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Molecular Motions in Ice

DISSERTATION

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ABSTRACT

This is a comprehensive analysis of a large amount of experimental data reflecting the internal motions of molecules in ice (reorientations and migration). Additional experiments are contributed in the fields of diffusion and n. m. r. relaxation of pure and HF-doped ice.

The comprehensive analysis suggests new concepts for the relative importance of lattice defects. Namely, vacant hydrogen bonds and molecular vacancies invested with one extra proton are complementary defects regarded as primordial as far as the random molecular motions are concerned. This leads to a new understanding of the low-temperature effects: molecular vacancies invested with two extra protons are quenched, in numbers exceeding normal equilibrium concentrations, while the corresponding mobile vacant hydrogen bonds keep contributing to the internal motions. Some ordering of the lattice according to the weakest electrostatic repulsions is thus allowed at low temperatures.

In addition to these basic perspectives, the detailed analysis contributes in the fields of dielectric relaxation, molecular dipole moment, molecular inter-proton distance, and low-frequency vibration spectrum. The dielectric analysis revives Debye's original definition of the molecular time-of-stay as related to the macroscopic bulk relaxation time. (A ratio 1/20 is derived). The molecular dipole moment in the solid phase is analysed to 2.25 Debye units from static dielectric data. The molecular inter-proton distance is analysed to 1.635 Å from n. m. r. free-induction decay shape measurements. The heat-capacity data show clearly the effect of low-frequency vibrations near 65 cm^{-1}, and once the harmonic contributions are subtracted, a discrepancy remains which can be represented by an activated rate process of 0.08 eV energy.

Finally, a set of equations is proposed which connects the observed apparent activation energies of the relaxation and diffusion processes with the activation energies for formation and migration of invested vacancies (V') and vacant bonds (L). The solution is: $E_{form(V')} = 0.47$ eV, $E_{migr(V')} = 0.16$ eV, $E_{migr(L)} = 0.08$ eV.