Raman Spectra of Gaseous, Liquid and Solid Hydrogen Sulfide

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Measurements of the infrared spectra,[1] as well as chemical and other evidence, indicate that the hydrogen sulfide molecule is of the symmetrical bent type, such as water, and belongs to the symmetry group, C_{2v}. Three vibrational frequencies are to be expected, all of which are permitted in both the infrared and Raman spectra. The only previous measurements resulted in the observation of one Raman line for the gas and the liquid.[2] Four Raman frequencies have been reported for the solid.[3]

We have photographed the Raman spectra of hydrogen sulfide in all three states, using the unfiltered radiation from a helical Pyrex arc such as described by Glockler and Davis.[4] The gas was at a pressure of about two atmospheres. Scattered lines were observed from both the 4358 and the 4047 mercury lines. The average of the results from four plates gives the frequency of the only line observed as 2615 cm^{-1} in agreement with the previous work on the Raman and infrared spectra. This line appeared on our plates within fifteen minutes, and exposures one thousand times as long failed to show any further scattered lines.

With the liquid kept at $-80°$ by means of a dry ice-alcohol bath, four spectra were obtained showing a single frequency of 2577 cm^{-1}, again in agreement with earlier work.

Photographs of the Raman spectra of the solid were obtained with the latter kept at liquid air temperatures. Two frequencies were observed of 2550 and 2523 cm^{-1}. The two frequencies of 80 and 2558 cm^{-1}, previously reported[3] were not present on our plates although an anti-Stokes line appeared (2523 cm^{-1}) in a one-hour exposure. An exposure of five hours failed to show anything different.

The precision in each case is about 5 cm^{-1}.

A preliminary experiment on D_2S gas shows one frequency of 1885 cm^{-1}, in fair agreement with infrared spectra.[1] The complete results will be reported later and will include measurements of liquid and solid D_2S as well as of HDS.

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[1] Bailey, Thompson and Hale, J. Chem. Phys. **4**, 625 (1936); Sprague and Nielsen, ibid. **5**, 85 (1937); Nielsen and Nielsen, ibid. **5**, 277 (1937).
[2] Bhagvantam, Nature **126**, 502 (1930).
[3] Sirkar and Gupta, Ind. J. Phys. **10**, 189 (1936).
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Low and High Raman Frequencies for Water

During the course of the last five years, many workers reported having observed a number of high and low frequency bands other than the 3200–3600 band for water. A systematic and thorough examination of these frequencies was recently made by Magat[1] and Hibben.[2]

As workers in this line ever since the discovery of the Raman effect, we were following with interest the results of different experimenters on this problem of water. The new frequencies reported by others were not unnoticed by us, but were rejected as either spurious mercury lines making their appearance during long exposures of the photographic plate, or genuine Raman bands of frequency 3200–3600, excited, not by the mercury line assigned by these authors, but out of other comparatively feeble lines of the mercury arc. Finding that even systematic investigations of the type of those of Magat and Hibben reveal these new lines, a critical study of the Raman spectrum of water was made by us which confirmed our previous interpretation.

Table I gives the results of our analysis, as compared with that of others.

TABLE I.

Assignment of Other Workers			Our Assignment		
$\Delta\nu$	ν_{Hg}	ν_R	λ_{Hg}	ν_{Hg}	$\Delta\nu$
175(32)	39412	39237	2345(4)	42622	3385
740(24)	"	38672	2378(6)	42032	3360
1145*	"	38267	2399(8)	41633	3396
2150(14)	"	37262	2464(4)	40570	3308
—	—	—	2482(6)	40276	—
3200 3400 (80) 3600	"	36012	2537(10R)	39412	3400
4023(47)	"	35389	2576(6)	38803	3414
5100(45)	"	34312	2652(8)	37695	3383
500(40)	"	38912	2464(4)	40571	1659
1659(?)	"	37753	2537(10R)	39412	1659

The Raman band noted with an asterisk was not pointed out by other workers. It is noted for the first time by us, but represents only the 3200–3600 band excited by the strong 2399 line of mercury.

The table clearly shows that the bands reported by other workers correspond not to different frequencies of water excited by the same 2537 line of the mercury arc, but to the same 3200–3600 band excited by lines other than the 2537 line. The excitation by these lines appears to have been entirely ignored by all these workers. We have systematically investigated excitation by all the other strong lines of the mercury arc both in the visible and ultraviolet regions and find not even a trace of these frequencies, though these exciting lines are nearly as intense as the 2537 line.

The only other frequency which we find to be genuine is of $\Delta\nu = 1659$ as is evident from the table.

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June 3, 1937.

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[2] J. H. Hibben, J. Chem. Phys. **5**, 166 (1937).