*Proton Resonance in Sulfamic Acid**

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Structural investigations on sulfamic acid by X-ray diffraction[1] and infrared absorption[2] measurements have shown the results to suggest the zwitter-ion form of $NH_3^+SO_3^-$ in crystal. Since nuclear magnetic resonance method is very straight-forward to distinguish two-proton system[3] from three-proton one[4], we have applied this method to the crystal of sulfamic acid. Evidences of zwitter-ion form will be shown here as well as the informations on the intramolecular rotation as the results of the measurements of line shape and widths.

Experimental.—The sample studied is crystalline powder with a purity of 99.95%. The proton resonance is observed at about 20 megacycles. The temperature range of the experiment is between −180°C and +60°C. The apparatus used is of the autodyne-detector type which has been described elsewhere[5]. Though efforts to make measurements below the temperature of liquid nitrogen were made, reliable record was not obtained as the sample was saturated.

The resonance curve has a shoulder over all the temperature range of the experiment and, furthermore, the second shoulder appears below −170°C outside of the first shoulder. Fig. 1 presents the half of the derivative of the resonance curves at several temperature ranges. With decreasing temperature, the line shape becomes of three-peaked form, the evidence of three-proton system[4]. This suggests that the zwitter-ion form can be taken plausible as the molecular configuration at this temperature range.

Fig. 2 shows the temperature dependence of the second moment of the resonance absorption curve. A constant value of about 6±0.5 gauss[2] is taken throughout the temperature range of the experiment higher than −170°C. It begins to increase in the range below −170°C, taking a value of about 12 gauss[2] at −180°C. This change in the second moments will suggest that the molecule begins to freeze at this temperature range.

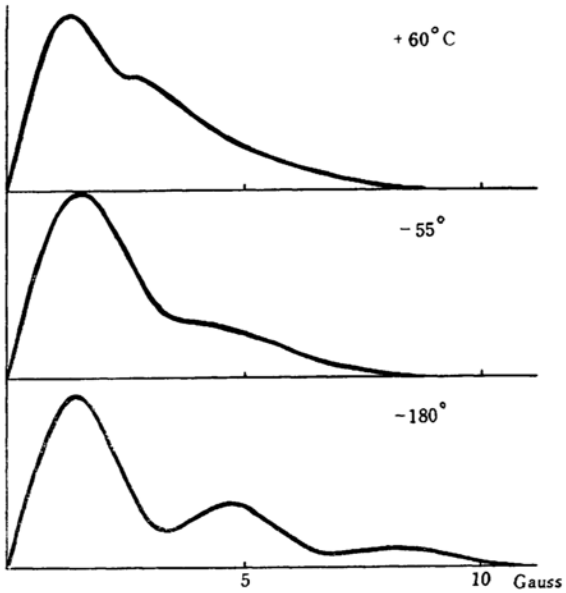

Fig. 1. Derivative of the proton resonance absorption curves for sulfamic acid at various temperatures.

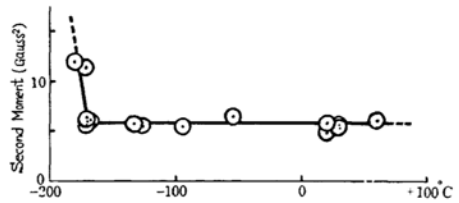

Fig. 2. Temperature dependence of the second moment.

Discussion of the Results. — Second moments are calculated for various models of the molecular structure: a) 30.7 gauss[2] for the model suggested by X-ray diffraction[1] where three protons in NH_3 group are taken equivalent, and b) 15~20 gauss[2] for the model of NH_2SO_3H having the same structure as a) with respect to the skeleton of heavy atoms. When NH_3 group in the model a) rotates freely about N-S bond axis, the second moment is expected to be reduced to 7.5 gauss[2].

According to the results shown above, we assume that the molecule takes zwitter-ion structure in crystal and reorientates about N-S bond axis in the temperature range higher than −170°C. Sano[6] reported a value of the second moment at room temperature almost the same as that obtained by the present authors. He

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explained this value by taking a model where molecules were rigid with the zwitter-ion form and N-H bonds in NH_3 groups were unusually elongated. This seems unplausible, however, since such an unreasonably deformed structure will show temperature dependence in the second moment values and, moreover, such a model can not explain the increasing tendency at around −180°C.

Another comment will be added here with respect to the zwitter-ion structure: asymmetrical derivative curve was obtained when the sample was moist. We assume that this curve is superposition of a narrow line and a broad one being different in resonance center. Since the intensity of the central narrow line is humidity dependent, it is attributed to the water molecules adsorbed by the sample. The asymmetrical curve was decomposed to show that the resonance center for the adsorbed water was shifted to the field higher than that for the broad line by 10^{-5}; in another words, proton in sulfamic acid is electronically less shielded than in water molecules. The asymmetrical figure of the derivative curve is not due to the saturation effect since the same result has been obtained when the polarity of the bias field is reversed.

A similar result of large positive shift has been reported with formamide[7], which is also considered to form zwitter-ion, and, therefore, the finding presented here may be taken as the characteristic nature of protons forming zwitter-ions.

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