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Phonon dispersion and heat capacity in polyfuran

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ABSTRACT

A study of the normal modes of vibration and their dispersion in polyfuran (Pfu) based on the Urey–Bradley force field is reported. It provides a detailed interpretation of IR and Raman spectra. Characteristic features of dispersion curves such as regions of high density-of-states, repulsion and character mixing of dispersive modes are discussed. Predictive values of heat capacity as a function of temperature are calculated.

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1. Introduction

Among the electrically conducting polymers, those from the five-membered heterocyclic compounds have attracted a great deal of attention because in addition to moderate electrical conductivity, they also show interesting properties such as electrochemical activity, stability and electrochromism [1–3].

Lopez and Hernandez, in a recent publication [4], have reported the vibrational dynamics of polyfuran (Fig. 1), including the dispersion of normal modes. However, their work suffers from several infirmities. They used the MNDO method and it is well known that the force constants obtained by the MNDO method are an over estimate of the real force constants, especially diagonal stretch terms [4]. The crowding of non dispersive modes is not reflected in the IR/Raman spectra. Similarly, the absence of regions of high density-of-states appears responsible for missing some of the spectral lines and these are not reported anywhere.

The structure of polyfuran has been reported as planar [5]. On the basis of this study and molecular modeling, we have taken planar geometry. A large number of studies have reported on polyfuran; for example, photo-excited IR spectrum [6], resonance Raman and FTIR spectra [7], electro synthesized Raman spectra [8], electronic structure [9], synthesis [10], etc. None of the studies on polyfuran except that reported by Hernandez and Lopez [4] contains dispersion curves. However, their study does not have a logical end by not evaluating thermodynamic parameters such as heat capacity. Further, the MNDO based force constants used by these authors take into account only limited interactions. Some of the important ones (torsional and nonbonded interactions) have been ignored.

In general the IR absorption, Raman spectra & Inelastic Neutron Scattering from polymeric systems are very complex and cannot be unraveled without the full knowledge of dispersion curves. Dispersion curves also give information on the extent of coupling along the chain and dependence of the frequency of a given mode upon the sequence length of ordered conformation. Thus the study of phonon dispersion in polymeric systems continues to be of topical importance.

In the present work we report a complete normal mode analysis of polyfuran using Urey–Bradley force field, phonon dispersion and heat capacity obtained via the density-of-states derived from dispersion curves. The experimental data of IR and Raman spectroscopic studies reported by previous authors [4] have been used. For assignment of modes band energy, band width, band shape, and P.E.D. scattering from similar molecule placed in similar environment have been used.

2. Theoretical approach

2.1. Normal mode calculation

The calculation of normal mode frequencies has been carried out according to the well-known Wilson's GF [11] matrix method as modified by Higgs [12]. It consists of writing the inverse kinetic energy matrix G and the potential energy matrix F in terms of internal coordinates. In the case of an infinite isolated helical polymer, there are an infinite number of internal coordinate that lead to G and F matrices of infinite order. Due to the screw symmetry of the

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Table 1
Internal coordinates and force constants (md A^{-1}).

Int. coord. stretches	Force constant value	Int. coord. in-plane bendings	Force constant value		Int. coord. out-of-plane bend	Force constant value
			Bonded	Nonbonded		
ν(C—C)	5.10	ϕ(C—C=C)	0.60	0.22	ω(CH)	0.06
ν(C=C)	5.40	ϕ(C=C—O)	0.40	0.22	τ(—C=C—)	0.001
ν(C—H)	5.13	ϕ(C=C—H)	0.34	0.21	τ(—C—C—)	0.001
ν(C—O)	3.40	ϕ(H—C—C)	0.22	0.19	τ(—C—O—)	0.001
		ϕ(C—O—C)	0.32	0.20		
		ϕ(C—C—O)	0.32	0.23		

polymer, a transformation similar to that given by Born and Von Karman can be performed that reduces the infinite problem to finite dimensions [13]. The vibrational secular equation, which gives normal mode frequencies and their dispersion as a function of phase angle, has the form:

$$IG(\delta)F(\delta) - \lambda(\delta)I = 0, \quad 0 \le \delta \le \pi \tag{1}$$

The vibrational frequencies $\nu(\delta)$ (in cm^{-1}) are related to the eigen values $\lambda(\delta)$ by the following relation:

$$\lambda(\delta) = 4\pi^2 c^2 \nu^2(\delta) \tag{2}$$

2.2. Calculation of specific heat

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

$$g(\nu) = \sum_j \left(\frac{\partial \nu_j}{\partial \delta}\right)^{-1} \Bigg|_{\nu j(\delta)=\nu} \tag{3}$$

with $\int g(\nu_j) d\nu j = 1$

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

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

The constant volume heat capacity C_v, given by equation is converted into constant pressure heat capacity C_p using the Nernst–Lindemann approximation [14,15].

$$C_p - C_v = 3RA_o \left(\frac{C_p^2 T}{C_v T_m{}^\circ}\right) \tag{5}$$

where A_o is a constant often of a universal value [3.9×10^{-9} (kmol/J)] and $T_m{}^\circ$ is the equilibrium melting temperature.

3. Results and discussion

The structure of polyfuran has been determined by using the Molecular modeling technique. Software used for this purpose is CS-Chemdraw. It consists of calculating the interatomic distances of atoms over all ranges of the dihedral angles which are of interest. One then selects a set of contact distances for the various kinds of atoms which are fully allowed and another which are considered as minimal. The fully allowed contact distances result in fully allowed regions of conformational space. In other words, the minimal contact distances result in limiting the region of conformational space. Thus all unfavorable steric overlaps are excluded from consideration. A planar conformation for polyfuran has been reported by McConnell et al. [5]. On the basis of this study and molecular modeling we have accepted planar geometry.

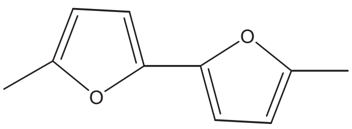

Fig. 1. Chemical repeat unit of polyfuran.

3.1. Vibrational modes

The number of atoms per residue in polyfuran is fourteen and hence there would be $14 \times 3 - 4 = 38$ normal modes of vibrations. The vibrational frequencies have been calculated for values of δ varying from 0 to π in steps of 0.05π. The optically active modes are those for which $\delta = 0, \pi, 2\pi$. The four zero frequencies at $\delta = 0$ correspond to acoustic modes, three representing translations along the three axes and the fourth one is rotation around the chain axis.

The assignments have been made on the basis of potential energy distribution, band position, band shape, band intensity and absorption/scattering in similar molecules having groups placed in similar environments. The Urey–Bradley force constants were initially transferred from the earlier work on molecules having similar groups and were further refined by using the least-square method as described earlier [16]. Final set of force constants for polyfuran are given in Table 1. Except for a couple of frequencies, most of the frequencies are better fitted within less than 1%. As mentioned earlier, the modes corresponding to $\delta = 0.0$ are both Raman and IR active. Therefore, the calculated frequencies are first fitted to the observed frequencies for this phase value. All vibrational modes along with their potential energy distribution are given in Tables 2 and 3 at $\delta = 0.0$ and $\delta = 1.0$, respectively.

The (C—H) stretching vibrations have been calculated in the neighbourhood of 3155 cm^{-1} showing a good agreement with the observed band at 3158 cm^{-1}. In our calculation, four frequencies have been calculated corresponding to (C=C) stretching with contribution of other modes at 1589, 1550, 1462 and 1398 cm^{-1} and they are assigned in the Raman spectra at 1597 and 1550 cm^{-1} and IR at 1472 and 1398 cm^{-1}, respectively. The frequencies calculated at 1292 and 1353 cm^{-1} are mainly due to (C—O) stretching in combination with contribution from (C—C) stretching. The frequency calculated at 1292 cm^{-1} is assigned to the observed frequency in Raman spectrum at 1283 cm^{-1}. Since no other frequency is observed either in Raman or IR, the frequency observed at 1353 cm^{-1} has been assigned another value at 1357 cm^{-1} calculated by ab initio method.

The assignments made by us agree with those made by others [4], except in a few cases as shown in Tables 2 and 3.

3.2. Dispersion curves

The dispersion curves below 1600 cm^{-1} are shown in Figs. 2(a) and 3(a). The modes above 1600 cm^{-1} are either

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