

Optical properties of potassium-doped polyacetylene

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Abstract

The optical reflectance of polyacetylene doped with high concentrations of potassium has been measured, and the optical properties estimated by Kramers–Kronig analysis. The samples, doped by a vapor-phase technique to $y \approx 0.08$ and 0.18 , showed strong doping-induced infrared absorption at ~ 900 , 1270 , and 1390 cm^{-1} . These experiments were motivated by calculations of the infrared absorption which showed that whereas there are only small differences in the infrared spectra for isolated solitons and isolated polarons, there is a dramatic difference between the high-concentration polaron and soliton lattices. The shapes of the absorption spectra are rather similar but the absorption for the polaron lattice is 13 orders of magnitude weaker than that of the soliton lattice. The observation of these features at high doping levels is inconsistent with both the polaronic metal and strongly disordered Peierls insulator models for highly doped polyacetylene and furthermore suggests that solitonic defects maintain their integrity to very high doping levels.

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1. Introduction

The physical model appropriate for describing the highly conducting, heavily doped phase of polyacetylene, $(\text{CH})_x$, is still being debated in the field of conjugated polymers, despite a considerable activity since its discovery [1]. A key issue is the nature of doped $(\text{CH})_x$ at doping levels above $\sim 6\%$; in contrast to the nonmagnetic, lightly doped case, this phase is highly conducting and possesses a finite Pauli paramagnetism. Early pictures [1] viewed the highly conducting state either as induced by a Mott semiconductor–metal transition or the result of doping eliminating the dimerization, leaving all the C–C bonds equal in length, thus providing a uniform charge distribution in a partially-filled band. Following the introduction of the soliton model, [2,3]

it was suggested that a highly disordered arrangement of dopant ions causes the soliton states to spread throughout the gap, destroying the dimerization at high concentrations [4,5]. Later, a number of other models were proposed. Transport, magnetic, and optical measurements of ClO_4^- -doped $(\text{CH})_x$ were used to support a model of doped polyacetylene as a gapless Peierls insulator [6,7]. The observation [8,9] of a first-order phase transition in the spin susceptibility of Na^+ -doped $(\text{CH})_x$ led to the proposal that the doped polymer is a polaronic metal [10]. There are also models based on the electronic structure of a soliton lattice, [11] finding that the heavily doped polymer is conducting and with a finite Pauli susceptibility [12–15]. Finally, there is considerable evidence in recent years for mixed-phase behavior, perhaps with metallic islands separated by disordered semiconducting regions [16,17]. Some of the variation in materials properties and consequently in applicable model may be attributed to differing methods of preparation of the polyacetylene or to the doping procedure. Nevertheless, it is fair to say that there is no consensus about the proper picture to apply to the “metallic” phases that occur above $\sim 6\%$ doping.

This paper describes a study of the infrared reflectance of $(\text{CH})_x$ doped with potassium into the “metallic” range. Our experiments were motivated by calculations of the infrared absorption by Hicks and Gammel [18], Choi and Mele, [19]

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and Hicks et al. [20] which show that whereas there are only small differences in the infrared spectra for isolated solitons and isolated polarons (in agreement with the earlier work of Horowitz [21]) there is a dramatic difference between the high-concentration polaron and soliton lattices. The shapes of the absorption spectra are rather similar but the absorption for the polaron lattice is *13 orders of magnitude* weaker than that of the soliton lattice. It appeared to us that a measurement of the strength of the doping-related infrared absorption at high concentrations should therefore be able to distinguish between these two possibilities.

The doping-induced infrared absorption [22] in lightly doped $(\text{CH})_x$ and the photoinduced infrared absorption [23,24] in undoped $(\text{CH})_x$ were important results for establishing the soliton model [2,3] of polyacetylene. These measurements observed intense absorption lines at approximately 1390, 1290, and 900 cm^{-1} with oscillator strengths which increased linearly with the concentration of charged centers produced either by doping [22,25] or by photo-excitation [23]. The theory of this effect was first given by Mele and Rice [26] and has been developed considerably over the years [18–21,27–29]. However, as shown initially by Horowitz, [21] infrared measurements at these low doping concentrations are not by themselves capable of distinguishing among various possible types of defects, because the absorption is determined by the lattice dynamics of the polyacetylene chain and differs only slightly for isolated solitons, polarons, or bipolarons.

Most previous infrared measurements on doped $(\text{CH})_x$ have been carried out at doping levels below 6%, the concentration where the susceptibility first becomes large. This concentration appears to be close to the maximum reached by acceptor doping with, for example, ClO_4^- or I_3^- . In contrast, it has been known for some time [30,31] that donor doping with alkali metals can produce dopant concentrations around 16%. Furthermore, K^+ - and Na^+ -doped $(\text{CH})_x$ exist in a series of ordered phases having simple ratios of dopant ion to CH unit, e.g., 1:16 (“6%”), 1:12 (“8%”), and 1:6 (“17%”).

2. Experimental details and analysis methods

We used a vapor-phase doping process [32] to prepare K^+ -doped $(\text{CH})_x$. An undoped film of Shirakawa $(\text{CH})_x$ was sealed in an evacuated glass tube along with a smaller glass ampoule containing K metal in vacuo. The K ampoule, which had a delicate break seal, was then broken and the tube placed in a two-zone furnace, which heated the $(\text{CH})_x$ to $\sim 180^\circ\text{C}$ and the K metal to $\sim 175^\circ\text{C}$. The purpose of keeping the $(\text{CH})_x$ warmer than the K metal is to minimize the amount of unreacted metal condensed on the $(\text{CH})_x$ film. K concentrations, determined by weight uptake, were $y = 0.08 \pm 0.02$ and 0.18 ± 0.02 in $[\text{CH}(\text{K})_y]_x$.

K^+ -doped $(\text{CH})_x$ is extremely reactive; in order to avoid degradation we found it necessary to transfer the doped

sample to a sealed infrared window cell in a high vacuum system. This was done for the $y \approx 0.08$ sample; the $y \approx 0.18$ sample was transferred in a glove box containing 1 ppm oxygen and consequently showed some discoloration. Near infrared/visible measurements for this sample were not possible on account of this degradation.

The reflectance of the doped samples was measured over 400–4000 cm^{-1} (0.05–0.5 eV) with a Digilab FTS-80 spectrometer and over 4000–20,000 cm^{-1} (0.5–2.5 eV) with a custom-built prism spectrometer. Data for the $y \approx 0.08$ sample extend to 20,000 cm^{-1} /2.5 eV whereas, on account of the degradation mentioned above, data for the $y \approx 0.18$ sample end at 4000 cm^{-1} /0.5 eV. All data were measured at room temperature (300 K).

The data were corrected for the measured losses associated with the window, for the known reflectance of the Al reference mirror, and (approximately) for the size of the sample. On account of the irregular shape and imperfect flatness of the polyacetylene film, there are systematic errors of perhaps $\pm 25\%$ in the calibration of the reflectance. However, relative features in the spectra reproduced to within $\pm 2\%$.

We used Kramers–Kronig analysis of the reflectance to estimate the phase shift upon reflection; the phase shift and reflectance determine the frequency dependent conductivity, $\sigma_1(\omega)$ and the real part of the complex dielectric function, $\varepsilon_1(\omega)$. Conventional extrapolation techniques were used. At low frequencies, we fit the data to a Drude–Lorentz model and used the parameters from the fit to generate reflectance data from 0 to 400 cm^{-1} . (A Hagen–Rubens reflectance is not a good description for a material with reflectance below 0.5.) For the $y \approx 0.18$ sample, the reflectance data for the $y \approx 0.08$ sample were scaled to the 4000 cm^{-1} data and used as an extrapolation over 4000–20,000 cm^{-1} /0.5–2.5 eV. We used a power-law reflectance at high frequencies: ω^{-2} between 2.5 and 125 eV and ω^{-4} above 125 eV.

3. Results

The upper panel of Fig. 1 shows the reflectance of the $y \approx 0.08$ sample over the entire range measured. There is noticeable structure in the midinfrared region and a broad maximum in the near infrared. The lower panel shows the optical conductivity, $\sigma_1(\omega)$, from the Kramers–Kronig analysis. The broad maximum leads to a strong peak at about 16,000 cm^{-1} (2 eV). This maximum is possibly related to the 1.4 eV interband transition of undoped $(\text{CH})_x$, which does shift to higher energies with doping [7,33]. Alternatively, it could be a “small-particle” absorption band, induced by a highly inhomogeneous doping distribution. Note that the 0.7 eV midgap absorption [33] of lightly doped $(\text{CH})_x$ is absent.

Fig. 2 shows the reflectance over 400–4000 cm^{-1} (0.05–0.5 eV) for both samples. The reflectance shows a broad plateau in the infrared, with strong features around

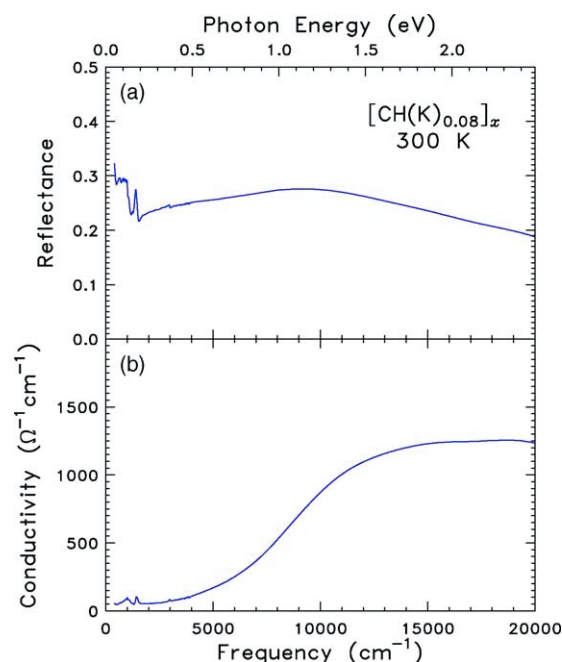


Fig. 1. (a) Room temperature reflectance of $[\text{CH}(\text{K})_y]_x$ with $y \approx 0.08$ over 400–20,000 cm^{-1} /0.05–2.5 eV. (b) Optical conductivity from Kramers–Kronig analysis of the reflectance.

900 and 1390 cm^{-1} . Weaker structure is observed at 1010, 1290, and 3000 cm^{-1} . The reflectance over the broad plateau is very similar for K concentrations of $y \approx 0.08$ and 0.18, consistent with the weak concentration dependence of the conductivity [31]. We note that the data in Fig. 2 resemble rather closely the previously measured [7] reflectance of $y \approx 0.06$ $[\text{CH}(\text{ClO}_4)_y]_x$.

Fig. 3 shows the frequency-dependent infrared conductivity of $y \approx 0.08$ and 0.18 $[\text{CH}(\text{K})_y]_x$ as determined by the Kramers–Kronig analysis. The low-frequency conductivity is nearly $120 \Omega^{-1} \text{cm}^{-1}$ for $y \approx 0.18$ and about

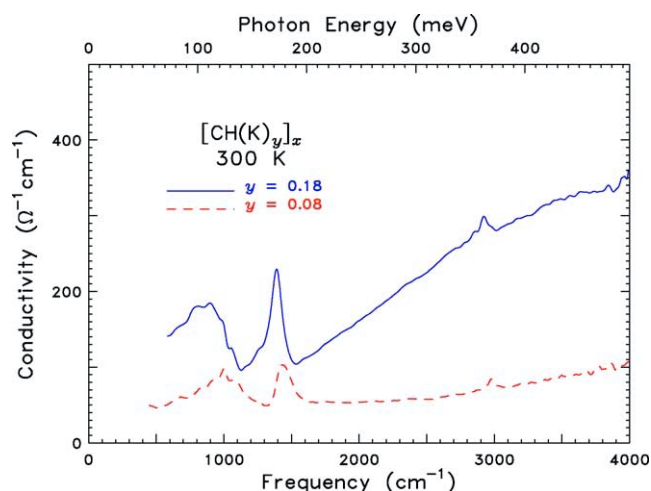


Fig. 3. Frequency dependent conductivity of $[\text{CH}(\text{K})_y]_x$ with $y \approx 0.08$ and 0.18 as determined by Kramers–Kronig analysis.

50 $\Omega^{-1} \text{cm}^{-1}$ for $y \approx 0.08$. These values are approximately a factor of 4 below those reported by Shacklette and Toth [31] but two to three times those estimated by Moses et al. [32] for donor-doped $(\text{CH})_x$. A broad and prominent band is seen in both samples in the 600–1100 cm^{-1} region. A sharper feature, also with great intensity, is seen at 1390 cm^{-1} . Weaker features are seen at 1010, 1180, 1290, and 3000 cm^{-1} . Note that the 1010 cm^{-1} line is the out-of-plane C–H bending mode of pristine *trans*-(CH)_x and is by far the strongest absorption there; here, it has about 1/20th of the oscillator strength of the 1390 cm^{-1} line.

Fig. 4 shows the real part of the complex dielectric function, $\epsilon_1(\omega)$, of $y \approx 0.08$ and 0.18 $[\text{CH}(\text{K})_y]_x$ as determined by the Kramers–Kronig analysis. For the $y \approx 0.08$ sample, $\epsilon_1(\omega)$ is positive over the entire measured range. In contrast, $\epsilon_1(\omega)$ for the $y \approx 0.18$ sample is clearly crossing zero at about 600 cm^{-1} and would appear to be negative in the far infrared.

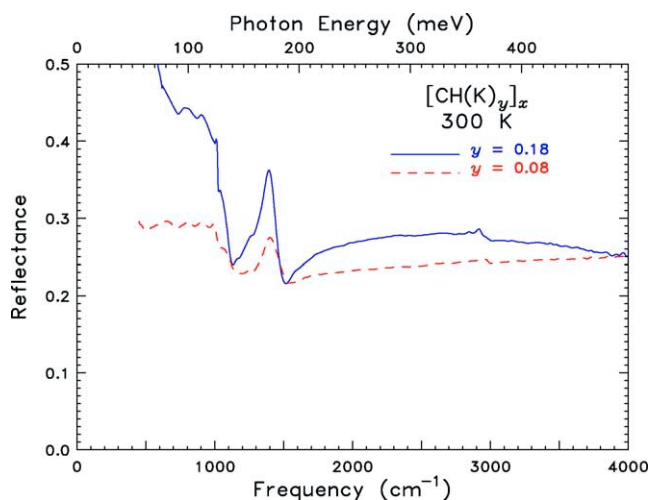


Fig. 2. Reflectance of $[\text{CH}(\text{K})_y]_x$ with $y \approx 0.08$ and 0.18 in the midinfrared region.

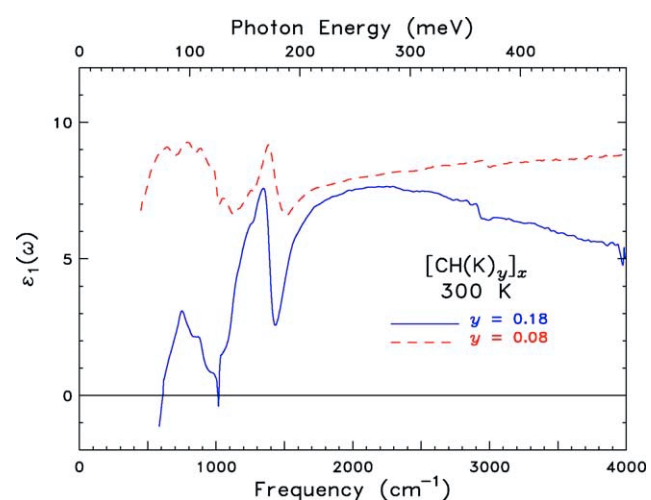


Fig. 4. Real part of the complex dielectric function of $[\text{CH}(\text{K})_y]_x$ with $y \approx 0.08$ and 0.18 as determined by Kramers–Kronig analysis.

4. Discussion

The strong feature in Fig. 3 at 1390 cm^{-1} is, within a three component theory of the lattice dynamics of $(\text{CH})_x$, attributed to a translational mode of the charged-defect containing polymer chain [34]. In our measurements, the strength (above the background) of the 1390 cm^{-1} line is seen to double as y increases from $y \approx 0.08$ to 0.18. This is the same behavior as seen in earlier studies [7,35–37] of acceptor-doped samples, which have shown that the strength of this doping induced absorption increases nearly linearly with doping concentration over the range $0 < y < 0.06$.

This behavior is demonstrated in Fig. 5, which shows the integrated oscillator strength of the 1390 cm^{-1} feature as a function of doping concentration. Previous data for I_3^- [25,35] and ClO_4^- -doped $(\text{CH})_x$ [7] are shown for comparison. The solid line is an extension of the best fit to the data from [25] for $(\text{CH})_x$ iodine doped over 0–1%.

The trend of increased oscillator strength with doping is clearly present in K^+ -doped $(\text{CH})_x$. Comparison with the previously measured [7,35] spectra reveals that the oscillator strength per dopant of the K^+ -doped samples appears to be about 30–50% of that of the hole-doped samples. Given the uncertainties of these measurements, however, we are not able to conclude that there is an actual difference between the two concentration ranges or dopant species. Indeed, there does appear to be a systematically smaller spectral weight for ClO_4^- doping and a still smaller value for K^+ doping. In the calculation by Salkola and Kivelson [16], there is a prediction of reduced oscillator strength above 6–8% doping, depending on the details of the model. Our measurements are more than accurate enough, however, to demonstrate that at the highest doping levels there is very strong doping-induced absorption in K^+ -doped $(\text{CH})_x$.

The infrared activity of the doping induced modes is a direct result of variations in charge density from site to site along the polymer chain; the modes are infrared inactive if

the charge density is uniform. For isolated defects (soliton, polaron, or bipolaron) the charge is that associated with the defect. At high dopant concentration, the order parameter for the polaron lattice is nearly constant, [19] leading to uniform charge density and hence to a nearly zero absorption. In contrast, the soliton lattice at high concentrations transforms into an incommensurate charge density wave, with sinusoidal order parameter [4,7] and the infrared activity remains. However, if the charge density wave is highly disordered, rendering the charge-density-wave ground state gapless, the infrared activity would disappear [38].

5. Conclusions

We find that the doping-induced infrared absorption in $[\text{CH}(\text{K})_y]_x$ increases approximately linearly as the dopant concentration increases from $y \approx 0.08$ to 0.18. Combining this result with earlier studies, [7,35] we conclude that the oscillator strength per dopant molecule of this absorption varies by no more than a factor of three as one changes dopant concentration from <1 to 18% and as one changes dopant species. This result appears to rule out the polaronic metal model [10] for highly doped polyacetylene as well as the picture of a strongly disordered Peierls insulator [4,7]. Our results are more consistent with the highly doped phase having a soliton lattice [12–15] or charge-density-wave ground state. Alternatively, there could be phase separation into metallic and less strongly doped regions, [16,17] although the volume fraction and/or the doping level in the less-strongly doped region would have to increase with the overall doping level. This behavior seems unlikely at doping levels of 18% (more than one dopant for every six C–H units).

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References

- [1] C.K. Chiang, C.R. Fincher Jr., Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, A.G. MacDiarmid, Phys. Rev. Lett. 39 (1977) 1098.
- [2] M.J. Rice, Phys. Lett. A71 (1979) 152.
- [3] W.P. Su, J.R. Schrieffer, A.J. Heeger, Phys. Rev. Lett. 42 (1979) 1698.
- [4] E.J. Mele, M.J. Rice, Phys. Rev. B 23 (1981) 5397.
- [5] W.P. Su, Solid State Commun. 42 (1983) 497.
- [6] M.J. Rice, S. Strassler, W. Schnieder, Lec. Notes Phys. 24 (1975) 282.

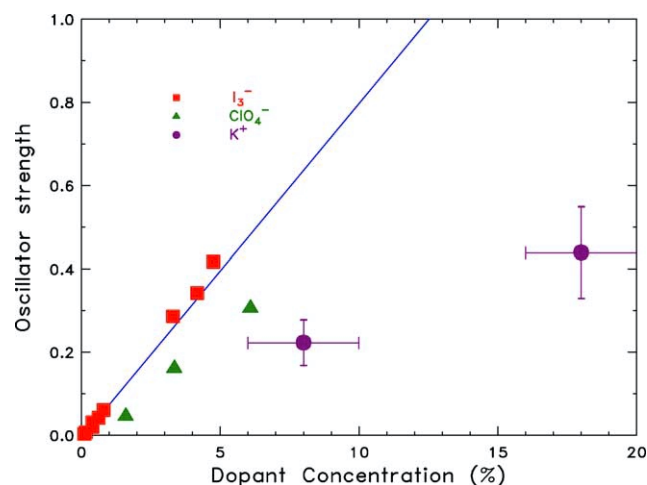


Fig. 5. Oscillator strength of the 1390 cm^{-1} mode as a function of dopant concentration.

- [7] X.Q. Yang, D.B. Tanner, M.J. Rice, H.W. Gibson, A. Feldblum, A.J. Epstein, *Solid State Commun.* 61 (1987) 335.
- [8] J. Chen, T.-C. Chung, F. Moraes, A.J. Heeger, *Solid State Commun.* 53 (1985) 757.
- [9] F. Moraes, J. Chen, T.-C. Chung, A.J. Heeger, *Synth. Met.* 11 (1985) 271.
- [10] S. Kivelson, A.J. Heeger, *Phys. Rev. Lett.* 55 (1985) 308.
- [11] M. Nakahara, K. Maki, *Phys. Rev. B* 24 (1981) 1045.
- [12] E.M. Conwell, S. Jeyadev, *Phys. Rev. Lett.* 61 (1988) 361.
- [13] E.M. Conwell, H.A. Mizes, S. Jeyadev, *Phys. Rev. B* 40 (1989) 1630.
- [14] E.M. Conwell, H.A. Mizes, S. Jeyadev, *Phys. Rev. B* 41 (1990) 5067.
- [15] S. Stafström, *Phys. Rev. B* 43 (1991) 9158.
- [16] M.I. Salkola, S.A. Kivelson, *Phys. Rev. B* 50 (1994) 13962.
- [17] J. Joo, G. Du, V.N. Prigodin, J. Tsukamoto, A.J. Epstein, *Phys. Rev. B* 52 (1995) 8060.
- [18] J.C. Hicks, J.T. Gammel, *Phys. Rev. Lett.* 57 (1986) 1320.
- [19] H.-Y. Choi, E.J. Mele, *Phys. Rev. B* 34 (1986) 5555.
- [20] J.C. Hicks, J.T. Gammel, H.-Y. Choi, E.J. Mele, *Synth. Met.* 17 (1987) 57.
- [21] B. Horowitz, *Phys. Rev. Lett.* 47 (1981) 1491;
B. Horowitz, *Solid State Commun.* 41 (1982) 593;
B. Horowitz, *Solid State Commun.* 41 (1982) 729.
- [22] C.R. Fincher Jr., M. Ozaki, A.J. Heeger, A.G. MacDiarmid, *Phys. Rev. B* 19 (1979) 4140.
- [23] G.B. Blanchet, C.R. Fincher, T.C. Chung, A.J. Heeger, *Phys. Rev. Lett.* 50 (1983) 1938.
- [24] H.E. Schaefer, R.H. Friend, A.J. Heeger, *Phys. Rev. B* 36 (1987) 7537.
- [25] D.M. Hoffman, A.J. Epstein, H.W. Gibson, D.B. Tanner, *Phys. Rev. B* 27 (1983) 1454.
- [26] E.J. Mele, M.J. Rice, *Phys. Rev. Lett.* 45 (1980) 926.
- [27] E. Ehrenfreund, Z. Vardeny, O. Brafman, B. Horovitz, *Phys. Rev. B* 36 (1987) 1535.
- [28] J.C. Hicks, J.T. Gammel, *Phys. Rev. B* 37 (1988) 6315.
- [29] A. Painelli, A. Girlando, L. Del Freo, Z.G. Soos, *Phys. Rev. B* 56 (1997) 15100.
- [30] R.H. Baughman, L.W. Shacklette, N.S. Murthy, G. G. Miller, R.L. Eisenbaumer, *Mol. Cryst. Liq. Cryst.* 118 (1985) 253.
- [31] L.W. Shacklette, J.E. Toth, *Phys. Rev. B* 32 (1985) 5892.
- [32] D. Moses, N. Colaneri, A.J. Heeger, *Solid State Commun.* 58 (1986) 535.
- [33] A. Feldblum, J.H. Kaufman, S. Etemad, A.J. Heeger, T.-C. Chung, A.G. MacDiarmid, *Phys. Rev. B* 26 (1982) 815.
- [34] B. Horowitz, Z. Vardeny, E. Ehrenfreund, O. Brafman, *Synth. Met.* 9 (1984) 215.
- [35] A.J. Epstein, H. Rommelman, R. Bigelow, H.W. Gibson, D.M. Hoffman, D.B. Tanner, *Phys. Rev. Lett.* 50 (1983) 1866.
- [36] Y.H. Kim, A.J. Heeger, *Phys. Rev. B* 40 (1989) 8393.
- [37] H.S. Woo, D.B. Tanner, N. Theophilou, A.G. MacDiarmid, *Mol. Cryst. Liq. Cryst.* 280 (1996) 169–174.
- [38] E.J. Mele, in: T. Skotheim (Ed.), *Handbook on Conducting Polymers*, Marcel Dekker, 1986.