The Raman Effect of Water Vapor

The Raman effect of water vapor has been observed with a Hilger E1 spectrograph by using Hg 2536 for excitation. The water was sealed in a quartz tube drawn into a horn at one end, and was illuminated by a water-cooled mercury arc. The tube with the water vapor was maintained at a temperature of approximately 135°C.

There was found but one Raman band shifted at its center 3654.5 cm^{-1} from the exciting line and extending for about 5 cm^{-1} on both sides of the center. It is not a sharp line for two much more intense and resolved mercury lines occupy only about the same distance on the microphotometer curve. Indeed, the limit of accuracy of the measurement is well within the half width of the line. Further than this there is no indication that the line is double, as was reported by Rank, Larsen and Bordner.[1]

As is well known the shift of the Raman line for ordinary water vapor is about 50 cm^{-1} greater than the corresponding fundamental frequency, while for heavy water vapor apparently the Raman line is close to the expected position of the fundamental.[2]

In an attempt to find an explanation for this discrepancy based on the location of the maximum of the vibration-rotation band, this band was worked out using the intensity factors for a symmetrical top[3] and using the positions derived from Mecke's[4] analysis of the infrared spectrum. The results indicate a strong group of lines corresponding to the Q-branch. Although the heavy water shows the greater relative intensity in this Q-branch the difference is not enough to account for its absence in ordinary water. The suggestion of Rank, Larsen, and Bordner[1] that the observed line consists of two members of the vibration-rotation band neglects the necessary presence of the rest of this band and appears to make use of lines forbidden by the selection rules.

A careful search was also made for a pure rotation band but none was found.

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[1] Rank, Larsen and Bordner, J. Chem. Phys. **2**, 464 (1934).
[2] L. G. Bonner, Phys. Rev. **46**, 458 (1934).
[3] Placzek and Teller, Zeits. f. Physik **81**, 209 (1933).
[4] R. Mecke, *et al.*, Zeits. f. Physik **81**, 313, 445, 465 (1933).