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The Raman Spectrum of Water Vapor

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The Raman spectrum of water vapor at atmospheric pressure was obtained. Special precautions were taken to avoid parasitic light and a search made for the 1648 cm^{-1}, and 984 cm^{-1} shifts reported by Johnston and Walker. These shifts were not observed. A line was found which might be correlated with Mecke's $\nu(\sigma)$ but the evidence in this case is not conclusive.

INTRODUCTION

THE Raman spectrum of water vapor has been investigated by Daure and Kastler,[1] who found a single Raman shift 3654 cm^{-1}. Johnston and Walker[2] have observed three Raman shifts: 3654 cm^{-1}, 1648 cm^{-1}, and 984 cm^{-1}, which they correlate with Dennison's[3] ν_3, ν_2, and ν_1, respectively. R. Mecke[4] has pointed out that the 984 cm^{-1} shift cannot be correlated with $\nu(\sigma)$ but might be attributed to the vibration of the associated molecule H_2O-OH_2. The author has attempted to find the Raman frequency corresponding to Mecke's $\nu(\sigma)$, which should lie near $\nu(\pi)$.[4, 5]

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental arrangement used was similar to that used by Professor R. W. Wood[6] in his work with gaseous hydrogen chloride at atmospheric pressure. The scattering tube was of Pyrex, about 130 cm long and 50 mm in diameter. A plane Pyrex window was sealed on to one end of the tube. The other end was drawn out into a cone and bent at right angles to the axis of the larger tube. A 100 cc flask was sealed on to the conical end, and provision was made for evacuation. The diaphragm used was of brass and had an 8 mm aperture. Water was placed in the flask, and the water vapor pressure was maintained at one atmosphere by having the flask immersed in a bath of boiling water, since all the other parts of the tube were maintained at a temperature greater than 100°C by means of the mercury arcs and suitable heaters.

The light source used consisted of two double mercury electrode Pyrex mercury arcs about 80 cm long. The one had an internal diameter of 36 mm and carried a current of 9 amperes, while the other was 25 mm in diameter and carried a current of 4 amperes. The arcs and scattering tube were enclosed in a cylinder of highly polished sheet aluminum.

Before being used for making exposures, the scattering tube was thoroughly baked out and repeatedly evacuated in order to clear the tube from any gases which might cause contamination.

The image of the diaphragm was focussed on the slit of the spectrograph by means of an achromatic lens of about 35 cm focal length, placed at a distance of about two meters from the scattering tube. The spectrograph employed was the same as that described by the author[7] previously. Exposures were made by using one or two prisms and an F 4.5 camera lens, which gave a dispersion of 100 and 50 Angstroms/mm respectively at λ4200. The slit width used was between 0.06 and 0.07 mm but because of reduction of the size of the image when using the F 4.5 camera lens, the width of the lines on the photographic plate was less than 0.02 mm.

It can be seen by referring to Fig. 1, A, that two black lines run across the spectrum horizontally. These are caused by the light which is diffracted from the diaphragm. These black lines automatically furnish blanks of the incident

1 Daure and Kastler, Comptes Rendus **192**, 1721 (1931).
2 Johnston and Walker, Phys. Rev. **39**, 535 (1932).
3 Dennison, Rev. Mod. Phys. **3**, 289 (1931).
4 R. Mecke, Zeits. f. physik. Chemie **B16**, 407 (1932).
5 R. Mecke, Phys. Zeits. **30**, 907 (1929).
6 R. W. Wood, Phil. Mag. **7**, 744 (1929).
7 D. H. Rank, J. Opt. Soc. Am. **23**, 84 (1933).

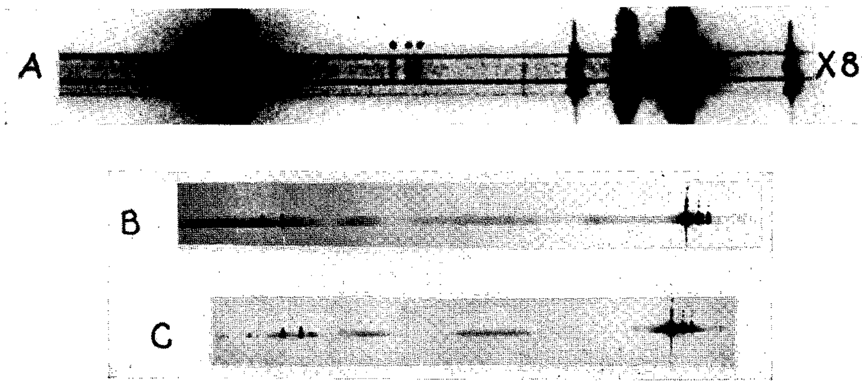

FIG. 1. A. The Raman spectrum of water vapor. B. The Raman spectrum of Pyrex glass. C. The spectrum of the mercury arc used.

radiation. Because of halation, faint Hg lines show up as dots on these black lines. Thus under the comparator, a Hg line looks much like a dumbbell while a Raman line does not have the knobs at both ends and is thus unmistakable. In order to furnish an additional blank of the incident radiation, a small finger mark was placed on the window just clear of the useful aperture. Sufficient light was reflected from this mark to give a complete blank spectrum. It can be seen by referring to the above figure that the Raman lines (3650 cm^{-1} excited by λ3650, λ3655, and λ3663), which are indicated by dots, are only in evidence between the two horizontal black lines; while Hg lines extend below the lower horizontal black line.

Using a single prism, the author was able to photograph the Raman lines $\Delta\tilde{\nu} = 3650$ cm^{-1} excited by λ3650, λ3655, λ3663, and λ4047 with an exposure time of only two hours. With an exposure time of 47 hours, a line $\tilde{\nu} = 21{,}950$ appeared which Johnston and Walker assign as a 984 cm^{-1} shift from λ4358. However, this line can be attributed within experimental error to a 3650 cm^{-1} shift from λ3906. This latter assignment seems most probable to the author, considering the great intensity of the 3650 cm^{-1} shifts and the increasing effectiveness of the shorter wave-lengths in exciting these long shifts. On these plates, taken with a single prism, the 3650 cm^{-1} shifts excited by λ3650 and λ3655 could be easily resolved.

Exposures were then taken with two prisms set for minimum deviation at λ4358. A 93-hour exposure showed all the lines which appeared on the plates taken with the single prism. In addition, on this plate a very weak line λ4238.6 appeared. This line might be assigned as a 3804 cm^{-1} shift from λ3650. However there is considerable doubt concerning this assignment, the increasing background preventing the observation of the two weaker lines excited by λ3655 and λ3663, which would definitely confirm this assignment. In order to test the very remote possibility of this line being due to double scattering from Pyrex, Mr. E. R. Bordner and the author have obtained the Raman spectrum of Pyrex. Use was made of a very fine bar of Pyrex which had been placed at our disposal through the courtesy of the Corning Glass Company. The filters used were the praseodymium filter, described by Wood and Collins,[8] and the sodium nitrite filter described by Pfund.[9] The excitation in this case is entirely by λ4358. Fig. 1, B, is an enlargement of one of the plates taken with Pyrex as the scatterer, while Fig. 1, C, shows the mercury as spectrum photographed through these filters. No lines were observed in the spectrum of Pyrex; only broad diffuse bands appear. The first of these bands has its center at 400 cm^{-1} and is about 150 cm^{-1} broad. The second has its center at 780 cm^{-1} and is about 50 cm^{-1} broad. These bands are only observable because they fall well within one of the praseodymium absorption bands. There seems to be a very heavy continuous Raman spectrum in the case of Pyrex in addition to the

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

[9] A. H. Pfund, Phys. Rev. **42**, 581 (1932).

band spectrum, as can be seen by referring to Fig. 1, B and C. It is absolutely certain that no Raman lines can be ascribed to double scattering from Pyrex in the light of these results.

The prisms were then set for minimum deviation at $\lambda 3900$, and a 120-hour exposure was taken. None of the lines reported by Johnston and Walker[2] in this region were observed. It was found that faint Hg lines would interfere with the measurements of all the new lines reported by the above authors with the exception of the 984 cm^{-1} Stokes shift from $\lambda 4078$ and the 984 cm^{-1} anti-Stokes shift from $\lambda 4078$. The author was unable to find any evidence for the existence of these lines. No evidence was found for the Stokes shift from $\lambda 4047$ which should fall midway between the pair of 3650 cm^{-1} Raman lines excited by $\lambda 3650$ and $\lambda 3655$ although this pair of Raman lines was easily resolved. No asymmetry of these lines could be noted. However all the Raman lines appeared to be about twice as broad as a sharp mercury line. Measurements of the plates give for the only Raman shift definitely observed 3650 $cm^{-1} \pm 3$ cm^{-1}.

Conclusion

The author was unable to find any evidence for the existence of the 984 cm^{-1} and 1648 cm^{-1} shifts reported by Johnston and Walker, although the intensity range used by the above authors appears to have been covered by a factor of two in the present investigation. One line which might be assigned as a 984 cm^{-1} shift from $\lambda 4358$ can also be attributed to a 3650 cm^{-1} shift from $\lambda 3906$ within experimental error. A line was found which, if excited by $\lambda 3650$, might be correlated with Mecke's $\nu(\sigma)$. However because of the increasing background, the corresponding shifts from $\lambda 3655$ and $\lambda 3663$ could not be observed if they existed. Double scattering from Pyrex was definitely eliminated as the source of this line.