

Some comments on the analysis of vibrational bands in strained polymers: polyethylene

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The Raman intensities of strained polyethylene (PE) chains are studied theoretically using quantum mechanical *ab initio* methods and subsequently discussed in conjunction with previously reported experimental Raman data on high-modulus PE fibres. The relevance of accounting for strain-dependent intensities is emphasized.

(Keywords: vibrational bands; strained polymers; PE)

INTRODUCTION

Vibrational spectroscopy has been known for a long time as a very useful tool in the study of polymers, enabling the study of quantities such as configuration, conformation, chemical composition and orientation¹. In recent years the study of strained polymers has been particularly focused on high-modulus fibres that exhibit relatively large frequency shifts. The use of micro-Raman spectroscopy in this field has been recently reviewed². Monofilaments of ultra-oriented high-modulus polyethylene (PE) fibres have been thoroughly investigated by experimental Raman spectroscopy^{3–10}. Some typical Raman spectra of high-modulus PE fibres in the C–C stretching range are shown in *Figure 1*. The asymmetric C–C stretching band is found near 1060 cm^{–1}, whereas the 1130 cm^{–1} band is the symmetric C–C stretching band. In relation to the mechanical experiment, the strongly shifted bands have been interpreted^{3–10} as coming from C–C stretching vibrations in the load-bearing fraction of the material, whereas the slightly shifted band originates from almost non-strained polymer chain segments. The experimentally observed shifts of Raman bands as a function of strain increase with increasing modulus of the PE fibre. In these Raman studies it has been assumed that the relative proportions of high load bearing C–C bonds and low load bearing C–C bonds could be obtained by taking the ratio of the corresponding Raman band areas. This was further substantiated by checking the polarization characteristics of these bands; the polarization ratio was found to be the same for both bands within experimental accuracy⁶.

However, this observation does not preclude a dependence of the Raman intensity upon the straining. In this paper we will therefore present quantum mechanically calculated Raman frequencies and intensities which will be interpreted along with the experimentally observed frequency shifts and intensities.

COMPUTATIONAL DETAILS

As a model for the PE chain, we chose n-octane. The size of this molecule still allows for *ab initio* calculation of the vibrational frequencies and intensities with acceptable computational effort. All calculations were performed with the Gaussian 90 suite of programs¹¹. The geometry of n-octane was fully optimized within *C*_{2h} symmetry using the 6-31G* basis set. Geometries were optimized until individual gradients were less than 2×10^{-4} hartree bohr^{–1} and the root mean force was less than 5×10^{-6} hartree bohr^{–1}. Thereafter we performed a force constant calculation to obtain the vibrational frequencies and the corresponding infra-red and Raman intensities.

To model the strained n-octane molecule we constrained the distance between the two terminal carbon atoms at a 10% larger value than was obtained for the optimized zero-strain *C*_{2h} structure. With this distance fixed, we performed a new optimization (within *C*_{2h} symmetry) followed by a force constant calculation.

RESULTS AND DISCUSSION

Calculated Raman frequencies and intensities

All *ab initio* calculations were carried out at the Hartree–Fock level. It is known that *ab initio* calculations at this level tend to yield frequencies which are

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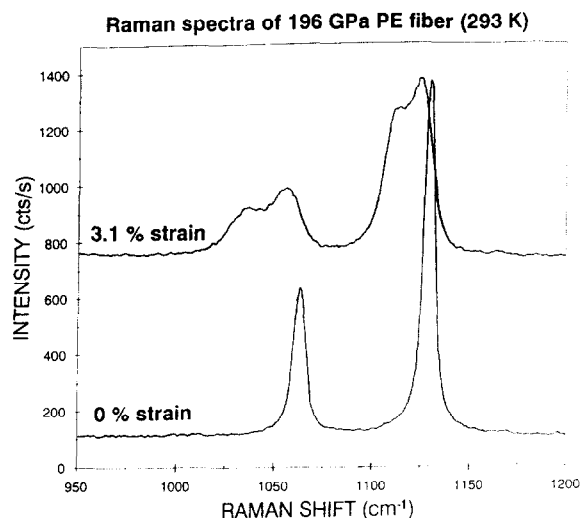


Figure 1 C–C stretching regions of the Raman spectra of a 196 GPa polyethylene fibre recorded at 293 K and strains of 0% and 3.1% (spectrum recorded approximately 8 min after applying strain). The spectra have been shifted along the intensity axis for clarity (reproduced from Van Eijk *et al.*⁶)

usually off by 10–20% (calculated frequencies are too large). But even when one improves on the accuracy of the absolute frequencies, still a larger uncertainty exists regarding *ab initio* calculated intensities. Because the comparison we are after, i.e. a comparison between experimental and calculated intensity changes upon straining the PE chains, has not been reported before, the theoretical part of the present study should be seen as a first qualitative investigation into the subject from which we intend to derive trends in frequencies and intensities that appear upon straining the PE chains.

We first discuss the frequencies. Calculated frequencies and intensities for both the zero-strain and the 10%-strained n-octane molecule are collected in Table 1. The calculated modes were identified with the experimentally observed modes by enumeration of the total number of observed Raman active modes in the range up to 1600 cm^{-1} , consideration of the symmetry of the modes and reference to the n-octane frequencies published by Snyder¹². The fact that three of the calculated frequencies of n-octane exhibiting Raman activity are identified with the single 1060 cm^{-1} band in PE is in accordance with the splitting observed when decreasing the length of the alkane (see Table V in the paper by Snyder¹²).

From the vibrational frequencies calculated for both the unstrained and the strained n-octane molecule (Table 1), the Raman shifts that occurred upon the application of strain were calculated. For the symmetric C–C stretching band (1130 cm^{-1} band in PE) we calculated a shift of 8.0 cm^{-1} per 1% strain (i.e. 1254–1174 cm^{-1} for 10% strain), and for the asymmetric C–C stretching band (1060 cm^{-1} band in PE) the corresponding shift was calculated as $16.8 \pm 2 \text{ cm}^{-1}$ per 1% strain. The given variation of 2 cm^{-1} in the latter value depends from which of the three A_g modes in n-octane at 1142 cm^{-1} , 1125 cm^{-1} and 1084 cm^{-1} (zero-strain frequencies) the shift is calculated. Experimental data for a fibre with $E = 196 \text{ GPa}$ have revealed^{7–9} shifts of approximately 8.7 cm^{-1} per 1% strain for the symmetric C–C stretching band (1130 cm^{-1}) and 14 cm^{-1} per 1%

strain for the asymmetric C–C stretching band (1060 cm^{-1})*. Even though we are comparing calculated data on n-octane to experimental data on PE, the agreement regarding frequency shifts that occur upon the application of strain is surprisingly good and almost quantitatively correct.

The dependence of the full width at half maximum (FWHM) for the two strongly shifted bands appearing at lower Raman frequencies upon the level of strain is shown in Figure 2. It can be seen from this figure, and also in the original spectra in Figure 1, that the highly shifted band originating from the unshifted 1060 cm^{-1} Raman band is broader than the highly shifted Raman band originating from the 1130 cm^{-1} band. From the calculated data compiled in Table 1 we can see that whereas the band with the high Raman shift (the equivalent of the 1130 cm^{-1} band of PE) simply shifts from 1254 cm^{-1} down to 1174 cm^{-1} upon the application of 10% strain, the calculated Raman bands at 1084 cm^{-1} and 1142 cm^{-1} (corresponding to the 1060 cm^{-1} PE band) are shifted to 910 cm^{-1} and 992 cm^{-1} for the same strain. This implies an increase in separation between these bands of 24 cm^{-1} when going from 0% to 10% strain. The increase is of the correct order of magnitude to explain the experimentally observed dependence of the FWHM on the applied strain. We think that the increase in frequency difference upon the application of strain is the origin of the stronger increase in the FWHM of the asymmetric C–C stretching band as compared to the increase in the FWHM of the symmetric C–C stretching band, since both bands had essentially the same FWHM at zero strain (Figure 2)†. Although we are comparing calculated data on n-octane to experimental data on PE, we can further substantiate our statement by pursuing a quantitative agreement between the experimental and calculated data. Since all experimentally observed shifts for high-modulus PE fibres^{3–10} have been found to vary linearly with applied strain^{3–10}, we may, as a first approximation, convert the 24 cm^{-1} increase in separation at 10% strain to a 7 cm^{-1} increase in separation at 3% strain. The experimental relative increase in the FWHM of the asymmetric compared to the symmetric C–C stretching band, as shown in Figure 2, equals 15 cm^{-1} at 3% strain. This value needs to be corrected for the difference between the applied macroscopic strain and the molecular strain as determined by Moonen *et al.*⁷, which brings the actual experimental value to 11 cm^{-1} . In view of the approximate nature of this initial straightforward attempt, this value compares favourably to the calculated value of 7 cm^{-1} .

We finally comment on the strain dependence of the Raman intensities. Since both experimentally and

* Both experimental values were corrected for the fact that the applied macroscopic strain does not necessarily equal the molecular strain. From a comparison between the applied macroscopic strain and the molecular strain at the crystalline level as determined by X-ray diffraction on a fibre with $E = 149 \text{ GPa}$, Moonen *et al.*⁷ obtained a molecular strain (elongation of the c axis) of 2.1% at an applied macroscopic strain of 2.8%.

† An alternative explanation for the broadening would be to assume a distribution of stresses. Although this possibility cannot be ruled out at present, there is no further evidence that there is such a distribution, and the proposed explanation for the line broadening provides a very satisfactory agreement between experimental observations and theoretically calculated data.

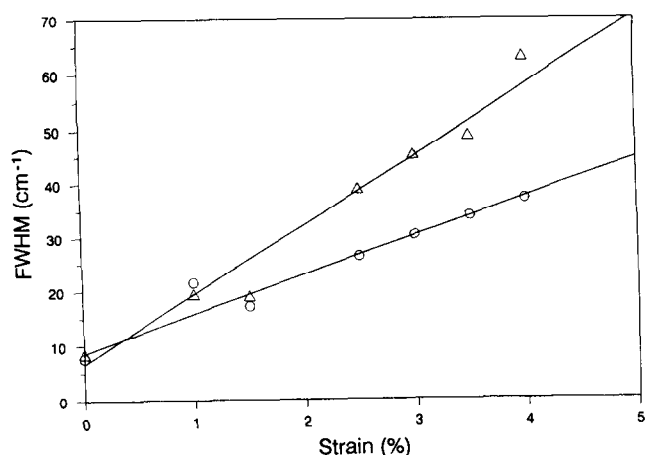


Figure 2 FWHM of the broad asymmetric (Δ) and symmetric (\circ) C–C stretching modes as a function of the applied strain for a 100 GPa (Young's modulus) polyethylene fibre (reproduced from Kip *et al.*⁸)

theoretically it is very difficult to obtain unambiguous absolute intensities, we will only discuss relative intensities. Let us first note that the calculated intensity of the symmetric C–C stretching band (experimental band at 1130 cm^{-1}) is lower than that of the asymmetric C–C stretching band (experimental band at 1060 cm^{-1}). This is the reverse of the experimental ratio, as can be seen from the spectrum displayed in Figure 1. However, the experimental relative intensities of these two bands depend strongly on the Raman scattering geometry and the degree of orientational order of the polymer chains in the material. We will pay no particular attention to these points because in the following we will only discuss relative intensity changes.

In the region of the symmetric C–C stretch (calculated frequency 1254 cm^{-1}), the calculated intensity increases from 17 (\AA^4 per a.m.u.) at 0% strain to 22 (\AA^4 per a.m.u.) at 10% strain. The overall Raman intensity for n-octane in the calculated region 1084–1142 cm^{-1} (asymmetric

Table 1 *Ab initio* (Hartree–Fock, 6-31G* basis set) calculated vibrational frequencies for n-octane, along with the symmetry of the mode and the calculated Raman activity. Only the modes in the range of interest with regard to the C–C stretching region of polyethylene are given. One band below and one band above this range have been included in order to emphasize further the correctness of the identification between calculated and experimental Raman bands. Some corresponding bands as measured experimentally for polyethylene are also given. The lines in the table indicate which band at zero strain corresponds to which band at 10% strain

Parameters	n-Octane at 0% strain	n-Octane at 10% strain	Corresponding experimental band for polyethylene at 0% strain
Frequency (cm^{-1})	972	784	890
Symmetry	A_g	A_g	
Raman activity	16.5	21.4	
Frequency (cm^{-1})	1044	814	
Symmetry	B_g	B_u	
Raman activity	0.5	0.00	
Frequency (cm^{-1})	1082	820	
Symmetry	B_u	B_g	
Raman activity	0.00	0.1	
Frequency (cm^{-1})	1084	878	1060 (asymmetric C–C stretch)
Symmetry	A_g	B_u	
Raman activity	4.5	0.0	
Depolarization ratio	0.56		
Frequency (cm^{-1})	1123	910	
Symmetry	A_u	A_g	
Raman activity	0.00	8.8	
Depolarization ratio		0.53	
Frequency (cm^{-1})	1125	922	1060 (asymmetric C–C stretch)
Symmetry	A_g	A_u	
Raman activity	8.2	0.0	
Depolarization ratio	0.48		
Frequency (cm^{-1})	1140	934	
Symmetry	B_u	B_u	
Raman activity	0.00	0.00	
Frequency (cm^{-1})	1142	945	1060 (asymmetric C–C stretch)
Symmetry	A_g	A_g	
Raman activity	24.1	41.9	
Depolarization ratio	0.73	0.73	
Frequency (cm^{-1})	1195	992	
Symmetry	B_u	A_g	
Raman activity	0.00	28.0	
Depolarization ratio		0.24	

Table 1 (Continued)

Parameters	n-Octane at 0% strain	n-Octane at 10% strain	Corresponding experimental band for polyethylene at 0% strain
Frequency (cm ⁻¹)	1254	1015	1130 (symmetric C–C stretch)
Symmetry	A_g	B_g	
Raman activity	16.9	1.0	
Depolarization ratio	0.15		
Frequency (cm ⁻¹)	1321	1101	
Symmetry	B_g	A_u	
Raman activity	0.85	0.00	
Frequency (cm ⁻¹)	1351	1134	
Symmetry	A_u	B_u	
Raman activity	0.00	0.00	
Frequency (cm ⁻¹)	1367	1174	
Symmetry	B_u	A_g	
Raman activity	0.00	21.9	
Depolarization ratio		0.14	
Frequency (cm ⁻¹)	1399	1270	
Symmetry	B_g	B_g	
Raman activity	3.0	3.6	
Frequency (cm ⁻¹)	1428	1307	
Symmetry	A_g	A_u	
Raman activity	0.3	0.00	
Frequency (cm ⁻¹)	1439	1336	
Symmetry	A_u	B_u	
Raman activity	0.00	0.00	
Frequency (cm ⁻¹)	1449	1366	
Symmetry	B_g	B_g	1296
Raman activity	60.6	0.5	
Frequency (cm ⁻¹)	1463	1395	
Symmetry	A_u	A_g	
Raman activity	0.00	0.4	
Frequency (cm ⁻¹)	1463	1419	
Symmetry	B_g	A_u	
Raman activity	0.0	0.00	
Frequency (cm ⁻¹)	1484	1436	
Symmetry	B_u	B_g	
Raman activity	0.00	54.4	
Frequency (cm ⁻¹)	1529	1448	
Symmetry	A_g	A_u	
Raman activity	0.4	0.00	
Frequency (cm ⁻¹)	1558	1451	
Symmetry	B_u	B_g	
Raman activity	0.00	12.7	

C–C stretch) amounts to 37 at 0% strain, whereas for the 10%-strained n-octane species this value increases to 79. These data suggest that a correct quantification of the relative band areas in strained PE does require taking account of the strain dependence of the Raman intensities. In fact, closer inspection of the experimental data reported by Van Eijk *et al.*⁶ provides evidence for a strain dependence of the Raman intensities of the C–C stretching bands. The normal zero-strain Raman spectrum of a 196 GPa PE fibre exhibits an intensity ratio $I_{1130}/I_{1060} = 2.4$. The same fibre strained at 2.8%

macroscopic strain, which equals 2.1% molecular strain⁷, has $I_{1130}/I_{1060} = 1.5^*$, as obtained from the ratio of the peak intensities. The band width, though, varies with applied strain, as illustrated in Figure 2. The ratio of the band widths for the '1130' and the '1060' bands for the 196 GPa fibre, with the Raman spectrum

*We use quotes around wavenumbers, 'X', to indicate that the numbers refer to strain-induced shifted bands being referred to by the zero-strain wavenumbers X

recorded at 240 K in order to suppress stress relaxation, is calculated as 0.9, this value being corroborated by other data⁶. As a consequence, the integrated intensity ratio I_{1130}/I_{1060} decreases to 1.4. These are experimentally derived Raman intensity ratios. Anticipating a linear dependence on strain, the theoretically calculated dependence of the intensities on strain suggests a 6% Raman intensity increase for the symmetric C–C stretching band and a 24% Raman intensity increase for the asymmetric band at 2.1% molecular strain. These data imply $I_{1130}/I_{1060} = 2.0$, as opposed to the experimental ratio $I_{1130}/I_{1060} = 2.4$ for the unstrained sample. Although there is a quantitative discrepancy, we see that the theoretical trend agrees with the experimental trend. Also, since the experimental data display an even larger difference between the ratios I_{1130}/I_{1060} and I_{1130}/I_{1060} than shown by the present theoretical intensities, this is further evidence that a correct quantification of the relative Raman band areas in strained PE requires taking account of the strain dependence of the Raman intensities.

As far as we can judge, this strain dependence of the Raman intensities does not, however, affect the observed⁶ relationship between the relative band area of the highly shifted component and the stress/strain ratio in the stress relaxation experiment, which for the first time indicates a relationship between the macroscopic creep and a molecular property.

CONCLUSIONS

Although we emphasize that all theoretical results presented in this paper should primarily be regarded as reliable at the qualitative level, we have shown that taking into account the strain dependence of the Raman

intensities is a prerequisite for a useful and reliable quantification of the C–C stretching frequency range of loaded PE. This effect is only significant, though, when the frequency shift is also considerable, i.e. when the molecular chains are strained.

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