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Heat capacity and phonon dispersion in polyselenophene in relation to the spectra of oligoselenophenes

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ABSTRACT

Normal modes and their dispersion have been obtained for polyselenophene (PSe) in the reduced zone scheme using Wilson's GF matrix method as modified by Higg's for an infinite polymeric chain. The Urey Bradley potential field is obtained by least square fitting to the observed infrared and Raman bands. The results thus obtained agree well with the experimental IR and Raman values. The characteristic features of dispersion curves such as repulsion and exchange of character, crossing, van Hove type singularities have been discussed and possible explanation has been given. Heat capacity has been calculated *via* density-of-states using Debye relation in the temperature range 0–450 K. Possible explanation for the inflexion region in the heat capacity variation is given. The spectra of the oligomers are checked with the finite–infinite spectral relationship and are found to be in agreement.

1. Introduction

Conducting polymers are a relatively new class of materials, which have gained increasing interest in recent years due to their reasonable price, facile large-scale synthesis, solution processability, and tunable properties [1]. Several polymers have been tested and found suitable in a variety of electronic devices including vapor sensors, electronic and photonic transistors, electrochromic devices, conductive adhesives, inks, photovoltaic cells, supercapacitors, batteries and nanoscale lasers [2–4]. They are attractive for sensor applications because they can directly convert the binding event into an electrical signal [5–7]. Development of nanowires of conducting polymers is a step toward device miniaturization [8,9]. These devices would be suitable to introduce built-in computers in space suits, with associated sensors to monitor the health of astronauts while they perform extra-vehicular activities. Due to the biocompatibility of some conducting polymers they may be used to transport small electrical signals, through the body, i.e. act as artificial nerves [10].

Polyselenophene (PSe) is an important member of conducting polymer family built from group VI five membered aromatic heterocycles having non-linear optical responses [11]. Polythiophene (PTh) is the most widely studied conjugated polymer. Its close Se analog polyselenophene has received a significant attention in recent years. It has been reported [12,13] that Se plays an important role in living organisms and that Se containing proteins are found to be components of various enzymes. The organic superconductors obtained from Se containing charge transfer complexes and the radical ion salts have led to a new promising Se chemistry. Research is being carried out to find new promising selenium-containing compounds for these purposes, and their structures are being studied [13,14]. Polyselenophenes exhibit some advantages [15] due to special nature of Se atom and selenophene and may even be superior to polythiophenes for some applications (i) improved interchain charge transfer due to intermolecular Se–Se interactions, (ii) lower oxidation and reduction potentials of polyselenophenes, (iii) polyselenophenes should have greater polarizability as compared to polythiophenes, (iv) due to the larger size of the Se atom, polyselenophenes should be able to accommodate more charge upon doping than polythiophenes, and (v) polyselenophenes should have a lower band gap than polythiophenes, resulting in opto electronic properties different from those of polythiophenes.

Polyselenophene has a rather low electrical conductivity (10^{-4}–10^{-3} S cm^{-1}) [16], as compared with polythiophene which is enhanced by doping [17]. However, the low conductivity observation is not supported by computational studies [18]. Considering the stronger conjugation in polyselenophene as compared to polythiophene and the intermolecular Se–Se interactions in bulk form, the conductivity of polyselenophene is expected to be of the same order of magnitude or even higher than that of polythiophene

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[18]. Polyselenophenes have excellent electrochromic properties [15]. They are highly transparent and have high contrast ratio and coloration efficiency. The UV–vis absorption spectrum of chemically synthesized polyselenophene film on glass coated with indium tin oxide (ITO) exhibits a λ_{max} at 440 nm [19]. The optical band gap of polyselenophene is 2.0 eV, which is nearly the same as that of polythiophene [20]. Oligo and polyselenophenes in the neutral undoped state are more difficult to twist is of fundamental importance to their development, since more substituents can be introduced onto their backbones than onto those of their thiophene analogs without distorting conjugate ion [18,21].

Vibrational spectroscopy is widely used to study structural and dynamic aspects of various molecular systems. FTIR spectroscopy is a major technique for investigating polymer sample in terms of composition as well as constituents' distribution. Apart from different chemical distributions in the sample, the spectroscopist is also able to visualize areas with different degree of crystallinity or preferred orientation and by these means ensures reliable data about the quality of the investigated sample, manufacturing process, etc. Raman spectroscopy is a nondestructive analytical technique and is complementary in nature to infrared spectroscopy. This can provide information from functional groups with vibration modes that are weak or unresolvable by FTIR. In general, the IR absorption, Raman spectra from polymeric systems are very complex and cannot be unraveled without the full knowledge of dispersion curves. One cannot appreciate the origin of both, symmetry dependent and symmetry independent spectral features without the knowledge of dispersion curves. The dispersion curves also facilitate correlation of the microscopic behavior of the long chain molecule with the macroscopic properties such as entropy, enthalpy, specific heat, etc. In continuation of our work on normal coordinate analysis and phonon dispersion in a variety of polymers in different conformations [22–25], we present here a complete normal mode analysis of PSe with phonon dispersion in the reduced Brillouin zone scheme using the Urey–Bradley force field (UBFF) [26].

Polyselenophene has been studied by Hasoon et al. [27] using IR and Raman spectroscopy. They have proposed the assignments on the basis of group theoretical species, an identification which ignores potential energy distribution completely. Their assignments are both incomplete and are based purely on symmetry. Ramirez et al. [28] have reported limited studies on the vibrational spectrum of PSe. Their study is focused on the dynamical and spectroscopic properties of the oligomers of selenophene $(Se)_n$ by semiemperical PM3 method. They have proposed the vibrational assignments for the in plane modes of the polymer. The force field used by them for a polymeric system is the same as that used for a tetramer in gas phase. By all logic long chain interactions are completely ignored. This is going to be an underestimate and hence needs a re-evaluation. Moreover their study is confined to zone center frequencies but in practice, there are absorption bands beyond the zone center. A study of the dispersion profile in the entire zone is necessary for thermodynamic behavior. We are not intending to underrate the importance of the work of previous authors. Our efforts are to fill in their gaps. We have analyzed the dispersive behavior of polyselenophene, including the van Hove type singularities [29], which give rise to additional absorption bands in turn affecting the thermodynamic behavior. The evaluation of normal modes and their dispersion has been taken to logical conclusion by calculating the heat capacity as a function of temperature. A satisfactory match and interpretation of the corresponding modes of vibration in oligomers [30] from the profile of dispersion curves of polymer provides reasonable justification of the structural similarity in the oligomeric and the polymeric forms. To the best of our knowledge such detailed studies leading to correlation between the microscopic behavior and macroscopic properties of this polymer have not yet been reported.

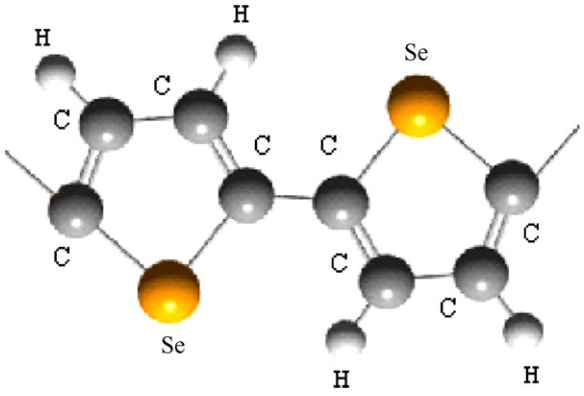

Fig. 1. One chemical repeat unit of PSe.

2. Theory

2.1. Calculation of normal mode frequencies

Normal mode calculations for an isolated polymeric chain have been carried out using Wilson's GF matrix method [31] as modified by Higg's [32] for an infinite chain. The vibrational secular equation to be solved is

$$|G(\delta)F(\delta) - \lambda(\delta)I| = 0 \qquad 0 \le \delta \le \pi \tag{1}$$

where δ is the phase difference between the modes of adjacent chemical units, the G (δ) matrix is derived in terms of internal coordinates, with its inverse being the kinetic energy, and the F (δ) matrix is based on the Urey–Bradley Force field.

The frequencies ν_i (δ) (in cm^{-1}) are related to the eigen values λ_i (δ) by

$$\lambda_i(\delta) = 4\pi^2 c^2 \nu_i^2(\delta). \tag{2}$$

A plot of ν_i (δ) versus δ gives the dispersion curve for the ith mode.

2.2. Calculation of heat capacity

Dispersion curves can be used to calculate the specific heat of a system. For a one-dimensional system the density of state function or the frequency distribution function expresses the way energy is distributed among the various branches of normal modes in the crystal. It is calculated from the relation

$$g(\nu) = \sum \left[\left(\frac{\partial \nu_j}{\partial \delta} \right)^{-1} \right]_{\nu j(\delta)=\nu j} \tag{3}$$

The sum is over all the branches j. If we consider a solid as an assembly of harmonic oscillators, the frequency distribution $g(\nu)$ is equivalent to a partition function. The constant volume heat capacity can be calculated using Debye's relation

$$C_\nu = \sum g(\nu_j) k N_A \left(\frac{h\nu_j}{kT} \right)^2 \left[\frac{\exp(h\nu_j/kT)}{\{\exp(h\nu_j/kT) - 1\}^2} \right] \tag{4}$$

with $\int g(\nu_i) d\nu_i = 1$.

3. Results and discussion

3.1. Geometric structure

One chemical repeat unit of PSe is shown in Fig. 1. The geometry of the oligomers of selenophene was optimized upto 8Se at DFT level using B3LYP/6-31G with Gaussian 03 program [33]. The