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NMR Relaxometry: The Canonical Case Glycerol

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Abstract

We present a quantitative description of the proton spin-lattice relaxation rate R1(T,ω) of glycerol including temperatures from 191 to 360 K and a frequency range 10 kHz < ω/2π < 20 MHz covered by the field-cycling technique. The analysis encompasses the data compiled by Noack and co-workers in 1971, so far, the most complete data set (10 kHz > ω/2π < 117 MHz). Applying frequency-temperature superposition, master curves are constructed extending over 15 decades in frequency/time. They are described by contributions reflecting translational and rotational dynamics mediated by inter- and intramolecular relaxation pathways. The rotational part of the spectral density/susceptibility shows high similarity with those reported by dielectric spectroscopy or photon correlation spectroscopy (PCS). In addition to a Cole-Davidson-like peak, a high-frequency "excess wing" has to be accounted for. Quantitative agreement with the PCS susceptibility is found which probes the same order of the rotational correlation function. The translational contribution is reproduced by applying the force-free hard sphere model, describing diffusion of dipolarly coupled spin systems. Rotational and translational time constants are compared to those from other techniques. Our approach is paradigmatic for the analysis of spin relaxation in glass-forming liquids. It also solves long-standing deficiencies regarding the analyses of deuteron relaxation. Moreover, the case of glycerol is special as its large separation of translation and rotation dynamics, probably because of its hydrogen bond network, is not found in nonassociated liquids.

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