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Application of Sum-Frequency Generation Spectroscopy for the Structural Studies of Polyaniline

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Infrared-visible sum-frequency generation (SFG) vibrational spectra were obtained from the conducting form of polyaniline (PANI), emeraldine salt (ES). Observation of the SFG signal indicated the presence of oriented non-planar structures in ES. It was suggested that the additional resonant enhancement due to the absorption of the visible beam by the polymer film operated in the investigated system. Resonances characteristic to different structural units, benzenoid rings and polarons, were detected in the SFG spectra. The C-C stretching and C-H deformation vibrations of benzenoid rings were detected at 1623 and 1192 cm^{-1}, while the polaronic ν(C~N$^+$) vibrational mode was observed at 1336 cm^{-1}. The stretching vibration of N-H bond was detected at 3273 cm^{-1} in the ssp-polarized SFG spectrum, indicating that the neighboring polymer chains in ES are connected by the N-H•••N interchain bridges.

Keywords: sum frequency generation, SFG, polyaniline, emeraldine salt.

1. INTRODUCTION

Conducting polymer polyaniline (PANI) has been among the most studied polymers, because of its excellent environmental stability [1] and technological importance in the fields of catalysis [2], biosensors [3], batteries [4], and electronic technology [5]. An understanding of the structure of the polymer in the conducting state requires experimental technique sensitive to the organization of polymer at molecular-level. Detailed information on the state and structure of polyaniline backbone might be obtained from vibrational spectroscopic studies.

Among the experimental techniques suitable for such studies, vibrational sum-frequency generation (SFG) spectroscopy seems particularly attractive. SFG emerges in 1987 [6] as the nonlinear interface specific vibrational probe with submonolayer sensitivity. Surface sensitivity and molecular specificity are the major advantages of SFG technique [7]. Surface sensitivity comes from the fact that the nonlinear generation of the sum-frequency signal from the overlapped visible and infrared beams is forbidden in the media of randomly oriented molecules or in the centrosymmetric media, but is allowed at the interfaces where inversion symmetry is necessary broken [7]. Molecular specificity of the technique arises from the possibility to record vibrational spectrum. Intensity of SFG signal enhances resonantly whenever the frequency of infrared or visible beam coincides with vibrational or electronic transition in molecule. Because frequency of the infrared beam is tunable in the wide frequency range the observed resonances correspond to the vibrational spectrum of molecule. Only vibrations those allowed both in the infrared and Raman spectra are monitored by SFG technique [7].

The successful applications of SFG spectroscopy for the analysis of the surfaces of polymers have been recently reported [8 – 12]. In such studies the surface composition and surface structure of biopolymer blends as a function of temperature and bulk blend concentration [8 – 11], and the orientation as well as conformation of alkyl side chains of polyimide [12] were analyzed.

In this manuscript we report the SFG spectra of emeraldine salt (ES). To the best of our knowledge, there was no report regarding the SFG study of polyaniline.

2. EXPERIMENTAL

Aniline has been distilled before use. PI-50-1 model potenciostat, arranged with a PR-8 model programmer was used in the electrochemical experiments. In this work we have used two type of polyaniline samples: (a) electrochemically synthesized, and (b) chemically synthesized. Electrochemical polymerization has been performed by deposition of the polyaniline on the Pt plate (10 × 50 mm) from the 0.5 M H_2SO_4 + 0.05 M aniline solution, at a constant anodic current density of ~ 1.5 mA/cm^2, applied for 5 min. Chemical polymerization has been performed by two steps [13]. It was demonstrated that the process proceeds through the autocatalytic mechanism [13]. First, polymer was deposited on the glass plates (25 × 76 mm) from the 22 mL solution containing 0.5 M H_2SO_4 + 0.05 M aniline + 0.0025 M $K_2Cr_2O_7$ for 1 hour. In the second step, an additional layer was deposited from the newly prepared the same solution for 15 min. After the polymerization the samples were placed in the 1 M HCl solution for 5 min and then dried.

The SFG spectrometer is based on a model-locked PL2143A Nd:YAG laser (EKSPLA Co.) generating 20 ps pulses at 1064 nm with 10 Hz repetition rate. The second harmonic radiation (532 nm) from this laser was used as visible beam. The tunable infrared pulses in the 2.3 – 10 μm range with the energies of 200 – 50 μJ respectively were produced in parametric generator PG401VIR/DFG (EKSPLA Co) by using third harmonic (355 nm) and fundamental radiations of the laser. The bandwidth of infrared beam was 6 cm^{-1}. To produce SFG spectra the

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infrared and visible beams were incident at angles of 53° and 60°, respectively, and overlapped at the sample within an area of 0.4 mm^2. Polyaniline absorbs in the visible spectral range [14 – 16]. In order to avoid complications associated with the sample photodegradation, the energy density of visible beam was kept at ~2 mJ/cm^2. The sum-frequency photons were filtered by holographic noch filter for the 532 nm line (Kaiser Optical Systems, Inc.) and monochromator and detected by a photomultiplier (Hamamatsu, Inc.) tube and gated electronic system. The SFG signal was averaged over 100 pulses for every data point taken at a 3 – 4 cm^{-1} interval. Wavenumber scale was calibrated by polystyrene film. The absolute frequency values are correct within ±2 cm^{-1}.

Raman spectra were recorded using near-infrared FT-Raman spectrometer (Perkin-Elmer, model Spectrum GX) with an excitation wavelength of 1064 nm. The laser beam was focused onto a spot with an area of ~1 mm^2, and the laser power at the sample was set to 300 mW. To reduce photo- and thermoeffects the sample was swung linearly with respect to the laser beam (~20 mm s^{-1}) [17]. No differences, except of lower S/N (signal to noise) ratio, were observed in the spectrum recorded with 30 mW laser power, indicating absence of photo- or thermo degradation effects of the sample. The experiments were carried out in 180° geometry. The instrument resolution was 4 cm^{-1}.

3. RESULTS AND DISCUSSION

Properties of polyaniline films among other factors depend on the preparation conditions [18]. To characterize the studied PANI films in this work we first recorded the resonance Raman (RR) spectrum (Fig. 1).

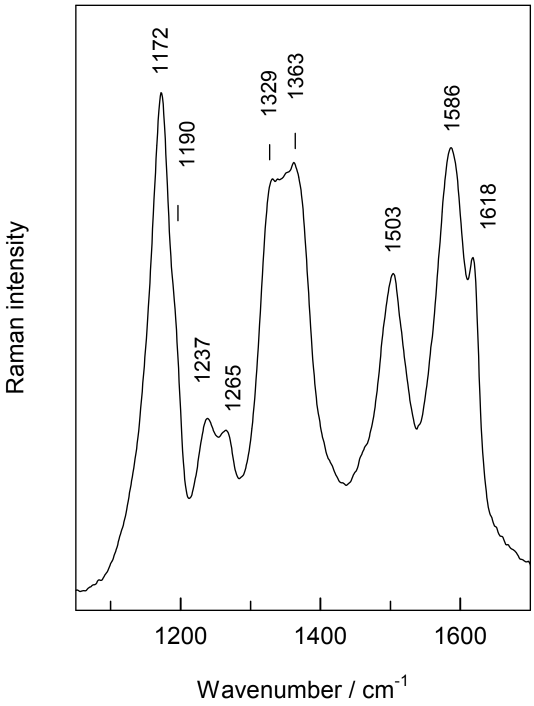

Fig. 1. RR spectrum of ES in the frequency region 1070 – 1700 cm^{-1}. The excitation wavelength is 1064 nm. Laser power at the sample is 300 mW. 200 scans were averaged

The near-IR laser line (1064 nm), used for the excitation of the spectrum, falls into the range of broad absorption band centered at ~1 eV. This band was ascribed to the polaron intraband transition in emeraldine salt [18]. Therefore, near-IR excitation line enhances the intensity of the bands associated with the charge carriers (oxidized protonated units) [15, 19] and provides possibility for detailed structural study of the molecular segments responsible for the conductivity. The main features in the spectrum correspond well with the frequencies reported in the literature [15, 20] for resonant-enhanced vibrations of oxidized units and unambiguously indicate that the studied film indeed resembles to conducting form of polyaniline, emeraldine salt. The most intense bands are associated with the vibrations of oxidized segments. Two intense peaks at 1172 and 1586 cm^{-1} correspond to the semiquinone-like (SQ) ring C-H in-plane bending and C-C stretching vibrations, respectively [15, 20]. Presence of the benzenoid rings in the emeraldine salt is evident from the low intensity and narrow peak at 1618 cm^{-1} due to the C-C stretching vibration. The corresponding C-H in-plane bending mode of benzenoid rings was seen as the shoulder at ~1190 cm^{-1}. The prominent peak at 1503 cm^{-1} we assigned to the ν(C=N) mode highly coupled with the ν(C-C) (*19a* according to the Wilson's notation of aromatic species modes) vibration as was proposed in the ref [21]. In the 1300 – 1400 cm^{-1} region, broad and intense feature (digitally decomposed in two Lorentzian-Gaussian components at 1329 and 1363 cm^{-1}) was observed. This spectral range is particularly interesting because comprises the stretching vibrations of charged nitrogen segments, ν(C~N^+), and provides information on the delocalization of the charge in the polymer chain [22 – 24]. Two ν(C~N^+) bands in the frequency range 1300 – 1400 cm^{-1} can be correlated with differently organized polarons. The lower frequency ν(C~N^+) band at 1329 cm^{-1} corresponds to the vibration of polaronic sites where C~N (CN bond intermediate between the single and double bonds) bond order is lowered and indicates the presence of more delocalized polarons. While, the higher frequency counterparent at 1363 cm^{-1} is associated with the more localized polaronic sites. The C~N bond order and ν(C~N^+) frequency increases upon charge localization due to the creation of bipolaronic-like structures. Finally, the low intensity doublet at 1237 and 1265 cm^{-1} was assigned to the N-benzene ring stretching and benzene ring deformation vibrations, respectively.

The SFG spectra from the chemically synthesized ES on glass substrate obtained with different polarization combinations (ssp and sps) in reflection geometry are displayed in Fig. 2. The most intense band in the ssp-spectrum at 1623 cm^{-1} was assigned to the in-plane C-C stretching vibration of the benzenoid rings. The clearly resolved peak at 1192 cm^{-1} was attributed to the in-plane C-H deformation vibration of the benzenoid rings. The shoulder at 1585 cm^{-1} was assigned to the stretching C-C vibration of SQ rings. The corresponding band was intense in the RR spectrum (Fig. 1). The low intensity resonance at 1481 cm^{-1} we tentatively attributed to the ν(C=N) vibration. Vibrations of charged polaronic sites can be clearly recognized from the broad 1336 cm^{-1} resonance

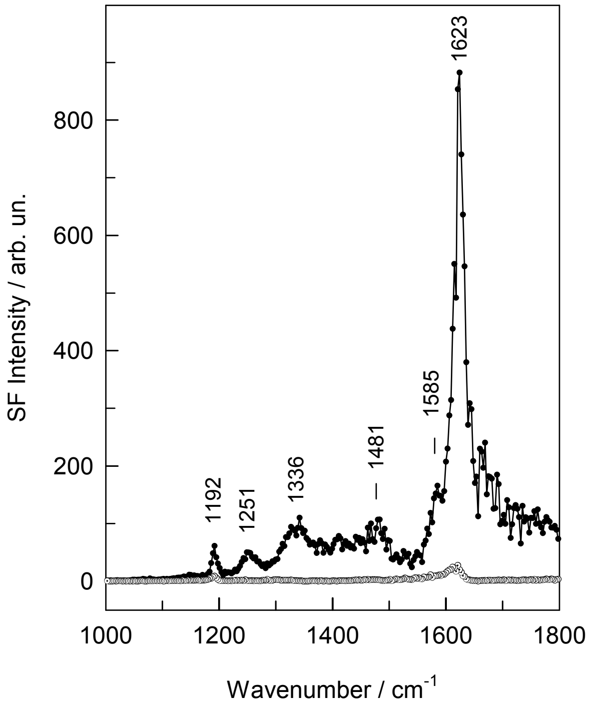

Fig. 2. Sum-frequency vibrational spectra in the middle frequency range (1000-1800 cm^{-1}) from the ES taken with two polarization combinations: (●●●) ssp (s-polarization for SF output, s-for visible input, p-for infrared input) and (○○○) sps

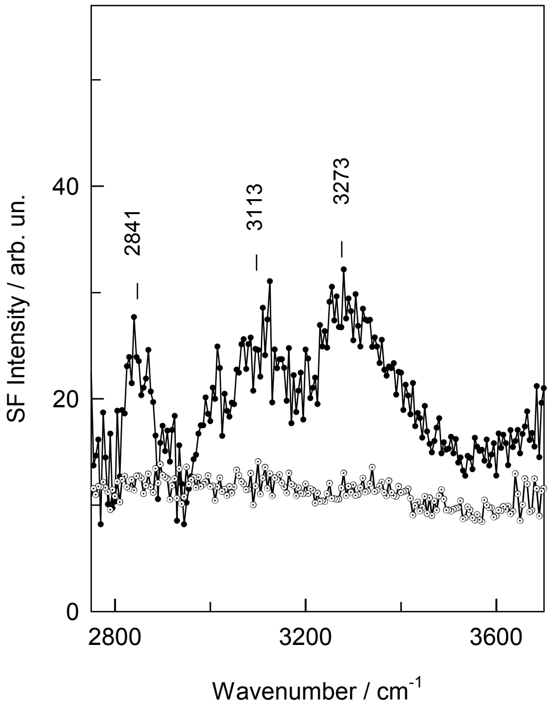

Fig. 3. Sum-frequency vibrational spectra in the high frequency range (2750 – 3700 cm^{-1}) from the ES taken with two polarization combinations: (●●●) ssp (s-polarization for SF output, s-for visible input, p-for infrared input) and (○○○) sps

due to the stretching ν(C~N$^+$) motion. The low intensity resonance at 1251 cm^{-1} we assigned to the N-benzene ring stretching vibration ν(C-N). It should be noted, that similar SFG spectra were obtained from electrochemically synthesized ES films on Pt. Although, relative intensities of the resonances were slightly different.

Comparison of SFG spectra obtained with different polarizations is useful in determining the average orientation of vibrating groups [12, 25]. In the ssp-spectrum the most intense resonances are associated with the vibrational modes with high value of perpendicular to surface transition dipole moment component. Thus ssp polarization probes only the vibrational modes normal to surface. On the other hand, vibrational modes with parallel dipole moment components to the surface are present in the sps-spectrum [12, 25]. As can be seen from Fig. 2, intensity of the SFG spectrum from ES obtained with sps polarization combinations decreases considerably. This observation indicates that the polymer chain segments responsible for the intense ssp spectrum are preferentially oriented perpendicularly with respect to surface.

Fig. 3 displays the SFG spectra from electrochemically synthesized ES on Pt substrate in the high frequency range (2750 – 3700 cm^{-1}) obtained with different polarization combinations**.** As can be seen intensity of SF resonances are considerably weaker in the high frequency range as compared with the middle frequency region. The broad peak centered at 3273 cm^{-1} we have assigned to the stretching vibration of N-H bonds. It is well known that frequency of the ν(N-H) mode is sensitive to the strength of hydrogen bonding [20, 26, 27]. For example, unbounded N-H groups of model compound BBB (N,N'-Diphenyl-1,4-benzenediamine, $C_6H_5NHC_6H_4NHC_6H_5$), dissolved in CCl_4 was observed at 3429 cm^{-1} [20]. In the solid state, formation of H-bonds resulted in the downshift of this mode by 44 cm^{-1} [20]. Observed ν(N-H) mode in SFG spectrum at 3273 cm^{-1} indicates that the neighboring chains, responsible for the SF signal, are connected by the N-H•••N interchain bridges.

Observation of intense SFG signal from the ES in 1000 – 1800 cm^{-1} spectral range provides insights into the structure of the polymeric chains. The selection rules for SFG spectroscopy require the vibrational mode to be both infrared and Raman active [7]. Assuming that polymeric chains are planar and infinite, the benzenoid rings are centrosymmetric. Sum frequency cannot be generated in such planar structures. Experimental observation of SFG signal implies that the structure of polymer is non-planar. The origin of the non-planarity most likely is associated with the rotation of the benzenoid rings around the C-N bond. The loss of inversion center might be associated also with the presence of defect sites, polarons, responsible for the conductivity of the polymer. Support for the last assumption comes from the second harmonic generation (SHG) studies of the polyaniline. Aktsipetrov et al. [29, 30] detected considerable increase in the SHG signal intensity in the vicinity of the insulator-to-metal transition.

The another conclusion comes from the analysis of the SFG signal intensity in ssp-polarized spectra. Comparison with intensity of stretching vibrations of methyl group of sodium dodecyl sulphate at the interface water/air revealed enhancement of the SFG signal from the ES roughly by 20 – 100 times. This indicates that additional resonant enhancement due to the absorption of visible beam by the polymer operates in the case of ES. Possibility of such double-resonant infrared-visible sum-frequency generation spectroscopy was recently demonstrated by Rasche et al. [31].

4. CONCLUSIONS

We have studied the structure of the conducting form of polyaniline, emeraldine salt, by the non-linear infrared-visible sum-frequency generation technique. Intense ssp-polarized SFG spectrum in the 1000 – 1800 cm^{-1} frequency region from the ES was observed for the first time.

It was suggested that the additional signal enhancement comes from the resonance of visible beam with the electronic transition in the polymer.

Because SFG is forbidden in centrosymmetric or randomly oriented media, the observation of SFG spectra indicates the deformation of the polymeric chains from the centrosymmetric geometry. It was suggested that the rotation of benzenoid rings around the C-N bond and the presence of charged defects, polarons, are responsible for the structural transformations in the ES.

Characteristic stretching and in-plane deformation vibrations of benzenoid rings were observed in the SFG spectra at 1623 and 1192 cm^{-1}, respectively. The stretching vibration of C~N (CN bond intermediate between the single and double bonds) bond was detected at 1336 cm^{-1}.

Considerably lower intensity SFG resonances were observed in the high frequency region (2750 – 3700 cm^{-1}). Based on the stretching N-H bond vibrational frequency, detected at 3273 cm^{-1}, it was concluded that the neighboring chains in the polymer are connected by the N-H•••N interchain bridges.

Presented data show that SFG spectroscopy opens the new and sensitive approach for studies of structural defects and non-planarity of polyaniline backbone.

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