Laser-excited Raman Spectra of Stretched Polyethylene Fibres

By P. J. HENDRA*
(*Department of Chemistry, University of Southampton*)
and H. A. WILLIS
[*Imperial Chemical Industries Limited* (*Plastics Division*), *Welwyn Garden City, Herts.*]

RECENTLY it has been demonstrated that it is possible to record useful Raman spectra of coloured, turbid, and even fluorescent materials with the helium–neon laser as a radiation source.[1] This development has been found particularly useful for measuring the spectra of polymers in the solid state, and data have been obtained recently on polypropene[2] and polyoxymethylene[3] which are either unique, or much superior to those previously reported.

Further, it has proved possible to obtain data on polarizability tensors, bond angles, and the assignment of spectral features to vibrational modes by examining the spectra of single crystals oriented in a number of senses in relation to the strongly polarised exciting radiation of the laser Raman spectrometer.[4] Thus, an obvious development is to examine oriented samples (*e.g.* drawn fibre or film) of partially crystalline polymers. Recently we reported data on oriented polypropene fibre and film.[5] Although there was agreement between the sense of the dichroism for the infrared and Raman measurements for most of the bands, there were some anomalies for which no explanation could be offered. Hence, it seemed worthwhile to examine a simpler system, and we report here on the Raman spectra of highly oriented fibres of linear polyethylene (1·8 methyl groups per 1000 carbon atoms). The fibres, of about 0·25 mm. diameter, and of draw ratio 10 : 1, were examined as a tight bundle about 5 mm. in diameter. The radiation in the Cary 81 laser Raman spectrometer is polarised with the electric vector vertical; thus, when the fibre bundle was held with its axis vertical against the plane surface of the hemispherical collection lens of the instrument, the electric vector of the radiation was parallel to the fibre axes. Two other spectra of the sample were obtained, *viz.* with the fibre axes horizontal, but oriented either at right angles, or parallel to the direction of propagation of the radiation. The spectra produced are shown in the Figure. Because the polyethylene molecules are aligned substantially along the fibre axes, but there is no preferred arrangement in other directions, the fibres may be regarded as having cylindrical symmetry. In the first experiment, parallel modes of vibration should be activated preferentially, while in the other two experiments bands due to the perpendicular modes should appear more strongly. Indeed, the latter two spectra are extremely similar, as expected.

In the Table are listed the Raman frequency shifts ($\Delta\nu$ cm.$^{-1}$), the relative intensities of the bands in the three experiments, the sense of the dichroism in relation to the molecular axis, and the assignments previously suggested by Schachtschneider and Snyder.[6]

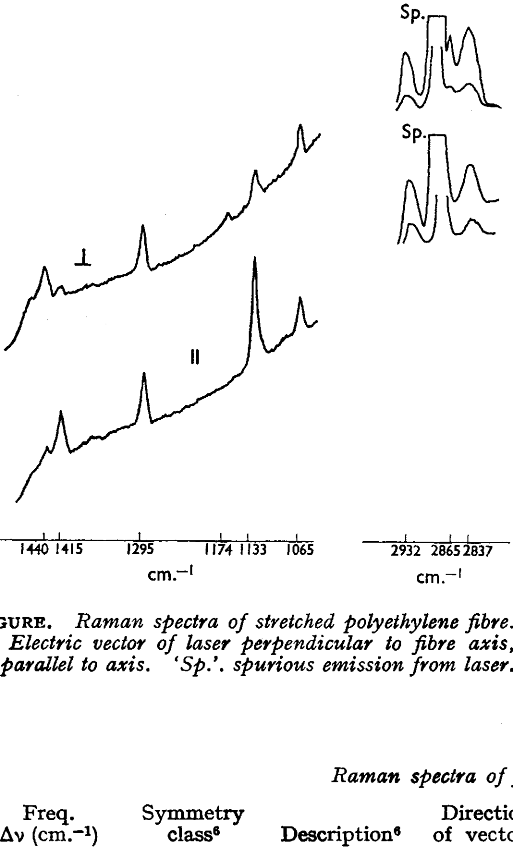

FIGURE. *Raman spectra of stretched polyethylene fibre. '⊥' Electric vector of laser perpendicular to fibre axis, '||' parallel to axis. 'Sp.'. spurious emission from laser.*

It is convenient to consult an article by Krimm[7] containing graphical representations of the vibrational modes of a polyethylene chain. Unfortunately, Krimm's description of the modes is not identical with that used in ref. 6 and so his definitions are included in the Table for reference purposes. It is clear that the A_g and B_{1g} class modes have vectors across the molecular axis and B_{2g} species have their motions centred along this axis. The lone B_{3g} class mode involves twisting of the CH_2 group relative to the skeletal chain. Although both the symmetric (A_g) and asymmetric (B_{1g}) C–H stretching modes are expected to be perpendicular, the dichroism of the former should be much greater. Indeed, the perpendicular dichroism of the A_g mode is found to be high, *i.e.* it has a maximum intensity when the electric vector of the radiation is oriented across the fibre axis. The dichroism of the B_{1g} mode may well be obscured by the imperfect orientation of the specimen. The bands at 1440, 1415, and 1174 cm.$^{-1}$ have the expected dichroism. The B_{3g} class twisting mode at 1295 cm.$^{-1}$ shows no dichroism, and a consideration of the molecular motion involved suggests that this is reasonable.

Turning now to the two lowest frequency modes, the skeletal vibrations of the A_g and B_{2g} classes, the dichroism of the line at 1133 cm.$^{-1}$ is the reverse of that expected. It is interesting to note that although the assignment of Schachtschneider and Snyder[6] is widely accepted and

TABLE

Raman spectra of fibres of polyethylene

Freq. $\Delta\nu$ (cm.$^{-1}$)	Symmetry class[6]	Description[6]	Direction of vectors[7]	Relative intensity of Raman Bands			Description (ref. 7)
				Fibres horizontal	Fibres vertical	Along fibres	
1456	—	—	—	3	0	1	—
1440	A_g	CH_2 bend	⊥ to axis	12	3	13	$\delta\ (A_g)$
1415	B_{2g}	CH_2 wag.	‖	2	15	2	$\nu_w(B_{1g})$
1295	B_{3g}	CH_2 twist	Twist	17	17	17	$\nu_t(B_{2g})$
1174	B_{1g}	CH_2 wag.	⊥ to axis	2	0	2	$\nu_R(B_{3g})$
1133	A_g	ν_{C-C} skel.	⊥	11	40	12	$\nu_+(0)(A_g)$
1065	B_{2g}	ν_{C-C} skel.	‖	12	12	12	$\nu_+(\ddot{u})(B_{1g})$
2932	B_{1g}	CH_2 asym. stretch	⊥	20	20	—	$\nu_a(B_{3g})$
2865	A_g	CH_2 sym. stretch	⊥	10	Small	—	$\nu_s(A_g)$

Assignment due to Schachtschneider and Snyder.[6]

supported by that due to Tasumi *et al.*,[8] a number of authors have suggested that the B_{2g} class skeletal vibration exceeds in frequency that of the A_g mode.[9] Our results tend to favour this latter conclusion.

It is worth emphasising that this new technique was applied to samples where polarized infrared radiation would have been valueless, *viz.* fibres of large diameter from a resin of high molecular symmetry. As is so often the case, Raman spectroscopy is proved complimentary to absorption measurements.

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