The Proton Magnetic Resonance Spectra of Hydrogen Selenide and HDSe

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The proton magnetic resonance spectrum of HDSe has not yet been observed. Our interest has been drawn to comparing the proton-deuteron coupling constant of HDSe with such other hydrides as HDS(1). After we had reported the multiplet structure of HDS in gas in a previous paper,(1) we observed the multiplet structures of both HDS and HDSe in liquid. Aluminum selenide(2) was placed in a bottle connected with a vacuum line and was treated with D_2O in a vacuum. In this case the impurity, H_2O, in D_2O was used as a source of the proton for HDSe. The D_2Se evolved, containing HDSe to a minor extent, was then introduced into a 5-mm. glass tube in a vacuum, with a small amount of TMS added as an internal reference. This liquid mixture of HDSe and D_2Se gave only a triplet signal of HDSe 0.85_5 p. p. m. upfield from that of TMS, as is shown in Fig. 1. The observed proton-deuteron coupling constant is 2.04±0.05 c. p. s. The proton-proton coupling constant for hydrogen selenide thus obtained is 13.28±0.33 c.p.s.; this magnitude is almost the same as that of HDS.(1)

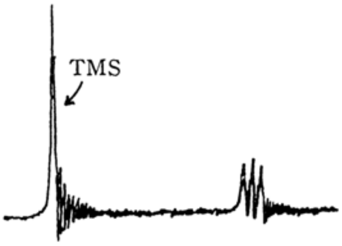

Fig. 1. The proton magnetic resonance spectrum of a liquid mixture of D_2Se and HDSe at 24°C in a sealed glass tube. The applied magnetic field increases from left to right.

Many factors may be considered to contribute to the coupling constants between two protons. In a way, it can be expressed as follows:

$$J_{ij}=A(r,\ \theta)\ \rho(i)\ \rho(j)$$

where $A(r, \theta)$ will be a function defined by the bond length, r, and the bond angle, θ, in a molecule, and where $\rho(i)$ and $\rho(j)$ express the electron densities around the protons in question, i and j respectively. In the case of the simple hydrides, H_nX, $\rho(H)$ will decrease with an increase in the electronegativity of X. Now we can compare the coupling constants of some simple hydrides, H_2O,(3) NH_3,(4) CH_4,(5) H_2S(1) and H_2Se. The order of the magnitudes of their coupling constants is approximately parallel to that of the decreasing electronegativities of the center atoms.

The isotope shift of HDSe with reference to H_2Se was also observed in the spectrum of the sample prepared by using a mixture of H_2O and D_2O as a reactant for aluminum selenide. The triplet of HDSe was centered 0.036±0.003 p. p. m. upfield from the hydrogen selenide resonance, which overlapped with one of the triplet lines of HDSe. Two satellites were observed on both sides of the center band; they may be due to the isotope of selenium-77, the natural abundance of which is 7.5%. The observed proton - selenium-77 coupling constant for hydrogen selenide is 60.5±0.5 c. p. s. As far as we know, this is the first case of a coupling constant observed in the direct H-Se^{77} bond. The signal of hydrogen selenide was also observed in the gaseous phase 1.78 p. p. m. upfield from TMS in contact with the liquid phase at 24°C,

The equilibrium constant of the following exchange reaction:

$$H_2Se + D_2Se \rightleftarrows 2HDSe$$

was estimated to be approximately 0.8 in liquid at 24°C by the use of the intensity measurement of the absorption signal of H_2Se and HDSe, and by the use of some approximations concerned with the initial concentration of hydrogen and deuterium. The rate of the above exchange reaction in liquid can be estimated to be slower than 0.5 sec^{-1} at 24°C. Details will be given later elsewhere.

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