

TIME DIFFERENTIAL PERTURBED ANGULAR CORRELATION STUDY OF VEGETABLE OILS

C. Oprea, A. Velichkov, I.A. Oprea, D.V. Filosofov, P. J. Szalanski

Joint Institute for Nuclear Research (JINR), Dubna 141980, Russian Federation

Abstract

We present a series of measurements of the time- and reactant-dependent interactions in the angular correlation of ^{111}In in vegetable oils. In our studies we employ Time Differential Perturbed Angular Correlation (TDPAC) of the $^{111}\text{In}/^{111}\text{Cd}$ γ - γ cascade from ^{111}In probe nucleus to investigate aspects related to physicochemical structure of vegetable oil (as for example, *Oleum embryonum tritici*). The above experiments are carried out using a home-made TDPAC spectrometer which consisting of a four detector fast-slow coincidence system using *NaI(Tl)* scintillators with a time resolution of 2.5 ns.

Keywords: TDPAC, ^{111}In , vegetable oil, Electric Field Gradient, physicochemical organization

Introduction

After the first paper of D. R. Hamilton (1940) on the theory of the directional correlation of γ - γ cascade, it took seven years before Brady and Deutsch (1947) realized the experimental adequate conditions to measure such a correlation. Then the perturbed angular correlation started as a nuclear physics technique used in measuring spins and parities.

Following the technological development of the experimental PAC installations, the perturbed angular correlation spectroscopy (PAC) has been widespread applied in a large variety of condense matter studies from the atomic scale to elementary defect itself and nowadays one uses the vacancy clusters as the object of investigation. The most common application of PAC is the time differential perturbed angular correlation (TDPAC) which measures the angular correlation between pairs of gamma rays emitted by radioactive nuclei, as fraction of the time the nucleus spends in the intermediate state.

During the present researches, the ^{111}In TDPAC measurements were conducted to explore the physicochemical structure and TDPAC dynamics of vegetable oil (as for example, *Oleum embryonum tritici* that was previously tested biologically). ^{111}In is frequently used in biomedical and pharmaceutical researches and it is readily available.

Theoretical background of TDPAC

This section reflects the nuclear physical origins of the quadrupole interaction and describes the magnetic interaction in hyperfine interactions (HFIs) that can be used in condense matter applications. The interaction of the magnetic moment and quadrupole moment of the probe nucleus with the extra nuclear magnetic field and electric field gradients respectively (HFIs) result in the perturbation of the angular correlation of γ - rays.

The basis of perturbed angular correlation consists in producing a radioactive nuclei (in excited state with nuclear spin $|I_i, m_i\rangle$) that decays over a $\gamma\gamma$ -cascade by emission of γ to the intermediate state I , followed by decay to the ground state $|I_f, m_f\rangle$ of the daughter nucleus I_f .

by emission of a second γ -quant γ_2 . The angular correlation function $W(\gamma_1, \gamma_2, t)$ is a measure of the probability that γ_1 is detected in direction $\rightarrow k_1$, and γ_2 is detected in direction $\rightarrow k_2$. Utilizing the density matrix formalism [4,5] it can be written as

$$W(\gamma_1, \gamma_2, t) = \sum_{mm'} \langle m | \rho(\gamma_2, 0) | m' \rangle \langle m' | \rho(\gamma_1, 0) | m \rangle, \quad (1)$$

where m, m' define the inhomogeneous population of the m -states of the intermediate state; the matrix elements $\langle m | \rho(\gamma_i, 0) | m \rangle$ are the probabilities of finding the system in an eigenstate m immediately after the i_{th} transition. Performing the mm' -sum the relative probability $W(\theta)d\Omega$ of detecting γ_2 in the solid angle $d\Omega$ with the angle θ in respect to γ_1 is obtained as Legendre polynomials

$$W(\theta) = \sum_{k=even}^{k_{max}} A_{kk} P_k(\cos\theta) \quad (2)$$

where $A_{kk} \equiv A_k(\gamma_1)A_k(\gamma_2)$ are the angular correlation coefficients and are depending of the angular momenta of the state and the multipolarities of the transitions; the sum is only over even k because the odd A_{kk} disappear as a consequence of parity conservation and $0 < k < \min(2I_s, l_i + l'_i)$ (Note: the polarization of the γ photons is not measured).

The summation is finite due to conservation of angular momentum. For the frequently used $I = 5/2$ the summation index limit is $k_{max} = 4$, thus

$$W(\theta) = 1 + A_{22}P_2(\cos\theta) + A_{44}P_4(\cos\theta) \quad (3)$$

Through the perturbation of the probe nucleus during the finite lifetime of the intermediate state from the hyperfine interaction of magnetic or electric extra field gradients of measured sample material the angular correlation function depends only on the angle between γ detections, θ , and time between detections, t as

$$W(\theta, t) = \sum_{\substack{k=0 \\ even}}^{k_{max}} A_{kk} G_{kk}(t) P_k(\cos\theta), \quad (4)$$

where $G_{kk}(t)$ is the perturbation factor containing the information about the interaction.

The interaction can occur between the nuclear magnetic dipole moment μ of the intermediate state I_s and the extranuclear magnetic field B or between the nuclear electric quadrupole moment Q and the extranuclear electric field gradient $V = \nabla^2 \Phi$.

Magnetic hyperfine interactions

The magnetic hyperfine interaction is measured by the Larmor-frequency

$$\omega_L = -\left| \frac{g\mu_N B}{\hbar} \right| \quad (5)$$

where g is the dimensionless g -factor (Land $é$ -factor) of the intermediate state; μ_N is the nuclear magneton ($\mu_N = 5.05 \cdot 10^{-27} \text{ J/T}$); B is the magnitude of the magnetic field at the probe, (*i.e.* the hyperfine magnetic field).

The magnetic hyperfine interaction splits the intermediate state into $|2I+1|$ equidistant sublevels with ΔE

$$\Delta E = \hbar\omega_L = -g\mu_N B \quad (6)$$

Electric hyperfine interactions

The electric hyperfine interaction between the charge distribution of the nucleus and the extranuclear static electric field occurs only for electric field gradients (EFG) that are strong enough to be measured.

The energy of the sublevels for axially symmetric EFGs is

$$E_Q = \left| \frac{eQV_{zz}}{4I(2I-1)} \right| \cdot (3m^2 - I(I+1)) \quad (7)$$

where Q is the quadrupole moment; V_{zz} is the the principal component of EFG with largest magnitude; e is the fundamental unit of charge; I is the total spin of the intermediate nuclear state.

The energy difference between two sublevels m and m' is given by

$$\Delta E_Q = \hbar\omega_0 \cdot 3|m^2 - m'^2| \quad (8)$$

where ω_0 is the quadrupole frequency.

It can be deduced from (8) that the splitting of the sublevels of electric quadrupole hyperfine interaction is non-equidistant since it depends on the angular momentum I of the sublevel. Practically is used the quadrupole coupling frequency ν_Q which measures the strength of the electric hyperfine interaction in time and is independent from the nuclear spin I

$$\nu_Q = \left| \frac{eQV_{zz}}{h} \right| \quad (9)$$

Experimental methodology

TDPAC sources

The PAC probe nucleus should to acts as a foreign agent that scopes out its environment and emits/decays by correlated γ - ray cascades. TDPAC method measures the angular

correlation as fraction of the time the nucleus spends in the intermediate state. For this the intermediate state needs to meet the following expectations:

- it must have a reasonably long lifetime so that the probe has time to “feel” the extra-nuclear fields and to interact with them;
- the γ - ray energies should to be sufficiently different so that γ_1 and γ_2 can be distinguished;
- the nuclear moments of the intermediate state, as well as the anisotropy of the angular correlation between γ - rays have to be large enough to allow the measurement of the perturbation function;
- the parent nucleus must be available, and it must have a long enough lifetime to be practical to work with.

The sensitive $^{111}\text{In}/^{111}\text{Cd}$ -PAC probe nucleus has been diffused into the oil material under study for experimental EFGs determination. ^{111}Cd is the decay product of electron-capture-decay of ^{111}In with a half-life of 2.83 days. The properties of the PAC pair parent-daughter probe nuclei relevant for TDPAC measurements are presented in Table 1.

Table 1: Relevant properties of PAC probe nuclei

Parent to probe decay	A_2	$T_{1/2}$	γ_1 [keV]	γ_2 [keV]	I	$t_{1/2}$ [ns]	g-factor	Quadrupole Moment
$^{111}\text{In} \rightarrow ^{111}\text{Cd}$	-0.18	2.83 d	171	245	5/2	85	-0.306	+0.83(13)

Note. $T_{1/2}$ is the half-life of parent nucleus; I and $t_{1/2}$ are nuclear spin and half-life, respectively, of the intermediate level in the γ_1 - γ_2 cascade; g-factors and quadrupole moments are of the intermediate state.

Although all the experiments were based on the measurement of the electric field gradient (EFG) at the probe sites, they have been performed with different biochemical reactivants concerning vegetable oil properties. In order to study the physicochemical structure of vegetable oil, the biochemical reactivants as ether, heptanol [$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$], and Dekan [$\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$], were employed in experimental measurements. They were used in different chemical complex solutions, as ^{111}In in ether + 14% HDPD, ^{111}In in 500ml $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$ + 13% HDPD, and ^{111}In in 21% HDPD + $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$.

TDPAC spectrometry

The above experiments are carried out using a home-made TDPAC spectrometer (Brudanin, NIMA 2005), which consisting of a 4-detector fast-slow coincidence system using $\text{NaI}(\text{Tl})$ scintillators (40 x 40 mm) arranged in the plane at 90° intervals. The fast timing signal is fed into the time-to-amplitude converter which allows to measuring the time the nucleus spent in the intermediate state of the cascade. The delayed coincidence counts $W(\theta, t)$ within a resolution time of 2.5 ns between the 90° and 180° detector pairs were recorded and stored as histograms.

Starting from the equation 2 the number of coincidences measured by the apparatus can be calculated as

$$N(\theta, t) = N_0 e^{-\lambda t} \cdot W(\theta) = N_0 e^{-\lambda t} \cdot (1 + A_{22} P_2(\cos\theta) + A_{44} P_4(\cos\theta)) \quad (10)$$

where N_0 is the total counting rate; λ the decay constant; the rest term describes the anisotropic emission probability; usually the coefficient A_{44} is much smaller than A_{22} ($A_{44} \ll A_{22}$). Then $A_2G_2(t)$ is defined as the ratio

$$A_2G_2(t) = 2 \frac{|N(180^\circ, t) - N(90^\circ, t)|}{|N(180^\circ, t) + 2N(90^\circ, t)|}, \quad (11)$$

The least-squares fitting from the angular correlation perturbation models for (*EFG*) parameter determination was used:

$$\begin{aligned} A_2G_2(t) &= a_0 + a_1 \exp(-\lambda_2 t) \text{ (dynamic)} \\ A_2G_2(t) &= a_0 + a_1 \cos(\omega_0 t) \exp(-\Lambda t) \text{ (static)}, \end{aligned} \quad (12)$$

where $G_2(t)$ is perturbation function extracted from the time spectra; λ_2 is relaxation parameter; Λ is width of the quadrupole frequency distribution relative to mean value of ω_0 .

Results

By the use of biochemical solutions the formation of homogeneous phases with similar local structures previously observed in the liquid state occurs (Figs 1-5). The spectra from the Figs 1-3 displays a superposition of signals corresponding at least to two different environments of the probes due to a degree of disorder around the radionuclide-probes. As it can be seen in figures, the error bars increase with time between γ -ray emissions.

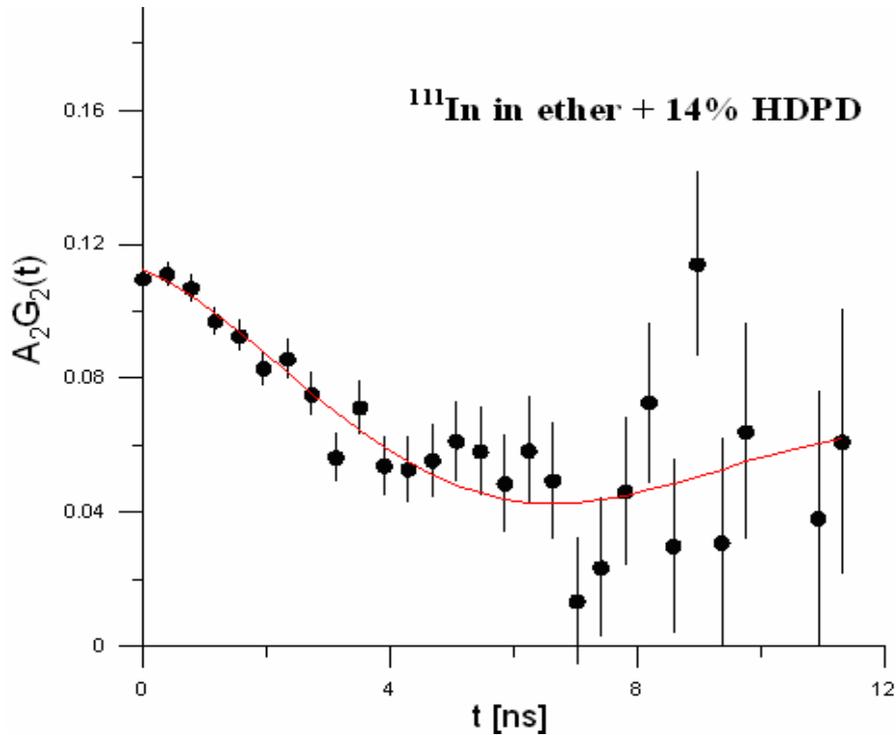


Fig. 1. TDPAC perturbation spectra of $^{111}\text{In}/^{111}\text{Cd}$ γ - γ cascade using ^{111}In in ether + 14% HDPD solution; $\nu_Q=137(12)$ MHz quadrupole frequency for axial symmetric EFG ($\eta=0$)

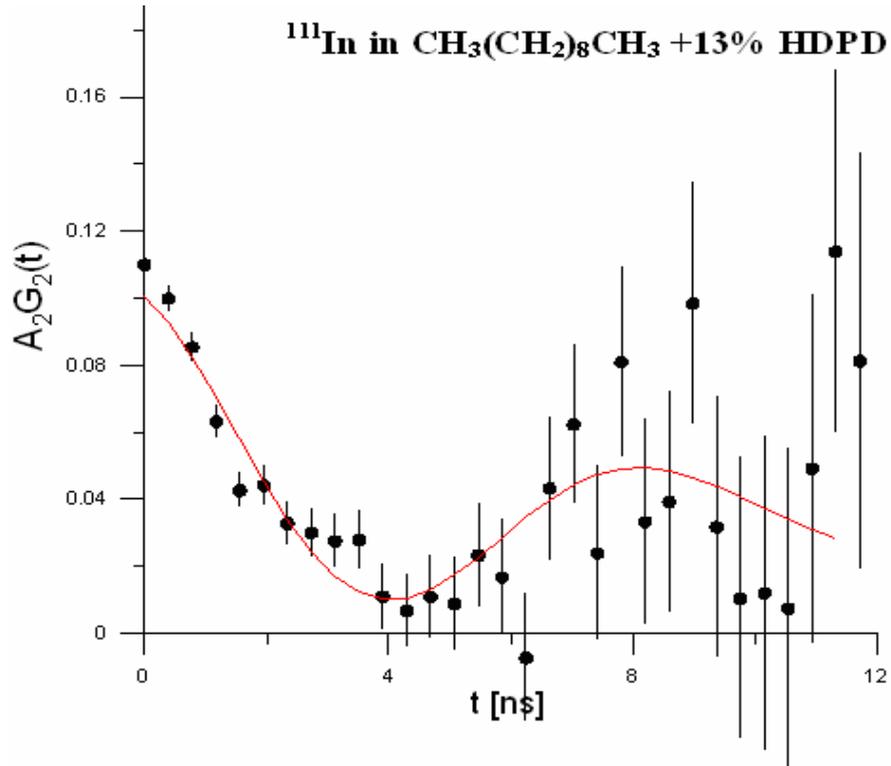


Fig. 2. TDPAC spectra of $^{111}\text{In}/^{111}\text{Cd}$ γ - γ cascade using ^{111}In in 500ml $\text{CH}_3(\text{CH}_2)_8\text{CH}_3 + 13\% \text{ HDPD}$ solution; $\nu_Q=218(10)$ MHz quadrupole frequency for axial symmetric EFG ($\eta=0$)

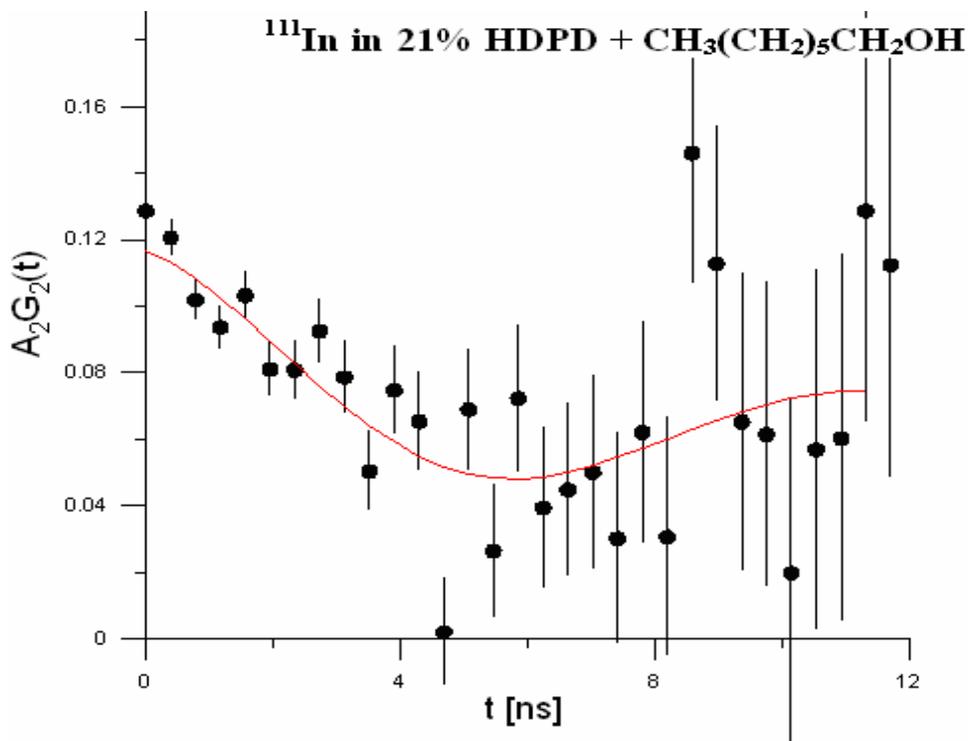


Fig. 3. TDDPAC spectra of $^{111}\text{In}/^{111}\text{Cd}$ γ - γ cascade using ^{111}In in 21% HDPD + $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$ solution; $\nu_Q=156(16)$ MHz quadrupole frequency for EFG ($\eta=0$)

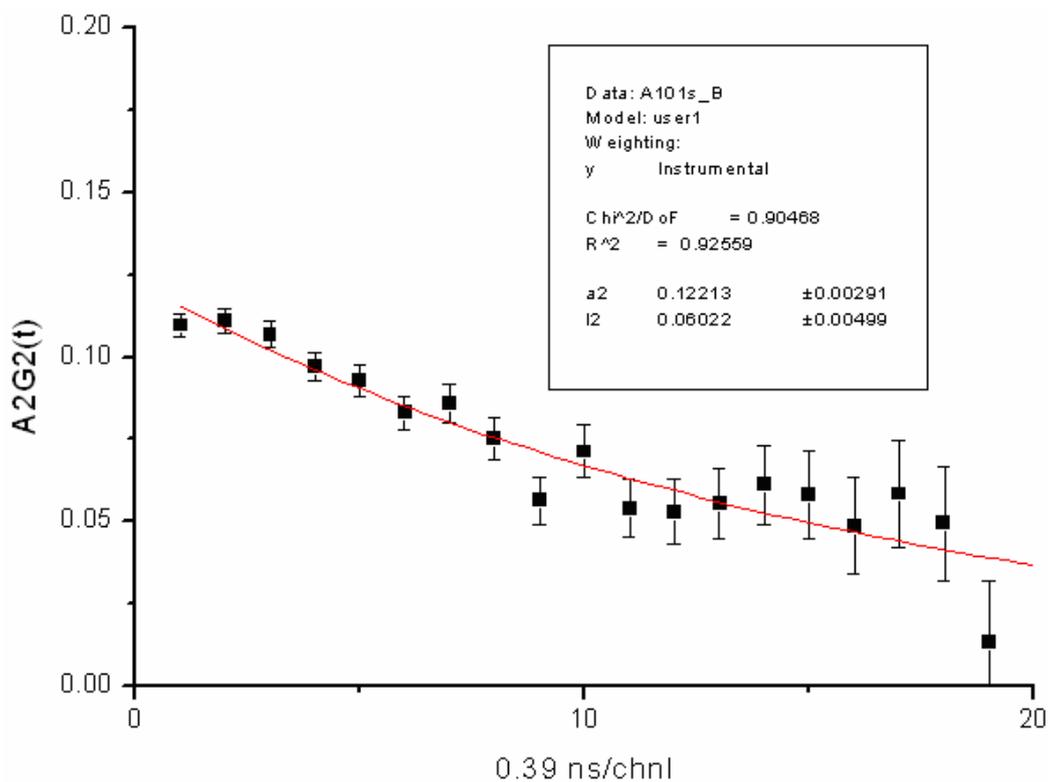


Fig. 4. Fitting χ^2 of the TDPAC spectra for ^{111}In in ether + 14% HDPD solution (Fourier transform display)

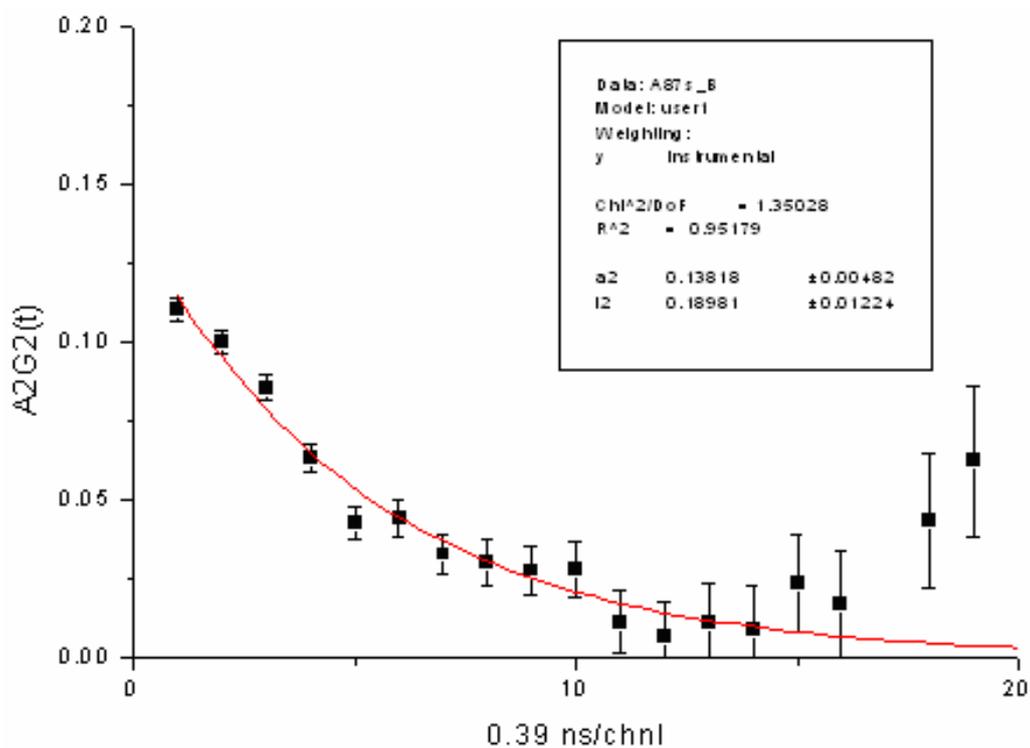


Fig. 5. Fitting χ^2 of the TDPAC spectra for ^{111}In in $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$ + 13% HDPD solution (Fourier transform display)

TDPAC perturbation spectra are fitted to a theoretical expression of the perturbation function by varying parameters in the model function until a χ^2 goodness of fit parameter is minimized (Figs 4-5) by using the DEPAC software. Best-fit values obtained from fits can provide information about physicochemical organization of the vegetable oil. From the fitting calculated parameters as a_0 , a_1 and v_Q , it results that these processes of diffusion of the PAC probe in oil are responsible for dynamic character of the perturbation of angular correlation.

Conclusions

It was shown the suitability of TDPAC method to analyzing the physicochemical organization in oil solutions. It was developed an experimental methodology by diffusing ^{111}In in several reactant solutions of preparation the vegetable oil analytical samples. Experimental and calculated electric field gradients (EFG) on ^{111}In probe atom diffused in different vegetable oil solutions were obtained.

The results were analyzed in terms of a diffusion process approach which explains the observed effects due to the dynamic character of the perturbation of angular correlation. It was obtained the minimization of the χ^2 fit parameter up to best-fit values for the TDPAC perturbation spectra to a full-line theoretical expression of the perturbation function by using the DEPAC software.

References

1. D.R. Hamilton, Phys. Rev. 58 (1940) 122
2. E.L. Brady and M. Deutsch, Phys. Rev. 72 (1947) 870
3. K. Krusch and J. Gardner, Phys. Rev. B 24 (1981) 4587
4. A. Lerf, T. Butz: Angew. Chem. Int. Ed. Engl. 26 (1987) 110
5. H. Frauenfelder and R. M. Steffen, in: *Alpha-, Beta- and Gamma-Ray Spectroscopy*, Ed. K. Siegbahn, North-Holland Publ. Comp. Amsterdam (1965)
6. G. Schatz and A. Weidinger: *Nuclear Condensed Matter Physics: Nuclear Methods and Applications* (John Wiley, New York, 1996)
7. Hemmingsen, L., T. Butz. *Encyclopedia of Inorganic Chemistry* (2008) DOI: 10.1002/0470862106.ia322.
8. Akselrod, Z.Z., D.V. Filosofov, et al. Z. Naturforsch. 55a (2000) 151
9. Brudanin, V.B., D.V. Filosofov, O.I. Kochetov, N.A. Korolev, et al. Nucl. Instrum. Meth. in Phys. Res. A 547 (2005) 389
10. C. Oprea, A. Velichkov, I.A. Oprea, D.V. Filosofov. *Proceedings of the XVIIth Int. Seminar on Interaction of Neutrons with Nuclei (ISINN-17)*, Dubna, RF (2010) 399