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Raman Spectra of Hydrogen and Deuterium Sulfides in the Gas, Liquid and Solid States

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Raman spectra have been obtained for H_2S and D_2S as gas, liquid and solid. Only one frequency has been obtained in the gas and liquid although three are permitted by the selection principles. In the solids, a single line and a close doublet have been obtained. With the available infra-red and Raman data, it is not possible to make quantitative calculations of isotope effect, force constants, angle or anharmonic factors.

1. INTRODUCTION

THE hydrogen sulfide molecule is known to belong to the symmetry group, C_{2v} and therefore three vibrational frequencies should be observed, both in the infra-red and in the Raman spectrum. Following the conventional nomenclature of Dennison,¹ we call ν_1 the symmetrical valence vibration, ν_2 the deformation vibration and ν_3 the antisymmetrical valence vibration. Previous work by Bhagavantam² resulted in but one frequency, 2615 cm^{-1} , in the Raman spectrum of H_2S gas and one frequency, 2578 cm^{-1} in the liquid. Sirkar and Gupta³ reported four frequencies in solid H_2S at 80, 2523, 2547 and 2558 cm^{-1} . The only work on the Raman spectrum of D_2S is that of Dadieu and Kopper⁴ who reported a single line of 1875 cm^{-1} . This frequency is certainly for the liquid since they also obtained 2578 cm^{-1} for H_2S . They report 1880 and 2585 cm^{-1} for HDS but this is obviously incorrect since these are the frequencies for H_2S and D_2S .

The older work on the infra-red absorption of H_2S is erroneous due to the presence of impurities. Recent work on vibration-rotation bands has been done with instruments of low

dispersion by Bailey, Thompson and Hale,⁵ under higher dispersion by Nielsen⁶ and collaborators and in the photographic infra-red by Cross⁷ and by Carvin. Similar experiments have been made on D_2S and HDS by Bailey, Thompson and Hale⁵ and by Nielsen and Nielsen.⁸

The purpose of the present work was to re-examine the Raman spectra of both H_2S and D_2S in all three states in the hope of obtaining better values for the three fundamental frequencies.

2. EXPERIMENTAL

The H_2S was drawn from a tank obtained from the Matheson Company, and was reported to be 99.7 percent pure. It was dried over P_2O_5 and frozen in liquid air. After several fractional distillations, the H_2S was distilled into the Raman tube at a pressure of about 2 atmospheres. The tube was made of Pyrex and was similar to that described by Teal and MacWood⁹ except that the platinum diaphragm used by them was omitted. The tube was 86 cm long and 3 cm in diameter. It was completely surrounded by a helical Pyrex arc containing neon and mercury as described by Glockler and Davis.¹⁰ The potential on the arc was approxi-

¹ In the descriptive system of Mecke, these are called $\nu(\pi)$, $\delta(\pi)$ and $\nu(\sigma)$, respectively.

² S. Bhagavantam, *Nature* **126**, 502 (1930).

³ S. C. Sirkar and J. Gupta, *Ind. J. Phys.* **10**, 227 (1936).

⁴ A. Dadieu and H. Kopper, *Nature* **136**, 235 (1935); *Akad. Anz.* **11**, 13 (1935). These are authors' abstracts of a paper presented before the Vienna Academy; the paper does not appear to have been published. The results are also quoted in *Tables Annuelles de Constantes et Données Numériques, No. 1. Deutérium et Composés de Deutérium*. G. Champétier. (Hermann et Cie., Paris 1937). A. Dadieu and W. Engler, *ibid.*, have reported Raman frequencies for H_2Se , D_2Se and HDS . The results for the latter appear to refer also to a mixture.

⁵ C. R. Bailey, J. W. Thompson and J. B. Hale, *J. Chem. Phys.* **4**, 625 (1936).

⁶ H. H. Nielsen and E. F. Barker, *Phys. Rev.* **37**, 727 (1931); H. H. Nielsen and A. D. Sprague, *ibid.* **37**, 1183 (1931); A. D. Sprague and H. H. Nielsen, *J. Chem. Phys.* **5**, 85 (1937).

⁷ P. C. Cross, *Phys. Rev.* **47**, 7 (1935); *J. Chem. Phys.* **5**, 370 (1937); F. D. Carvin, *ibid.* **5**, 159 (1937).

⁸ A. H. Nielsen and H. H. Nielsen, *J. Chem. Phys.* **5**, 277 (1937).

⁹ G. K. Teal and G. E. MacWood, *J. Chem. Phys.* **3**, 760 (1935).

¹⁰ G. Glockler and H. M. Davis, *J. Chem. Phys.* **2**, 881 (1934).

mately 3000 volts and the current through it was about 350 milliamperes. A Schmidt and Haensch Universal spectrograph was used with 2 Rutherford prisms. The dispersion in the region of the Raman lines was about 16.5Å per mm. A lens of 7 cm focal length was used to focus the scattered radiation on the slit and to insure that no light scattered by the walls should enter the spectrograph. With a slit width of 0.1 mm, satisfactory exposures of the gas could be obtained in about 100 hours, although the Raman line could be seen on the plates after an hour or two. Eastman spectroscopic plates, type I-J were used and standard Fe lines were used for a comparison spectrum. The plates were measured on a comparator giving readings reproducible to ± 0.001 mm.

For observations on the liquid and the solid, smaller Raman tubes were used which were supported in an unsilvered Dewar flask. The latter was surrounded with a helical arc of similar design to that described above. The Raman tubes were cooled with dry ice alcohol for the liquid and liquid air for the solid. Satisfactory exposures were obtained for the liquid and solid in about 4 hours.

D₂S was prepared from pure aluminum sulfide and 99.6 percent D₂O with subsequent distillation as in the preparation of H₂S.

3. EXPERIMENTAL RESULTS

The experimental results are shown in Table I. The frequencies given in Table I are average values as determined from two or more plates. In some cases, scattering was observed from both the 4358Å and 4047Å mercury line. Agreement between two or more plates in each case was better than ± 2 cm⁻¹. The Raman line in the gas and in the liquid is quite sharp. In the solid, the close doublet is rather diffuse and about half as intense as the single line. The latter is quite sharp. In the experiments on the solids, we also observed a Raman line of liquid oxygen, the frequency of which was in good agreement with the experiments of McLennan and McLeod.¹¹

¹¹ J. C. McLennan and J. C. McLeod, *Nature*, **123**, 160 (1929).

TABLE I. Observed Raman frequencies (cm⁻¹ in vacuum) of H₂S and D₂S (gas, liquid and solid).

	GAS	LIQUID	SOLID
H ₂ S	2610.8 — —	2573.6 — —	2520.8 2545.8 2553.7
D ₂ S	1891.6 — —	1866.3 — —	1832.5 1848.5 1853.4

4. DISCUSSION

The gas

The single frequency obtained in the gas is undoubtedly ν_1 . The fact that the other two frequencies do not appear is probably a matter of intensity. It is not possible at present to make any calculations on the relative intensities of Raman lines since very little is known regarding the change of polarizability with displacement. A qualitative explanation of the appearance of only one frequency may be given however. If the molecule were linear and hence belonged to the symmetry group, $D_{\infty h}$, ν_1 would be the only frequency active in the Raman effect. As the angle becomes less than 180°, this frequency will probably still remain more intense in the Raman effect than the other two frequencies which were inactive in the linear molecule. This fundamental vibration has not been observed in the infra-red for either H₂S or H₂O. Van Vleck and Cross¹² have offered the following explanation for the inactivity of ν_1 in the infra-red spectrum of H₂O. As the hydrogen atoms approach the oxygen atom, the molecules become more ionic in character and the accompanying migration of charge averages out in such a way that there is no appreciable change in the electric moment. The same argument applies to H₂S and also shows that in this mode of vibration there will be a maximum change in the polarizability and hence the line should appear in the Raman effect with considerable intensity. Although the resolving power of our spectrograph was sufficiently great to separate ν_1 from ν_3 and ν_2 , no trace of them could be seen on plates given exposures over 400 times as

¹² J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.*, **1**, 357 (1933).

long as that needed to photograph ν_1 . It can thus be said that ν_1 appears in the Raman effect with an intensity of more than 400 times that of ν_2 or ν_3 .

Although ν_1 does not appear in the infra-red as a fundamental, it is active in combination bands in both H_2O and H_2S . In the former case, both ν_1 and ν_2 as observed in the Raman effect¹³ have frequencies about 50 cm^{-1} greater than the corresponding calculated results obtained from infra-red spectra.¹⁴ A similar discrepancy appears to exist in D_2O also.¹⁵ No satisfactory explanation has yet been given for this shift but it has been assumed that the behavior is shown only by H_2O and D_2O . While there seems to be no reason why the Raman and infra-red frequencies should be different, we should like to point out that there is no definite experimental proof that H_2O is a unique case. In H_2O , H_2S and HCN ,¹⁶ the fundamental frequency has been observed only in the Raman effect. In other cases, such as NH_3 and SO_2 , the infra-red frequencies have been observed but complete rotational analyses have not been made and there is some doubt about the origin of the bands. In other cases, the Raman effect has only been obtained on the liquid. It is not possible to say whether there is a difference between the infra-red and Raman spectra in H_2S and D_2S from the present experimental data. Since ν_1 has not been observed in the infra-red it is necessary to calculate its frequency from the position of overtone and combination bands and this can only be done if the anharmonic factors in the vibrational energy are known. Nine observed frequencies are required to calculate these factors and there are not nine bands for H_2S known with certainty since the frequencies as determined by different investigators are not in complete agreement. Conclusions have been drawn concerning the presence or absence of a collected Q branch from the general appearance of the rotational structure or of the band envelope and while the appearance will probably be similar to the charts of Dennison,¹⁷

transitions involving J values greater than 4 and intensity changes may alter the appearance considerably. We therefore believe that calculations of anharmonic factors, angle and force constants of H_2S and of D_2S based on the present data are of doubtful value unless a complete rotational analysis can be made such as that of the band at 9911 cm^{-1} by Cross.⁷

The liquid

The shift of the Raman frequency accompanying a change of state from gas to liquid has been discussed by Buchheim¹⁸ and his considerations may be extended to the shift from liquid to solid. The changes in the spectrum due to association in solution have been discussed by Wolkenstein¹⁹ and these results may also be extended to liquids and solids. The experimentally observed shift, $\Delta\nu = \nu(\text{gas}) - \nu(\text{liquid})$ is 37.2 cm^{-1} or 1.4 percent for H_2S and 25.3 cm^{-1} or 1.3 percent for D_2S . The shift is towards lower frequencies which is observed in most polar compounds. However, in some cases, as for example, liquid ethane,²⁰ the shift is in the opposite direction for two of the vibrational frequencies. For nonpolar compounds, the shift is usually less than 0.5 percent.

The solid

Our experimental results²¹ on H_2S are in good agreement with earlier work of Sirkar and Gupta.⁸ They, however, have observed a frequency of 80 cm^{-1} both as a Stokes and anti-Stokes line. We have not attempted a measurement in this region since the experimental difficulties attending the recognition and correct assignment of a frequency so near the exciting line introduce considerable uncertainty²² concerning the meaning of such lines of low frequency.

The close doublet is probably to be associated with ν_1 , although one should expect it to be more intense than the other line. Taking the center of gravity of the doublet, the ratio of gas

¹⁸ W. Buchheim, *Physik. Zeits.* **36**, 694 (1935).

¹⁹ M. Wolkenstein, *Acta Physicochim.* **4**, 357 (1936).

²⁰ G. Glockler and M. M. Renfrew, *J. Chem. Phys.* **6**, 295 (1938).

²¹ In a preliminary communication, G. M. Murphy and J. E. Vance, *J. Chem. Phys.* **5**, 667 (1937), we reported only two lines in the solid. These results were obtained with somewhat smaller dispersion than that used here.

²² See, for example, I. R. Rao and P. Koteswaram, *Phil. Mag.* **25**, 90 (1938).

¹³ H. L. Johnston and M. K. Walker, *Phys. Rev.* **39**, 535 (1932); D. F. Bender, *ibid.* **47**, 252 (1935).

¹⁴ L. G. Bonner, *Phys. Rev.* **46**, 458 (1934).

¹⁵ G. W. King, *J. Chem. Phys.* **5**, 405 (1937).

¹⁶ K. N. Choi and E. F. Barker, *Phys. Rev.* **42**, 777 (1932).

¹⁷ D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

frequency to solid frequency is 0.98 for both H_2S and D_2S . A splitting of this type has been observed in other solids²³ and is usually attributed to the effect of electric fields in the crystal lattice.

The single remaining frequency cannot be associated with ν_2 since this deformation frequency is usually much lower than the other two. Taking the gas frequencies for H_2S and D_2S from the work of Nielsen^{6,8} as 2685 and 2000 cm^{-1} for ν_3 , $\Delta\nu = 164 \text{ cm}^{-1}$ or 6.1 percent for H_2S and 167.5 cm^{-1} or 8.4 percent for D_2S . The ratio of gas to solid frequency is 0.74, for both H_2S and D_2S .

From x-ray data, Vegard²⁴ has concluded that H_2S is linear in the solid state. This conclusion conflicts with the fact that ν_1 and ν_3 appear in the Raman spectrum of the solid. Further, this interpretation of the data has been disputed by Sirkar and Gupta²⁵ who concluded from their

own Raman data and the x-ray results of Vegard that the molecule is bent, the angle being about 108° . However, their arguments are based upon erroneous conclusions of Dadiou and Kohlrausch²⁶ who obtained an angle of 90° from the spectroscopic data. While the angle is not known definitely, it is almost certainly not 90° . Both Dadiou-Kohlrausch and Sirkar-Gupta have used a simplified valence-force potential energy curve for the molecule. As shown above and in many other places, this sort of potential energy function may not be used except as a rough approximation for actual molecules. Moreover, the angle is very sensitive to slight changes in the frequency and for the latter, the actual mechanical frequency corrected for anharmonic terms must be used and not the observed frequency. All questions regarding angle, force constants and isotope effect can only be settled with more and better experimental data.

²³ A. A. Sidorova, *Acta Physicochim.* 7, 193 (1937).

²⁴ L. Vegard, *Nature* 126, 916 (1930).

²⁵ S. C. Sirkar and J. Gupta, *Ind. J. Phys.* 11, 119 (1937).

²⁶ A. Dadiou and K. W. F. Kohlrausch, *Physik. Zeits.* 38, 165 (1932).

Fractionation of the Lithium and Potassium Isotopes by Chemical Exchange with Zeolites*

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A study has been made of the fractionation of the lithium isotopes by electrolysis and of the lithium, potassium, and nitrogen isotopes by chemical exchange with zeolites. The fractionation factor obtained by a "batch" electrolysis of lithium chloride solution was 1.039. The normal abundance ratio of the lithium and potassium isotopes was determined and found to be 11.71 ± 0.14 for $\text{Li}^7 : \text{Li}^6$ and 14.10 ± 0.09 for $\text{K}^{39} : \text{K}^{41}$. The fractionation factor for the lithium isotopes in exchange with sodium zeolite was found to be 1.022. A partial separation of the lithium, potassium and nitrogen isotopes has been affected using long columns filled with zeolites. Both an increase and a decrease of about 25 percent from the normal abundance ratio has been obtained for the lithium isotopes and a change of about 10 percent for the potassium and nitrogen isotopes. Some of the factors involved in the mechanism of the process are discussed.

INTRODUCTION

RECOURSE may be had to a number of different methods in attempts to separate the isotopes of an element. One may choose a

method more or less directly dependent on physical properties related to the masses of the isotopes such as diffusion, distillation, or deflection in an electric and magnetic field using large capacity mass spectrographs. Electrolysis or reaction velocity may also lead to some fraction

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