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F. Coter [a], Z. Vardeny [a], O. Brafman [a], E. Ehrenfreund [a] & J. Ashkenzai [a]
[a] Physics Department and Solid State Institute, Technion, Haifa, Israel
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RESONANT RAMAN SCATTERING OF TRANS POLYACETYLENE UNDER PRESSURE

F.COTER, Z.VARDENY, O.BRAFMAN, E.EHRENFREUND, J.ASHKENZAI-
Physics Department and Solid State Institute, Technion, Haifa, Israel

Abstract The three resonantly enhanced Raman lines of Polyacetylene(PA)are studied under hydrostatic pressure up to 8kbar, with various laser excitation wavelengths. The results are interpreted in the framework of the Amplitude Modes theory (AM), with varying interchain coupling.

Polyacetylene is a quasi 1D Pererls semiconductor with a large anisotropy between the interchain and intrachain transfer integral. Previous studies of the interband absorption under hydrostatic pressure showed that the main effect is an increase in the interchain coupling. Here we study the effect of pressure on Resonant Raman Scattering (RRS) and show that the results can be accounted for by the AM theory while taking into account the increase of the interchain coupling with pressure. When excited in red, RRS spectrum of PA shows[3] three lines. At higher excitation energies satellites appear which shift to higher frequencies.

RRS in a back scattering geometry was taken from free standing films mounted in a pressure cell[2] for pressures up to 10 kbars. The measurements were reproducible for pressures greater than 1.2kbar. The results are: 1. The intensities decrease as the pressure increases (Table 1, Fig 1&2). The first line is more affected than the third one in both $(CH)_x$

Table 1

	ω_1	ω_2	ω_3	λ_L
$(CH)_x$	0.80 0.03	—	0.80±0.03	4579 A
$(CH)_x$	0.68 ±0.03	—	0.80±0.03	6300 A
$(CD)_x$	0.75±0.03	0.73±0.03	0.85±0.03	6300A

$I^R(P)/I^R(o)$- Intensity ratio at 8kbar and 1.4kbar.

and $(CD)_x$ though generally $(CH)_x$ is more sensitive to pressure (in red). For the 4579Å excitation wavelength the lines 1&3 of $(CH)_x$ are equally reduced (Table 1).2. The widths of all the lines increase with increasing pressure. In fig. 3 the pressure dependence of FWHM of the first line of $(CH)_x$ is plotted and is shown to be linear. 3. The peak frequency shifts are small (2-4 cm^{-1}). The well defined second line of $(CD)_x$ shifts by 3cm^{-1}; this is important for the analysis.

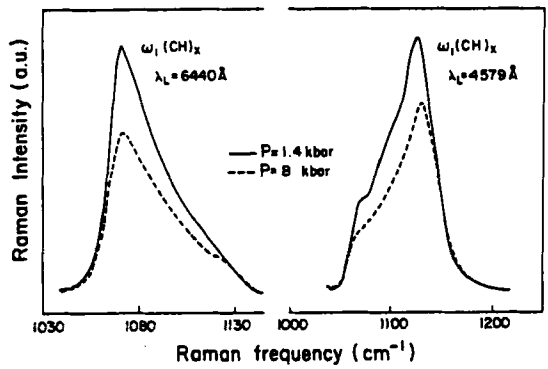

Fig.1. Pressure dependence of the first line of trans $(CH)_x$.

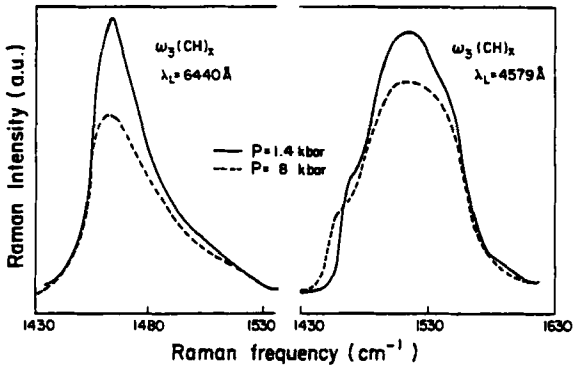

Fig.2. Pressure dependence of the third line of trans $(CH)_x$.

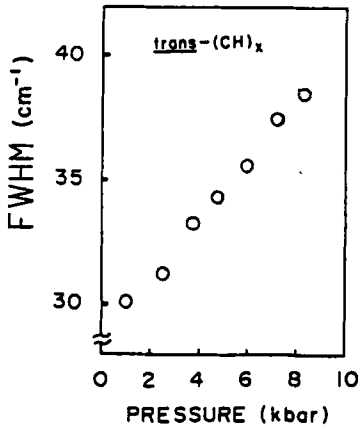

Fig. 3. Pressure dependence of the FWHM of the first line of trans $(CH)_x$.

The crossection of RRS from AM is given[3] by:

$$\frac{d^2\sigma}{d\Omega\, d\omega} \sim |f(\omega_L/E_g)|^2 Im \frac{-D_0(\omega)}{1+(1-2\tilde{\lambda})D_0(\omega)}$$

$$D_0(\omega) \equiv \sum_n \frac{\lambda_n}{\lambda} \frac{(\omega_n^0)^2}{\omega^2-(\omega_n^0)^2} = \frac{-1}{1-2\tilde{\lambda}}$$

$$f(x) = \frac{1}{2} - \frac{x^2}{1-x^2} + \frac{1-2x^2}{x(1-x^2)^{3/2}} \tan^{-1}\frac{x}{\sqrt{1-x^2}} \qquad x<1$$

$$f(x) = \frac{1}{2} + \frac{x^2}{x^2-1} + \frac{2x^2-1}{2x(x^2-1)^{3/2}} \ln\frac{x-\sqrt{x^2-1}}{x+\sqrt{x^2-1}} + \frac{\pi i}{2x\sqrt{x^2-1}} + \frac{\pi i}{4(x^2-1)} \qquad x>1$$

where $X=h\omega_L/Eg$, ω_n^R is the Raman Shift, ω_n^o is the bare phonon frequency. $D_o(\omega)$ changes by less than 1% for a shift of about 3 cm^{-1} in ω_n^o : $D_o(\omega)$ depends on intrachain parameters whereas the hydrostatic pressure affects mainly the interchain transfer integral. On the other hand, $|f(x)|^2$ contains the 1D density of states with a typical strong divergence at X=1. (See fig. 4).

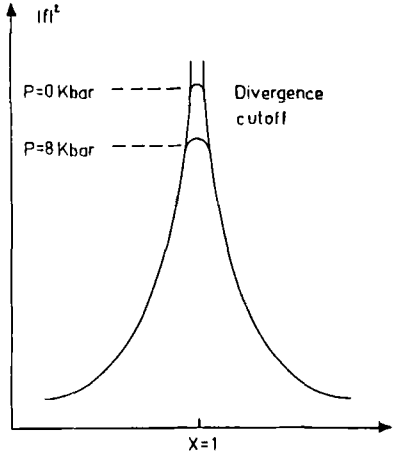

Fig.4. Schematic picture of $|f(x)|^2$.

This divergence is suppresed by the finite interchain coupling. One expects a change in the suppression of the 1D singularity when hydrostatic pressure is applied[4]. Indeed, increasing pressure causes an increase in the three dimentionality and thus an increase in the interchain transfer integral. This lowers the divergence cutoff with two consequences: the line intensity decreases and the line FWHM increases. Given this simplified model, one can regard the width of $f(x)$ at the cutoff hight as a rough measure of the interchain coupling. Within those assumptions the pressure dependence of line intensity and FWHM should be approximately linear. Indeed, a simple calculation shows that: (within the given pressure range): The decrease in line intensity is about 30-40% (See table 1); The slope of FWHM(p) is about 2x10 kbar while a least square fit of the data of Fig. 3 gives 4.6×10^{-2} $kbar^{-1}$.

Conclusions: 1. As hydrostatic pressure is applied, both the line intensity and the line width change. This can be accounted for within the framework of RRS from AM. 2. The changes in RRS spectrum are smaller at higher excitation wavelengths. 3. Since the RRS crossection diverges much more rapidly than the quasi 1D density of states, one expects the decrease in RRS intensity to be about 5 times larger than the decrease in the absorption. Indeed, this is true, in view of our data and those of Ref. 1.

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