_2\text{--O}_2$ flame at about 1500 °K is shown in Fig. 3. This result illustrates the increasing width and structure of the band at higher temperatures.

CROSS SECTIONS

The water-vapor vibrational Raman-scattering cross-section measurements were performed using both vapor in the cell and in the open laboratory atmosphere. The observed light was that summed over polarization, scattered into a 10° half-angle cone about a direction perpendicular to the propagation and (electric field) polarization of the plane-polarized incident beam. The resulting cross sections describe that type of right-angle scattering, and backscattering irrespective of the polarization state of the incident light. Dependence of the cross sections on polarization and scattering angles is discussed elsewhere.^{19,20} The water-vapor molecule number density in the atmosphere was determined using a precision psychrometer. In the cells, this density was controlled by the cold-finger temperature. For observations of the water-vapor scattering, the double-monochromator slits were set at 400 μm (entrance), 3000 μm (intermediate), and 2000 μm (exit), yielding a nearly rectangular spectral pass band approximately 31 cm^{-1} wide at half-maximum. These wide slit set-

tings were chosen in order to integrate the Raman scattering over the entire Q-branch.

Some of the rotational-vibrational wings might also be included within this measurement. An indication of the possible magnitude of the wing contribution is given by the depolarization ρ of the observed scattering, which we measured to be $\leq 6\%$. The theoretical depolarization of the wings⁹ is $\frac{3}{4}$. If we designate the depolarization of the Q-branch by ρ_Q , then that fraction of the observed scattering intensity which is due to the rotational-vibrational wings is

$$F_R = 7(\rho - \rho_Q)/(1 + \rho)(3 - 4\rho_Q).$$

Thus, the largest possible contribution of the rotational-vibrational wings to our measurement is 13.2%, which would result if $\rho_Q = 0$. The weakness of the rotational-vibrational wings shown in Fig. 1 suggests that the actual contribution is much smaller. This conclusion is supported by our measurements made with exit slits increased from 2000 to 3000 μm , which revealed no systematic increase in the cross section results.

For observations of the nitrogen vibrational Raman scattering, the exit slit was reduced to 800 μm , yielding a spectral pass band 12 cm^{-1} wide at half-maximum. This width is sufficient to integrate over the Q branch, and includes only a negligible amount of the rotational-vibrational wings of nitrogen.

The spectrometer-detector system was calibrated for wavelength and polarization response by use of a calibrated lamp and polarization filters. This procedure has been described elsewhere.¹⁶

We made two types of cross-section measurements. First, at incident-light wavelengths of 488.0 and 514.5 nm, we determined the relative intensities of scattering from water vapor and nitrogen. These ratios were used with our previously determined values for the nitrogen cross section,⁵ which agree closely with other recently measured values,⁶⁻⁸ to obtain absolute values for the water-vapor cross section at those wavelengths. The results are shown in Table I. Note that the nitrogen cross sections used here are those for scattered light summed over polarization, and thus are slightly larger than those given in Ref. 5.

The expected errors shown in Table I come primarily from the uncertainty of water-vapor-density measurements, and secondarily from the uncertainty of the spectral calibration. No systematic variation of re-

TABLE I. Water-vapor cross sections, summed over polarization, for scattering through 90° from directions of polarization and propagation of a linearly polarized incident beam. The absolute cross sections in the last two columns are in units of $(\text{cm}^2/\text{sr}) \times 10^{-30}$.

Incident wavelength (nm)	Scattered wavelength (nm)	$\frac{\sigma_{\text{H}_2\text{O}}}{\sigma_{\text{N}_2}}$	σ_{N_2}	$\sigma_{\text{H}_2\text{O}}$
488.0	593.9	$2.5 \pm 10\%$	$0.56 \pm 5\%$	$1.4 \pm 11\%$
514.5	633.6	$2.5 \pm 10\%$	$0.44 \pm 5\%$	$1.1 \pm 11\%$

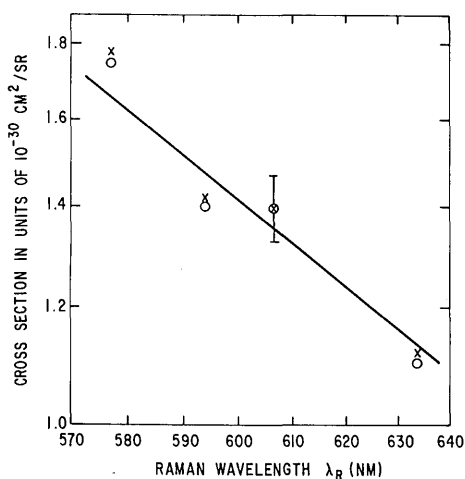


FIG. 4. Dependence of the water-vapor Raman scattering cross section on exciting wavelength. Note that these cross sections are presented on a log-log plot as a function of the corresponding Raman wavelengths, shifted from each exciting line by 3654 cm^{-1} .

sults between open-atmosphere and cell measurements was observed in the several separate measurements of each type that we performed over a three-year span. The variations observed in the relative measurements are well within the stated expected error. Therefore we present only the average of each set of measurements.

In the second type of cross-section measurement, we determined the water-vapor vibrational RS cross section at incident-light wavelengths 476.5, 496.5, and 514.5 nm relative to its value at 488.0 nm. These measurements were made to determine if the cross section follows the expected $(1/\lambda_R)^4$ dependence over the wavelength range from 476.5 to 514.5 nm. The results, shown in Fig. 4, agree with this dependence within experimental error.

CONCLUSIONS

There is only one strong vibrational band in the Raman scattering from water vapor. This band, centered at a shift of approximately 3654 cm^{-1} , has appreciable intensity over a spectral interval of about 20 cm^{-1} near room temperature. The measured cross section for the band is $2.5 \pm 10\%$ times larger than the

corresponding cross section for Q-branch vibrational scattering from N_2 , for incident-light wavelengths of 488.0 and 514.5 nm. This cross section appears to follow a $(1/\lambda_R)^4$ dependence for the incident wavelengths 476.5, 488.0, 496.5, and 514.5 nm.

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