The Proton Magnetic Resonance Spectrum of Hydrogen Sulfide and HDS

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The proton magnetic resonance spectrum of HDS has not yet been observed. Our interest is drawn to the proton-deuteron coupling constant of HDS and its isotope shift with reference to hydrogen sulfide. The equilibrium of the following exchange reaction, another point of interest, has been studied by many authors:[1]

$$H_2O + HDS \rightleftarrows H_2S + HDO$$

This equilibrium suggests one possibility of observing the multiplet spectrum of HDS if the exchange rate is not too rapid. We have estimated that the gas phase is suitable for observing the spectrum of HDS because we can easily expect a slower exchange rate in gas than in liquid.

About equal volumes of D_2O and liquid hydrogen sulfide were therefore introduced into a 5 mm. glass tube in a vacuum, using a small amount of tetramethylsilane as an internal reference. Measurements for a gaseous mixture of hydrogen sulfide and HDS were carried out at about 24°C in contact with a liquid mixture of hydrogen sulfide and D_2O in a sealed glass tube; we could thus estimate the total pressure of hydrogen sulfide and HDS to be about 20 atmospheres. This mixture of hydrogen sulfide and D_2O gave the signal of hydrogen sulfide 0.25 p. p. m. downfield from that of tetramethylsilane in the gas phase. The triplet of HDS was centered 0.028 ± 0.003 p. p. m. upfield from the hydrogen sulfide resonance, as is shown in Fig. 1, in which one of the triplet lines of HDS seems to overlap with the signal of hydrogen sulfide. The observed proton-deuteron spin-spin coupling constant is 2.1 ± 0.2 c. p. s. The proton-proton spin-spin coupling constant for hydrogen sulfide can be readily obtained by multiplying the experimentally-determined J_{HD} by the ratio of the gyromagnetic ratios, $\gamma_H/\gamma_D = 6.51$; we thus get $J_{HH} = 13.7 \pm 1.3$ c. p. s. It can be estimated that the rate of the exchange reaction between hydrogen sulfide and HDS in the gas phase, with the saturated vapor pressure at 24°C, is slower than $0.5\ \mathrm{sec}^{-1}$, a value which is derived from the observed proton-deuteron coupling constant. Without D_2O, the signal of hydrogen sulfide is observed 0.89 and 0.25 p. p. m. downfield from tetramethylsilane in the liquid and gas phases respectively. The difference of 0.64 p. p. m. between the chemical shifts of the liquid and the gas of hydrogen sulfide may be due to the weak hydrogen-bonded association of hydrogen sulfide in a liquid, as has previously been discussed by Schneider et al.[2]

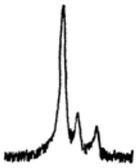

Fig. 1. The proton magnetic resonance spectrum of a gaseous mixture of H_2S and HDS at 24°C in contact with a liquid mixture of H_2S and D_2O in a sealed glass tube. The applied magnetic field increases from left to right.

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[1] For example, J. Garaud and R. Amanrich, *J. Chim. Phys.*, **56**, 532 (1959); R. Haul, H. Behnke and H. Dietrich, *Angew. Chem.*, **71**, 64 (1959).

[2] W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).