Laser-Raman Spectrum of Polyethylene under High Pressure

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Summary Correlation splitting due to pressure in the laser-Raman spectrum of polyethylene has been observed at room temperature; anisotropic studies on the doublet components are discussed.

THE vibrational spectrum of crystalline polyethylene consists of the vibrational modes of the molecule considered in isolation (line-group modes) modified in symmetry and energy by the fact that two chains traverse the unit cell (space-group modes). This complication arises because each fundamental of each chain can vibrate either in-phase or out-of-phase with its neighbour in the unit cell, and results in 'correlation' (or 'Davydov') splitting. This situation is well understood both theoretically and experimentally and the subject has been reviewed recently.[1]

In the Raman spectrum, a number of bands has been shown to have close doublet character[2] at low temperatures, whilst the broad complex bands near 1440 and 2900 cm^{-1} are sensitive in profile to temperature and are thought to arise from modes affected by both 'correlation' effects and Fermi resonance.

In principle another method of observing correlation effects is to pressurise the sample, but to date the technique does not seem to have been applied extensively to polymers.[3] It should lead to the computation of force fields associated with the interchain forces, because it is simple in principle to determine the compressibility of the material, and one should be able to record Raman spectra over a range of pressures.

In this communication we report the effect of high pressure applied to polyethylene specimens of high crystallinity.

Two samples of polyethylene, a small pellet of high crystallinity (unoriented) material and a piece of rolled sheet (*ca.* 3 × 2 × 2 mm, rolled 3:1) were studied in a steel high-pressure cell. The cell had sapphire windows set at 90°, a collection aperture of *ca.* *f*/8 and was designed to be pressurised with water from a hydraulic system at pressures of up to 2·5 kbar. Raman spectra were recorded on a Cary 82 spectrometer powered by a Model 165 Spectra Physics Argon ion laser.

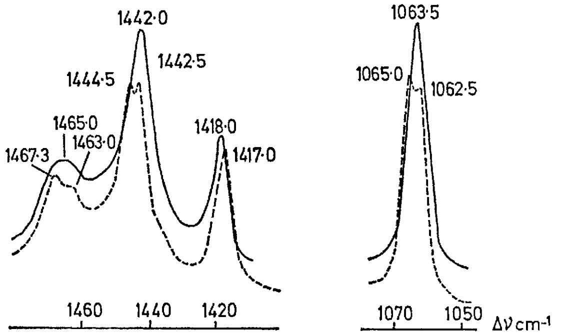

FIGURE. *Spectrum at atmospheric pressure*——; *at* 2 kbar ----.

An example of the effect of a pressure of 2 kbar on the Raman spectrum of un-oriented polyethylene is shown in the Figure. For a comparison with the effect of lowering the temperature of polyethylene see reference 2.

The effects of applied pressure on the non-oriented specimen can be summarised as follows:—

(*a*) The general appearance of the spectrum is not altered, thus, it is unlikely that a change in crystalline from of the specimen has occurred. If a modification to the paraffinic crystalline form containing one chain per unit cell had occurred, then the band system near $\Delta\nu$ 1440 cm^{-1} would have become a simple doublet and the band at $\Delta\nu$ 1418 cm^{-1} would have disappeared.[5]

(*b*) The band at 1063·5 cm^{-1} splits into a doublet at 1062·5 and 1065·0 cm^{-1}. The splitting appears to be somewhat less than 1 cm^{-1} kbar^{-1}.

(*c*) The complex set of bands at 1418, 1442, and 1465 cm^{-1} change in profile and frequency.

(*d*) The prominent bands at 1296 and 1129 cm^{-1} do not alter significantly with pressure except that in the latter case the frequency rises slightly.

If we then consider the oriented specimen under pressure and arrange polarisations and directions of illumination and view to give us two spectra, one of geometry X(ZZ)Y in the Porto nomenclature[1,4] [molecular axis Z] and the other X(ZX)Y [X and Y are not distinguished in this case, hence the second spectrum arises from changes in $(\alpha_{ZX} + \alpha_{ZY} + \alpha_{XZ} + \alpha_{YZ})$], we find clear indications of anisotropy dissimilar from that of the specimen at atmospheric pressure. For example, the doublet near 1063 cm^{-1} has characteristics 1065·2 and 1062·5, both bands being observed in the second orientation only. The $\Delta\nu$ 1063 cm^{-1} band observed at atmospheric pressure is thought[6] to arise from a b_{2g} class skeletal mode whilst in the crystal this has two forms of B_{2g} and B_{3g} symmetry. The observation of a clear doublet in the X(ZX)Y experiment under pressure seems to confirm that this assignment is correct.

The band system near 1440 cm^{-1} shows anisotropy in agreement with our earlier suggestion[1] that the feature at $\Delta\nu$ 1418 cm^{-1} and a contribution to the broad shoulder near 1455 cm^{-1} are due to A_g components.

Thus, we demonstrate that the application of pressure has a somewhat similar effect to that of lowering the temperature on the Raman spectrum of polyethylene. The technique is more versatile in studying interchain forces because anisotropic measurements can be made (cooling makes most polymers very turbid) and pressure can be varied at will over a large range. We hope shortly to be able to report results at higher pressures.

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[1] P. J. Hendra, M. J. Gall, C. J. Peacock, M. E. A. Cudby, and H. A. Willis, *Spectrochim. Acta*, 1972, **38A**, 1485.

[2] J. L. Koenig and F. J. Boerio, *J. Chem. Phys.*, 1970, **52**, 3425.

[3] Nicol verbally announced at the recent 3rd International Conference on Raman Spectroscopy (Rheims, September 1972) that he had succeeded in recording a Raman spectrum of polyethylene under very high pressure.

[4] For a full explanation of anisotropic scattering see T. R. Gilson and P. J. Hendra, 'Laser-Raman Spectroscopy,' Wiley, London, 1970.

[5] R. G. Snyder, *J. Mol. Spec.*, 1969, **31**, 464.

[6] Reference 1 and references therein.