

Change in Electronic Structure of the ICl_2^- Anion in NH_4ICl_2 Crystals due to an Excitation of Reorientational Motion of the Ammonium Ion

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Two ^{35}Cl NQR frequencies, $\nu_a = 9.148$ and $\nu_b = 28.286$ MHz, were observed at 77.3 K in NH_4ICl_2 . ν_a and ν_b showed a strong temperature dependence with positive and negative temperature coefficient, respectively. This anomalous temperature dependence is explained by a temperature dependence of the mole fraction of the hydrogen-bonded ICl_2^- ion. The energy difference, ΔE_{anion} , of the anion between the hydrogen-bonded and the non-bonded states was derived as $\Delta E_{\text{anion}} \approx 700$ K (5.8 kJ mol^{-1}) and as $\Delta E_{\text{anion}} \approx 640$ K (5.3 kJ mol^{-1}) for NH_4ICl_2 and ND_4ICl_2 , respectively. The temperature dependence of the spin-lattice relaxation time T_1 showed a clear minimum in the $\ln T_1$ vs. $10^3 \text{ K}/T$ plots, which can be interpreted as due to EFG modulation by the reorientational motion of the ammonium ion. The reorientation of the ammonium ion among stable and meta-stable orientations is expected to be responsible to the temperature variation of electronic structure of the ICl_2^- anion.

Key words: Hydrogen Bond; Electronic Structure; Ammonium Ion; Reorientaion; NQR.