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New insights into the nature of the metastable structures in supercooled liquid 2-biphenylmethanol

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Abstract

The experimental work to be presented and analyzed here focuses on the investigation of the molecular hydrogen-bonded compound 2-biphenylmethanol in a supercooled liquid state using FT-IR spectroscopy measurements. In the IR spectra, some attributes of the beginning of a new crystalline phase formation, as the temperature is raised from the glass transition to the room temperature has been observed. At the room temperature a continuous transformation of the IR spectra, which is intimately related to the crystallization, extends over 60 min. The IR spectrum of the so produced crystalline phase has been found to be quite different from that of the stable phase.

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1. Introduction

Experiments on glass-forming liquids reveal many universal features associated with the non-exponential behavior of their dynamics at a crossover temperature, $T_c \sim 1.2\ T_g$, of mode-coupling theory [1,2]. Below the crossover temperature the dynamical properties of a liquid change from an 'ordinary', Arrhenius-like temperature dependence, to an 'anomalous', that is stronger than Arrhenius one. Such an anomalous dependence, which is observed in all kinds of liquids irrespective of their detailed molecular properties, is an evidence of a collective phenomenon involving a cooperative motion of a large number of molecules [3–5]. These correlated clusters of molecules, the so-called dynamical heterogeneities, play a crucial role in the slowing-down of the dynamics when the temperature is decreases. However, up to now, many aspects of the characterization of these dynamical heterogeneities have remained elusive. For instance, there is no clear consensus on their shape, their size, and their evolution with temperature [8–10].

In our previous study, we have pointed out that 2-biphenylmethanol (2BPM) can remain in a supercooled state at room temperature for as long as one likes (for example, a year). The only possibility to initiate the crystallization in this compound is to quench the liquid 2BPM down to a low temperature and then reheat it [11]. It should be noted, that there exists a number of glass-formers which can easily be vitrified without crystallization on cooling, while they are crystallized after melting of their glassy state. The examples are: benzophenone, salol, *o*-benzylphenol, *o*-terphenyl, and so on. The fact that a liquid sample is not crystallized indicates that it does not contain nuclei, while nuclei emerge during the cooling procedure. We have found by means of a differential scanning calorimetry (DSC) that the temperature at which nuclei appear in the

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supercooled liquid 2BPM is equal to 283 K. Earlier it has been shown that a metastable phase of benzophenone is obtained from the liquid supercooled to 243 K [12]. Interestingly, the temperatures of 283 K for 2BPM and 243 K for benzophenone turn out to be close to the crossover temperature, T_c, which was determined using optical Kerr effect experiments. It has been found that T_c is equal to 290 ± 4 K for 2BPM and 250 ± 4 K for benzophenone [6,7]. These experimental findings were interpreted by us as the evidence that the origin of the crossover at T_c is related to the formation of the microscopic structure, namely, to the appearance of fluctuating nuclei in the supercooled liquid, whose radii are less than the critical one. At low temperatures ($T < T_g$) nanometric scale nuclei turn out to be incorporated in the glass structure, while at high temperatures ($T > 283$ K) where the rearrangements of the molecules become larger, nuclei get the possibility to grow rather easily to a bulk crystal.

Another important result, which we have received from X-ray experiments [11], was that the structure of the so produced bulk crystal (hereafter referred to as metastable) is monoclinic and consists of hydrogen-bonded chains of molecules. The structure of the metastable phase differs substantially from that of the stable phase, which is triclinic and consists of the cyclic tetramers of 2BPM molecules [13]. It should be noted, that organic molecular compounds often crystallize in more than one modification. In many cases, a metastable form can be obtained from a strongly supercooled melt. Benzophenone is an example. According to [14], the metastable phase of benzophenone is monoclinic and consists of linear chains of molecules, arranged parallel to the monoclinic 2_1 axis, whereas the stable phase of benzophenone is orthorhombic.

In the present investigation, we report for the first time the IR spectroscopic studies of the structural transformations within a supercooled liquid 2BPM and their evolution with time. This study was motivated by our previous results (DSC and X-ray [11]) concerning the formation of the metastable phase in supercooled liquid 2BPM. We wish to note that using the DSC method, we could observe only macroscopic processes, such as the glass transition, crystallization, and melting. In the vicinity of the glass transition temperature the state of a highly supercooled liquid offers propitious conditions for nucleation. However the process of nucleation, being a relatively microscopic process, is not directly observable by the DSC method. Thus, the investigation of the structural transformations in the supercooled phase remains beyond the possibility of the DSC method. On the other hand, the easily accessible melting point ($T_{\text{melt}} = 326.8$ K) and the glass transition temperature ($T_g = 240$ K) in 2BPM, as well as its very low rate of crystallization, provides a convenient temperature range where the supercooled liquid can be studied by means of IR spectroscopy.

We will focus on a careful analysis of the IR spectra upon different courses of the temperature change from a liquid to glassy state and back, and their time evolution at room temperature in order to confirm and complement the DSC and X-ray results [11].

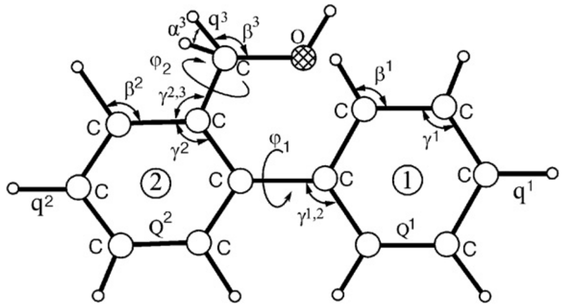

Fig. 1. The structure and vibrational coordinates of 2BPM molecule, proposed in Ref. [15].

2. Experimental

2BPM [$C_6H_5C_6H_4CH_2OH$] serves as a model system for our investigation. The structure and vibrational coordinates of 2BPM molecule are shown in Fig. 1. It contains two phenyl rings and a methanol group CH_2–OH. The hydroxyl groups (OH) form intermolecular hydrogen bonds.

FTIR absorption spectra were recorded at different temperatures in transmission on Bruker model IFS–88 Fourier-transform infrared spectrometer at 2 cm^{-1} resolution and 32 scans were accumulated for an individual spectrum. Data processing was performed with OPUS software. For the IR measurements, the sample of powder 2BPM was inserted in a cell with two KBr discs at room temperature and then melted. Such a cell with a liquid 2BPM was then fixed in a cryostat providing for a temperature variation.

3. Results and discussion

Before discussing the results we wish to note that 2BPM molecules have a strong ability to form an intermolecular hydrogen bonding. The hydroxyl group (–OH) in 2BPM molecule (Fig. 1) acts as a donor towards the O atom and thus forms the hydrogen bonding that defines O–H⋯O distances between the neighboring molecules. The greater is the hydrogen bond energy, the closer are the molecules. In the IR spectra, the intermolecular hydrogen-bonded interaction results in a decrease of ν(O–H) stretching vibration frequency compared to that in a free molecule. This frequency shift, consequently, can be used as an evidence of the changes in the distances between the hydrogen-bonded molecules. Thus, the IR spectra in the OH stretching vibration region (3000–3600 cm^{-1}) can provide additional information about structural transformations.

Fig. 2 (solid curve d) shows the fragment of IR spectrum of liquid 2BPM in the OH stretching vibration region recorded at room temperature. This liquid phase of 2BPM was obtained by a melting of the crystalline sample at 330 K. The structure of the liquid state contains both