

INFRARED ABSORPTION IN K-DOPED $(\text{CH})_x$

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Abstract

The infrared absorption of polyacetylene doped with high concentrations of potassium has been studied. The samples, doped by a vapor-phase technique to $y \approx 0.08$ and $y \approx 0.18$, showed doping-induced infrared absorption at ~ 900 , 1270 , and 1390 cm^{-1} which was comparable in strength to that seen in $[\text{CH}(\text{ClO}_4)_y]_x$ with $y \approx 0.06$. 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 lattice and soliton lattice. 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 soliton lattice. The observation of these features at high doping levels appears to be inconsistent with the polaronic metal and strongly disordered Peierls insulator models for highly doped polyacetylene.

I. Introduction

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,¹ Choi and Mele,² and Hicks, Gammel, Choi and Mele,³ 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 Horowitz⁴ there is a dramatic difference between the high-concentration polaron lattice and soliton lattice. 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.

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 time⁵ that donor doping with alkali metals can produce dopant concentrations around 16 %. Furthermore, K-doped 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 %"). Experiments at these high dopant concentrations are relatively few in number.

Infrared studies of doping-induced absorption⁶ in lightly doped $(\text{CH})_x$ and of photoinduced absorption⁷ in undoped $(\text{CH})_x$ were important factors in establishing the soliton model^{8,9} 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 or by photoexcitation. However, as shown by Horowitz,⁴ 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.

Soliton and polaron models have been employed to discuss the nature of the form of doped $(\text{CH})_x$ which occurs around 6 % doping levels and which is highly-conducting and possesses a finite Pauli paramagnetism. Initially, it was suggested that a disordered arrangement of dopant ions causes the soliton states to spread throughout the gap, destroying the dimerization at high concentrations.¹⁰ More recently, 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.¹¹ The observation¹² of a first-order phase transition in the spin susceptibility of Na-doped $(\text{CH})_x$ led to the proposal that the polymer had become a polaronic metal.¹³

II. Experimental details

We prepared K-doped $(\text{CH})_x$ by a vapor-phase doping process.¹⁴ An undoped film of Shirakawa- $(\text{CH})_x$ was sealed in an evacuated glass tube along with an glass ampoule containing K metal. The ampoule was 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 was to minimize the amount of unreacted metal deposited on the $(\text{CH})_x$ film. K concentrations, determined by weight uptake, were $y = 0.08 \pm 0.02$ and $y = 0.18 \pm 0.02$ 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 $y=0.08$ sample; the $y=0.18$ sample was transferred in a 1 ppm oxygen glove box and 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 the 400-4000 cm^{-1} (0.05-0.5 eV) range with a Digilab FTIR spectrometer and over the 4000-20000 cm^{-1} (0.5-2.5 eV) with a custom-built prism spectrometer. Data for the $y=0.08$ sample extend to 20,000 cm^{-1} / 2.5 eV whereas, on account of the degradation mentioned above, data for the $y=0.18$ sample end at 4000 cm^{-1} / 0.5 eV.

III. Results

Fig. 1 shows the reflectance over $400\text{--}4000\text{ cm}^{-1}$ ($0.05\text{--}0.5\text{ eV}$). The data shown here have been corrected for the measured losses associated with the window 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 $\pm 2\%$.

The reflectance shows a broad plateau in the infrared, with strong features around 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 0.08 and to 0.18 , consistent with the weak concentration dependence of the conductivity.⁵ The data resemble rather closely the previously-measured¹¹ reflectance of $y \approx 0.06$ $[\text{CH}(\text{ClO}_4)_y]_x$. Note that the 1.4 eV interband transition and the 0.7 eV midgap absorption of lightly-doped $(\text{CH})_x$ are absent in both cases.

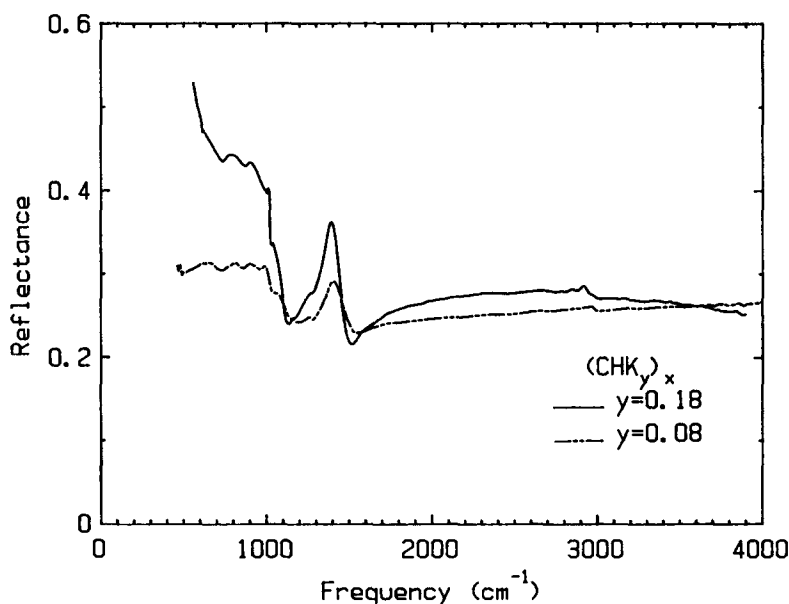


Fig. 1. Room-temperature reflectance of $[\text{CH}(\text{K})_y]_x$ with $y \approx 0.08$ and $y \approx 0.18$.

We have used Kramers-Kronig analysis of the reflectance to determine the frequency dependent conductivity, $\sigma_1(\omega)$. Conventional extrapolation techniques were used: a Hagen-Rubens reflectance at low frequencies and a power-law reflectance at high frequencies. For the $y \approx 0.18$ sample the reflectance of the $y \approx 0.08$ sample was scaled to the data and used as an extrapolation over $4000\text{--}20000\text{ cm}^{-1}$ / $0.5\text{--}2.5\text{ eV}$. Note that systematic errors in the reflectance calibration (i.e., multiplicative factors) leave the Kramers-Kronig-determined phase unchanged but lead to errors of similar magnitude in the conductivity scale.

Fig. 2 shows the frequency-dependent infrared conductivity of $y \approx 0.08$ and $y \approx 0.18$ $[\text{CH}(\text{K})_y]_x$ as determined by the Kramers-Kronig analysis. The low-frequency conductivity is nearly $200 \Omega^{-1}\text{cm}^{-1}$ for $y \approx 0.18$ and about $50 \Omega^{-1}\text{cm}^{-1}$ for $y \approx 0.08$. These values are approximately a factor of 3 below those reported by Shacklette and Toth⁵ but 2 to 3 times those estimated by Moses *et al.*¹⁴ A broad and prominent band is seen in both samples in the $600\text{--}1100 \text{ cm}^{-1}$ region. A sharper feature, also with great intensity, is seen at 1390 cm^{-1} . Weaker features are seen at 1010 , 1180 , and 1290 cm^{-1} . Note that the 1010 cm^{-1} line is the out-of-plane C-H bending mode; it is by far the strongest absorption in undoped $(\text{CH})_x$; here it has about $1/20$ th of the oscillator strength of the 1390 cm^{-1} line.

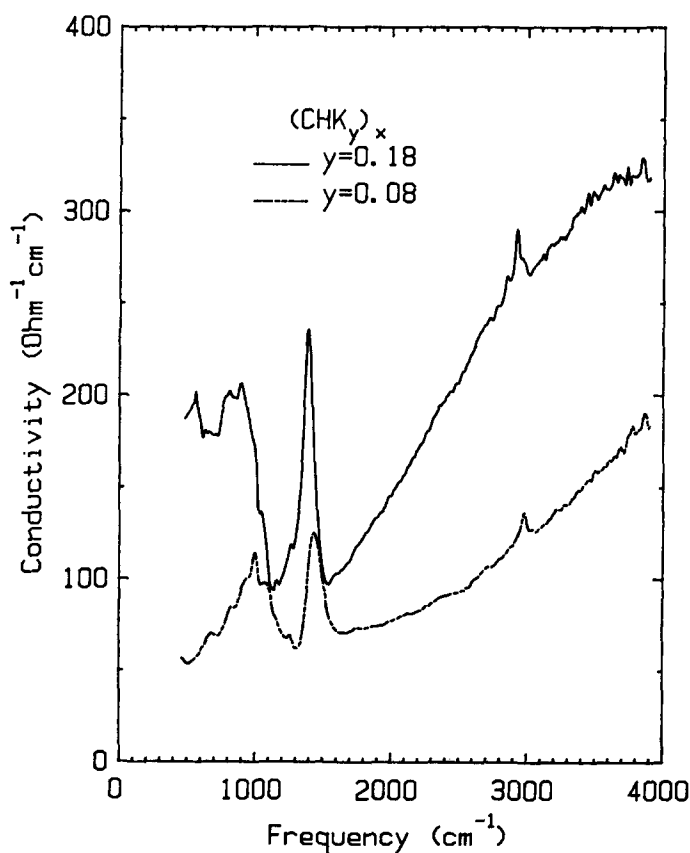


Fig. 2. Frequency dependent conductivity of $[\text{CH}(\text{K})_y]_x$ with $y \approx 0.08$ and $y \approx 0.18$ as determined by Kramers-Kronig analysis.

IV. Discussion

The strong feature in Fig. 2 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.¹⁵ 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 $y \approx 0.18$. This is the same behavior as seen in earlier studies^{11,16} of acceptor-doped samples, which have shown that the strength of this doping-induced absorption increase linearly with doping concentration over the range $0 < y < 0.06$. This trend appears to continue in K-doped $(\text{CH})_x$ at higher concentrations. A direct comparison with the previously measured¹¹ infrared conductivity of $[\text{CH}(\text{ClO}_4)_y]_x$ reveals that the oscillator strength per dopant of the K-doped samples appears to be about 70 % of that of the ClO_4 doped samples. Given the uncertainties of these measurements, however, we are not able to determine that there is an actual difference between the two concentration ranges or dopant species. The measurements are more than accurate enough to demonstrate that at the highest doping levels there is strong doping-induced absorption in K-doped $(\text{CH})_x$.

The infrared activity of the 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,² 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^{10,11} 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.¹⁷

V. 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 $y \approx 0.18$. Combining this result with earlier studies^{11,16} we conclude that the oscillator strength per dopant molecule of this absorption is (within a factor of two or so) independent both of dopant concentration and dopant species. This result appears to rule out the polaronic metal model¹³ for highly-doped polyacetylene as well as the picture of a strongly disordered Peierls insulator.^{10,11} Our result is consistent with the highly doped phase being having a soliton lattice or charge-density-wave ground state.

Acknowledgements

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