PHYSICAL REVIEW B VOLUME 26, NUMBER 12 15 DECEMBER 1982

Frank-Condon approach for optical absorption and resonance Raman scattering in *trans*-polyacetylene

H. Kuzmany,* E. A. Imhoff, D. B. Fitchen, and A. Sarhangi
Cornell University, Department of Physics, Ithaca, New York 14853

(Received 6 August 1982)

The Frank-Condon approach for resonance Raman scattering and optical absorption was used to explain the dispersion effect for the C=C stretch mode in *trans*-$(CH)_x$ quantitatively. The results are consistent with disturbed and undisturbed areas in the polymer. The Frank-Condon electron-phonon coupling constant was found 3.9 eV/Å, and the anomalous broad resonance cross section is interpreted as uncertainty broadening due to soliton-antisoliton generation from excited electron-hole pairs.

Recently strong interest has been focused on the conjugated polymer polyacetylene (CH_x) because of its unusual electrical and magnetic properties.[1–3] Wide agreement has been achieved for the interpretation of the magnetic properties of the undoped trans-isomer as due to highly mobile chargeless spin carriers (solitons[3,4]) which have been classified recently by Jackiw and Schrieffer as spin masked fractional charged particles.[5] In particular, electron-nuclear double resonance (ENDOR) experiments proved that the spin diffusion is highly one dimensional and leads to a well-expressed Overhauser effect.[6] Charged solitons were suggested to be generated either by doping[4] or by decay from photoexcited electron-hole pairs.[7] The later process is of particular importance since photogenerated solitons are not bound to dopant impurities. Experimental evidence for the decay process was drawn recently from results on the difference in photoconductivity[8] and luminescence[8,9] in *cis*- and *trans*-CH_x. In addition to these results Raman experiments attracted strong attention because unusual scattering was observed in the sense that line shape and line position for modes containing the C=C stretch motion depend on the frequency of the exciting laser.[10–12]

In this paper we show that the application of the Frank-Condon approach to the calculation of resonance Raman intensities leads to a quantitative explanation of the Raman line shapes and relative Raman intensities as a function of the laser excitation frequency and of the optical absorption. From a fit of both results to experimental data, the Frank-Condon coupling constant is determined and the existence of an ordered and a disordered phase is shown. The percentage of material in either phase is obtained. The interpretation of the experimental results suggests that photogeneration of soliton-antisoliton pairs occurs. For this case the lifetime of the excited electron-hole pair can be estimated for the first time from the measured width of the resonance effect.

A quantitative description of the dispersion effect of the Raman lines was first given by Kuzmany[11] using a model in which the polymer consists of a Gaussian distribution of segments of undisturbed conjugations and a simplified version of the *A* term of the Albrecht theory[13] for the description of the resonance effect. Further evidence for this model was obtained from a force field analysis for the frequency range of the dispersion.[14] Samples prepared under a highly oxygen-free condition were observed by Lichtmann *et al.*[15] to exhibit a double peak structure for the resonance enhanced modes and an inverse power-law distribution for the undisturbed segments on the chain.[9] Since all previous interpretations of the Raman results have suggested a predominance of short segments, Raman scattering has become a critical experiment with respect to a model of highly mobile solitons.

Raman spectra for the C=C stretch mode of highly oxygen-free (good) *trans*-CH_x have been recorded by standard techniques as shown in Fig. 1 where the nonresonant mode at 1290 cm^{-1} was used as an internal standard for good samples and only a small correction for the experimentally observed weak energy dependence of the scattering cross section for this mode was necessary. For less good (bad) samples the mode at 1290 cm^1 is not a good standard any more. Relative intensities were determined in this case from a simultaneous excitation of the Raman spectrum of polystyrene used as a cover for CH_x. Optical absorption of thin films of *trans*-CH_x was recorded as shown in Fig. 2. The quality of these samples as determined by Raman was less good than the quality of those of Fig. 1.

In the model calculation the energy of the lowest π-π^* optical transition for the various segments and the corresponding frequency for the C=C stretch mode was determined from the well-known particle in the box model of Kuhn[16] and from experimental results on finite polyenes,[10] respectively. The damping constant of the excited electronic state γ_e (full

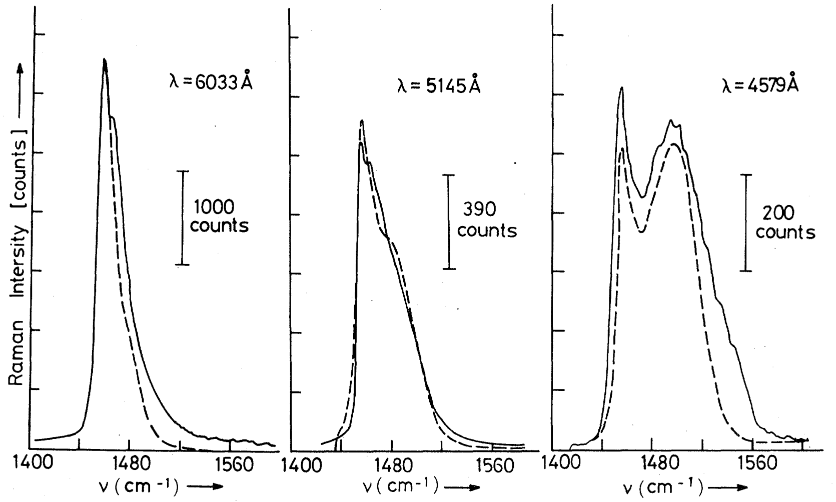

FIG. 1. Line profiles for the C=C stretch mode in *trans*-CH$_x$ as measured (——) and as calculated (– – –) for excitation with three different laser lines.

width half maximum), the parameters of the distribution function and the Frank-Condon coupling constant were used as fitting parameters. The first-order Raman tensor for scattering from total symmetric modes is[17]

$$\beta^{10}_{gm} = \rho^2_{gm} \sum_{\vec{v}} \frac{\langle \vec{0}|\vec{v}\rangle\langle \vec{v}|\vec{1}\rangle}{\nu_{\vec{v},0} - \nu_{\text{laser}} + i\gamma_e/2} \tag{1}$$

with

$$\nu_{\vec{v},0} = \epsilon_g + \sum_{i,k} v_{ik}\nu_{ip} \;.$$

$\vec{v}$ is a multidimensional vector in the phonon subspace and $\langle \vec{0}|\vec{v}\rangle$ and $\langle \vec{v}|\vec{1}\rangle$ are the Frank-Condon integrals which can be evaluated in terms of the Frank-Condon coupling constant B_i.[17,18] ρ_{gm} is the matrix element for the electronic transition from state g to m. Since the square of this quantity is proportional to the oscillator strength for the transition it was assumed proportional to the square root of the number of π electrons $2N$. This assumption is in very good agreement with a very recent quantum-mechanical calculation on the basis of a Longuet-Higgins-Salem Hamiltonian.[19] Similar to Eq. (1) the optical absorption α_{gm} can be calculated from

$$\alpha_{gm}(\nu) = \rho^2_{gm} \sum_{\vec{v}} \frac{\nu_{\vec{v},0}|\langle \vec{0}|\vec{v}\rangle|^2\gamma_e}{|(\nu - \mu_{\vec{v},0})^2 + (\gamma_e/2)^2|} \;. \tag{2}$$

The evaluation of β and α for the distributed segments proceeds by weighted summation over N from 5 to 150 double bonds with $\epsilon_g = 1.40$ eV, and an effective mass for the electrons of $m^* = 1.15m_0$ as described in Ref. 11. Two resonance enhanced modes around 1050 and 1500 cm^{-1} have been considered. With respect to the absorption edge the fit could be improved by linearizing $\gamma_e(N)$ between two limiting values γ_{e1} and γ_{e2}.

The distribution of the segments was described by an inverse power law of the form $P(N) = 1/(N+1)^x$. Calculated line shapes were matched to experimental curves only for the peak position for red laser light excitation. From a fit of the calculated line shapes to the experimental results for the good samples the parameters $\gamma_{e2} = 4600 \pm 1000$ cm^{-1}, $\gamma_{e1} = 2600 \pm 1000$ cm^{-1}, $B = 1.3 \pm 0.2$, and $x = 2.1$ were obtained. Very good agreement between calculated measured line shapes has been observed as shown in Fig. 1. Using the same parameters for calculating the optical absorption reveals similar good agreement as shown in Fig.

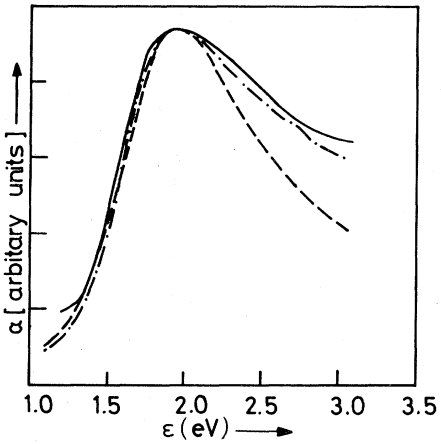

FIG. 2. Optical absorption for *trans*-CH$_x$ as measured (——) and as calculated for good (– – –) and bad (—·—·) samples.

2, except for the blue region. The dash-dotted line corresponds to a distribution with increased concentration of short segments.

The values for fitting parameters shown in parentheses describe the range where a reasonable fit to the experimental results can be obtained. Thus, within these limits the parameters are well defined. It was further checked explicitly that the inverse power law with $x = 2.1$ is equivalent to two log-normal distributions peaking at $N = 40$ and 5 double bonds, respectively. For the calculations of the line shape of the bad sample a distribution with less material in long segments was used and similar good agreement was obtained. However, the total scattering intensity as measured and as calculated for blue laser light was strongly enhanced. Figure 3 finally shows calculated scattering cross sections for the low-frequency peak of the C=C stretch mode for various values of γ_e as compared to corrected experimental results of Lichtmann.[9,20] The calculated curves were matched to the experiment at 1.96 eV and are thus forced to intersect there.

The good agreement between experimental and calculated line shapes and relative intensities for good and bad materials suggests that the observed dispersion in CH_x is mainly due to the length distribution for undisturbed conjugations. The fact that this distribution corresponds to two log-normal distributions with different peak value is consistent with the existence of a disordered and an ordered phase in CH_x as suggested previously from an x-ray analysis.[21] For the parameters given only 10% of the material is in very short segments. Calculating the amount of material in long segments altogether yields, e.g., ~70% of the polymer in segments longer than 30 carbons in reasonable agreement with an observed crystallinity of 80% from x rays.[21] As compared to very recent results from neutron scattering[22] the evaluated conjugation length is about a factor of 2 smaller than the minimum coherence length parallel to the chain. This may be due to an underestimation of scattering from long segments for which the Frank-Condon approach is not a good approximation. For the dashed-dotted line in Fig. 3 only 50% of the material are in segments with more than 30 carbons.

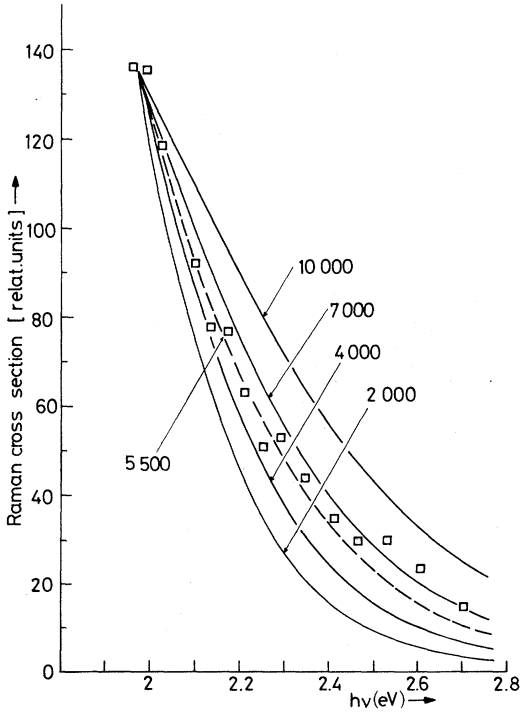

FIG. 3. Relative Raman cross section as calculated for various damping constants γ_e of the excited state, as compared to corrected experimental results of Lichtmann (Ref. 9).

The strong Overhauser effect requires a relative free motion of the soliton. The defects we are discussing here need not interrupt the conjugation and may therefore be transparent to solitons. Typical defects of this kind are locked in single *cis*-segments or strain-induced bending or twisting of the backbone.

The question arises whether solitons generated by a decay of photoexcited electron-hole pairs can by themselves intersect the conjugation and thus account for the described distribution of undisturbed conjugations. Though this idea is tempting, there is good experimental and theoretical evidence against it. From the results reported above it is, e.g., evident, that the distribution of undisturbed segments is determined by sample quality and not by the laser light. Also, we have performed a two beam experiment where one laser was used for photoexcitation and a second laser was used for scanning the Raman spectrum of the excited polymer.[20] There was no influence of the photoexcitation on the spectrum. Finally, a soliton tends to equalize bond alternation and it is transparent to electronic wave functions.[23] It can therefore not be expected to interrupt a conjugation, at least not in the same sense as a static defect which increases bond alternation.[19]

The Frank-Condon coupling constants B_i describe the shift of the vibrational equilibrium position between the ground and excited state. From the work of Tang and Albrecht[13] this quantity can be shown to be related to the electron phonon coupling constant h_{ep} by $h_{\mathrm{ep}} = KB(h/\mu\omega)^{1/2}$ where K, μ, and ω are the force constant, the reduced mass, and the angular frequency of the mode, respectively. With $B = 1.3 \pm 0.2$ this yields 3.9 ± 0.6 eV/Å in reasonable agreement with results between 3.5 and 8 eV reported from force field calculations.[4,24,25] The difference of the two values probably arises from the relaxation of the excited state for the coupling according to the Frank-Condon mechanism in contrast to the pure deformation potential interaction considered so far.

The observation of the high value for γ_{e2} is surprising. A trial and error fit to the experimental results of Fig. 3 (broken lines in Fig. 3) revealed an even slightly larger value of 5500 cm^{-1} for the electronic damping. Typical values for this quantity in finite conjugated systems are 900 cm^{-1}.[18] A resonance effect from transitions into higher states in the π^* band might account for the broadening of the cross section. However, the matrix elements for this transition showed a rapid decrease with increasing transition energy. This and the lack of a similar result for the *cis*-polymer makes it unlikely that such transitions can explain the effect. The theoretically predicted fast decay of photoexcited electrons and holes into charged soliton-antisoliton pairs[7] renders the energy of the excited state, on the other hand, highly undefined according to the uncertainty principle. From the work of Su and Schrieffer[7] a typical decay time would be $\Delta\tau = 4 \times 10^{-15}$ sec whereas the uncertainty principle $\Delta\tau = 1/2\pi c \gamma_e$ yields $\Delta\tau = 1.1 \times 10^{-15}$ sec for an experimentally observed damping constant of approximately 5500 cm^{-1}. The experimental result is definitely of the right order of magnitude and thus allows one for the first time to estimate the characteristic time constants for photogeneration of solitons. The fact that the evaluated time constant is smaller than calculated probably results from the neglect of the higher excited states in the evaluation process.

In conclusion we showed that introducing the Frank-Condon approach into the model of distributed length of undisturbed conjugation allows one to explain quantitatively the dispersion effect and relative scattering intensities from Raman measurements, and the shape of the optical absorption. The Frank-Condon electron phonon coupling constant was determined to 3.9 eV/Å. The results suggest that the polymer consists of a highly ordered and disordered phase and are in agreement with a soliton model for CH_x. They give particular support to the possibility of a photogeneration of these quasiparticles.

ACKNOWLEDGMENTS

We acknowledge valuable discussion with A. C. Albrecht, J. A. Krumhansl, and P. Vogel. The work was partially supported by the NSF through the Material Science Center, and by the Fonds zur Foerderung der Wissenschaftlizhen Forschung in Austria. One of us (H.K.) acknowledges support from the Max Kade Foundation.

---

*Present address: University of Vienna and L. Boltzmann Institute in Vienna, Vienna, Austria.

[1] Y. W. Park, A. J. Heeger, M. A. Druy, and A. G. MacDiarmid, J. Chem. Phys. 73, 46 (1980).

[2] Y. Tomkiewicz, T. D. Schulz, H. B. Brom, A. R. Taranko, T. C. Clarke, and G. B. Street, Phys. Rev. B 24, 4348 (1981).

[3] B. R. Weinberger, E. Ehrenfreund, A. Pron, A. J. Heeger, and A. G. MacDiarmid, J. Chem. Phys. 72, 4749 (1980).

[4] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B 21, 1 (1980).

[5] R. Jackiw and J. R. Schrieffer, Nucl. Phys. B190, 253 (1981).

[6] M. Nechtschein, F. Devreux, R. L. Greene, T. C. Clarke, and G. B. Street, Phys. Rev. Lett. 44, 356 (1980).

[7] W. P. Su and J. R. Schrieffer, Nat. Acad. Sci., N. Y. 77, 5626 (1980).

[8] L. Lauchlan, S. Etemad, T. C. Chung, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B 24, 3701 (1981).

[9] L. S. Lichtmann, thesis (Cornell University, 1981) (unpublished).

[10] I. Harada, M. Tasumi, H. Shirakawa, and S. Ikeda, Chem. Lett. 1411 (1978).

[11] H. Kuzmany, Phys. Status Solidi (b) 97, 521 (1980).

[12] L. S. Lichtmann, D. B. Fitchen, and M. Temkin, Synth. Met. 1, 139 (1979/80).

[13] J. Tang and A. C. Albrecht, in *Raman Spectroscopy,* edited by A. Szymanski (Plenum, New York, London, 1970), Vol. 2, p. 33.

[14] F. B. Schügerl and H. Kuzmany, J. Chem. Phys. 75, 953 (1981).

[15] L. S. Lichtmann, A. Sarhangi, and D. B. Fitchen, Chem. Scr. 17, 149 (1981).

[16] H. Kuhn, J. Chem. Phys. 17, 1198 (1949).

[17] W. Siebrand and M. Z. Zgierski, J. Chem. Phys. 71, 3561 (1979).

[18] L. C. Hoskins, J. Chem. Phys. 74, 882 (1981).

[19] P. Surian, M. Kertesz, and H. Kuzmany (unpublished).

[20] D. B. Fitchen, Mol. Crys. Liq. Crys. 83, 1127 (1982).

[21] T. Akaishi, K. Miyasaka, K. Ishikawa, H. Shirakawa, and S. Ikeda, J. Polym. Phys. Ed. 18, 745 (1980).

[22] C. Riekel, H. W. Hässlin, K. Menke, and S. Roth (unpublished).

[23] J. T. Gammel and J. A. Krumhansl, Phys. Rev. B 24, 1035 (1981).

[24] E. J. Mele and M. J. Rice, Phys. Rev. Lett. 45, 926 (1980).

[25] S. Strässler and L. Pietronero, Mol. Crys. Liq. Crys. 83, 1243 (1982).