

On the Constitution of Spring Water

Tatsuo TOKUIHRO

The Osaka University of the Liberal Arts and Education

(Received for publication May 20, 1961)

1. Introduction.

Various solutes in spring water have been analyzed spectroscopically, chemically, both qualitatively and quantitatively, and results of analysis as well as physiological effects of solutes have been widely reported. However, a molecular structure of spring water itself, that is, spring water as a solvent has been studied very little so far. Now in this experiment I tried to find out the structural difference between common water and spring water by examining their molecular structure by means of Raman effects.

2. Experimental

The experimental arrangement used in this experiment is shown in fig. 1. The spectrograph of high luminosity, which was designed and made by author, consists of three 60° prisms ($16\text{cm} \times 13\text{cm}$) and two achromatic lenses (diameter 10cm; focal length=50cm). This gave dispersion of 10\AA per mm. at 4000\AA . As a light source a mercury lamp (1 KW. Mitsubishi Electric Co.) was used, and Raman-tube of Pyrex glass make is 3cm in diameter and 30cm in length and is put in larger outer tube so that it may be cooled by water. As experimental samples I used spring water of Arima spa, Takedao mineral spring, and our drinking water.

3. Results

The micro photometric curves of Raman spectra of spring water are reproduced in fig. 2.

The wave-lengths of the mercury arc lines are marked and the Raman bands of water indicated by arrows. The left one is excited by the 3650-63 group (Hg-q, Hg-p, Hg-o line) and the right by the 4047 line (Hg-k line). The curve for sample 1. (spring water of Arima spa.) clearly showed that each of the bands consists of two components the one towards the right being sharper and the another towards the left being greater in intensity.

The curve for sample 2. (Takedao mineral spring) also rise to two components the one towards the left being sharper and the another towards the right being greater in intensity.

In sample 3. (our drinking water), there is clearly change in the form of micro-photometric curve corresponding to the band. of the two maxima which are clear in the curves for water in sample 1 and sample 2, the left component has considerably diminished in

intensity.

The following table contains the Raman frequencies of H_2O calculated from the micro-photometric curves given above. As the bands very diffuse, the exact position of the maxima could not be located for measurement with a micrometer. Hence the wave-lengths are determined by measuring distances on the photometric curves themselves using the mercury arc lines as the standards.

The values given in the table are for the band excited by the 4047 line (Hg-k line) alone. The other due to excitation by the 3650-63 group (Hg-q, Hg-p, Hg-o line) is a mixture bands arising from the three components of the group and hence is not simple enough to give accurate values of frequency.

Table 1. Raman Frequencies of the H_2O Band

Sample	Raman frequencies of maxima in cm	
Sample 1. Arima spa	3416 (2.93)	3292 (3.04)
Sample 2. Takedao mineral spring	3435 (2.91)	3310 (3.02)
Sample 3. Common Water	3424 (2.92)	

The values given within brackets below each value of $\delta\nu$ are the corresponding infra-red wave-lengths in μ .

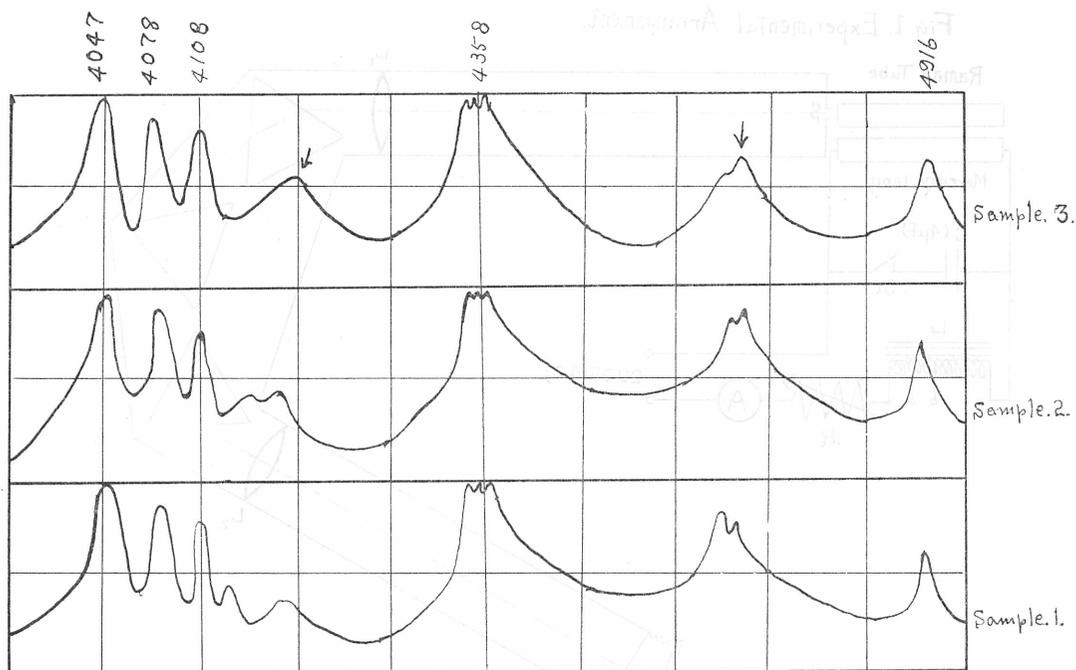


FIG. 2. Microphotometer curves of Raman bands of water.

As it is not possible to draw any conclusions from the simple micro-photometric curves, the intensities of the bands are calculated according to the method already discribed. ①

The following Tables 2-4 contain the calaulated results of the intensity distribution of the band excited by the 4047 line (Hg-k line) in each sample.

Table 2. Intensity Distribution of the H₂O Band of Sample 1.

λ in A. U.	ν in cm ⁻¹	$\delta\nu$ in cm ⁻¹	λ I. R in μ	Intensity
4771	20959	3750	2.66	0
4750	21052	3657	2.73	7
4726	21159	3550	2.82	13
4706	21249	3460	2.89	36
4695	21299	3410	2.93	40
4680	21365	3384	2.95	38
4669	21417	3292	3.04	45
4649	21510	3199	3.12	35
4637	21566	3143	3.18	18
4614	21673	3039	3.29	5

Fig. 1. Experimental Arrangement.

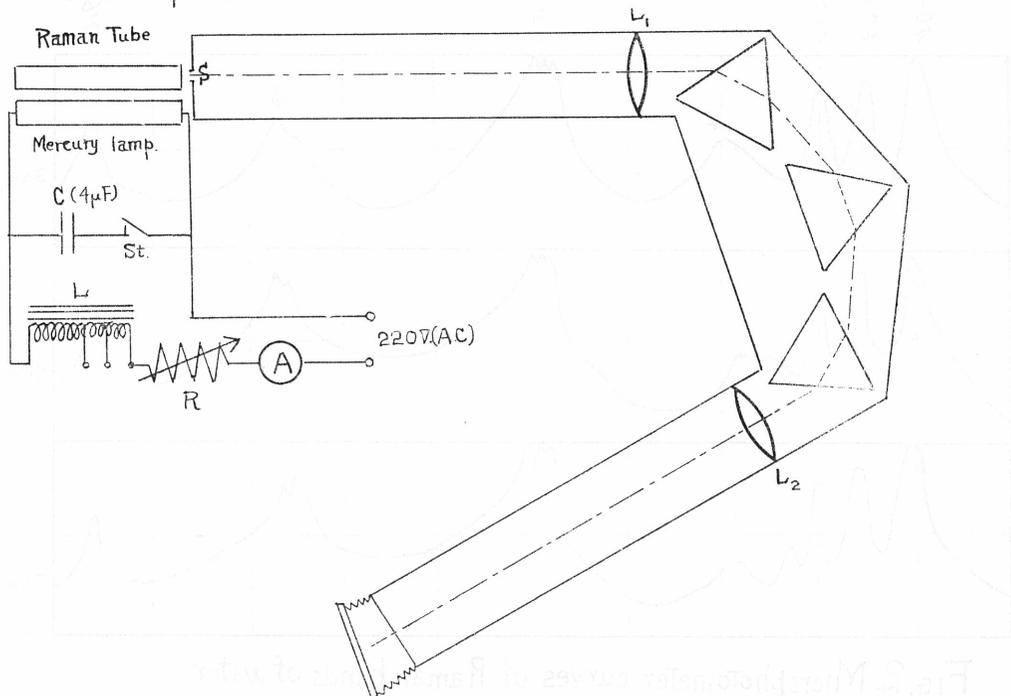


Table 3. Intensity Distribution of the H₂O Band of Sample 2.

λ in A. U.	ν in cm ⁻¹	$\delta\nu$ in cm ⁻¹	λ I. R in μ	Intensity
4770	20964	3745	2.67	5
4748	21061	3648	2.74	15
4725	21164	3545	2.82	35
4706	21249	3460	2.89	42
4700	21274	3435	2.91	44
4693	21309	3400	2.94	42
4678	21376	3333	3.00	31
4673	21399	3310	3.02	38
4664	21440	3269	3.06	33
4668	21514	3195	3.13	10
4629	21603	3106	3.22	2

Table 3. Intensity Distribution of the H₂O Band of Sample 3.

λ in A. U.	ν in cm ⁻¹	$\delta\nu$ in cm ⁻¹	λ I. R in μ	Intensity
4811	20785	3924	2.55	1
4711	20959	3750	2.66	11
4745	21704	3635	2.75	25
4725	21164	3545	2.82	32
4706	21249	3460	2.89	42
4698	21258	3424	2.92	45
4690	21321	3388	2.95	43
4678	21376	3333	3.00	27
4669	21417	3292	3.04	25
4649	21510	3199	3.12	18
4632	21584	3125	3.20	10
4623	21633	3076	3.25	3

The results given in Tables 2-4 are represented graphically in fig. 3. The wave-lengths are taken along the abscisa and intensities along the ordinates.

The solid line corresponds Arima spa (sample 1) and consists of two distinct maxima at 2.93 μ and 3.04 μ , the latter being much stronger in intensity than the former. The two maxima 2.91 μ and 3.02 μ of the band for sample 2 (Takedao mineral spring) are much more pronounced in its intensity curve which is represented by the dotted line. The band for common water (sample 3) represented by alternate dots and dashes is not resolved at all, showing only a single maximum at 2.93 μ .

4. Explanation of the above Results.

According to I. R. Rao,^② Sutherland,^③ Dennison^④ etc., there are three types of molecules arising out of the association of single molecules, viz., (H_2O) , $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O})_3$. These three types of molecules are supposed to give rise to the three components of Raman band of water with frequencies 3650 cm^{-1} (2.74μ), 3435 cm^{-1} (2.91μ), and 3280 cm^{-1} (3.04μ) respectively. And (H_2O) , $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O})_3$ represent vapour, water and ice respectively.

According to Hückel,^⑤ ice particles are combined one another through hydrogen-bond and their combination is gradually broken with the rise of temperature but ice-structure still remains. I shall examine the results with those things in mind.

Water-vapour gives rise to a Raman line at 2.74μ . In the liquid state the position of the maximum is at about 2.9μ , and the band for ice consists of a larger maximum at 3.04μ . The analysis reveals in general three components at 2.74 , 2.9 and 3.04μ respectively.

Since the first component corresponds to the Raman line for the vapour state, it will be called the vapour component and the single molecules which give rise to it will be called the vapour molecules. The second component should correspond to the higher polymer, the double molecules, and since it is conspicuous in the liquid state, the molecules which give rise to it will be called the water molecules. The third component most conspicuous in ice is supposed to arise on of the triple molecules which on account of their preponderance in this state, will be called the ice molecules.

On the basis of the above assumptions, the intensity curve for sample 1 is analysed in the manner represented in fig. 4.

On the assumption that the ice component will have its maximum in the same position as that of the larger maximum in the resultant curve, a line is drawn through the latter parallel to the ordinate. As it is assumed that the component intensity curves will be symmetrical about their maximum, this line is taken as the line of symmetry for the ice component. Since the contribution to the resultant intensity curve to the extreme right will be due only to this component to some extent, the extreme portion of the curve is also taken as a portion of the curve due to the ice component. With this as the starting-point, a small curve is drawn on the left of the line of symmetry which appears as the inversion of the actual extreme portion of the resultant curve about this line. The curve so drawn is smoothly extended to meet the line of symmetry at some point. With this extended curve as the left half of the actual ice component, the right portion is completed. This complete curve which is drawn as discontinuous in the figure is taken as representing the curve for the ice molecules. To get the water component, a line is drawn parallel to the ordinate with its abscissa equal to 2.9μ which corresponds to the maximum of the water component. The ordinate differences between the resultant curve and the ice component, complete above, are plotted against their corresponding abscissa and a portion of the water component thus obtained. The inversion of this curve about the line of symmetry is also drawn and produced to meet this line at some point. With this point as the maximum of the water component in the curve for sample 1, the whole component is completed. On subtracting the intensities of the above two components from the resultant,

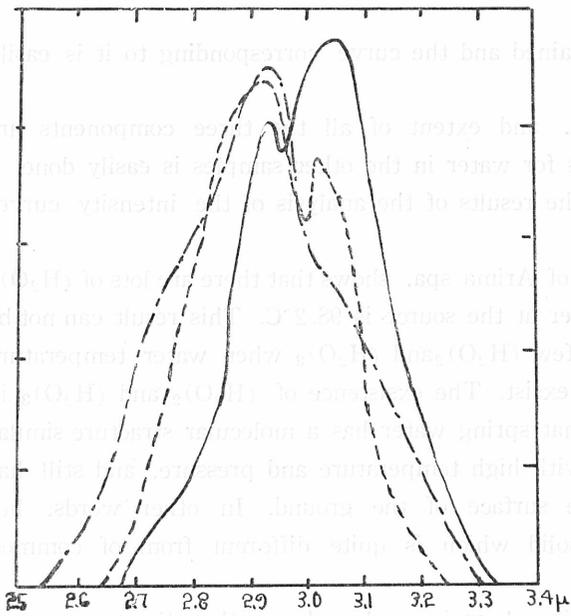


Fig. 3. Intensity curves for Raman of water.

Sample. 1. — ; Sample. 2. - - - - ;
 Sample. 3. - · - · - ;

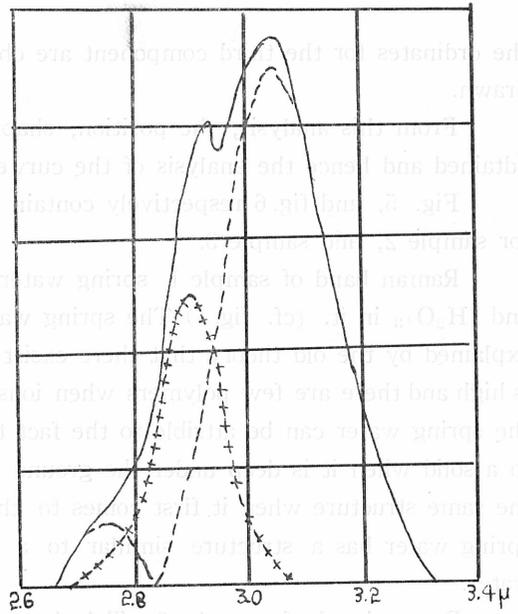


Fig. 4. Analysis of the curve for sample 1.

Resultant curve —
 ice component - - - -
 water component - · - · -
 vapour component · · · · ·

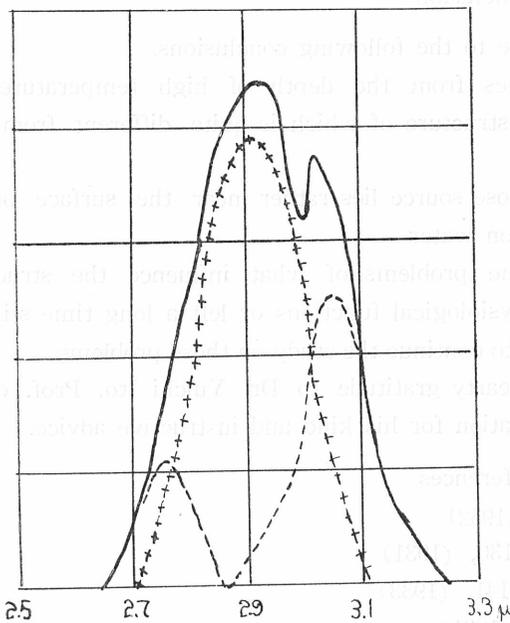


Fig. 5. Analysis of the curve for sample 2.

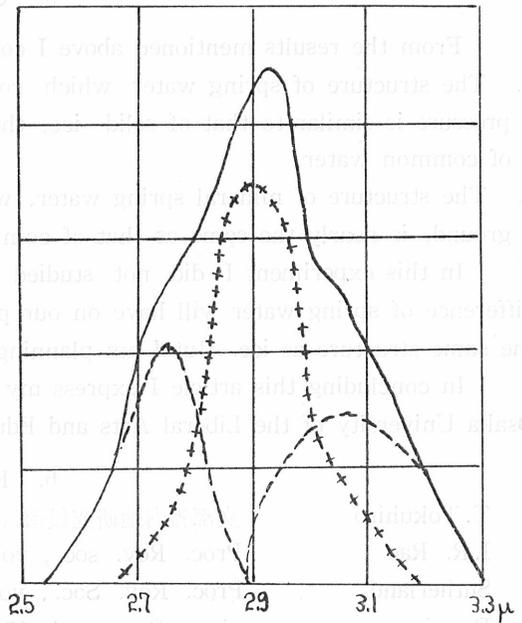


Fig. 6. Analysis of the curve for sample 3.

the ordinates for the third component are obtained and the curve corresponding to it is easily drawn.

From this analysis, the position, shape, and extent of all the three components are obtained and hence the analysis of the curves for water in the other samples is easily done.

Fig. 5, and fig.6 respectively contain the results of the analysis of the intensity curves for sample 2, and sample 3.

Raman band of sample 1, spring water of Arima spa, shows that there are lots of $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ in it. (cf. fig.4) The spring water at the source is 98.2°C . This result can not be explained by the old theory that there exist few $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ when water temperature is high and there are few polymers when ions exist. The existence of $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ in the spring water can be attributed to the fact that spring water has a molecular structure similar to a solid when it is deep under the ground with high temperature and pressure, and still has the same structure when it first comes to the surface of the ground. In other words, hot spring water has a structure similar to a solid which is quite different from common water.

Raman band of sample 2, Takedao mineral spring, also shows that there are some $(\text{H}_2\text{O})_2$ and some $(\text{H}_2\text{O})_3$ in it, but they are far less in number than in sample 1. This is because, perhaps, the mineral spring lies shallow under the ground and its temperature is not so high.

Raman band of sample 3, common water, shows that it also contains some $(\text{H}_2\text{O})_2$, and some $(\text{H}_2\text{O})_3$, but they are far less in comparison with sample 1.

5. Conclusion

From the results mentioned above I come to the following conclusions.

1. The structure of spring water which comes from the depth of high temperature and pressure is similar to that of solid-ice, the structure of which is quite different from that of common water.
2. The structure of mineral spring water, whose source lies rather near the surface of the ground, is nearly the same as that of common water

In this experiment I did not study the problems of what influence the structural difference of spring water will have on our physiological functions or left a long time still has the same structure as ice. But I am planning to continue the study on those problems.

In concluding this article I express my hearty gratitude to Dr. Yuichi Ito, Prof. of the Osaka University of the Liberal Arts and Education for his kind and instructive advice.

6. References

1. T. Tokuhira 文部省内地研究員報告 (1952)
2. I. R. Rao Proc. Roy. soc., vol.130, (1931)
3. Sutherland Proc. Roy. Soc., vol.141, (1933)
4. Dennison phys. Rev., vol. 17. (1931)
5. Huckel Z. Elektrochem. 34 (1928)