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Resonant raman scattering of conducting polymers

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RESONANT RAMAN SCATTERING OF CONDUCTING POLYMERS +

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A combined study of electronic absorption data and Resonant Raman spectra yields valuable information on the structure and electronic properties of conducting polymers. The role of the electron-phonon interaction in determining the absorption bandshape and the Resonant Raman intensities is discussed. A case of weak (cis-polyacetylene) and strong (polyiodide chains) electron-phonon interaction is considered and a few results concerning the applications of the Resonant Scattering to investigate the nature of the band gap in polyacetylene and the structure of polyiodide chains in iodine-doped polymers are briefly reported.

INTRODUCTION

Resonant Raman (RR) Spectroscopy can play a major role in investigating the electronic properties and the structure of conducting and semiconducting polymers and their dopants.

Electronic absorption bandshapes and RR intensities can be conveniently studied within the framework of the theory of Resonant Secondary Emission[1]. This formalism yields analytical expressions for both the absorption coef-

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ficient and the Raman Excitation Profile (REP), which are treated in a self consistent way. A combined study of the absorption and Raman spectra can therefore provide quantitative information on phonons, electronic transitions and their mutual interactions.

In this note we give a brief outline on the theoretical approach used and preliminary results for the case of cis-polyacetylene and polyiodide chains are presented. These systems represent two examples of weak and strong electron-phonon (e-p) interaction respectively.

THEORY

In our approach we treat the ground and excited electronic states involved in the optical absorption and in RR scattering as two localized levels for which there is no dispersion in the wavevector space. Moreover only linear e-p interactions are considered. Phonon anharmonic interactions and phonon dispersion are phenomenologically taken into account through the linewidth of the vibronic states.

The final expressions for the RR cross section as a function of the laser frequency involve some parameters (V, the linear e-p interaction, M_{ug}, the electronic dipole matrix element, Ω_{ug} the electronic frequency in the rigid lattice approximation and γ, the vibronic linewidth) which can be obtained from the analysis of the absorption spectrum.

We give here only the final expressions for the absorption coefficient and the RR intensities for the case of the electron interacting with only one dispersionless phonon mode. A complete derivation of these formulae, together with the approximations implied in our model can be found in previous papers[2,3].

Two limiting cases can occurr:

i) Weak coupling

The absorption spectrum consists of a few vibronic lines generally well resolved. The absorption coefficient is given by:

$$\alpha(\Omega) = \frac{\Omega}{N(\Omega)} I(\Omega) \qquad (1)$$

where Ω is the frequency of the light beam, $N(\Omega)$ is the refractive index and:

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$$I(\Omega) = e^{-S} |M_{ug}|^2 \sum_{n=0}^{\infty} \left(\frac{V^2}{\omega^2}\right)^n \frac{1}{n!} \frac{\gamma}{\gamma^2 + (\Omega - \Omega_0 - n\omega)^2} \quad (2)$$

This equation is valid only in the low-temperature limit and/or when high energy phonons are involved, as in the case of cis-polyacetylene which we will discuss later. S is the Huang-Rhys factor ($S=V^2/\omega^2$), V is the linear e-p coupling constant and Ω_0 is the zero-phonon frequency. This equation describes a sum of individual vibronic transitions of Lorentzian lineshape, centered at $\Omega = \Omega_0 + n\omega$ whose intensity is given by $(V^2/\omega^2)^n e^{-S}/n!$.

The corresponding RR cross section for the k^{th} Stokes process is given by[3]:

$$\frac{d^2\sigma}{d\omega d\phi} = |M_{ug}|^4 \left(\frac{V^2}{\omega^2}\right)^k \frac{1}{k!} \left| \sum_{j=0}^{k} (-1)^j \binom{k}{j} R(\Omega - j\omega) \right|^2 \quad (3)$$

where:

$$R(\xi) = e^{-S} \sum_{n=0}^{\infty} \left(\frac{V^2}{\omega^2}\right)^n \frac{1}{n!} \frac{\gamma + i(\xi - \Omega_0 - n\omega)}{\gamma^2 + (\xi - \Omega_0 - n\omega)^2} \quad (4)$$

ii) Strong coupling

In this case the absorption spectrum consists of a broad structureless band, whose halfwidth is much larger than typical phonon frequencies and their linewidth. The intensity distribution can be approximated by a Gaussian curve, which is the envelope function of the multiphonon processes taking place in the excited state[2]. In this case we get:

$$I(\Omega) = \frac{|M_{ug}|^2}{\sqrt{2M_2}} \exp\left[-\frac{(\Omega - \Omega_{ug})^2}{2M_2}\right] \quad (5)$$

where:

$$M_2 = V^2(2n_\omega + 1) = W^2/8\ln 2 \quad (6)$$

W being the halfwidth of the absorption band and Ω_{ug} is the absorption frequency corresponding to the band peak (Frank-Condon energy). M_{ug}^2, Ω_{ug} and M_2 represent the zero, first and second moment of the distribution given in eq.5. The zero moment is the oscillator strength M_{ug}^2 and it is related to the integrated area of the band, the first moment corresponds to the energy of the Frank-Condon transition, the second moment M_2 is related to the e-p coupling, and hence to the halfwidth, through eq.6.

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The same parameters are also responsible for the excitation profile of the RR scattering, whose cross section is given by:

$$\frac{d^2\sigma}{d\omega d\phi} = (n_\omega+1)^n \frac{|M_{ug}|^4}{2\pi}\left(\frac{\Omega_L}{c}\right)^4 \delta(\Omega-n\omega)\left(\frac{V^2}{\omega^2}\right)^n \frac{1}{n!}\left|\sum_{k=0}^{n}(-1)^k\binom{n}{k} S(\Omega_L-\Omega_{ug}-k\omega)\right|^2 \quad (7)$$

where:

$$S(\xi) = \sqrt{\frac{\pi}{2M_2}}\, e^{-\xi^2/2M_2} + i\, e^{-\xi^2/2M_2}\, F\left(\frac{1}{2},\frac{3}{2};\frac{\xi^2}{2M_2}\right) \quad (8)$$

$F(\alpha,\beta;\gamma)$ being the hypergeometric function.

APPLICATION TO CONDUCTING POLYMERS

i) Polyacetylenes

The electronic absorption spectrum and the RR scattering spectra of polyacetylenes contain a number of features, whose interpretation is still controversial[4].

In particular the trans isomer exhibits, above the absorption edge, continuum absorption which is typical of the onset of band-band transitions and its RR spectrum[5] displays weak overtone scattering, whose intensity rapidly decays with the order of the process.

On the other hand the absorption spectrum of the cis isomer shows a resolved vibronic structure[4] due to the backbone phonons (c-c and c=c stretching) interacting with the excited electronic state. Its RR spectrum displays a long sequence of overtones and combination bands[5] (superimposed to a strong luminescence background) of the two fundamentals, similar to the multiphonon scattering series observed in inorganic semiconductors[6].

In order to account for the different behaviour of the optical and the electrical properties of the two isomers, some authors[7] have postulated the formation of localized exciton states in the cis isomer upon irradiation. The problem of the RR scattering from localized excitons in semiconductors has been already treated in details in a previous paper[8] and a brief outline of the relevant equations has been given in the previous section.

In the following we present the results of the calculations of the absorption cofficient (eq.2) and of the RR overtone scattering (eqs.3,4) for the cis polyacetylene based on this simple model, namely a localized exciton interacting with two dispersionless phonon modes.

The proper shift of the phonon frequencies (ω_1:1251

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--> 976 cm^{-1} and ω_2: 1541 --> 1470 cm^{-1}) upon deuteration has been considered in our calculations, as available experimental data only include absorption spectra[4] for the hydrogenated and Raman Scattering [5] for the deuterated polymer respectively.

In figure 1 and 2 the absorption coefficient and the RR scattering calculated on the basis of the model described above are compared with the experimental data. The following parameters have been used: V_1=800 cm^{-1}, V_2=550 cm^{-1}, $\gamma_1=\gamma_2$=450 cm^{-1}. The zero phonon line has been taken at 16870 cm^{-1} according to the experimental data.

It can be noticed that the absorption spectrum is reproduced fairly well by the calculation, apart from minor

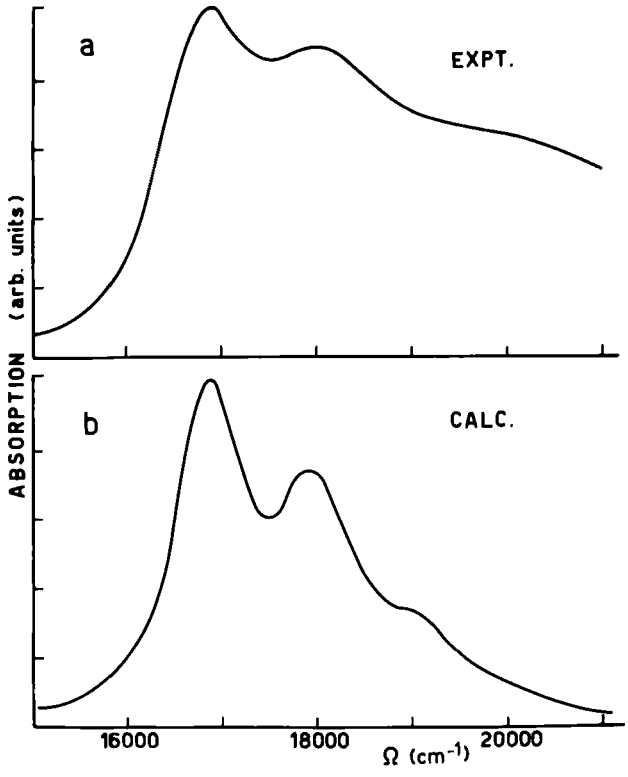

FIGURE 1 Experimental (a) and calculated (b) electronic absorption spectrum of cis-polyacetylene.

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discrepancies in the high-frequency tail of the spectrum. Also the rather erratical intensity ditribution of the multiple order Raman scattering experimentally observed, is properly accounted for by the theory (see fig.3), whose predictions could be better checked when more complete experimental data will become available.

Erratical intensities of the multiple order Raman scattering have been observed also in gaseous I_2[9] and in β carotene. According to our model this behaviour can occurr whenever the laser light is in resonance with resolved vibronic structures (namely scattering from phonon states which have long lifetime), while a regular decrease of the RR intensities with the order of the process is expected for scattering from an absorption continuum, as in the case of trans-polyacetylene.

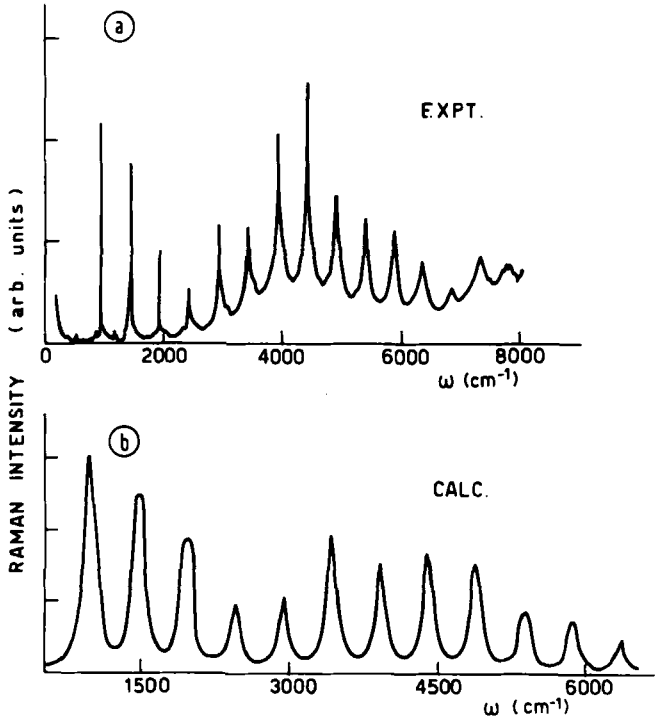

FIGURE 2 Experimental (a) and calculated (b) overtone scattering of cis-polyacetylene at 514.5 nm. Notice: i) the difference of scale ii) the experimental data have not been corrected by the luminescence background

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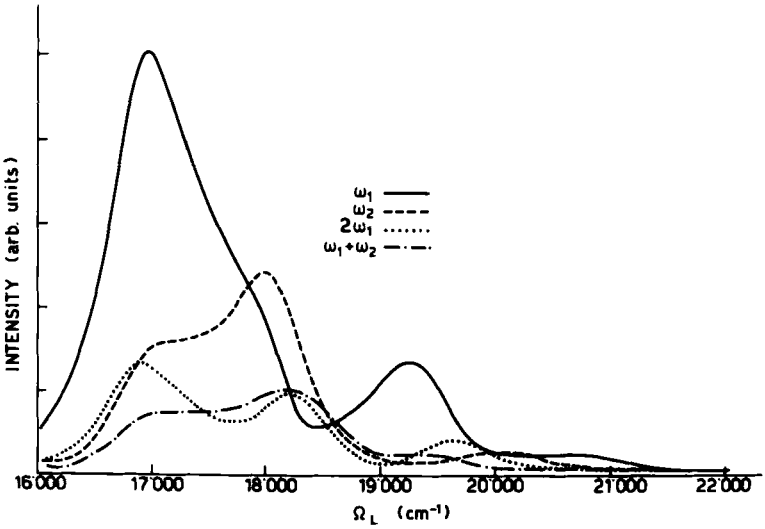

FIGURE 3 RR intensities of selected overtone and combination bands of cis-polyacetylene as a function of the exciting frequency.

The overall good agreement between the experiments and these preliminary results seems provide support to the hypothesis of the formation of localized excitations in cis-polyacetylene, when visible light is absorbed.

ii) Polyiodide chains

RR studies have been performed in our laboratory on starch-I_2 complex[2] and I_2 doped $(SN)_x$[10]. We summarize here only a few relevant results.

Polyiodide chains give rise to broad structureless absorption bands, whose halfwidth is larger than typical phonon frequencies (strong e-p coupling). The blue starch-iodine complex and iodine-doped polysulfurnitride $(SN)_x$ and polyacetylene $(CH)_x$ exhibit two strong fundamentals at ~110 and ~160 cm^{-1}, which show selective RR enhancement, as the laser frequency is tuned across the visible region.

The calculations based on the theory previously sketched account for this behaviour, which has some structural implications on the chromophore contained in all these compounds.

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An exhaustive treatement of systems containing polyiodide chains can be found in our previous papers[2,10] to which we refer for any further detail.

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