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Raman Effect in Water Vapor

With the use of a high speed glass spectrograph and a very intense light source we have been successful in obtaining the Raman spectrum of water vapor excited by the total radiation of the mercury arc in the visible and near ultraviolet regions of the spectrum. The water vapor was sealed in a Pyrex tube and was at a temperature of about 275°C and at a pressure of between two and three atmospheres.

The observed Raman lines correspond to shifts of 3654 (± 5) cm^{-1} , 1648 (± 5) cm^{-1} , and 984 (± 10) cm^{-1} . On the basis of the selection rules which apply in Raman spectra¹ these are interpreted as pure vibration frequencies and represent the three fundamentals to be expected for the water molecule. The two longer shifts correspond to infrared frequencies of 2.73 μ and 6.06 μ , respectively, and must be the counterparts of the strong absorption bands near 2.66 μ and 6.26 μ which were first classed as fundamentals by Hettner.² The third shift corresponds to infrared absorption at 10.16 μ which is very nearly inactive in ordinary absorption or emission spectra although some weak absorption does show in this region. This shift is probably to be correlated with Dennison's³ ν_1 which would be nearly inactive for suitable force constants within the molecule. The 3654 cm^{-1} shift probably corresponds to Dennison's ν_3 since the latter motion would closely approach that of mutual vibration of an hydrogen atom with an oxygen atom and since this frequency so nearly corresponds to the vibration of the normal OH molecule, 3568 cm^{-1} . Mecke⁴ has previously attributed the 2.7 μ fundamental to the OH band. The 1648 cm^{-1} frequency must then represent Dennison's ν_2 .

Our observations of the 3654 cm^{-1} shift confirm the work of Daure and Kastler⁵ who reported a Raman frequency of 3655 (± 5) cm^{-1} in an exposure of 50 to 70 hours duration. On one of our clearest plates this frequency shift made its appearance in a 16 hour exposure, scattered from the exciting lines $\lambda 3650$ and $\lambda 3655$. Considerably longer exposures showed scattering of the same frequency from $\lambda 3663$ and from $\lambda 4047$.

Evidence for the 1648 cm^{-1} vibration frequency rests on Raman scattering to the long wave-length side of $\lambda 3650$, $\lambda 3655$ and $\lambda 4047$

and the further appearance of two lines close to positions calculated for anti-Stokes lines from $\lambda 4047$ and $\lambda 4358$. The frequency shifts computed from all of the Raman lines are in good agreement. The scattering from $\lambda 3650$ and $\lambda 3655$ was particularly intense and showed clearly on the 16 hour exposure referred to above. The long wave-length shift from $\lambda 4047$ and the anti-Stokes lines from $\lambda 4078$ and $\lambda 4358$ appeared on plates exposed from 114 to 140 hours.

The existence of the 984 cm^{-1} vibration frequency is indicated by the appearance of Raman lines on the long wave-length side of $\lambda 4078$ and $\lambda 4358$ and by the appearance, on long exposures, of a line 989 cm^{-1} to the short wave-length side of $\lambda 4078$. Although no clear indications of the 984 cm^{-1} scattering appeared on plates of less than 70 hours exposure the conclusion can not be drawn that this vibration frequency is more weakly scattered than the others. Observation of this scattering from the more favorable exciting lines, $\lambda 3650$ and $\lambda 3655$, is precluded by the low ultraviolet transmission of our prisms. Likewise, scattering from $\lambda 4047$ falls, fortuitously, midway between the pair of 3654 cm^{-1} Raman lines excited by $\lambda 3650$ and $\lambda 3655$, and can not be separately resolved.

A more detailed account of our investigations will be published elsewhere (probably in the Journal of the American Chemical Society). We will also include application of this data to the computation of the high temperature heat capacity curve of water vapor.

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¹ Rasetti, Nature **123**, 757 (1929).

² Hettner, Zeits. f. Physik **1**, 345 (1920).

³ Dennison, Rev. Mod. Phys. **3**, 289 (1931).

⁴ Mecke, Phys. Zeits. **30**, 907 (1929).

⁵ Doure and Kastler, Comptes Rendus **192**, 1721 (1931).