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SOLID ECHOES AND MOLECULAR REORIENTATION OVER UNEQUAL POTENTIAL BARRIERS

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Introduction

The solid spin-echo technique is based on the application of two pulses ($90^0{}_Y$ and $90^0{}_X$) separated by a time interval τ [1]. Anisotropic random thermal reorientation of molecular groupings can have significant effects on the solid echo amplitudes and for the cases of molecular reorientations between the equivalent potential wells this problem was considered in [2]. At the last time the complex molecular motions between two or more unequal potential barriers have been of interest to reseaches in the field of molecular dynamics of solids [3,4].
In this report we consider the effect of the molecular jumps between nonequivalent sites on the solid echo amplitudes. Our main goal is to investigate how the results obtained in [2] are changed when molecular group reorients in asymmetrical potential wells.

Results and discussion

The solid echo amplitude in solids with molecular mobility is defined by the expression [2]

$$V(2\tau)=\exp\left[-\tfrac{1}{2}\left(\int_0^{\tau}dt'\int_0^{\tau}h(t'-t'')dt''-2\int_0^{\tau}dt'\int_{\tau}^{2\tau}h(t'-t'')dt''+\int_{\tau}^{2\tau}dt'\int_{\tau}^{2\tau}h(t'-t'')dt''\right)\right], \quad (1)$$

where

$$h(t'-t'')=\frac{Tr\left(\langle[H_d(t'),[H_d(t''),I_X]]\rangle I_X\right)}{Tr\left(I_X^2\right)} \quad (2)$$

is the correlation function for stochastic dipolar Hamiltonian $H_d(t)$.
In the case of unequal barrier wells, the correlation function $h(t'-t'')$ may be written as [3,4]

$$h(t'-t'')=K_0+\sum_{i=1}^{n}K_i\exp\left(-\frac{|t'-t''|}{\tau_{ci}}\right), \quad (3)$$

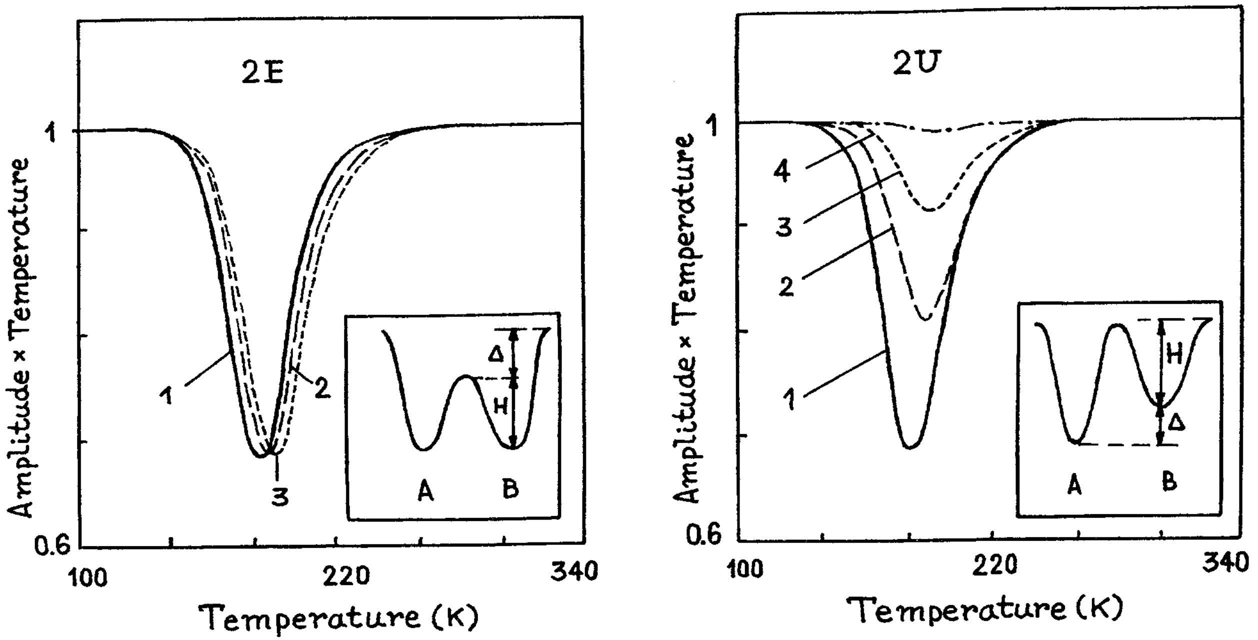

Fig.1. A normalised plot of Curie law corrected solid echo amplitude (τ = 5μs) versus temperature for the different double-minimum potentials and various values of Δ : 1 - Δ=0 kJ/mol; 2 - Δ=2.5 kJ/mol; 3 - Δ=4.2 kJ/mol; 4 - Δ=8.4 kJ/mol. H=29 kJ/mol, $\Delta M_2\tau^2 = 1$.

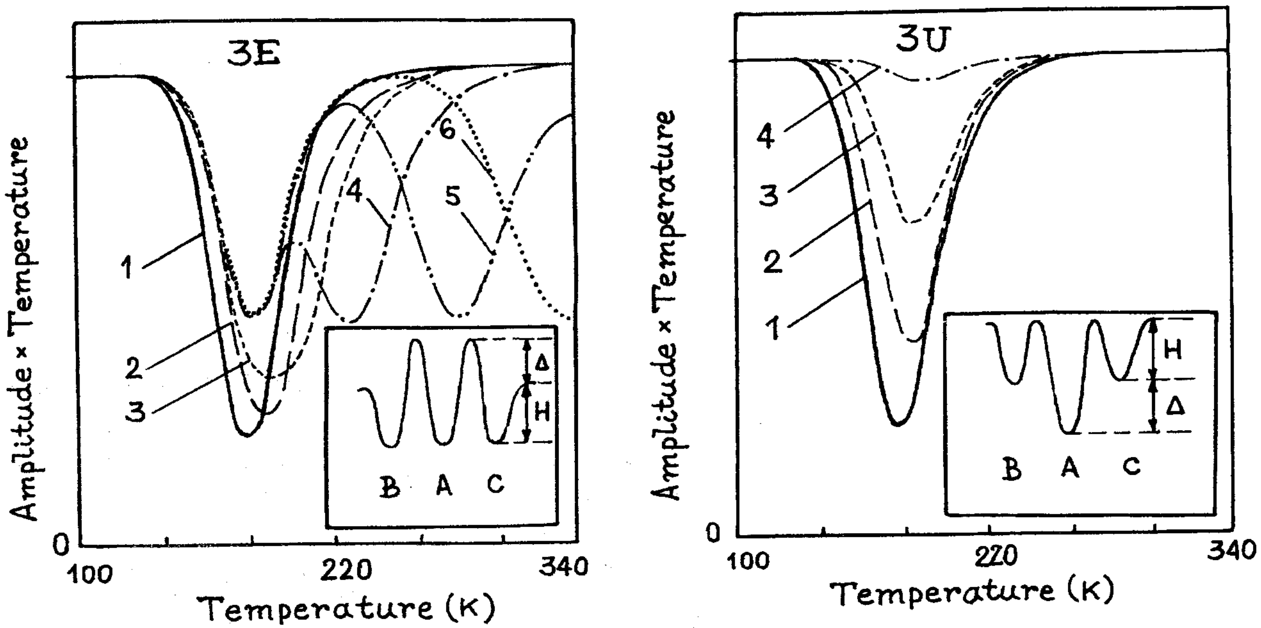

Fig.2. A normalised plot of Curie law corrected solid echo amplitude (τ = 5μs) versus temperature for the different triple-minimum potentials and various values of Δ :1- Δ=0 kJ/mol;2- Δ=2.5 kJ/mol;3- Δ=4.2 kJ/mol;4- Δ=8.4 kJ/mol;5- Δ=16.7 kJ/mol;6- Δ= 25 kJ/mol.H=29 kJ/mol,$\Delta M_2\tau^2$= 1.

where K_i $(i=0,1,...n)$ are the structural parameters which are depended on the shape of the potential well and τ_{ci} are the correlation times, characterizing n modes of reorientation [3,4]. Using eq.(3) we obtain the following expression for the amplitude of the solid echo signal

$$V(2\tau) = \exp\left[-\sum_{i=1}^{n} K_i \tau_{ci}^2 \left(1 + 2\frac{\tau}{\tau_{ci}} - (2 - e^{-\tau/\tau_{ci}})^2\right)\right]. \quad (4)$$

The temperature dependences of the solid echoes amplitude for the different potentials considered in [4] are shown in Fig.1 and Fig.2. So as in the case of the temperature dependence of the NMR second moment [4], the temperature dependence of the solid echo amplitude for 2E potential well is almost independent on Δ. The temperature dependence of the solid echo amplitude for the 2U and 3U potential wells shows a strong dependence on Δ. The interesting dependence of the solid echo amplitude on temperature is observed for the 3E potential well. For this potential well the two resolved minima in the temperature dependence of the solid echo amplitude may be observed. The temperature at which the low-temperature minimum is observed depends on the energy H, while the temperature at which the high-temperature minimum takes place is determined by the energy H+Δ.

The obtained results demonstrate clearly that the study of the temperature dependence of the solid echo amplitude can yield valuable information about the shape of potential well in solids.

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