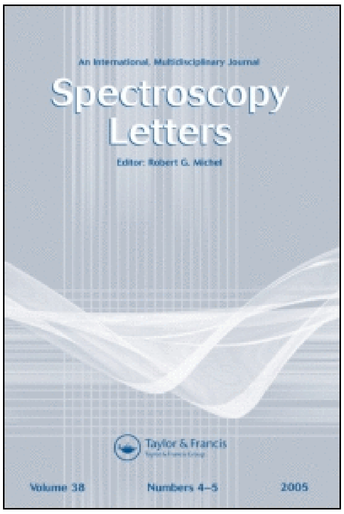

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Raman Spectrum of Crystalline Polyethylene at 15K

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To cite this Article Butler, Ian S. and Neppel, Anton(1983) 'Raman Spectrum of Crystalline Polyethylene at 15K', Spectroscopy Letters, 16: 6, 419 — 423
To link to this Article: DOI: 10.1080/00387018308062360
URL: http://dx.doi.org/10.1080/00387018308062360

SPECTROSCOPY LETTERS, 16(6), 419-423 (1983)

RAMAN SPECTRUM OF CRYSTALLINE POLYETHYLENE AT 15K

Key Words: polyethylene, Raman spectroscopy,
correlation splitting

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INTRODUCTION

Polyethylene, $-(CH_2-CH_2)_n-$, is one of the simplest polymers known and its ir and Raman spectra have been extensively studied over the past 25 years. In its crystalline state, at ambient temperature, the polymer has a primitive orthorhombic lattice (Pnma, D_{2h}^{16}) with two molecular chains per Bravais unit cell[2]. There is evidence that the vibrations of these neighbouring chains interact because correlation splitting has been observed at 77K for most of the ir-active fundamentals[3-5] However, while similar splittings have been detected for a few bands in the Raman[1,6], it is clear that the data are far from complete. Several of the Raman fundamentals reported as single peaks ought theoretically to be split into doublets under high enough resolution, and moreover, these splittings should be more easily

0038-7010/83/1606-0419$3.50/0

TABLE 1

Vibrational Spectra of Crystalline Polyethylene (cm^{-1})

Ir (77K)[a]	Raman (15K)[b]	Assignment	
2917		b_{2u}, b_{3u}	$\nu_a(CH_2)$
2848		b_{2u}, b_{3u}	
	2883[c]	a_g	
	2881[c]	b_{1g}	
	2846	a_g, b_{1g}	$\nu_s(CH_2)$
1475		b_{3u}	$\delta(CH_2)$
1460		b_{2u}	
	1466	b_{1g}	$\delta(CH_2)$ overtones and Fermi resonance
	1453[a]	a_g	
	1442	a_g, b_{1g}	
	1415	a_g	
	1371	b_{2g}, b_{3g}	wag(CH_2)
	1296	b_{3g}	twist(CH_2)
	1293	b_{2g}	
1174		b_{1u}	wag(CH_2)
	1173[d]	b_{1g}	rock(CH_2)
	1171[d]	a_g	
	1133	a_g, b_{1g}	ν_s(C-C)
	1064	b_{2g}	ν_a(C-C)
	1062.5	b_{3g}	
1050		b_{1u}	twist(CH_2)
733		b_{3u}	rock(CH_2)
721.5		b_{2u}	
	137	b_{1g}	rotation about chain axis
	110	a_g	
110		b_{2u}	translation of chain
72		b_{3u}	

discerned at very low temperatures. With this in mind, we have now examined the Raman spectrum of highly-crystalline polyethylene at 15K and we present the results here.

RESULTS AND DISCUSSION

A group theoretical analysis for crystalline polyethylene yields the following for one repeat unit on the basis of D_{2h} symmetry:[7,8]

$$\Gamma^{vib}_{gen} = 3a_g + a_u + 2b_{1g} + b_{1u} + 2b_{2g} + 2b_{2u} + b_{3g} + 2b_{3u}$$

Taking into account the complete interaction of one molecular chain with the other in the Bravais unit cell affords the following irreducible representations:

$$\Gamma^{vib}_{int(cryst)} = 5a_g + 5b_{1g} + 3b_{2g} + 3b_{3g} + 2a_u + 2b_{1u} + 4b_{2u} + 4b_{3u}$$

Footnotes to Table 1

[a] Data for an oriented sample, ref. 1.

[b] Measured on a Jarrell-Ash model 25-300 spectrometer using 488.0-nm argon-ion laser excitation (∿200 mW at sample). The polyethylene sample studied was Fortiflex RS-187 (Soltex Polymer Corp., Houston, Texas, U.S.A.); the powdery flakes were sealed in a Pyrex capillary tube. The various spectral regions were studied under high-resolution conditions (0.75-1.00 cm^{-1} slit widths) and the low temperature was achieved using a Cryogenic Technology Inc. model 21 variable-temperature cryostat (±0.1K).

[c] Calculated splitting at room temperature (2904 - 2899 = 5.0 cm^{-1}), ref. 9.

[d] Calculated splitting at 77K (1177.3 - 1174.3 = 3.0 cm^{-1}), ref. 6.

$$\Gamma^{vib}_{ext(cryst)} = a_g + b_{1g} + b_{2u} + b_{3u}$$

$$\Gamma_{acoustic} = b_{1u} + b_{2u} + b_{3u}$$

In actual fact, every active fundamental of the isolated chain is predicted to split into a doublet in the spectra of the crystal except for the b_{1u} modes. The complete correlation diagram is available in ref. 8: a_g and b_{1g} modes should split into $a_g + b_{1g}$ components, b_{2g} and b_{3g} into $b_{2g} + b_{3g}$ components, a_u and b_{1u} into $a_u + b_{1u}$ components, and b_{2u} and b_{3u} into $b_{2u} + b_{3u}$ components. As in the case of the isolated chain, the rule of mutual exclusion holds and all "g" modes are Raman active, whereas all "u" modes, with the exception of a_u, are ir active.

Infrared data have been published for crystalline polyethylene at 77K and these are given in Table 1 together with our Raman data obtained at 15K. The vibrational assignments shown are those currently accepted in the literature[1]. Our Raman band positions are very similar to those recorded earlier at 77K[1,6], except that more of the bands are split into doublets in accord with the group theoretical predictions for correlation splitting. There is no evidence for a phase change and the observed splittings (1.5 - 3.0 cm^{-1}) are in excellent agreement with those calculated earlier[6,9]. Our results show that crystalline polyethylene behaves almost precisely as expected in view of its orthorhombic crystal lattice and the data provide an excellent example of a factor group analysis for a polymer.

ACKNOWLEDGMENTS

This research was supported by funds from the Natural Sciences and Engineering Research Council of Canada and the Government of Quebec. We thank Drs. E.A. Vogelfanger and M.D. Baker (Soltex Polymer Corp.) for donating the polyethylene sample and A.N. acknowledges the Social Sciences and Humanities Research Council of Canada for the award of a graduate scholarship.

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Received: March 8, 1983
Accepted: March 29, 1983