Asian Journal of Chemistry Vol. 3, No. 2 (1991), 232–235

NOTES

NORMAL COORDINATE ANALYSIS OF POLYVINYLIDENE FLUORIDE AND ASSIGNMENTS OF RAMAN AND INFRARED BANDS

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The laser Raman spectra of the two forms of polyvinylidene fluoride have been recorded on a Cary model 82 grating spectrophotometer. The infrared and far infrared spectra have also been recorded on Perkin-Elmer IR 781 and Polytech FIR 30 spectrophotometers respectively. The vibrational analysis has been carried out assuming C_{2v} symmetry for form I and C_s symmetry for form II.

The normal coordinate calculations of poly (vinylidene fluoride) was earlier reported by Boerio *et al*[1] and Kobayashi *et al*[2]. They carried out these calculations employing valence field, with two preferred conformations. (i) a planar (all-*trans*) zig zag conformation representation called as form I. (ii) TGTG' conformation associated with form II. In the present investigation the laser and the infrared spectra have been recorded and the vibrational analysis has been carried out employing general quadratic valence force field. The vibrational assignment has been further verified through normal coordinate calculations.

The two forms of poly (vinylidene fluoride) were obtained from M/S Aldrich Chemicals, USA and used as such. The laser Raman spectrum of two forms have been recorded on a Cary model 82 grating spectrophotometer using 488 nm line of Ar^+ for excitation in the region 50-4000 cm^{-1} and using a 4W argon laser.

The values of bond length and bond angles are assumed from Sutton Table[3]. Internal coordinates for the out-of-plane vibrations are defined as recommended by IUPAC. The general quadratic valence force field is adopted for both inplane and out-of-plane vibrations. The initial set of force constants have been transferred from polyethylene[4] for methylene group and from polytetrafluoroethylene[5] for the difluoromethylene group. The normal coordinate calculations have been performed using the program given by Schachtschneider[6].

The observed frequencies along with their relative intensities are presented in Tables 1 and 2. The isolated chain for the planar zig zag model is isomorphous to the point group C_{2v}. The optically active fourteen fundamental modes are distributed as:

$$= 5A_1 + 3B_1 + 2A_2 + 4B_2$$

All the modes are active in both Raman and infrared but A_2 mode is infrared inactive. For TGTG' model the isolated chain is isomorphous with point group C_s. It contains two chemical repeat units per translational repeat unit. The 32 optically active modes split between A′ and A″ The A′ modes vibrate in phase in the two monomer units whereas A″ modes vibrate out-of-phase.

The bands around 3000 cm^{-1} are assigned to C-H stretching vibrations. In line with the above conclusion the bands at 3015 cm^{-1} and 2990 cm^{-1} are assigned to C–H asymmetric and symmetric stretching respectively in form I. Similarly the bands at 3025 cm^{-1} and 2980 cm^{-1} are assigned to C–H asymmetric and symmetric stretching respectively in form II. The above assignments are in good agreement with the values reported by Bellamy[7]. The CH_2 twisting modes are assigned to the bands at 985 cm^{-1} in form I and 974 cm^{-1} in form II. The bands at 1441 cm^{-1} in form I and 1435 cm^{-1} in form II are assigned to CH_2 bending modes. (Table 1 and 2)

TABLE 1

OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION FOR PLANAR POLY (VINYLIDENE FLUORIDE) FORM I

Species	Observed frequency and Intensity		Calculated frequency	Description/PED%
	Infrared	Raman		
A_1	2990vw	2982s	2992	CH_2 symmetric stretching (94)
A_1	1441w	1443s	1445	CH_2 bending (91)
A_1	1187s	1182s	1180	CF_2 symmetric stretching (77)
A_1	884s	889s	886	CF_2 symmetric stretching (80)
A_1	502s	507m	512	CF_2 bending (72)
A_2		985w	992	CH_2 twisting (86)
A_2		260m	269	CF_2 twisting (91)
B_1	1407s	1398w	1403	CH_2 wagging (90)
B_1	1065m	1061m	1067	C–C stretching (85)
B_1	474s	482w	484	CF_2 wagging (89)
B_2	3015vw	3020vs	3025	CF_2 asymmetric stretching (85)
B_2	1270s	1259w	1264	CF_2 asymmetric stretching (81)
B_2	842s	844vs	849	CH_2 rocking (94)
B_2	494w	496w	490	CF_2 rocking (94)

vs = very strong; s = strong; m= medium; w = weak; vw = very weak

Rao *et al*[8] assigned the bands in the region 1100-1300 cm^{-1} to C-F stretching vibrations. In accordance with their assignments the bands at 1187 cm^{-1} and 1270 cm^{-1} in form I are assigned to CF_2 symmetric and asymmetric stretching respectively. Similar in form II the bands at 1294 and 1247 cm^{-1} are assigned to CF_2 asymmetric stretching and the bands at 1170 and 1147 cm^{-1} are assigned to CF_2 symmetric stretchhing respectively. The CF_2 bending vibrations are assigned to the bands at 507 cm^{-1} and 516 cm^{-1} in form I and in form II respectively. The bands at 260 cm^{-1} in form I and 283 cm^{-1} in form II are assigned to CF_2 twisting vibrations. The CF_2 rocking and CF_2 twisting vibrations are given in the Tables 1 and 2. The values are in good agreement with literature values[9,10].

TABLE 2
OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION FOR TGTG′ POLY (VINYLIDENE FLUORIDE) FORM II

Species	Observed frequency and Intensity		Calculated frequency	Description/PED%
	Infrared	Raman		
A′	3025w	3023w	3020	CH_2 asymmetric stretching (95)
	3001w	2989w	2995	CH_2 stretching (87)
	1435m		1432	CH_2 bending (79)
	1407s	1403m	1405	CH_2 scissoring (82)
		1294m	1293	CF_2 asymmetric stretching (76)
	1149s			CF_2 symmetric stretching (80)
	1065m	1071w	1073	C–C stretching (88)
		974m	970	CH_2 twisting (72)
	874m		878	CF_2 symmetric stretching (84)
	841s	846s	849	CH_2 rocking (80)
	615m	617m	612	CF_2 wagging (74)
		483w		CF_2 rocking (71)
	413w	411m	417	C–C–F bending (67)
	283w		289	CF_2 twisting (81)
	214m		219	C–C–F bending (65)
		67m	63	C–C torsion (84)
A″	3015w	3010vw	3012	CH_2 asymmetric stretching (94)
	2980w		2985	CH_2 stretching (83)
	1424m	1429m	1421	CH_2 scissoring (77)
	1380s		1376	CH_2 wagging (70)
		1250m	1247	CF_2 asymmetric stretching (81)
	1170s	1174s	1173	CF_2 symmetric stretching (77)
	1065m	1064m	1061	C–C stretching (73)
	944m		942	CH_2 rocking (70)
	901s	904m	907	C–C stretching (67)
		811Vs	814	CH_2 rocking (66)
	757w	753w	754	C–C–C bending (69)
		516m	513	CF_2 bending (73)
	407m		411	C–C–F bending (75)
	379w	365m	371	CF_2 wagging (61)
	270w	278vw	273	C–C–F bending (78)
		113w	110	C–C torsion (79)

vs = very strong; s = strong; m= medium; w = weak; vw = very weak

The C-C skeletal stretching vibrations are assigned to the bands at 1065 cm^{-1} in form I and 1071 cm^{-1} in form II. The assignments are in good agreement with Piseri *et al*[11].

ACKNOWLEDGEMENT

One of the authors (ARP) expresses his thanks to CSIR New Delhi for the award of a Senior Research Fellowship which enabled him to pursue this investigation.

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[Received: 6 April 1990; Accepted: 12 July 1990] AJC–175