Raman Spectrum of Heavy Water

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The Raman spectra of two samples of heavy water, one 18 percent and the other 80 percent, were excited by the 2536 line of mercury. The 18 percent heavy water gave the usual band ($\Delta\nu=3445$) and a new band ($\Delta\nu=2623$). The new band is probably due to the molecule H^2OH^1. With 80 percent heavy water the new band was much stronger than the 3445 band but was shifted slightly towards shorter wave-lengths. With the 80 percent sample the 3445 band was shifted slightly toward the red with respect to ordinary water. From the amount of shift it is concluded that molecules containing only one atom of heavy hydrogen give two bands, $\Delta\nu=2623$ and $\Delta\nu=3500$, while the molecules made of two heavy hydrogen atoms give a single band $\Delta\nu=2517$. These bands have been photographed as lines in the case of heavy water vapor.

THE Raman spectrum has been obtained of two samples of heavy water, one of 18 percent prepared by John W. Murray of the Chemistry Department and the other of 80 percent loaned by Professor Hugh Taylor of Princeton University. The irradiation tube was of fused quartz 6 mm internal diameter and 35 cm long with a circular disk of the same material, optically worked, and fused within the slightly widened end of the tube, the oxy-hydrogen flame being played against the outer wall only and never making contact with the disk. In this way all distortion of the optical surface was avoided. The other end was drawn down in an oblique direction and painted black. It was clamped in close contact with a vertical Hanovia high potential quartz mercury vapor tube 50 cm long, and the light issuing from the irradiation tube reflected to the spectroscope by means of a quartz total reflection prism. The vertical position has two advantages. It abolishes a temperature gradient across the diameter of the tube which, if present, causes curvature of the rays, the interior of the tube appearing bent into an arc when viewed through the window. This prevents the light from the further end of the fluid column from reaching the spectroscope and enables parasitic light from the fluorescent walls of the tube to enter the instrument. Gas bubbles are sometimes set free by the ultraviolet radiations which accumulate along the upper side of the tube if it is mounted in a horizontal position.

With a tube of such large ratio of length to diameter very careful lining up with respect to the collimator is necessary if full efficiency and complete absence of fluorescence light from the tube wall are to be secured.

As it appears likely that the introduction of heavy hydrogen into organic chemistry will be accompanied by an intensive study of Raman spectra of materials obtainable only in small quantities, a brief description of an easy and rapid method of securing this adjustment may be worth putting on record.

We shall require a double concave lens of the same focus as that of the lens employed for forming an image of the window of the quartz tube on the slit of the spectrograph, preferably a quartz fluorite achromat of about 20 cm focus, if we are operating with ultraviolet excitation. By holding the concave lens before the eye, we can view the window of the Raman tube through the center of the achromat and make sure of its proper orientation. A candle is mounted at a distance of about two meters from the slit of the spectrograph and brought into such a position that it appears at the center of the field of the camera lens when the latter is viewed from the position of the photographic plate. A cardboard screen, perforated with a hole slightly smaller than the window of the tube is next mounted close against the flame on the side facing the spectrograph and an image of the illuminated aperture focussed on the slit of the spectrograph with the achromat. The candle is now removed, the prism mounted against the hole and the ir-

radation tube brought over the prism. We now have to so adjust the prism and tube that the reflected image of the tube is exactly parallel to the axis of the collimator.

A pin is mounted at a distance of about 30 cm from the aperture in such a position that its head appears over the center of the aperture when we view it through the center of the achromat and the concave lens. We now view the aperture with the pupil of the eye immediately behind the pinhead, and by adjusting the prism and Raman tube bring the reflected image into such a position that we are looking directly down its axis at the circular black background at its further end. The pin is now removed and the adjustment checked by again viewing the aperture through the two lenses, moving the eye over the whole area of the lens to make sure that no part of it receives light from the fluorescent wall of the tube. If the aperture is too large one sees also a thin ring of blue light surrounding the black background, and the Raman spectrum will be photographed with a line of continuous spectrum at the top and bottom, punctuated at points with black dots which mark the mercury lines and are useful for distinguishing the latter from the true Raman lines. If the blue ring is exactly focussed on the slit, these horizontal lines will be blurred and partially obscure the Raman spectrum because of the astigmatism of the spectrograph.

To secure the correct position of the projecting lens back the aperture with the mercury tube and mount a narrow horizontal wire across it. Focus this on the slit (which can be lightly smoked by burning magnesium wire), and then make a trial photograph. The wire will probably be found to be out of focus all along the spectrum (for the same reason that dust on the slit is never in focus when the lines are sharp). We now move the lens a millimeter or two away from the slit and make another photograph. If this has made matters worse, move it nearer to the slit, and continue until a sharp image of the wire is obtained.

The spectrograph employed in the present work was furnished with a large Cornu prism and lenses of 100 cm focus by Hilger and was constructed in the laboratory shop. It was found that both samples of heavy water were slightly fluorescent at first, the continouus spectrum almost blotting out the Raman band characteristic of ordinary water, but after a twelve hour exposure the fluorescence disappeared, the background appearing quite black. The 18 percent heavy water gave the usual band $\Delta\nu = 3445$ and a new band $\Delta\nu = 2623$ bordering the mercury line 2700 on the long wave-length side. This sample had the composition 0.034 H^2OH^2, 0.30 H^2OH^1, and 0.66 H^1OH^1 and since the proportion of water molecules made of one atom of light and one of heavy hydrogen to those made of two heavy atoms was about 9 : 1 we can regard the new band as due largely to the former. The intensity ratio of the two bands was 4 : 1, determined by comparing photographs taken with different times of exposure.

With 80 percent heavy water the new band was much stronger than the 3445 band, and no trace of any additional band was found. By taking photographs of both concentrations of heavy water with times of exposure so regulated that the new band had the same intensity in each it was at once clear that with the 80 percent heavy water the band was shifted slightly towards the region of shorter wave-lengths with respect to the band obtained with the 18 percent sample. The faint band of longer wave-length, obtained with the 80 percent sample, was shifted slightly towards the red with respect to the band obtained with ordinary water. By estimating the amount of the two shifts, which could only be done roughly, we arrive at the following conclusions.

The molecules containing only one atom of heavy hydrogen give two bands, $\Delta\nu = 2623$ and $\Delta\nu = 3500$, while the molecules made of two heavy hydrogen atoms give a single band $\Delta\nu = 2517$. Ordinary water gives also a single band $\Delta\nu = 3445$. This band is frequently reported as double, but no trace of this appeared in any of the photographs made with the narrow tube.

On a spectrogram made last year with the same lamp and a longer and much wider tube, there was a slight indication of a region of less intensity near the center of the band. Photographs of the bands are reproduced in Fig. 1.

The exciting line, 2536 lies to the left at a distance nearly equal to the length of the spectrogram. The narrowness of the slit is indicated by the mercury lines. The percent of heavy water is

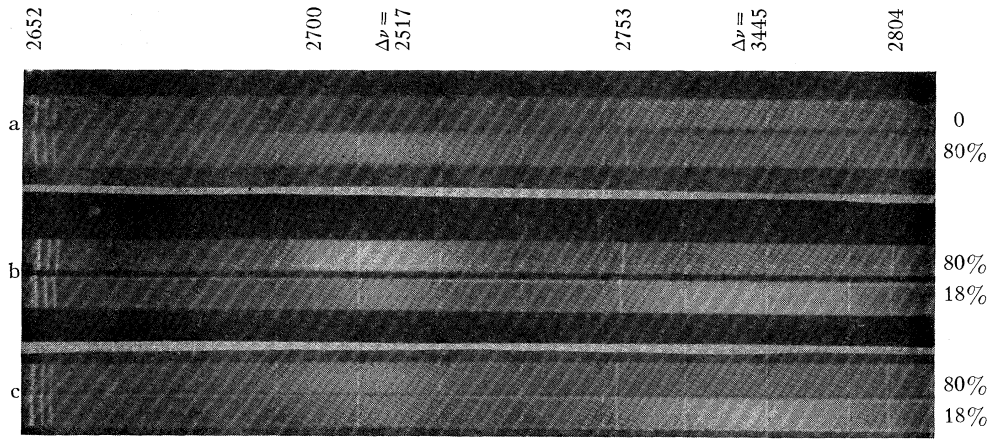
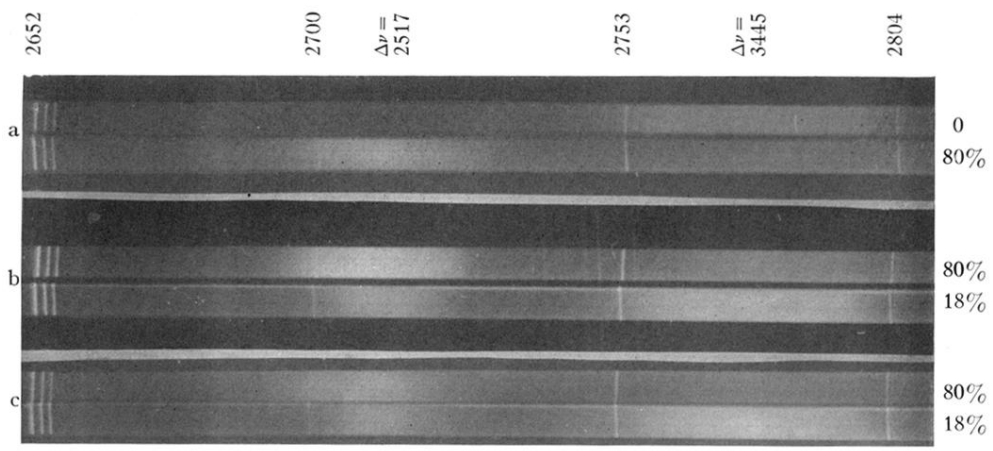


FIG. 1. Photographs of the Raman bands of 18 percent and 80 percent heavy water.

indicated at the right of each spectrogram. Each of the three enlargements were made from two negatives mounted film to film, with the spectra in coincidence. Fig. 1a, is of ordinary water and the 80 percent sample, the latter made up of 0.64 of H^2OH^2, 0.32 of H^1OH^2 and 0.04 of H^1OH^1. The band of longer wave-length, due chiefly to the half heavy molecules is seen to be shifted to the right with respect to the band due to the light water. Fig. 1b, fully exposed spectrograms of 80 percent and 18 percent heavy water and Fig. 1c, the same but with exposure times adjusted to equalize the intensities of the 2517 and 2623 bands to bring out the shift.

The Raman band of ordinary water is shifted towards shorter wave-lengths with respect to the line found by Rank[1] for water-vapor for which the $\Delta\nu = 3650$. Cross and Van Vleck[2] have calculated the values for H^2OH^1 as 3750, 2720 and 1400, the latter not having been found in the Raman spectrum. These values were for the vapor, and the values for the liquid reported in the present paper correspond to bands shifted in the same direction, i.e., towards shorter wave-lengths. Experiments are now under way on the determination of the Raman spectrum of a 66 percent sample in the vapor condition at a pressure of two atmospheres. The line $\Delta\nu = 3550$ has been obtained and also a trace of the double line of shorter wave-lengths but better spectrograms will be produced very shortly.

[1] Rank, J. Chem. Phys. **1**, 504 (1933).
[2] Cross and Van Vleck, J. Chem. Phys. **1**, 350 (1933).



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