Vibrational and Orientational Dynamics of Polyatomic Molecules in Liquids by the Raman Spectroscopy Data

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ABSTRACT

The methodology of applying vibrational spectroscopy to the investigation of the interactions and dynamics of molecules and polyatomic ions in liquids and solutions is set out. The results of the study of a number of dipolar aprotic solvents are given.

KEY WORDS: molecular interactions, orientational relaxation, Raman spectra, vibrational relaxation.

1. INTRODUCTION

Vibrational spectroscopy (IR and Raman) is one of the most informative experimental methods for the study of the condensed state of matter and provides information which is usually inaccessible to other experimental methods of research. Vibrational spectra of molecules are characterized by the maxima positions of bands, their intensities and shapes. Studying a change taking place in these parameters under the influence of intermolecular interactions, one can obtain information on the structure of liquids and the presence of relatively long–lived complexes and associates in them, and also investigate molecular dynamics.

In the liquid, the existence of a relatively long–lived local order, associated with the formation of various complexes and associates, is indicated by the intramolecular vibrational frequency change. The discrete character and the diversity of such local environments result in several discretely shifted spectral bands, the number of which is determined by that of the associates formed in the liquid. The intensities of these bands depend on the concentration of a particular type of associates.

2. MEASUREMENTS AND RESULTS

A rather simple picture of interparticle interactions in dipolar aprotic solvents (DAS) (dimethylsulfoxide /DMSO/ dimethylformamide /DMF/, acetonitrile /AN/, propylencarbonate /PC/, acetone /AC/) and their distinct manifestations in vibrational spectra allow detailed information to be drawn on

molecular association [1] and its influence upon molecular dynamics.

The association of the molecules of these solvents reveals itself in the complex structure of band contours arising from the atomic vibrations by means of which the interaction is preferentially realized. From these contours, one can separate four components pertaining to monomeric molecules and molecules incorporated in chain and cyclic dimers; in the latter, both synphase and antiphase vibrations are possible [1].

The parameters determining the Raman band shapes are described by the derivative of the molecular polarizability tensor by the normal coordinate corresponding to a given mode. For optically inactive molecules this tensor may always be reduced to the diagonal form and generally resolved into the isotropic and the anisotropic components. The anisotropic part of the Raman tensor determines the sensitivity of the depolarized band contour shape to the molecular reorientation conditions. The isotropic part of the tensor is responsible for the polarized bands whose contour shape is independent of molecular reorientations.

The isotropic scattering spectrum is related to the isotropic polarizability only and thus does not depend on the orientational molecular motion conditions. The anisotropic scattering spectrum is related to both the vibrational and the orientational motion. This provides a possibility to separate the effects due to the vibrational and the orientational motion of molecules. The extraction of such information from the spectral band contour shape involves certain difficulties, associated with the acquisition of the real spectral band

contours. The most serious of them stems from the spectral band overlap. Thus it is first necessary to resolve the complex spectrum into individual components, ascribed to monomeric or associated molecules, and to determine their contours, which then provides access to the information on molecular dynamics. In the component analysis of the spectrum no firm restrictions on the component contour shapes are allowed, as this would predetermine the result. In our study, the shape of individual components was approximated by the symmetric curves of the Gaussian or Lorentzian function product shape. Such a curve does not impose firm restrictions on the band contour shapes so that one may use the analytical form of integral Fourier transformations that are necessary for calculating the molecular dynamics parameters.

The vibrational relaxation of molecules in liquids is determined mainly by intermolecular interactions. Three mechanisms of relaxation of intramolecular vibrations can be pointed out: 1) energy relaxation – the dissipation of energy of intramolecular vibrations to all the other degrees of freedom of motion, i.e. to the thermostat including the translational and vibrational molecular motions as well as other vibrational modes; 2) phase relaxation – the modulation of the intramolecular vibration phase by collisions with surrounding molecules, or, in other words, by the local field fluctuations; 3) resonance energy exchange – the exchange of quanta of intramolecular vibration energy between oscillators of one type. The pulse picosecond laser investigations show that the time of the energy relaxation of intramolecular vibrations in most liquids is nearly two orders of magnitude larger than the time of vibrational relaxation. In

the majority of liquids studied to date, the phase relaxation is the predominant mechanism of vibrational relaxation.

The resonance energy exchange may contribute significantly to the shape of band contours in pure liquids with sufficiently strong intermolecular interactions. Its manifestation in the vibrational spectra of liquids was the subject of many theoretical and experimental studies [2–5]. It was established that, besides causing band contour broadening in liquids with strong intermolecular interactions of directed character, the resonance energy exchange should bring about the noncoincidence of the positions of maxima for bands arising from the same mode in the spectrum of isotropic and anisotropic Raman scattering. The band maximum frequency in the anisotropic spectrum, ν_{anis} , should be higher than that in the isotropic one, ν_{is} , and the frequency difference, $\delta\nu = \nu_{anis} - \nu_{is}$, should be positive. This effect of noncoincidence was discovered for many liquids. But the $\delta\nu$ behaviour upon changing the density of the liquid or diluting it in a solvent of a different nature cannot always be explained by the the resonance energy exchange. Thus, in recent literature, the idea has been expressed that the current approaches to the explanation of this effect should be revised [6].

The most favourable conditions for the resonance energy exchange are found in self–associated liquids, including DAS. The noncoincidence effect here is observed with the bands of the stretching modes of the bond with the strongest polarity in a molecule. But, as already mentioned, these bands have complex structure due to self–association of molecules. In literature, the resonance energy exchange in these solvents is correlated

with the noncoincidence of the maxima positions of the resulting complex contours in VV – and VH – spectra. In our view, the correlation of this noncoincidence with the resonance exchange of the energy of intramolecular vibration is incorrect. The noncoincidence of maxima of such complex VV – and VH – spectral contours is due to the different intensity and degree of depolarization of the components and depends on the concentration of associates of different types in the liquid. For correct estimation of the values of noncoincidence caused by the resonance energy exchange one has to compare the isotropic and anisotropic spectral maximum positions for components pertaining to the same type of the associate.

It appears meaningless to regard the effect when averaged for associates of different types, i.e. when maximum positions of the resulting complex contours are compared, because different associates offer different conditions for intermolecular exchange of vibrational energy. Figure 1 shows the result of the component analysis of complex band contours in isotropic and anisotropic spectra.

Table 1 gives the positions of band maxima in pure liquids in isotropic and anisotropic spectra for monomeric molecules and molecules in different associates, as obtained by the component analysis of complex contours [7]. The error of determination in all cases does not exceed 1.0 cm^{-1}. It can be seen from the table that, within the limit of error of determination, the positions of component maxima in the isotropic and anisotropic spectra coincide. This allows the assertion to be made that in the case of associated liquids the main reason for noncoincidence of maxima must lie in the association of molecules. The

noncoincidence of maxima is observed only for the bands having complex structure due to molecular association. Other vibrations of these molecules whose bands are single and are insensitive to molecular association do not exhibit this effect.

The assignment conducted for the individual components of the complex band contours of the vibrational modes of the DAS functional molecular groups allows the calculation of the relaxation parameters for monomeric molecules and molecules entering into associates (Table 2). Also given are the values of the coefficients k_{is} which characterize the isotropic scattering band contour shapes and are equal to the ratio of the reverse value of the Lorentzian contribution halfwidth to the sum of the reverse halfwidths of the Gaussian and Lorentzian contributions to the total band contour shape. The contour shape is Lorentzian when $k_{is} = 1$, and Gaussian when $k_{is} = 0$. The data show that the interacation between molecules in DAS leads to the increase of the Gaussian contribution to the stretching band contour shape. The stochastic model of phase relaxation relates the Gaussian band contour shape to the limit of the slow modulation of intramolecular vibrations by the environment, when the environment of a given molecule remains unchanged during the lifetime of the excited vibrational state [8,9]. Thus, in terms of this model, the increased Gaussian contribution points to the decreased lifetime of the excited vibrational state of molecules in the associates.

The Fourier–transformation of the spectral functions allows one to obtain the expression for the orientational relaxation correlation functions and the orientational correlation functions of the Raman polarizability tensor and the dipole moment.

Figures 2 and 3 give the orientational relaxation correlation functions for monomeric and associated molecules as calculated from the dimethylsulfoxide ν(SO) and acetonitrile ν(CN) bands [7]. The figures also show the theoretical correlation functions, calculated on the basis of the stochastic model of phase relaxation according to

$$G_\nu(t) = \exp(-M_2 \cdot \tau_c)$$

and

$$G_\nu(t) = \exp(-M_2 \cdot t^2/2)$$

in the limits of fast and slow modulation respectively.

Here τ_c is a certain characteristic time associated with the second frequency moment M_2 of the band in the isotropic scattering spectrum and with the vibrational relaxation time τ_V by the following correlation:

$$\tau_C = (M_2 \cdot \tau_V)^{-1}.$$

Their rather good agreement allows the assumption to be made that the vibrational relaxation of monomeric and associated molecules in the DAS under study has predominantly phase character, but its parameters differ considerably. For monomeric DAS molecules the modulation is fast, while for the molecules incorporated in cyclic and, especially, chain dimers, the modulation decelerates.

The numerical integration of the corresponding correlation functions provided the orientational relaxation times [10 –12] (Table 2) for monomeric molecules, τ_V^{mon}, and for molecules incorporated in cyclic, τ_V^{cyc}, and chain, τ_V^{chain}, dimers. The times decrease in the series $\tau_V^{mon} > \tau_V^{cyc} > \tau_V^{chain}$.

Since the orientational relaxation times for associated molecules are larger than for monomeric molecules and are

characterized by a more slow modulation, it may be assumed that for the molecules in dimers, processes of energy relaxation play a significant role.

The condensed phase quantized rotation of molecules is as a rule excluded, thus no discrete rotational structure is observed in molecular spectra. In liquids, rotational motion is of strongly decelerated diffuse character. To describe such a motion, the Debye, or the rotational diffusion, model is used, which presumes that reorientation of molecules at large angles occurs as a sequence of turns at infinitesimal angles due to weak intermolecular collisions. The most frequently used formalism for the orientational motion of molecules in the liquid is the Kubo stochastic model, which contains both limiting cases, rotational diffusion and free rotation. For highly symmetric molecules, the orientational correlation function in this model is as follows:

$$G_{2R}(t) = \exp\{-\tau_c[\exp(-t/\tau_c) - \tau_c + t] / \tau_R\},$$

where τ_R is the orientational relaxation time.

In the limits of free rotation and rotational diffusion, this model will yield

$$G_{2R}(t) = \exp(-t^2/\tau_c \cdot \tau_R)$$

for free rotation and

$$G_{2R}(t) = \exp(-t/\tau_R)$$

for rotational diffusion.

This model allows the calcuation of the angular steps of diffusion, ε_o:

$$\varepsilon_o = \frac{1}{6\,\tau_R} \cdot \sqrt{\frac{I}{k \cdot T}},$$

where I is the moment of inertia for the molecular symmetry axis turn.

The same correlations are employed in the study of the orientational motion of low–symmetry molecules. In this case, however, they do not afford one to judge upon the rotation of the molecule about one particular axis but give the result which appears to be the average for the rotations about three spatial axes.

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LEGENDS

Fig. 1. Contour of the ν(CO) band in acetone in isotropic and anisotropic spectra and the result of its component analysis.

Fig. 2. Orientational relaxation correlation functions $G_v(t)$, calculatedfrom the dimethylsulfoxide ν(SO) band for chain (a) and cyclic (b) dimers, and for monomers (c).Models of fast (1) and slow (2) modulation, the experimental curve (3).

Fig. 3. Orientational relaxation correlation functions $G_v(t)$, calculated from the acetonitrile ν(CN) band for chain (a) and cyclic (b) dimers, and for monomers (c). Models of fast (1) and slow (2) modulation, the experimental curve (3)

Table 1.

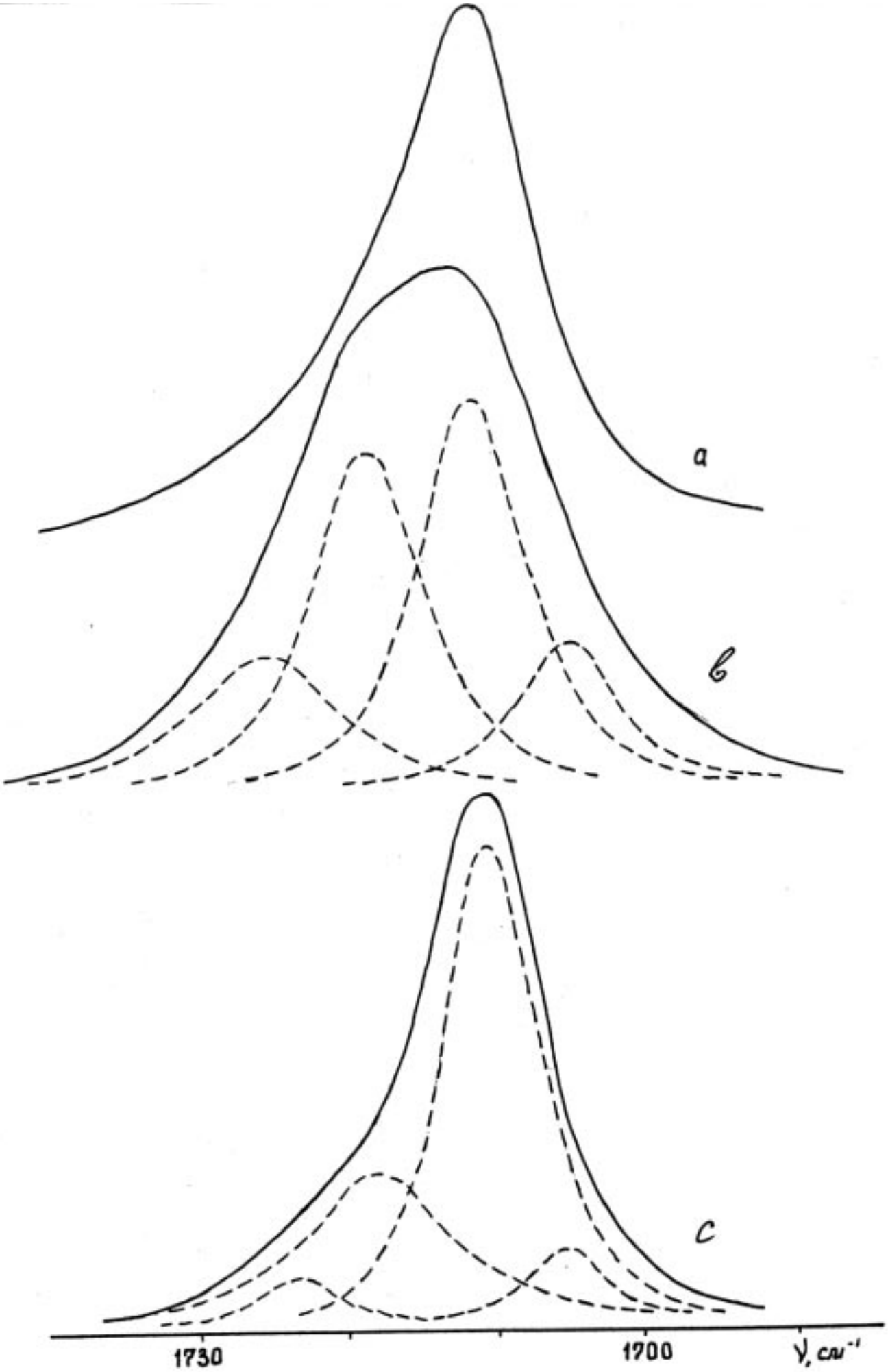
Maxima positions of bands in the isotropic, ν_{is}, and anisotropic, ν_{anis} , spectra and the value of non-coincidence, $\delta\nu$, of the resulting complex contours for molecules in monomeric state and in different types of associates (cm^{-1}).

Solvent and mode		monomer			chain dimer			cyclic dimer					
								synphase mode			antiphase mode		
	$\Sigma\ \delta\nu$	ν_{is}	ν_{anis}	$\delta\nu$	ν_{is}	ν_{anis}	$\delta\nu$	ν_{is}	ν_{anis}	$\delta\nu$	ν_{is}	ν_{anis}	$\delta\nu$
Propylencarbonate ν(C=O)	8.5	1819.1	1818.6	–0.5	1771.0	1771.4	0.4	1781.2	1781.8	0.6	1793.2	1793.7	0.5
Acetonitrile ν(C≡N)	0.5	2257.0	2257.5	0.5	2247.2	2247.0	–0.2	2251.8	2252.2	0.4	2254.0	2254.0	0.2
Dimethylsulfoxide ν(S=O)	12.0	1072.2	1071.9	–0.3	1027.8	1027.2	–0.6	1045.0	1044.3	–0.7	1058.8	1058.5	–0.3
Dimethylformamide ν(C=O)	13.8	1686.8	1687.1	0.3	1660.4	1660.6	0.2	1666.5	1665.8	–0.7	1675.6	1676.4	0.8
Acetone ν(C=O)	4.0	1715.5	1714.9	–0.6	1709.0	1709.8	0.8	1711.2	1711.5	0.3	1713.0	1713.4	0.4

Table 2

Parameters of vibrational and orientational relaxation of associated and non-associated molecules of DAS

	PC			DMSO			DMF			AN			AC		
	mon	cyc	chain	mon	cyc	chain	mon	cyc	Chain	mon	cyc	chain	mon	cyc	chain
k_{is}	0.9	0.5	0.4	0.9	0.5	0.6	0.8	0.4	0.5	0.9	0.4	0.4	0.9	0.6	0.6
τ_{v}, ps	2.1	1.7	1.4	0.9	0.7	0.5	1.0	0.8	0.6	5.8	2.7	2.0	4.0	2.2	2.1
τ_{2R}, ps	1.0	1.5	1.1	0.6	1.5	0.9	1.2	2.3	1.3	5.2	6.7	7.7	2.2	4.8	3.6
ε_{O}, grad	8.1	5.4	7.5	7.3	3.0	5.0	4.5	2.3	4.1	0.8	0.7	1.6	8.4	1.2	1.6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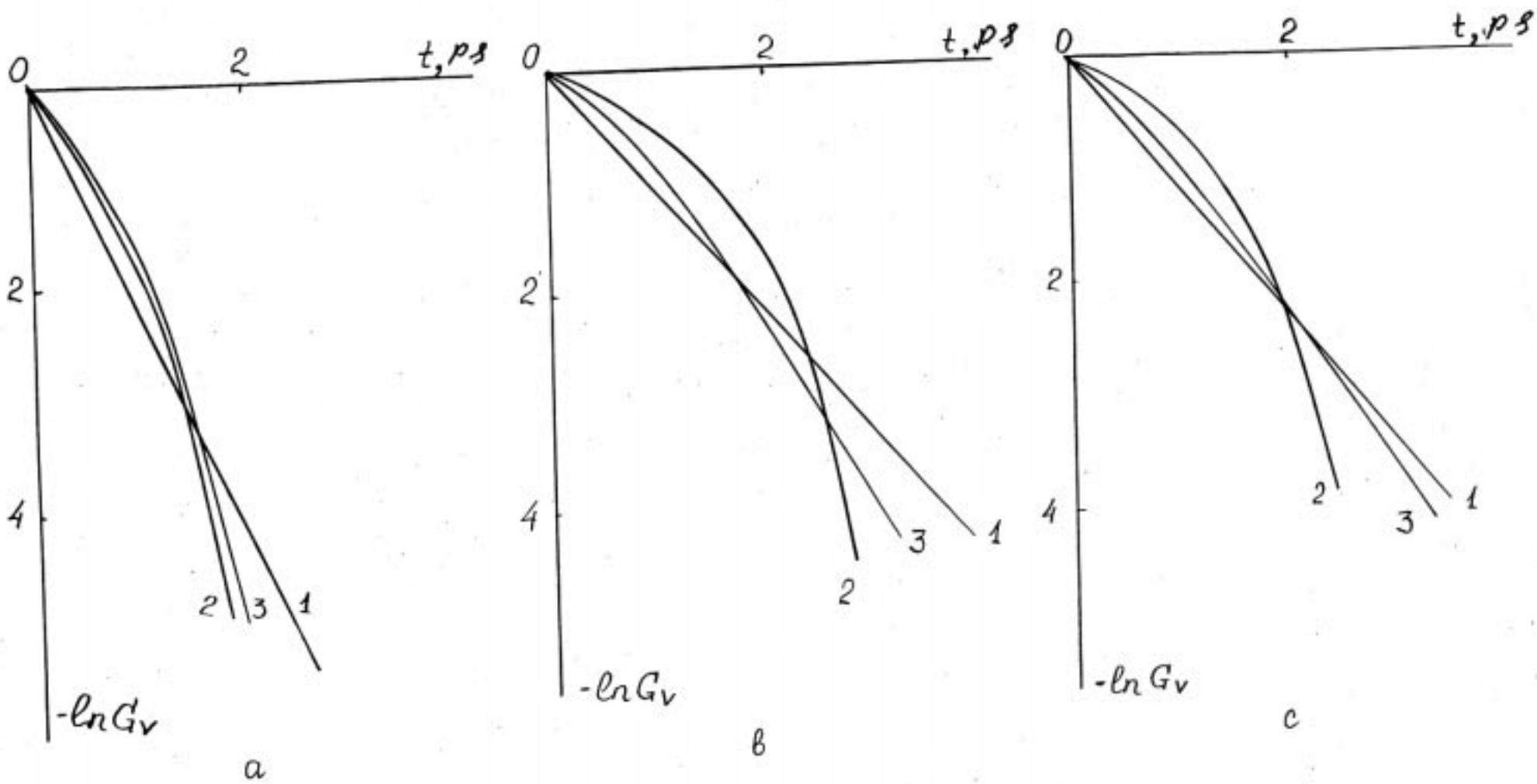
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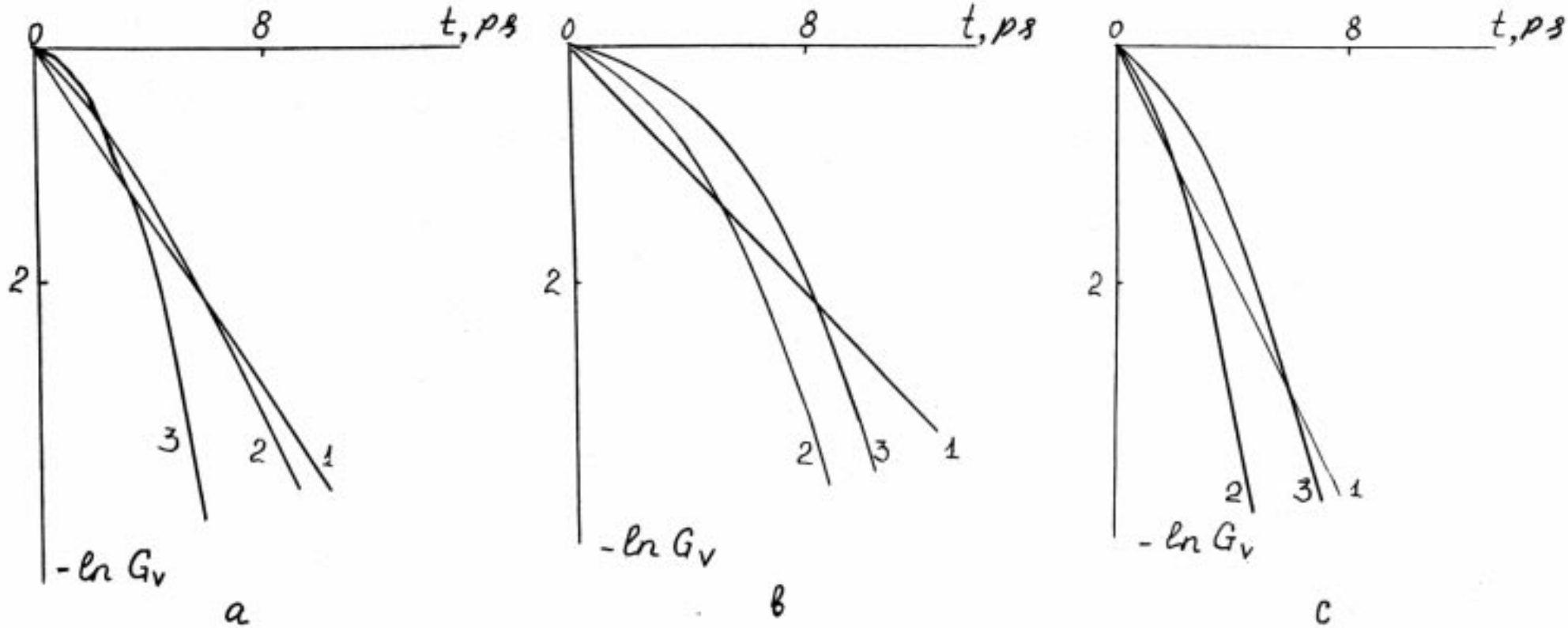
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