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The influence of phase transformations on the frequencies of molecular vibrations in films of 2-methylbenzimidazole perchlorate $C_8H_8N_2$-$HClO_4$

© B.B. Krichevtsov[1], S.I. Pavlov[1], A.V. Redkov[2], E.V. Balashova[1]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] Institute of Machine Science Problems of the Russian Academy of Sciences,
St. Petersburg, Russia
e-mail: boris@mail.ioffe.ru

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Films of 2-methylbenzimidazolium perchlorate $C_8H_8N_2$-$HClO_4$ (MBI·$HClO_4$) were grown on sapphire $Al_2O_3(0001)$ substrates. The frequencies of molecular vibrations of MBI·$HClO_4$ were studied during phase transitions from the ionic crystal (IC) state to the intermediate phase and to the ionic liquid (IL) phase. Raman spectra were obtained in the range of $80-3300\,cm^{-1}$, as well as infrared absorption and reflectance (FTIR) spectra in the range of $650-5000\,cm^{-1}$. It was shown that in the IL phase, as in the IR phase, the MBI molecule remains protonated as the MBI-H^+ cation, and perchloric acid is present as the ClO_4^- anion. Analysis of the FTIR spectra showed that the ionic liquid crystal state is realized in the intermediate phase.

Keywords: ionic liquid, ionic liquid crystal, ionic crystal, Raman spectroscopy, infrared spectroscopy.

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Ionic liquids (ILs) and ionic liquid crystals (ILCs) currently attract significant interest due to their wide range of potential applications [1,2]. In particular, ILs have found important uses in creating organic solvents with low vapor pressure, thermal energy storage devices, supercapacitors, and solar cells. Additionally, organic ionic plastic crystals (IPCs), materials for ammonia production, gas separation, and ionogels are synthesized on the basis of ILs [3]. ILCs, which combine the properties of both ILs and liquid crystals (LCs), are of no less interest and can be used as ion-conducting materials, anisotropic solvents, functional nanostructured materials, and energy storage devices [4]. In this connection, intensive work is underway to search for and study new ILs and ILCs. Various organic and semi-organic compounds are used for their synthesis, in particular, imidazole-based compounds with various organic chains attached [5]. The chain length determines the properties of the IL, particularly the lower temperature at which the IL state is realized.

Recently, in a study by the co-authors of this article, a new semi-organic crystal, 2-methylbenzimidazole perchlorate (MBI·$HClO_4$) was synthesized by combining organic 2-methylbenzimidazole $C_8H_8N_2$ (MBI) and perchloric acid $HClO_4$ [6]. At room temperature, MBI·$HClO_4$ crystallizes in a centrosymmetric lattice with space group $P2_1/n(14)$. The unit cell contains 4 formula units. At this temperature, the ionic crystal (IC) phase is realized, composed of protonated MBI-H^+ molecules and ClO_4^- anions (Fig. 1).

Upon heating, two first-order phase transitions occur in the crystal. The low-temperature phase transition occurs at $T^h_{c2} = 161.3\,^\circ C$ (upon cooling at $T^c_{c2} = 127.7\,^\circ C$), and the high-temperature transition at $T^h_{c1} = 168.4\,^\circ C$ (upon cooling at $T^c_{c1} = 157.8\,^\circ C$) [6]. The high-temperature transition results in the IL state, as evidenced by dielectric measurements. In this state, the low-frequency conductivity is 7 orders of magnitude higher than at room temperature in the IC phase. At the low-temperature transition, the crystal enters an intermediate state, which is also characterized by high conductivity, 2–3 orders of magnitude higher than in the IC state but lower than in the IL state. Dielectric studies of MBI·$HClO_4$ films grown on various substrates showed lower transition temperatures from IC to the intermediate

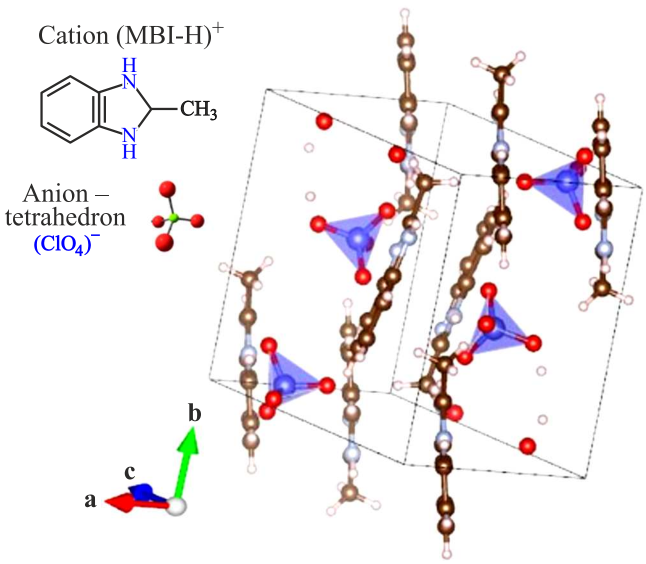

Figure 1. Crystal structure of MBI·$HClO_4$. Left: images of the MBI-H^+ cation and ClO_4^- anion.

phase and to the IL phase. Polarization-optical studies of the films indicated that the intermediate phase exhibits properties characteristic of the liquid crystalline state [7], i.e., the ILC state is realized in this phase. Information about the state of the ions forming the IC, ILC, or IL, particularly their bonds, can be obtained from the frequencies of ionic molecular vibrations, which can be measured using Raman or infrared spectroscopy. The aim of this work was to study molecular vibrations in MBI·$HClO_4$ films grown on sapphire substrates during phase transitions from the IC state to the intermediate phase and to the IL phase.

MBI·$HClO_4$ films with thickness $h \sim 10\,\mu$m were grown on $Al_2O_3(0001)$ substrates by evaporation from an aqueous solution of purified single crystals of MBI·$HClO_4$. The grown films were textured structures with crystallographic planes ($h0h$) oriented parallel to the film surface. Studies of the dielectric properties of films grown on interdigital transducers showed that, as in crystals, two first-order phase transitions are realized, with changes in conductivity at the phase transitions similar to those observed in single crystals [7]. After heating above the transition temperature to the IL state and subsequent cooling, the texture disappeared, and the films had a polycrystalline structure.

Raman scattering spectra in the spectral range $\nu = 80-3300\,\mathrm{cm}^{-1}$ were obtained using a confocal microscope Alpha 300R (Witec, Germany) in backscattering geometry with a diode laser operating at a wavelength of 532 nm. Measurements were performed in the temperature range 295−450 K. The laser beam was focused on the sample to a spot diameter of $\sim 1\,\mu$m, which allowed spectra to be obtained from individual droplets formed during the film transition to the IL state.

Infrared absorption and reflection spectra were measured in the temperature range 295−450 K using an IRPrestige-21 Fourier infrared spectrometer (Shimadzu, Japan) in the range $\nu = 650-5000\,\mathrm{cm}^{-1}$ at temperatures corresponding to the IC phase, intermediate state, and IL phase.

At room temperature in the IC phase, the Raman scattering spectra of MBI·$HClO_4$ single crystals in the studied frequency range consist of a large number of lines associated with molecular vibrations of the protonated MBI-H^+ molecule and ClO_4^- tetrahedra [6]. The interpretation of these lines, based on comparison of Raman spectra in crystals and liquids containing MBI and $HClO_4$, molecules, as well as theoretical works, is given in [6]. Raman scattering spectra measured in MBI·$HClO_4$ films at 90 °C (IC phase) also consist of a set of lines (Fig. 2, *a*), the frequencies of which nearly coincide with those observed in MBI·$HClO_4$ single crystals.

Raman spectra measured at 165 °C after the film transition to the IL state are similar but somewhat differ from the spectra obtained in the IC phase (Fig. 2, *b, c*). The main difference is that in the crystalline phase, 9 lines associated with vibrations of bonds in distorted ClO_4^- tetrahedra are observed, whereas in the IL phase, only 4 lines remain.

The free ClO_4^- ion has T_d symmetry, corresponding to four main vibrations: a non-degenerate symmetric stretching mode ν_1 (A1), a doubly degenerate bending (deformation) mode ν_2 (E), a triply degenerate asymmetric stretching mode ν_3 (F2) and a triply degenerate asymmetric bending mode ν_4 (F2) [8]. In the MBI·$HClO_4$ crystal, the ClO_4 tetrahedron is strongly distorted due to the low positional symmetry $C1$ (Fig. 1). This leads to lifting of the degeneracy of the ν_2, ν_3 and ν_4 (F2) modes in the crystal [6]. The non-degenerate stretching mode ν_1 appears at 933 cm^{-1}; the ν_2 mode at 466 and 458 cm^{-1}; the ν_3 mode at 1122, 925, 909 cm^{-1}; the ν_4 mode at 619, 626, 650 cm^{-1}. Lines corresponding to these modes are also observed in the Raman spectra of films in the IC phase at 90 °C (Fig. 2, *b, c*), both before the transition to the IL state and after cooling from the liquid phase. In the Raman spectrum measured at 165 °C in the IL phase, the number of lines associated with ClO_4^- tetrahedron vibrations decreases. The remaining lines are at $\nu = 934\,\mathrm{cm}^{-1}$ (ν_1), 466 cm^{-1} (ν_2), 1122 cm^{-1} (ν_3), 626 cm^{-1} (ν_4) (Fig. 2, *b, c*). Note that in aqueous solutions of perchloric acid and perchlorate salts, as well as in the MBI·$HClO_4$, melt, lines at $\nu = 934, 462, 1122, 629\,\mathrm{cm}^{-1}$, corresponding to the T_d tetrahedron symmetry are observed [9,10].

The degeneracy of the modes associated with ClO_4^- tetrahedron vibrations in the IL phase indicates that the tetrahedron shape is close to ideal, and the ClO_4^- tetrahedron is very weakly bound to the MBI-H^+cation. This also confirms the conclusion that in the IL phase, the MBI molecule remains protonated, i.e., present as the MBI-H^+ cation, and perchloric acid as the ClO_4^- anion. Unfortunately, observation of Raman spectra in the intermediate state was impossible due to strong luminescence. The luminescence intensity in this phase is approximately two orders of magnitude higher than the Raman scattering intensity. Upon transition from the IL state to the intermediate state and then to the IC phase, the luminescence abruptly appears and disappears.

Unlike Raman spectra, infrared absorption spectra are well measured over the entire studied temperature range (Fig. 3 *a*). As in the case of Raman spectra, the frequencies of FTIR lines measured at room temperature are close to those observed in MBI·$HClO_4$ single crystals [6]. The FTIR spectra contain lines that appear in all phases; upon transition to the IL phase, the frequencies of some lines remain nearly unchanged (660, 820, 895, 1030, 1150, 1220, 1290 cm^{-1}), others slightly increase (1258, 2828, 2880, 2938, 2992, 3080 cm^{-1}) or decrease (754 773, 932, 954, 997 cm^{-1}) (Fig. 3, *a*). The temperature changes in the frequencies of these lines are reversible. Some lines (868, 891, 1001, 1121, 1184, 1946, 3024 cm^{-1}) do not appear in the IL phase. There are also a number of lines whose energies exhibit temperature hysteresis (Fig. 3, *b, d*).

Changes in the frequencies of molecular vibrations upon transition to the liquid state are evidently associated with the breaking of bonds between ions forming the crystalline lattice at low temperature. In the IL state, these ions are in a free state in their most symmetric form. Breaking of interionic bonds can be accompanied by both increases and decreases in the energies of intramolecular bond vibrations.

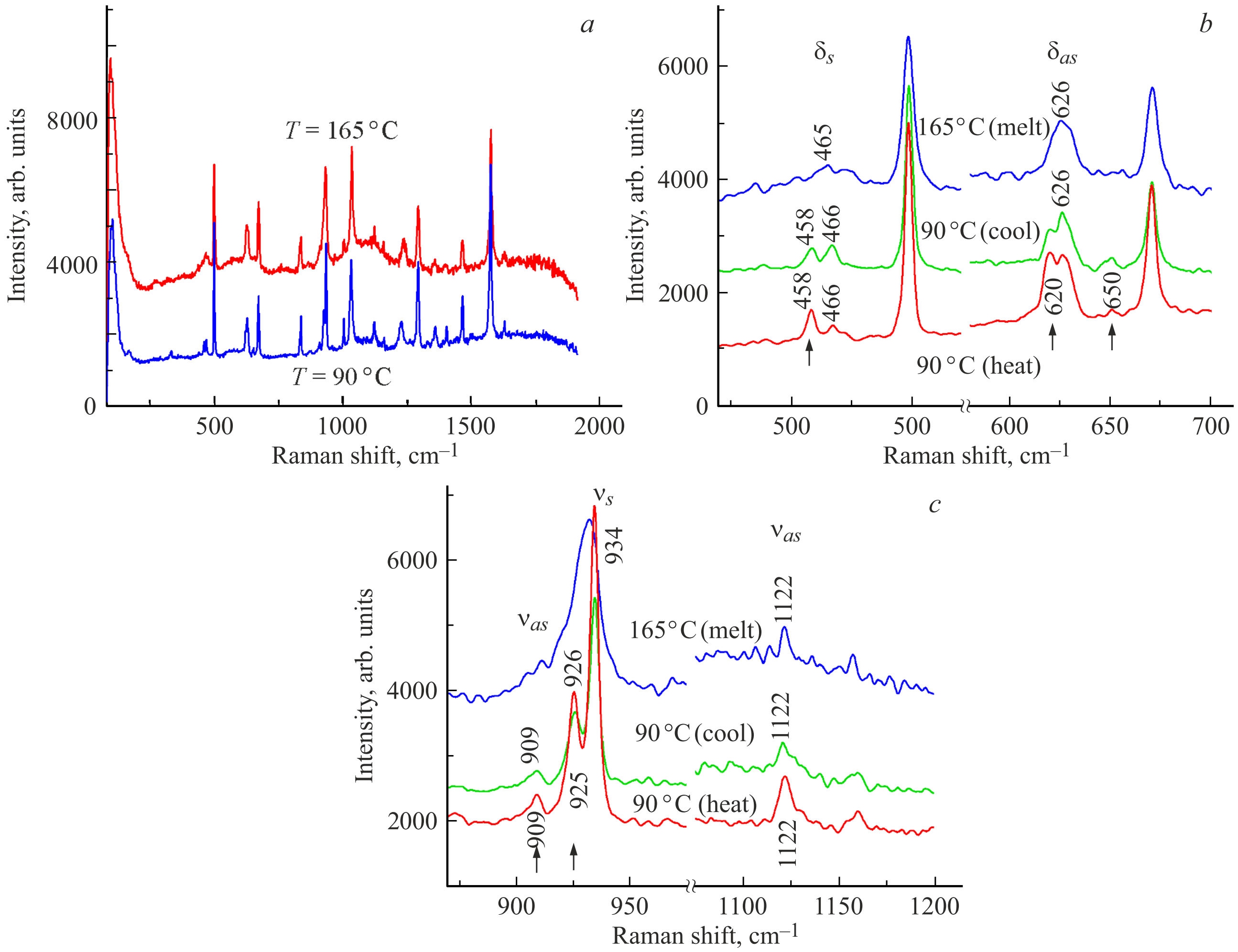

Figure 2. (a) Raman scattering spectra in the MBI·$HClO_4/Al_2O_3$ film in the IC phase ($T = 90\,^\circ C$) and IL phase ($T = 165\,^\circ C$). Raman scattering spectra in the ranges $450-700\,cm^{-1}$ (b) and $900-1200\,cm^{-1}$ (c) at $T = 90\,^\circ C$ after heating from room temperature (IC phase, red lines), at $T = 165\,^\circ C$ (melt, IL phase, blue lines), and at $T = 90\,^\circ C$ after cooling from the melt (IC phase, green lines). δ_s and δ_{as} show bending symmetric (ν_2) and antisymmetric (ν_4) vibrations; ν_s and ν_{as} — show stretching symmetric (ν_1) and antisymmetric (ν_3) vibrations. Arrows indicate lines that disappear in the IL phase.

Lines for which the temperature change from 295 to 450 K and back is accompanied by hysteresis are of particular interest. In the IC state, the frequencies of these modes remain nearly unchanged with increasing temperature. Upon transition to the IL state, the frequencies of these modes increase, and upon cooling—up to the transition to the IC state—they remain the same as in the IL state. The frequencies of these lines in the IC state, intermediate state, and IL state, as well as their interpretation, are given in the table.

The lines exhibiting temperature hysteresis are associated with C–H bond vibrations present in the MBI-H^+ molecule in both the benzene and imidazole rings. The fact that the frequencies of these lines remain nearly unchanged upon transition from the IL phase to the intermediate phase indicates that the cations in the intermediate phase remain free, suggesting the realization of the liquid crystalline state in this phase.

Thus, temperature studies of Raman line frequencies in MBI·$HClO_4$ films in various phases (IC, intermediate phase, IL) showed that the transition to the IL state is accompanied by the ClO_4^- tetrahedra approaching the ideal tetrahedron shape. This is evidenced by the reduction in the number of lines associated with tetrahedron vibrations in the IL phase compared to the IC phase. Observation of lines associated with tetrahedra in the IL confirms the conclusion that both IC and IL are formed by MBI-H^+ cations and ClO_4^- anions. FTIR infrared absorption spectroscopy studies showed that in both the IL phase and the intermediate phase, MBI molecules remain free, indicating the formation of the liquid crystalline state in this phase. This confirms the results obtained earlier using optical polarization spectroscopy.

Additional information about the intermediate state of the films can be obtained using XRD measurements at various temperatures. Luminescence studies observed in the intermediate phase are also planned. Experiments using

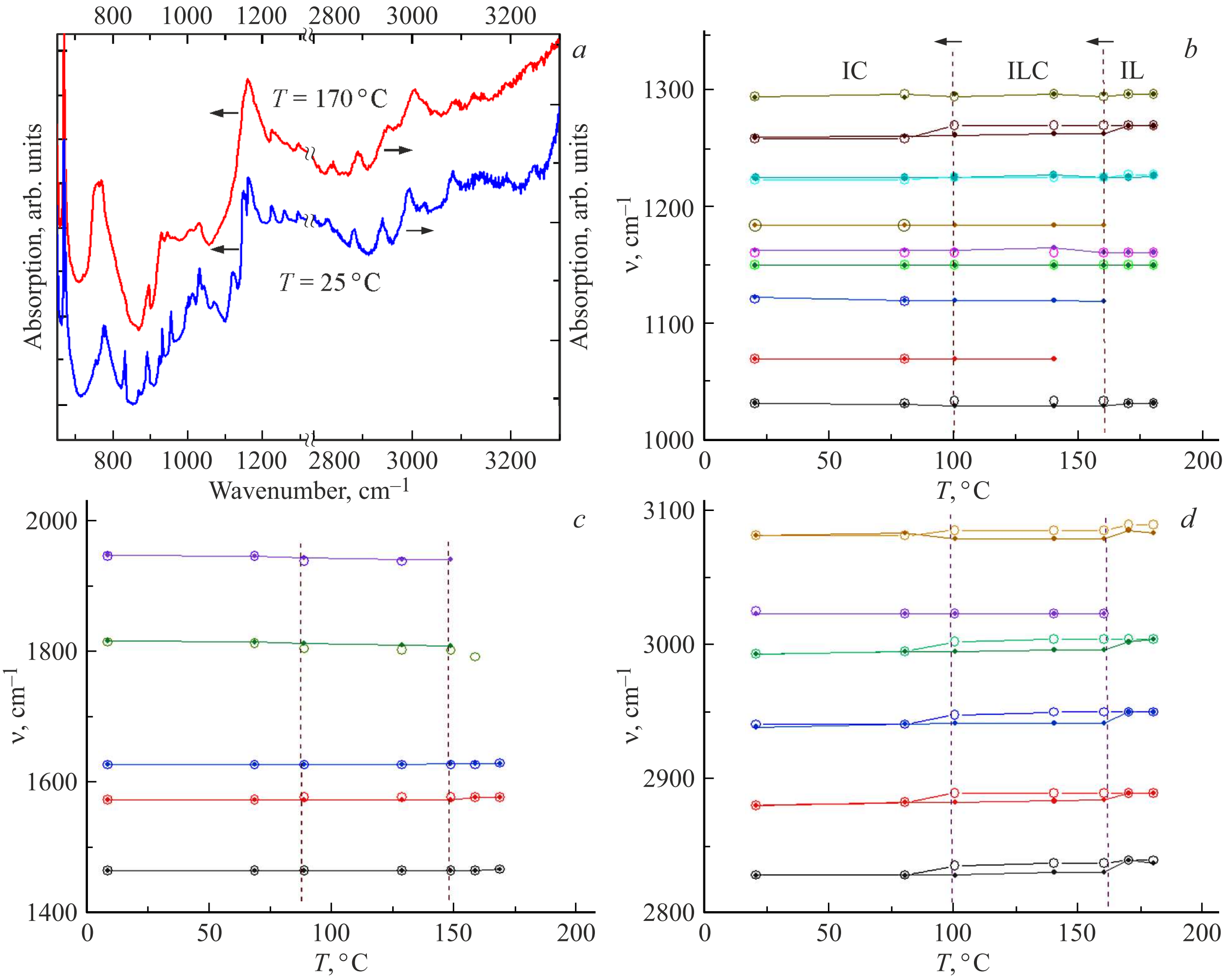

Figure 3. (a) Infrared absorption spectra at $T = 25\,^\circ$C (IC), $179\,^\circ$C (IL) in the spectral ranges 700–1300 cm^{-1} and 2800–3300 cm^{-1}for clarity, the spectra are shifted along the ordinate axis. Temperature dependences of resonant frequencies of FTIR lines appearing in the ranges 1000–1300 cm^{-1} (b), 1300–2000 cm^{-1} (c), 1800–3100 cm^{-1} (d). Filled circles correspond to heating, open to cooling. Dashed vertical lines schematically denote the IL (IL), intermediate phase (ILC), and ionic crystal (IC) regions upon cooling from the IL phase.

Raman and infrared spectroscopy under an applied electric field in the IL phase, when double electric layers form at the metal electrode–IL interface, are of great interest.

Conflict of interest

The authors declare that they have no conflict of interest.

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