Photoinduced ir-Active Vibrations in *trans*-$(CD)_x$: A Three-Mode System

In a recent Letter Blanchet *et al.*[1] have extended photoinduced absorption measurements of *trans*-polyacetylene to lower energy than obtained before[2] for both isotopes, $(CH)_x$ and $(CD)_x$. While in $(CH)_x$ three strong ir-active vibrations (IRAV) are photoinduced, only two IRAV were observed in $(CD)_x$, at $\omega_1 = 400$ cm^{-1} and at $\omega_2 = 1045$ cm^{-1}. This appeared strange, since from doping-induced IRAV and from resonant Raman scattering (RRS) it is known that $(CD)_x$ is also a three-mode system.[3,4] Because of the asymmetry of the mode at 1045 cm^{-1}, it was suggested that two vibrations may be contained in this line, but high-resolution examination of the line failed to resolve it.[1]

We report a high-resolution photoinduced absorption measurement of $(CD)_x$ at 80 K obtained with a double integration technique using a setup described before,[2] in which we have observed the third IRAV in $(CD)_x$. As shown in Fig. 1 ω_3 peaks at 1225 cm^{-1} and its relative intensity I_3 is more than an order of magnitude smaller than I_2 ($I_2/I_3 \simeq 14$). Its location and small intensity may explain why this mode was not observed before.[1] On the other hand both its location and intensity were recently predicted with use of the amplitude-mode formalism[3] to describe the strongly coupled phonons in polyacetylene.[4]

When charges are added to the chain the induced absorption $\Delta\alpha(\omega)$ is given by[3]

$$\Delta\alpha(\omega) \sim \omega D_0(\omega)/[1+(1-\alpha_p)D_0(\omega)], \quad (1)$$

where

$$D_0(\omega) = \sum_{n=1}^{3} [(\omega/\omega_n{}^0)^2 - 1]^{-1}\lambda_n/\lambda .$$

In Eq. (1), $\omega_n{}^0$ and λ_n are the bare phonon frequencies and their relative e-p coupling and α_p is a pinning parameter.[3] The IRAV are the poles of Eq. (1) and satisfy the equation $D_0(\omega) = -(1-\alpha_p)^{-1}$. $D_0(\omega)$ for $(CD)_x$ was inferred from RRS measurements[4] and is plotted in Fig. 1. The intersections of $D_0(\omega)$ with the horizontal line drawn at $-(1-\alpha_p)^{-1}$ with $\alpha_p = 0.055$ give accurately the experimental IRAV frequencies. These include the two modes ω_2 and ω_3 (observed at 1045 and 1225 cm^{-1}) as well as the lowest mode ω_1 ("pinned mode") which, however, could not be reached with our equipment, but it is reported at $\omega_1 \simeq 400$ cm^{-1} [Ref. (1)]. The dashed line describing the "pinned mode" is a normalized theoretical[3] prediction for its line shape based on a Gaussian distribution for α_p centered around 0.055 and with a width of 0.025.

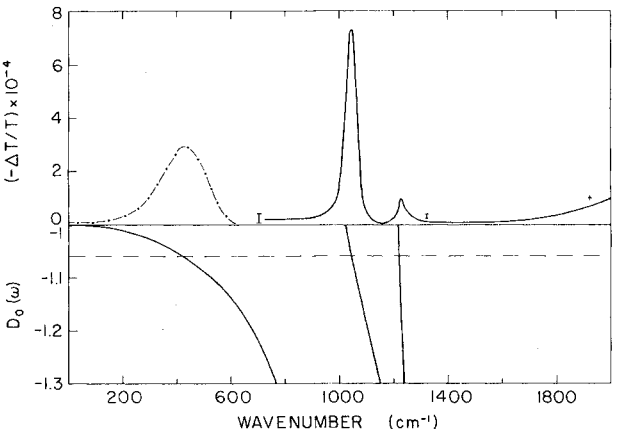

FIG. 1. Photoinduced absorption spectrum of *trans*-$(CD)_x$ at 80 K. The dot-dashed line is theoretical. $D_0(\omega)$ is displayed and the horizontal line intersections give the IRAV frequencies.

In this model the IRAV relative intensities I_n are proportional to ω times the residues [in Eq. (1)] at each pole ω_n. This residue is inversely proportional to the derivative $D' = \partial D_0(\omega)/\partial\omega$ at $\omega = \omega_n$. This explains the relative intensities in Fig. 1: $I_1 > I_2 \gg I_3$ while the order is reversed in D'.

The measurements were done during my stay at Brown University in the National Science Foundation–Materials Research Laboratory Optical Facility and I thank Professor J. Tauc for his hospitality. I thank Professor J. Tanaka for supplying me with a thin film of $(CD)_x$ and Professor B. Horovitz, Professor E. Ehrenfreund, and Professor O. Brafman for stimulating discussions. This work was supported in part by the Israli Academy for Basic Research.

Zeev Vardeny
Department of Physics, Solid State Institute
Technion, Haifa 32000, Israel

Received 15 August 1983
PACS numbers: 78.30.Cp

[1]Graciela B. Blanchet, C. R. Fincher, T. C. Chung, and A. J. Heeger, Phys. Rev. Lett. 50, 1938 (1983).
[2]Z. Vardeny, J. Orenstein, and G. L. Baker, Phys. Rev. Lett. 50, 2032 (1983).
[3]B. Horovitz, Solid State Commun. 41, 729 (1982).
[4]Z. Vardeny, E. Ehrenfreund, O. Brafman, and B. Horovitz, to be published.

