

Phase transition and peculiarities of acoustic wave spreading in benzophenone

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Using ultrasonic methods, two main matters have been studied: the reliable establishment of phase transition glass-supercooled liquid and determination of the medial order value in glassy benzophenone. The glass-supercooled liquid phase transition has been fixed at $T = 216 \pm 3$ K. The medial radius order of $R = 33$ Å for glassy benzophenone has been determined for the first time.

С использованием акустических методов исследованы два основных вопроса: надёжное установление фазового перехода стекло-переохлаждённая жидкость и определение среднего порядка в стеклообразном бензофеноне. Был зафиксирован фазовый переход стекло-переохлаждённая жидкость при $T = 216 \pm 3$ K. Впервые для стеклообразного бензофенона определена величина радиуса среднего порядка $R = 33$ Å.

Benzophenone $\text{CO}(\text{C}_6\text{H}_5)_2$ is a molecular crystals exhibiting some interesting physical properties. It exists in several phase modifications: two crystalline ones, glassy state and state of the supercooled liquid [1]. The crystals show a considerable piezoelectric effect [2]. The compound shows chemo- and electroluminescence under certain conditions [3, 4]. Benzophenone and its derivatives are used to manufacture a wide class organometal compounds, light-resistant dyes, polymer materials [5–7], etc. Due to effective intramolecular conversion under optical excitation, only the phosphorescence caused by emissive decay of triplet excitons is seen in emission spectra [8]. Benzophenone is an object of numerous and various physical and applied investigations, reviewed in part in [8, 9].

There are only incomplete and unsystematic literature data on phase transitions and structure of various benzophenone phases. The reliable information on X-ray phase analysis is available only on one crystalline (stable) benzophenone modification [10]. As to glass-supercooled liquid transition, it was observed before only visually [1].

Fig. 1 shows the temperature dependence of longitudinal ultrasonic waves propagation speed in benzophenone for two is benzophenone forms: stable phase crystals and glassy state. The monotonic drop of sound speed with increasing temperature in a crystal is caused by scattering on phonons and relevant relaxation of sound wave energy. A peculiar temperature dependence of acoustic wave speed in glassy benzophenone within 77 to 215 K temperature range seems to be caused by "curing" of defects at microblock boundaries at temperature elevation. As a result, the sound speed increases. It is seen in Fig. 1 that the acoustic signal vanishes near the temperature $T = 216 \pm 3$ K and at $T > 216 \pm 3$ K, it appears again, its speed decreasing sharply due to dispersion already in liquid benzophenone. Such temperature dependence of sound speed is typical of the first-order phase transitions [9]. This result is in agreement with the preliminary data on thermal properties of benzophenone obtained before by differential scanning calorimetry (DSC) (in the DSC-diagrams, a low-intensity peak was observed near $T = 217$ K presumably identified to

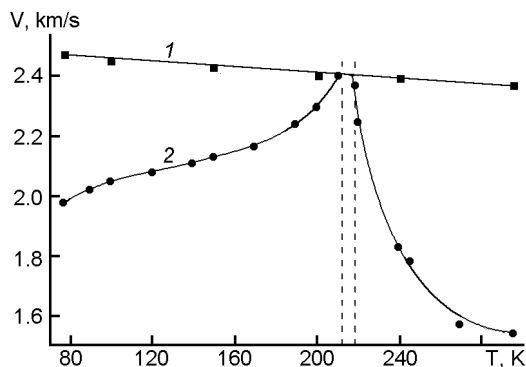


Fig. 1. Temperature dependence of longitudinal acoustic waves speed in various benzophenone modifications: crystal (1); glass-liquid (2).

glass-supercooled liquid phase transition at $T = 217$ K [12]).

Of particular interest is to establish the structure and energy distribution in glassy benzophenone. In spite of the fact that glassy systems are explored rather intensively during last decades, till now, there is no complete understanding of their structure. Since the X-ray methods are poorly suitable for structure establishment of various disordered systems, other examinations are necessary to provide indirect information on structure of glasses.

One of the concepts of a glass state being under successful development to date is the hypothesis about connection of physical properties of a glass with its nanostructure [13–15]. Various experiments have evidenced for a long time some universal structural formations of several nanometer size in glasses. In the glassy state and amorphous structures, the so-called medial order is inherent, while crystal bodies having translation symmetry exhibit the long-range order. Within the frame of conceptions of the disordered state nature [14], the disorder and chaotic character in glasses and amorphous bodies are not absolute: their homogeneity is broken on the medial order scale due to presence of some formations of ordered structure, such as crystalline ones. This ordering is maintained at a distance of several coordination spheres, and then is broken. The specified formations are not individual islands in a disordered medium but represent fragments constituting the amorphous bodies and glasses as wholes.

The presence of spatial inhomogeneities in structure amorphous and glassy solids with radii values characteristic of the medial order results in occurrence of a series

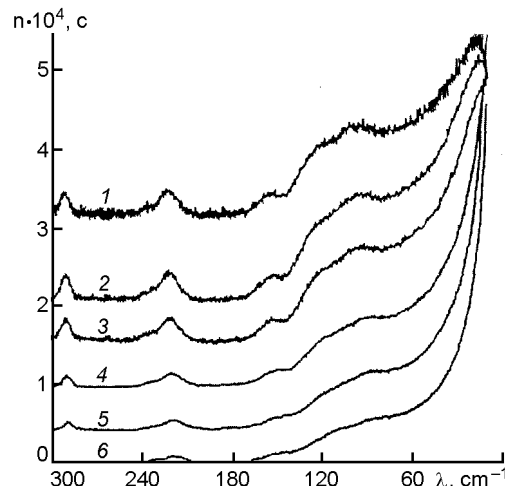


Fig. 2. Temperature dependences of Raman spectra for glassy benzophenone [12]: 160 (1); 190 (2); 210 (3); 260 (4); 300 (5); 324 (6).

of universal properties. Those are, in turn, anomalous as compared to the crystalline analogs: redundant density of vibrational states, singularities in temperature dependences of heat capacity and thermal conductivity, the ratio $T_g/T_m \sim 2/3$ (T_g , T_m are glass transition temperature and melting point, respectively) valid for most glasses, etc. In particular, for many glasses, irrespective of their chemical composition (metals, semiconductors, dielectrics, organics), the characteristic bands appear in low energy region (<100 cm^{-1}) of the Raman spectra (RS) caused by redundant density of vibrational states. Those bands are referred to as benzophenone peak (BP). There are no BP in RS of corresponding crystals.

It has been shown before [13, 15] that the BP position is related to the size of structural inhomogeneities characterized by the medial order radius, the latter value being in proportion to the ratio of sound speed to the BP frequency. In a previous work by the authors [12] considering the temperature dependence of RS, a BP with $\nu = 17$ cm^{-1} has been revealed (Fig. 2). According to [13], the medial order radius value is determined by the following relationship:

$$R = k \frac{V_d}{\nu c}, \quad (1)$$

where ν is the BP frequency (cm^{-1}); c , light speed; k , a dimensionless coefficient depending on the cluster shape (for sphere, $k = 1$); V_d , Debye sound speed [17].

$$V_d = \left[\frac{1}{3} \left(\frac{2}{V_t^3} + \frac{1}{V_l^3} \right) \right]^{1/3}, \quad (2)$$

where V_l and V_t -velocities of longitudinal and transversal acoustic wave, respectively in glass state benzophenone. Using the experimental values and the BP frequency, we obtain the value for $R = 33 \text{ \AA}$.

It is to note that this value defines the order of magnitude of the medial order radius but not its absolute value, as the formula is approximate, the cluster shape is not quite known, etc.

To conclude, the glass-supercooled liquid phase transition has been fixed at $T = 216 \pm 3 \text{ K}$ basing on the analysis of temperature dependence of longitudinal acoustic wave speed in benzophenone. The value of the medial order radius $R = 33 \text{ \AA}$ for glassy benzophenone has been determined for the first time. It characterizes the medial size of structural inhomogeneities in this substance.

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Фазові перетворення та особливості поширення акустичних хвиль у бензофеноні

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З застосуванням акустичних методів досліджено два головних питання: надійне встановлення фазового переходу скло-переохолоджена рідина та визначення середнього порядку в склоподібному бензофеноні. Зафіксовано фазовий перехід скло-переохолоджена рідина при $T = 216 \pm 3 \text{ K}$. Вперше для склоподібного бензофенону визначено величину радіусу середнього порядку $R = 33 \text{ \AA}$.