

ASYMMETRIC POTENTIAL BARRIER DISTRIBUTION OF MOBILE GUEST MOLECULES IN ORGANIC GLASSES: ^2H NMR INVESTIGATIONS

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Structural properties of organic glasses have been studied via ^2H NMR by doping deuterated guest molecules as benzene or hexamethylbenzene (HMB) into the protonated host matrix. Due to the high degree of rotational mobility of the guests the ^2H spin lattice relaxation becomes sufficiently short to allow detailed NMR investigations¹⁾. In addition, the rotational correlation time τ and its activation energy E are dependent on the local environment of the individual guest molecule. Because of the topological disorder in the glasses, the ensemble of guest molecules experiences a distribution of activation energies $g(E)$ for the molecular rotation. As a direct consequence of a thermally activated process, a temperature independent distribution $g(E)$ leads to a temperature dependent distribution of correlation times $G(\ln\tau)$, which broadens proportional to $1/T$ when the temperature is lowered.

A relatively simple method to obtain $g(E)$ is the analysis of the ^2H NMR line shape as a function of temperature²⁾. The line shape is given by a superposition of only two subspectra corresponding to molecules in the

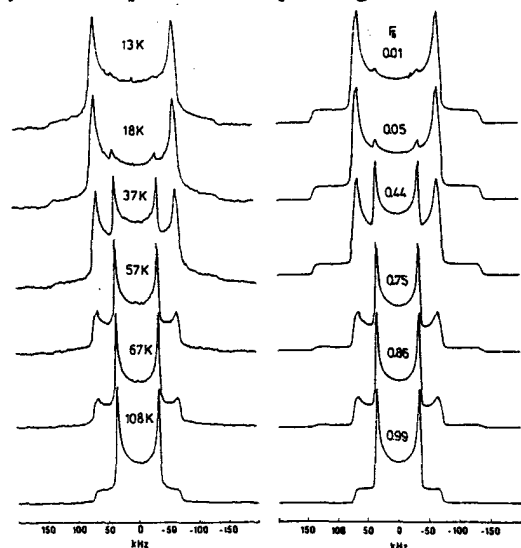


Fig. 1: ^2H NMR lineshape of benzene in LCPS (see text) at various temperatures.

limit of fast and of slow rotation, respectively. The spectral intensity from molecules with intermediate τ is negligible, because of the great width of $G(\ln\tau)$. The intensity ratio of the sub-spectra has a characteristic temperature dependence and is closely related to $g(E)$. This is illustrated in Fig. 1 for the system 10.0 % benzene in the liquid crystal polysiloxane with fluorene as mesogenic side group (LCPS). Experimental spectra obtained at various temperatures are compared with numerical calculations. For each temperature, the fraction $F_0(T)$ of molecules in the limit of fast rotation can easily be determined from the lineshape. The derivative $d/dT(F_0(T))$ directly yields $g(E)$. In Fig. 2, $g(E)$ for benzene (straight line) in LCPS is compared with results obtained for other amorphous systems [benzene in phthalic acid di-n-butyl ester (PDB), HMB (dotted line) in polystyrene (PS) and HMB in PDB]. An asymmetry of $g(E)$ is found, with a maximum on the low energy side. The degree of asymmetry and the shape of $g(E)$ depends on the system. This result is in good agreement with spin lattice relaxation measurements³⁾.

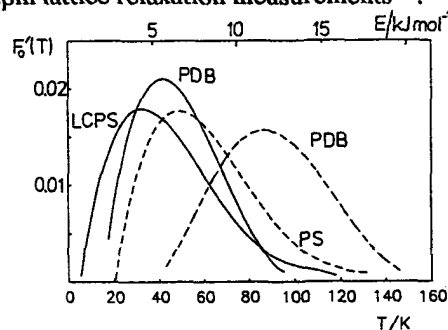


Fig. 2: $d/dT(F_0(T))$ for benzene in LCPS, comparison with other amorphous systems (see text).

- 1) Jansen-Glaw, B., Rössler, E., Taupitz, M. and Vieth, H.-M., *J. Chem. Phys.* **90** (1989)
- 2) Rössler, E., Taupitz, M., Börner, K., Schulz, M., Vieth, H.-M., submitted to *J. Chem. Phys.*
- 3) Rössler, E., Taupitz, M. and Vieth, H.-M., submitted to *J. Phys. Chem.*