The Raman Spectrum of Heavy Water Vapor

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in the original distillations made by simple evaporation 2 mm of Hg above the triple point pressure. The hydrogen used in these experiments was prepared electrolytically from cells which had been freshly filled with ordinary water. The hydrogen discharged from these cells, as is now known, should contain considerably less deuterium than natural hydrogen. It seems reasonable to assume that the hydrogen used in these experiments contained about 1 part deuterium in 25,000. The ratio of the original volume of liquid hydrogen to the final volume was approximately 4000. Substituting in the Rayleigh equation,[3] it is found that the final sample should have contained approximately 1 part in 200 of deuterium instead of 1 part in 1100 as found by the mass-spectrograph analysis. Or, if the observed fractionation factor is calculated using 1 part in 25,000 for the original concentration, and one part in 1100 for the final concentration, one obtains 2.1 for the ratio of the vapor pressure of hydrogen to that of hydrogen-deuterium at 13.92°K. Because of its low surface tension and density, boiling liquid hydrogen readily forms a spray which is carried along with the vapor in a distillation. It appears, therefore, that the enrichment secured was about what should be expected from the theory.

The Raman Spectrum of Heavy Water Vapor

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The Raman spectrum of heavy water vapor was obtained by using water having a $d^{20}{}_{20}$ = 1.073, at two atmospheres pressure. A line $\Delta\nu = 2666$ cm^{-1} was found for D_2O and $\Delta\nu = 2718$ cm^{-1} for HDO. The other line expected from the work of Wood on liquid heavy water in the region $\Delta\nu = 3700$ cm^{-1} was not found. The line $\Delta\nu = 3650$ cm^{-1} of H_2O was resolved into a doublet $\Delta\nu = 3646.1$ cm^{-1} and $\Delta\nu = 3653.9$ cm^{-1}. An attempt has been made to explain the Raman spectrum of H_2O empirically by using the data of Mecke on the infrared absorption spectrum of H_2O.

EXPERIMENTAL

THE apparatus used in the present investigation was essentially the same as that employed by one of us[1] previously in obtaining the Raman spectrum of ordinary water.

In order to utilize a long scattering tube to the best advantage it is necessary to make the distance from the condensing lens to the scattering tube large compared to the distance from the lens to the slit of the spectrograph. Necessarily the fulfillment of this condition produces a very small image, which must be accurately focussed on the slit of the spectrograph. This adjustment can be made quite accurately in the following manner. After the scattering tube has been lined up, the achromatic condensing lens is put in the proper position to focus the image on the slit of the spectrograph. The prisms are then removed from the spectrograph and an auxiliary telescope is aimed down the collimator and the slit brought into sharp focus. The condensing lens is then adjusted until the two tiny arcs of light caused by the light diffracted by the diaphragm in the scattering tube come into sharp focus. The necessity for a critical focus of this small image is best appreciated when one considers the fact that in the present case the actual useful length of the spectral lines on the photographic plate was only 0.25 mm.

From a sample of heavy water $d_{20}{}^{20} = 1.048$ the Raman spectrum of the liquid was obtained. A reproduction of this spectrogram is shown in Fig. 1b. This sample had been purified by a distillation from alkaline $KMnO_4$. However, in spite of this treatment it fluoresced so badly that the spectrum was only obtainable by the use of strong filters. We were unable to obtain any results from this sample in the vapor phase because of the strong fluorescence.

The second sample of heavy water which we used had a $d_{20}{}^{20} = 1.073$, which should contain on a basis of pure probability approximately 11.5 percent H_2O, 45.0 percent HDO and 43.5 percent D_2O. This sample was much better than
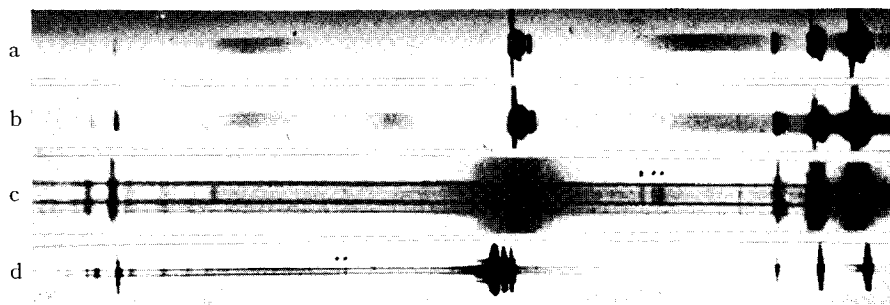
FIG. 1a, Raman spectrum of liquid H_2O; b, liquid heavy water $d_{20}^{20} = 1.048$; c, Raman spectrum of H_2O vapor; d, Raman spectrum of heavy water vapor $d_{20}^{20} = 1.073$. These spectra have been taken with several different spectrographs and are enlarged so as to make the mercury lines approximately correspond.

the previous one and we were able to obtain the modified lines from it. However, there was still a considerable amount of fluorescence. The heavy water was removed from the scattering tube and sealed in an ampule with a quantity of $KMnO_4$ and held at a temperature of 100°C overnight. After a distillation from the $KMnO_4$ the material was pure enough to yield a spectrum which was practically free from fluorescence.

Numerous plates were obtained by using from one to four prisms in the dispersing train. The best plates were obtained by using four prisms which gave a dispersion of 40A/mm at λ4500 and 27A/mm at λ4200. The entire spectrograph is installed in a constant temperature room, the temperature of the prisms being held constant to ±0.1°C. The time of exposure varied from 3 to 7 days with the highest dispersion used. Any lines which did not appear on the 7-day exposure could not have been made to appear upon longer exposure because of the increasing background from the unmodified scattering and unavoidable parasitic light from the scattering tube. A 3-day exposure showed two Raman lines which were excited by λ4047. The mean of all the measurements for these two lines yielded a $\Delta\nu = 2666$ cm^{-1}±3 cm^{-1} and $\Delta\nu = 2718$ cm^{-1}±3 cm^{-1}, respectively, for these shifts, their intensity being approximately in the ratio of 3 to 2, the 2666 shift being the stronger. A reproduction of one of the plates showing these lines appears in Fig. 1d, the Raman lines being indicated by means of ink dots below the spectrum. These results had been reported by one of us[2] previ-

ously. The longer exposures were made in an attempt to find a line in the region $\Delta\nu = 3700$ cm^{-1} which one would expect from the work of Wood[3] on liquid heavy water. This particular shift falls in an unfavorable place for observation by λ4047 excitation because of the presence of a number of weak mercury lines in this region. However, by λ3650 excitation this line should fall in a place which is quite favorable for its observation. We have been unable to find this line and it seems safe to say that if this particular line appears in the spectrum of the vapor it must be considerably weaker than the other two lines which do appear. A vapor pressure of about two atmospheres was maintained in the scattering tube for all these exposures.

It appeared to be worth while to obtain more accurate measurements on the modified lines in the spectrum of H_2O, since the dispersion used in the present work was double that used in the earlier work. It had also been noted in the previous work that all the Raman lines were somewhat broader than a sharp mercury line. A 15-hour exposure with H_2O in the scattering tube showed the 3650 cm^{-1} shift excited by λ3650 to consist of a close pair of lines of equal intensity. The measurements yielded $\Delta\nu = 3646.1$ cm^{-1}±1.5 and 3653.9 cm^{-1}±1.5 for these shifts, respectively. The definition on this plate was particularly good and this doublet was clearly resolved. An attempt was made to resolve the corresponding line shifted from λ3654. Since this line is considerably weaker than λ3650 several days' exposure was necessary to photograph it

[2] D. H. Rank and G. H. Fleming, Florida Meeting Am. Chem. Soc.

[3] R. W. Wood, Phys. Rev. 45, 392 (1934).

properly and unfortunately the definition could not be maintained as sharp for the longer period of time. The third member of the triplet naturally could not be resolved, since the exciting line $\lambda 3663$ is itself a close doublet of 0.38 Angstrom separation. This state of affairs would contract the pattern to an extent far beyond the photographic resolving power of the spectrograph.

DISCUSSION

The Raman spectrum of liquid water has been obtained by numerous investigators. This spectrum is characterized by an extremely broad diffuse band whose center lies approximately 3445 cm^{-1} from the exciting line. The Raman spectrum of the vapor consists of a sharp line ($\Delta\nu = 3650$ cm^{-1}) in contrast to the band observed in the liquid. Shifting of the center of the bands in the liquid to lower frequencies compared to those observed for the vapor, is well known from work on the infrared spectrum of water.[4] The infrared spectrum of water vapor shows these bands, which have been analyzed by Mecke and his co-workers[5, 6, 7] to exhibit the structure predicted from the theory developed by Kramers,[8] Dennison[9] and Nielsen.[10] In the liquid state these infrared absorption bands no longer show

this "many lined" fine structure but appear to be continuous.[4] The reason for this phenomenon is probably to be found in the action of the stray fields of neighboring molecules on the absorbing molecules in such a manner that the energy levels are no longer discrete. This phenomenon is quite marked in the Raman spectrum of liquid H_2O, HDO and D_2O, while the spectrum of liquid CS_2 apparently yields quite sharp lines.[11] From the work of Wood[3] on the liquid it is interesting to note, that the shift of the center of the band to lower frequencies in the spectrum of liquid D_2O compared to the line observed in the spectrum of the vapor, when compared to the effect observed for H_2O, appears to be proportional to the frequency.

In Table I we have arranged the available data on the infrared and the Raman spectrum of both ordinary and heavy water.

Mecke's[5] analysis of the infrared absorption bands of H_2O vapor leads to the values for the fundamentals given in Table I. $\nu(\sigma)$ and $\delta(\pi)$ appear as fundamentals in the infrared absorption spectrum. However, $\nu(\pi)$ makes its appearance only in the combination bands. In the Raman spectrum $R\nu(\pi)$ is observed by the appearance of a line $\Delta\nu = 3650$ cm^{-1}. A line $\Delta\nu = 3804$ cm^{-1} has been observed[1] which (though somewhat doubtful) might be correlated with $R\nu(\sigma)$. It is observed from the infrared data that $\nu(\sigma) - \nu(\pi) = 156$ cm^{-1} while from the Raman effect $R\nu(\sigma) - R\nu(\pi) = 154$ cm^{-1}. This agreement which is well within experimental error may be significant. The answer to the discrepancy between the absolute value of $R\nu(\pi)$ and $\nu(\pi)$ is probably to be found in the rotational structure of the spectrum. It is difficult to see how the Raman frequencies can be correlated with Q branch lines as is the case in diatomic molecules.*

TABLE I.

	H₂O			HDO			D₂O		
	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$
Mecke[5]	3756	3600	1595						
Johnston and Walker[12]		3655	1648						
Rank[1]	3804	3650							
Rank		3646.1							
Larsen					2718			2666	
Bordner		3653.9							
Wood[3]		3445*		3500*	2623*			2517*	

* These values are obtained from the spectrum of the liquid and must not be compared with the values obtained from the vapor. Due to the well-known broad diffuse character of these bands the measurements obtained from the spectrum of the liquid cannot be of comparable accuracy with those obtained from the spectrum of the vapor.

[4] Schaefer and Matossi, *Das Ultrarote Spektrum*, p. 242.

[5] R. Mecke, Zeits. f. Physik **81**, 313 (1933).

[6] W. Baumann and R. Mecke, Zeits. f. Physik **81**, 445 (1933).

[7] K. Freudenberg and R. Mecke, Zeits. f. Physik **81**, 465 (1933).

[8] H. A. Kramers and G. P. Ittman, Zeits. f. Physik **53**, 553 (1929).

[9] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[10] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

[11] R. W. Wood and George Collins, Phys. Rev. **42**, 386 (1932).

* The apparent absence of a Q branch was noted by Langseth and Nielsen (A. Langseth and J. Rud Nielsen, Zeits. f. physik. Chemie **B19**, 427 (1932)) in the Raman spectrum of gaseous CO_2. They interpreted the lines which they found as maxima of P and R branches. Nielsen (Phys. Rev. **44**, 911 (1933)) has calculated the intensities of the Raman lines associated with this transition. However, the calculations do not explain the difficulty since they show that the Q branch should be considerably stronger than the P and R branches.

The observation in the present work that $R\nu(\pi)$ consists of a close pair of lines enables us to attempt an empirical explanation of the apparent discrepancy noted above. If we assume that $R\nu(\sigma)$ also consists of a close pair of lines, we find from the infrared data of Mecke that the mean of the two transitions

$(2_{-2} \rightarrow 1_{-1} = 3802.6$ cm^{-1}, $2_0 \rightarrow 1_1 = 3807.9$ cm^{-1})

in the R branch of the 1,0,0 band yields a value of 3805.2 cm^{-1}, which is in excellent agreement with the value found for $R\nu(\sigma)$ (3804 cm^{-1}). The corresponding transitions in the 0,0,1 band would yield a value the mean of which is 1646.7 cm^{-1}, which would be in good agreement with the line $\Delta\nu = 1648$ cm^{-1} found by Johnston and Walker.[12] The doublet separation in this case would be 10.3 cm^{-1}. Unfortunately the rotational constants are not available for the 0,1,0 band. If we assume them to be sensibly the same as in the 1,0,0 band the value obtained for the mean of the corresponding transitions in the 0,10, band would be 3649.0 cm^{-1} in excellent agreement with the value found for $R\nu(\pi)$ (3649.5 cm^{-1}). However, if the same rotational constants were used as in the 1,0,0 band the doublet

separation would be too small by about 30 percent to check the observed value (7.8 cm^{-1}).

If the numerical agreement using the empirical assignment outlined above, for the observed Raman transitions, is not fortuitous the selection rules for the rotational quantum numbers would appear to be $J \rightarrow J-1$, $K \rightarrow K+1 \neq 0$. (These selection rules as stated would correspond to anti-stokes transitions.) The rule $K+1 \neq 0$ would explain the absence of the $1_{-1} \rightarrow 0$ transition. If the $K+1 \neq 0$ rule did not apply one would obtain a triplet for the $2 \rightarrow 1$ transitions instead of the observed doublet. Unfortunately the transitions involving higher values of J, excited by $\lambda 3650$ would be masked by the $2 \rightarrow 1$ transitions excited by $\lambda 3654$ and $\lambda 3663$. $\lambda 2536$ excitation would remove the experimental difficulties cited above and enable one to obtain these higher transitions providing they appear with appreciable intensity.

We wish to acknowledge our indebtedness to Mr. G. H. Fleming of the Chemistry Department for his assistance in the preparation of the heavy water.

Note added in proof:

Since this paper was written a communication has appeared by R. W. Wood[13] in which he gives 2601 and 2674 cm^{-1} for the Raman frequencies of D_2O and HOD vapors, respectively. The values given in the present were obtained using much higher dispersion and should accordingly be considerably more accurate.

[12] H. L. Johnston and M. K. Walker, Phys. Rev. 39, 535 (1932). It is a curious fact that this transition does not appear in the Raman spectrum of the liquid. Professor Wood[3] using $\lambda 2536$ excitation did not obtain it either for H_2O or D_2O. $\lambda 2536$ excitation should be quite favorable for the observation of this frequency because of the absence of other exciting lines. One of us[1] previously was unable to find this transition in the spectrum of the vapor.

[13] R. W. Wood, Phys. Rev. 45, 732 (1934).