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The reason for the revision of conjugated polymers Raman bands attribution

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The bands similar to D and G-bands of carbonaceous materials and bands of conjugated polymers were observed in polyvinyl alcohol (PVA)-iodine complex Raman spectra. It contradicts to their common attribution because PVA has no C=C bonds. Based on this result it is supposed that treatment of *sp*^{2} hybridized carbon structures Raman behavior should be revised.

Keywords: polyvinyl alcohol, PVA-iodine complex, hybrid interpolymeric complexes, conjugated polymers.

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Introduction

There are two main bands named D and G in Raman spectra of carbonaceous materials. G-band usually is observed at 1550−1600 cm^{-1} and attributed to *sp*^{2} hybridized carbon structures, and D-band at 1300−1400 cm^{-1}, is commonly associated with disordered structure [1,2] There are similar two main bands at 1400−1600 and 900−1300 cm^{-1} in conjugated polymers Raman spectra [3–12]. The first band (G-like) is attributed to C=C stretch (probably mixed with C−H) vibration and the second one (D-like) to C−C stretch vibrations. Recently we observed similar bands in polyvinyl alcohol (PVA)−CdS, compound which has no C=C bonds [13]. The idea was put forward that these bands can be attributed to polymeric chain vibrations in vicinity of objects with high anisotropic polarizability like graphite layers, conjugated polymeric chains, SERS (Surface Enhanced Raman Scattering) substrates and so on (SERS-like effect). It was suggested to use this effect for hybrid interpolymeric complex formation verification. This idea was not welcomed by expert community and the effect was suggested to attribute to PVA conversion under exciting radiation. It caused to undertake this additional investigation of PVA-iodine Raman scattering. PVA-iodine is well known hybrid interpolymeric complex with iodine in form of linear polymeric chains: $-(I_3-)_n-$ or $-(I_5-)_n-$ [14–17]. In our study, we have observed Raman spectra of PVA-iodine compounds with different iodine content. Therefore, the aim of this research is the verification of earlier obtained result concerning distinctive features of PVA based hybrid interpolymeric complexes' Raman spectra. It turned out that our result is in contradiction with the existing interpretation of Raman spectra of conjugated polymers and G-band of carbonaceous structures, what is the reason for this interpretation revision.

Experimental

PVA of 16/1 grade, produced by VECTON Co., „analytically pure " I_2, NH_4I and acetone were used for samples preparation.10 wt.%- aqueous solution of PVA was poured in Petry-dish and dried before gelation. Then, I_2-NH_4I water solution was added (3 g I_2 dissolved in 100 ml saturated NH_4I water solution). Excess of the solution was removed after 4 h soaking at room temperature and PVA was dried completely 24 hours at room temperature forming a film. Iodine ratio in this initial sample was determined as 12 wt.%. The aim of this treatment was producing of saturated initial (stoichiometric) PVA-iodine complex apt for stretching (producing of structure oriented specimens). According to the existing concept, PVA-iodine complex represents itself linear iodine chains inside PVA helix. Then, we extracted iodine by soaking of stretched film in 50% water acetone solution 7 days at 277 K. We expected to conserve PVA helix structure as a matrix for further nanostructures producing. The photo of initial, partly and nearly completely deiodinated films is represented at fig. 1. Deiodination predictably leads to increase of films transparency. Deiodonated films are enough transparent to check their stability under excitation.

Raman measurements were carried out with Bruker RFS-100/S spectrometer equipped by 1064 nm excitation source and with Horiba Jobin-Yvon T64000 spectrometer equipped with 514.5 nm laser. In the first case, irradiation power was nearly 25 mW at a sample and spot diameter app. 0.1 mm In the second case, irradiation power nearly 2 mWt was focused at 0.05 mm spot on a sample surface. All spectra were measured at room temperature with resolution 4 cm^{-1}. Registration conditions at room temperature were chosen in such a way as not to cause local heating of the films by laser radiation.

Figure 1. Stretched PVA-iodine (*a*), initial, (*b*) partly and (*c*) nearly completely deiodinated films.

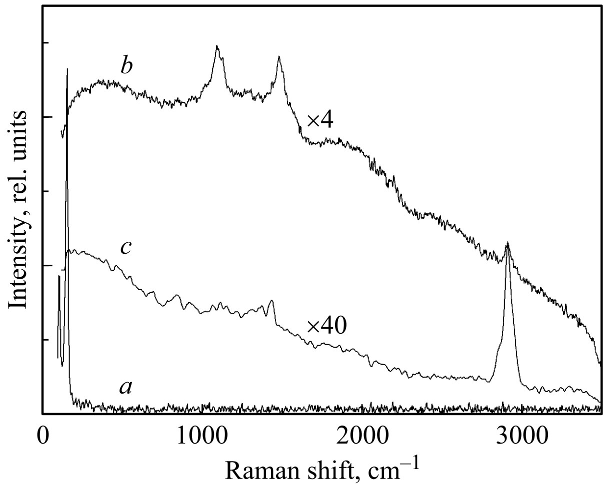

Figure 2. Raman spectra of (*a*), initial PVA-iodine sample, (*b*)partly deiodinated sample and (*c*) nearly completely deiodinated sample when excited at a wavelength of 1064 nm.

Results and discussion

Spectra of PVA-iodine samples are represented in fig. 2 and 3. It was observed that Raman spectrum of initial sample indicates strong narrow lines at 107 and 155 cm^{-1} (at 1064 nm excitation) or at 111 and 165 cm^{-1} (at 514.5 nm excitation) which can be attributed to iodine molecular vibrations. Distinct dependence of Raman spectra from excitation wavelength is indicated. This result is in general accordance with other report of iodine (not with PVA) complexes' Raman spectra [18], where I_3^- vibration was observed in iodine complexes at 111, 165 and 200 cm^{-1} with 413 and 647 nm excitation, However, the dependence of line position on excitation frequency has not previously been reported. It should be emphasized that we observed though shifted but evidently the same (iodine) bands at different excitation wavelengths. There are no PVA's bands observed in the spectrum of initial sample. Raman spectrum of our sample with nearly completely extracted iodine at 1064 nm excitation is quite weak and similar to reported pristine PVA spectra [19,20] (fig. 2). At 514.5 nm excitation Raman spectrum indicates prominent background, residual iodine bands at 111 and 165 cm^{-1}, and absence of PVA's bands (fig. 3, 4). Thus, we can see crucial influence of excitation wavelength on the Raman spectrum which might be attributed to resonance Raman scattering at excitation wavelength near PVA-iodine complex absorption as it was done for other iodine complexes [18]. The most interesting is the Raman spectrum of the sample with partly extracted iodine. It is turned out similar to spectra of different conjugated polymers with typical two bands at 1110 and 1480 cm^{-1} at 1064 nm excitation. PVA 2910 cm^{-1} band is also observed. At 514.5 nm excitation two main bands appear at 1130 and 1515 cm^{-1} (and weak band at 1295 cm^{-1}). Obviously, enhancement of two bands takes place for partly deiodinated sample in comparison with two others (SERS-like effect). Commonly, 1515−1480 cm^{-1} band (analog of carbonaceous materials' G band) could be attributed to C=C bond stretch vibration in conjugated polymers [3–7], but PVA $[-(C_2H_3OH)_n-]$ has no such structures. They can appear as the result of PVA dehydration [20] but there is no reason for such dehydration in our experiment. Therefore, the attribution of conjugated polymers' G-like band to sp^2-hybridized carbon structures vibration becomes questionable.

Raman scattering is quite complicate effect stipulated by influence of atomic vibrations on electronic properties (polarizability) of substance. In our opinion, some effects like SERS and dependence of Raman spectra from excitation wavelength have not exhausting explanation yet. We suppose that the cases of PVA-iodine and similar complexes indicate that treatment of Raman scattering behavior of conjugated polymers is not satisfactory enough. We hope that investigations of PVA complexes should contribute to it better understanding. We suggest two ideas which can help to explain observed effects.

1. High polarizability's anisotropy should be taken into account. The idea has been put forward that oscillations along and across to the direction(s) of preferable polarizability should differently participate in scattering spectrum formation [20]. It is caused by signal increase from transversal modes and suppression from parallel vibrations. This mechanism is similar to field-effect transistor operation having a „channel“ with high conductivity in one direction, which could be, for example, a nanotube [21]. Electric field transversal to the „channel“can modulate electric current flowing through the „channel“what yields amplified signal. In our case PVA's molecular vibrations of the polymer chain produce alternating electric field which can modulate polarization current in inorganic polymer like polyiodine chain, what causes light scattering enhancement for correspondent Raman band with an appropriate frequency shift. Conjugated polymeric chain itself can serve as conducting „channel“. Therefore, similar Raman spectra

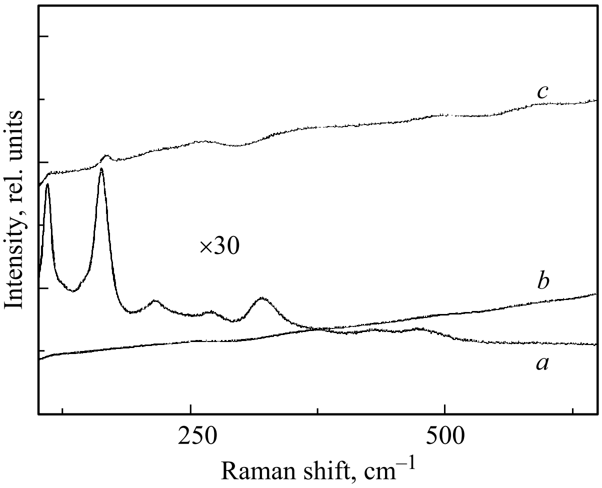

Figure 3. Raman spectra of (*a*), initial PVA-iodine sample, (*b*)partly deiodinated sample and (*c*) nearly completely deiodinated sample when excited at a wavelength of 514.5 nm. Iodine bands region.

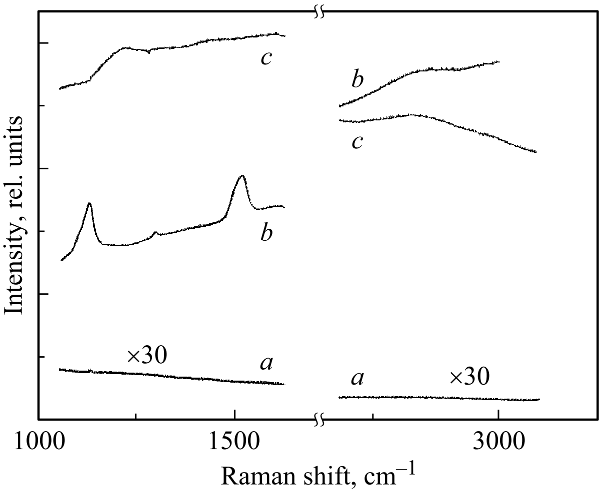

Figure 4. Raman spectra of (*a*), initial PVA-iodine sample, (*b*)partly deiodinated sample and (*c*) nearly completely deiodinated sample when excited at a wavelength of 514.5 nm. PVA bands region.

should be observed for conjugated polymers and hybrid interpolymeric complexes.

2. It can be also proposed that D and G-like bands can be actually treated as manifestations of vibrational-polarization resonances (quasiparticles) taking place at some conditions. This supposition is supported by the observations that: a) there are no clear correspondence between PVA's bands and D and G-like bands of the PVA's complexes; 2) prominent „amplification" of these bands in comparison with genuine PVA bands takes place. Highly polarizing species like carbon layers or intramolecular conjugated bonds or external complexing iodine chains or polymeric CdS or SERS substrates can serve as „amplifiers".

Conclusion

The result of this research indicates that Raman spectra of PVA-iodine complex can not be explained based on common attribution of carbonaceous materials Raman bands. Seemingly, this attribution needs in revision.

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Conflict of interest

The authors declare that they have no conflict of interest.

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