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# Infrared Spectrum of Solid Hydrogen Disulphide

by

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# Infrared Spectrum of Solid Hydrogen Disulphide

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The infrared absorption spectra of crystalline hydrogen disulphide is measured within the optical interval of 290–5000 cm-$^1$, the fundamentals and several combinations bands of fundamentals-lattice vibrations have been observed. The band located at 1070 cm-$^1$ has been assigned as a combination due to $\nu_6$ and a frequency combination of the order 202 cm-$^1$, the torsional frequency $\nu_4$ which has not been detected yet. This fundamental is the only oscillation that can be used to prove the possibility of $C_2$ configuration of hydrogen disulphide.

## INTRODUCTION

Wilson and Badger (1) have measured the infrared spectrum of gaseous hydrogen disulphide in the region 1,5 to 15 microns and they observed fundamental vibrations $\nu_2$ and $\nu_5$, and combination band of $\nu_3+\nu_5$, $\nu_5+\nu_6$, $\nu_1+\nu_5$.

Fehér and his co-workers (2,3) have studied the Raman shifts, one of them of 509 cm-$^1$ has been assigned as $\nu_3$ which could not be observed as a single band in the infrared spectrum. However, no structural investigation of the crystalline $H_2S_2$, either by x-ray diffraction or spectroscopy has been reported yet. It is this lack of data that has been main source of difficulty encountered in the interpretation of solid state spectra studied in the present work.

The infrared spectrum of the solid $H_2S_2$ is also of significance with respect to,

i) The analogy of the molecular structure to that of hydrogen peroxide

ii) The absence of hydrogen bonding in the hydrogen persulphide.

## EXPERIMENTAL PROCEDURE

The sample of the $H_2S_2$ used for the present work was prepared after the method prescribed by Butler and Maass (4). Sodium polysulphide used as the raw material to obtain hydrogen disulphide, was produced by heating on a water bath, a mixture of sulphur, sodium sulphide crystals ($Na_2 S.9 H_2O$) and water. Sodium polysulphide solution was added into the hydrocloric acid cooled to – 20° C from a dropping funnel. Thus, the preparation resulted in an emulsion of crude hydrogen polysulphide, with suspended sulphur in an acid solution of sodium chloride. The yellow mixture settling to the bottom was decanted and diluted with water. Then polysulphide layer was drown off a flask by using a separating funnel. Ample amount phosphorus pentoxide was added and the mixture was allowed to rest.

İsolation of $H_2S_2$: Since hydrogen disulphide decomposes rapidly in the presence of alkali, the Pyrex system used for distillation was previously treated with gaseous HCl. Fractionation of the hydrogen polsysulphide was made at 120°C under vacuum.

The distilling system was equiped with five successive traps, all containing $P_2O_5$ except the last. The traps were isolated from one another by vacuum stop-cocks. The second trap was held at –40°C during distillation, to collect $H_2S_2$, while the first one, in which the higher polysulphide were collected, remained at room temperature.

During the first phase of distillation, traps numbered 3,4 and 5 were isolated from the system. In the second phase the first stop-cock was closed, and the rest were opened and connected to the vacuum. Three successive fractional distillations at –80°C were sufficient to yield a clear, colorless liquid, free from higher polysulphides and water.

The final product collected in the last trap remained stable when kept at dry-ice temperature and in the dark.

No analyses of purity were caried nor needed, due to the fact that in the spectra no band belonging to the $H_2S$ absorption was traceable. As a matter of fact, Walton and Parson (5) reported 99, 98% purity after only the first phase of distillation.

A special vacuum absorption cell similar to that of Wagner and Hornig (6) was used to take spectra (Fig. 1). The central window of the cell was in thermal contact with the cooling tube by a Kovar and Housekeeper,-copper-glass joint. Metallic parts of the cell were plated with silver.

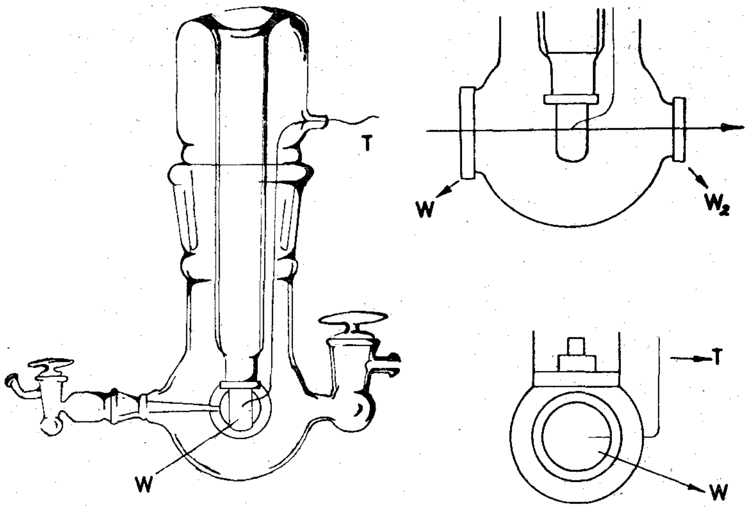

Fig. 1. Vacuum absorption cell

During the recording of spectra, the observed temperatures of central window were about 5 °C higher than that of the liquid air, despite the fact that thermal conductivity between the disks and the silver plated copper block was improved by using finely powdered silver in between. The temperature of the sample was measured through copper-constantan thermocouple imbedded into the disk on which the sample was deposited.

Transparent films of the solid $H_2S_2$ were easily obtained by depositing on the diks of NaCl orCsI (depending on the spectral region) cooled to the liquid air temperature. The cell was evacuated by means of an high vacuum system.

The background was taken by using the single beam spectroscopy technique. From the amount of the liquid used, the surface area of salt disk and metal support, the thickness of thickest crystalline film was estimated to be of the order of 10 microns.

The infrared absorption was measured within the possible optical interval of 290–5000 cm$^{-1}$ with a Perkin-Elmar spectrometer, model 12–C, single beam, double pass, with automatic scanning and recording on a speedomax, using prisms of NaCl, CsBr and KBr and also Perkin-Elmar spectrometer modal 121-A grating instrument with the same absorption cell. The single beam spectrometer was calibrated by usual method (7).

## DISCUSSION OF RESULTS

Various bands observed in the low and high frequency regions are shown in Fig. 2.

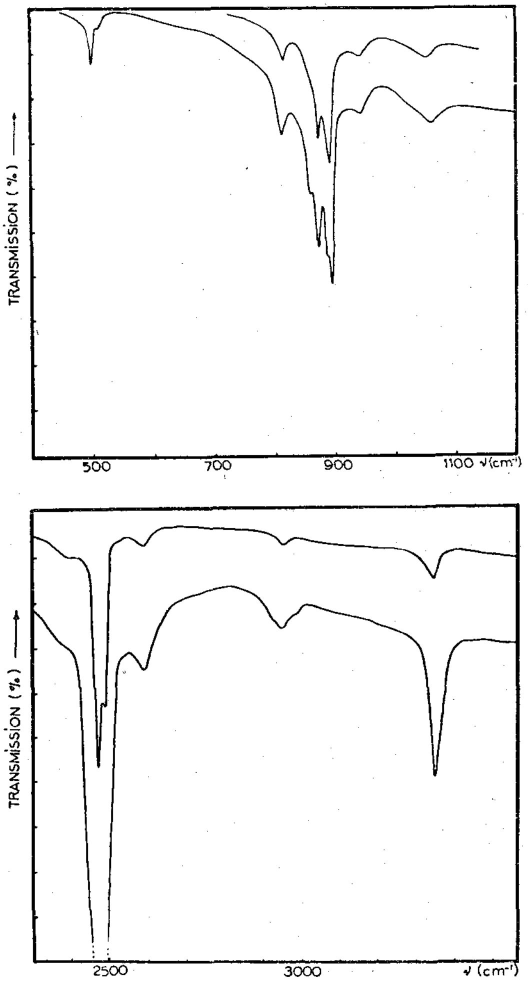

Fig. 2. Infrared absorption spectra of crystalline $H_2S_2$ for two films of different thicknesses

No fundamental or combination bands were observed between 1100 and 2200 cm$^{-1}$ and in the frequency region higher than 5000 cm$^{-1}$

The frequencies of the absorptions maxima are listed in table 1. Due to the weakness of the intermolecular forces, the vibrational frequencies of the free molecule showed, as expected, little variation for the liquid and solid phases. For the same reason, the $H_2$ $S_2$ bands are much sharper than those given by $H_2O_2$, the oxigen analogue of the hydrogen disulphide (8).

Table 1.

Band frequencies in the infrared spectra of solid hydrogen disulphide

| Bands (cm$^{-1}$) | Intensity | Fundamentals | Combinations |
|---|---|---|---|
| 501 | w | $\nu_3$ | |
| 518 | vw | | |
| 814 | w | | $\nu_6-\nu_T$ |
| 857 | vw | $\nu_6$(i) | |
| 868 | vs | $\nu_6$ | |
| 881 | vw | $\nu_2$(i) | |
| 890 | vs | $\nu_2$ | |
| 940 | vw | | $\nu_6+\nu_T$ |
| 1070 | m | | $\nu_6+\nu_4$ |
| 2380 | vw | | $\nu_5-\nu_R$ |
| 2480 | vs | $\nu_5$ | |
| 2495 | s | $\nu_1$ | |
| 2590 | w | | $\nu_5 + \nu_R$ |
| 2930 | vw | | |
| 2960 | w | | $\nu_3 + \nu_5$ |
| 2995 | vw | | $\nu_5 + \nu_6$ |
| 4840 | vw | | $\nu_1 + \nu_5$ |

The first low frequency band located at 501 cm$^{-1}$ with weak satellite at 518 cm$^{-1}$ is the doublet of S–S stretching vibration ($\nu_3$) chich corresponds to the 509 cm$^{-1}$ shift in the Raman spectra for liquid.

Strong absorption region between 800 and 900 cm$^{-1}$ is due to the S–H bending fundamentals. Very strong band located at 868 cm$^{-1}$ is identified $\nu_6$ since it should be lower than $\nu_4$ with a center at 881 cm$^{-1}$ for the solid and 886 cm$^{-1}$ for the gas phase.

Sum-difference combinations of the bending frequency $\nu_6$, appeared together with a lattice vibration of 65-70 $cm^{-1}$ located at 814 $cm^{-1}$ and 940 $cm^{-1}$.

The strong band at 890 $cm^{-1}$ is ascribed to the symmetrical bending mode $\nu_2$, which is stronger than $\nu_6$, observed in the Raman spectrum with a shift of about 882 $cm^{-1}$. The very weak shoulder at 857 and 881 $cm^{-1}$ of about 10 $cm^{-1}$ seen on the low frequency sides of the two main peaks, were only detected by the thickest films. These shoulders might be conceivably attributed to the isotopic molecules $H{-}S^{32}{-}S^{34}{-}H$ which have a natural abundance of about 4 %. They show roughly the same relative intensity as observed for the isotopic bands of $SO_2$ (9). An other single band observed at medium intensity at 1070 $cm^{-1}$ must be a combination band due to $\nu_6$ and a frequency of the order 202 $cm^{-1}$, the torsional frequency which has not been detected yet.

The unsymmetrical stretching fundamental $\nu_5$ gives strongest absorption near 2480 $cm^{-1}$ region. This fundamental also yields strong absorption in the gas phase at 2577 $cm^{1-}$ The shoulder at 2380 $cm^{-1}$ and the rather weak band located at 2590 $cm^{-1}$, too, show sum-difference combinations with a lattice frequency of about 120 $cm^{-1}$

The symmetrical S-H stretching frequency $\nu_1$ which is not observed in the gas gives as expected a strong band at 2495 $cm^{-1}$ very close to unsymmetrical S-H stretching fundamental. The Raman shift of this fundamental is 2509 $cm^{-1}$ which is 14 $cm^{-1}$ higher than the infrared frequency of solild $H_2S_2$.

Finally, the combination band at 2960, 3345 and 4840 $cm^{-1}$ corresponds to the already observed gas-phase ınfrared bands $\nu_3+\nu_5$, $\nu_5+\nu_6$, $\nu_1 + \nu_5$ respectively.

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## ÖZET

Daha önce, $H_2S_2$ molekülünün bazı temel titreşimleri ile bunların kombinezonları tesbit edilmiştir; fakat 200 $cm^{-1}$ mertebesinde olması gereken $\nu_4$ ün kombinezonlarına rastlanmadığı gibi, 1,5–15 mikron aralığında yapılan çalışmalarda bu titreşimin harmonikleri bölgesine de girilememiştir. Moleküller arası etkilerin zayıf olduğu bu maddede, temel titreşimlerin her üç fazda da biribirine yakın olması beklenirdi ve böyle bir sonuç gözlenmiştir. Katı hâl spektrumlarında genellikle gözlenen örgü titreşimleri $H_2S_2$ de de gözlenmiştir. Ancak 1070 $cm^{-1}$ de gözlenen orta şiddette bandın ne bir temel titreşim ve ne de bunların kombinezonlarına uymadığı görüldü. Bu band şiddeti de göz önünne alınarak $\nu_6$ ile 202 $cm^{-1}$ mertebesinde başka bir bandın kombinezonu olarak tefsir edildi. Benzeri moleküllere kıyasla hesaplanan mertebede olması beklenen ve ölçü sınırları dışında bulunan bu titreşim, $H_2S_2$ nin çift düzlemli $C_2$ simetrisine sahip olmasını gerektiren ve ne sıvı ne de gaz fazlarda gözlenemeyen $\nu_4$ burulma titreşimi olmalıdır

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