Some Structural and Dynamical Properties of Liquid $POCl_3$

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The liquid $POCl_3$ (chlorine oxide of phosphor) is known as a main component of a mixture, constituting the liquid based laser system (typical composition: $POCl_3$ + $SnCl_4$, activated by Nd^{3+} ions) [1]. If the chemical properties and electron excitation spectrum of this liquid are widely studied, the information, concerning with its molecular structure and microdynamics is very scarce. At the same time it is well established, the elementary excitation spectrum of phonon subsystem and its correlation with electronic excitations are directly related to the nature of electron excitation transfer, its relaxation and quenching [2]. This is why we have undertaken a set of neutron scattering experiments on liquid $POCl_3$ with the spectrometer DIN-2PI, using it in diffraction as well as in inelastic scattering modes. The present report contains the short information about our first results.
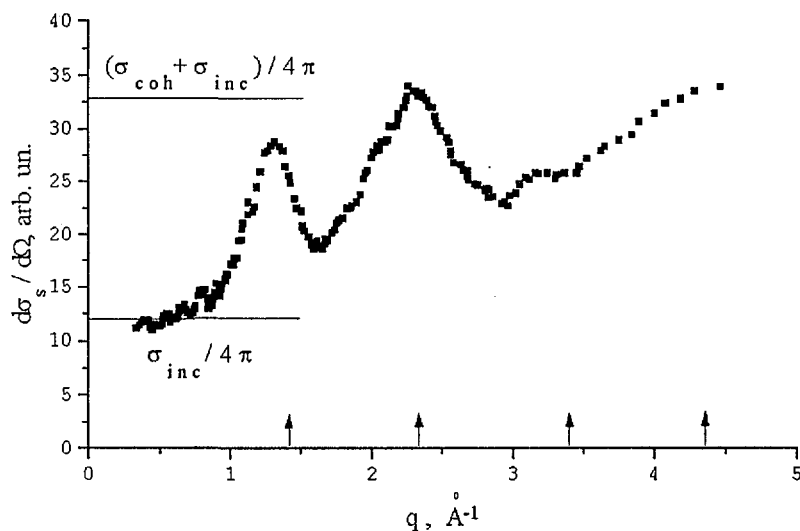

Fig. 1. Angular differential scattering cross section for liquid $POCL_3$

Fig. 1 shows the angular differential scattering cross section. The arrows point to the positions of the coherent peaks, found by X-ray diffraction [3]. The double differential scattering cross sections, measured at small scattering angles, where coherent effects can be neglected (see initial part of $d\sigma/d\Omega$ on fig.1), were used to extract the generalized frequency distribution (GFD) of chlorine atoms (87% of scattering events on $POCl_3$ molecule are connec-ted with chlorine) by application of the method, elaborated for incoherent scatterers [4] (fig. 2). The arrows show the location of the intramolecular modes, discovered in optical experiments by IR- absorption and Raman scattering of light [5]. It can be concluded from fig. 2, the region of intramolecular modes to be restricted by the energy transfers $\varepsilon \geq 20\text{meV}$. Thus, the part of GFD to the left from these energies can be related to the intermolecular modes. It should be supposed, that the wide peculiarity with the maximum about $\varepsilon\sim(4\text{-}5)$ meV contains effects of molecular vibration motions (hindered translations) as well as effects of molecular librations in the force field of neighbours. There is no information about the intermolecular interactions in the liquid under study, but in [6] the method is suggested to estimate the frequency of intermolecular vibrations for liquids on the basis of their evaporation heats. Taking for $POCl_3$ $H_{ev}\cong 8$ kCal/mole, we get $\varepsilon_{tr} \sim (7\text{-}8)$ meV. If we suppose the intermolecular part of GFD

can be described by superposition of two Gaussians, we get one centered near $\varepsilon\sim(7-8)$ meV (supposed, translational), and the second (librational) near $\varepsilon\sim(4-5)$ meV (see inset of fig. 2). The wide overlap of these curves can be explained by the proximity of effective masses, which molecule participates in these two kinds of motions with.

The analysis of the quisielastic component of scattering in the region of small q has allowed to estimate the selfdiffusion coefficient for $POCl_3$ liquid as $D \sim(1.6\pm0.2)$ cm^2/c.
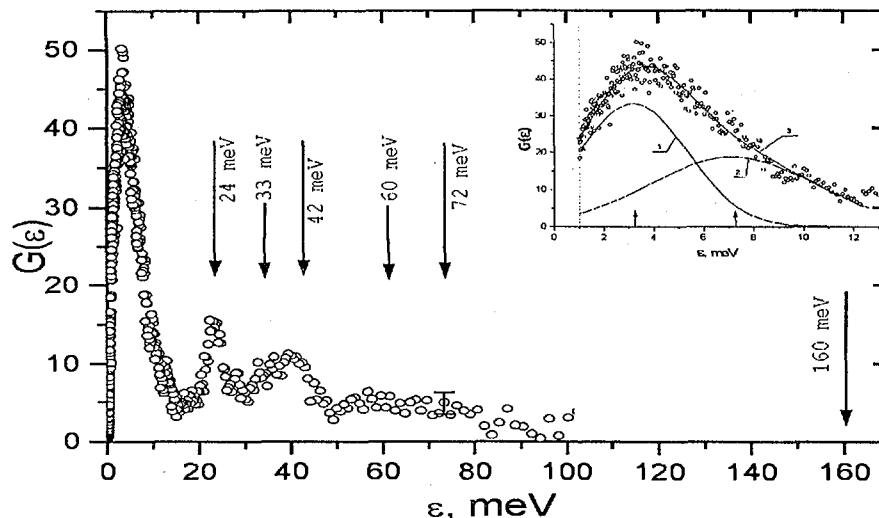

Fig. 2. Generalized frequency distribution $G(\varepsilon)$ for chlorine atom in POCL$_3$ molecule. Inset: intermolecular part of $G(\varepsilon)$. 1 -libration mode; 2 -translation mode; 3 - common approximating curve.

References

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