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Anomalous Hole Burning in Polymers with Inhomogeneous Broadening

by

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ANOMALOUS HOLE BURNING IN POLYMERS WITH INHOMOGENEOUS BROADENING

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ABSTRACT

For inhomogeneously broadened media such as polydiacetylene-4BCMU films, a phenomenological model is proposed to calculate the imaginary part of the optical susceptibility as a function of the pump field intensity. It is shown that the model can qualitatively account for the anomalous behavior of the absorption hole observed in recent experiments. Possible cause of the anomaly is discussed.

INTRODUCTION

Studies of transient optical effects have become important in the development of coherent optical spectroscopy and fast response nonlinear optical materials. Many experiments have been carried out by the pump-probe technique in which the strong pump laser induces the nonlinear optical response of the sample to be examined by the weak probe laser. Spectral hole burning or bleaching accompanied by a dynamical Stark shift has been observed in such experiments on various materials such as semiconductor quantum wells[1] and conjugated polymers.[2] A phase-space filling model has been proposed[3] which provides a good explanation for the hole burning and excitonic Stark effect in low-dimensional semiconductors.

It is well-known that polymers exhibit giant nonlinear optical susceptibilities with fast responses.[4] They have attracted much attention in recent years for their potential applications in future generations of high-speed signal processing devices. It is therefore of great interest to investigate the mechanism responsible for the nonlinear optical behavior.

In recent experiments on polydiacetylene (PDA)-4BCMU,[5] the hole width measured in the absorption spectrum is found to change with the pump laser intensity in an unexpected fashion. It decreases first and then increases as the intensity of the incident beam increases. On the other hand, the absorption depth increases slowly at first and rises sharply as the pump intensity steadily increases. We attempt in this paper to understand these anomalous phenomena from a model of exciton-phonon coupling system with inhomogenous broadening.

THE MODEL

For inhomogeneously broadened materials such as a PDA-4BCMU film which contains linear chains of various lengths, there is a distribution of the exciton resonance. The situation is reflected in the observed absorption spectrum shown in Fig. 1(a),[6] where the pump frequency is indicatad by an arrow. It is clearly seen from the curve that the exciton resonance at 2.35 eV (~527.5 nm) and its vibrational sideband at 2.60 eV are inhomogeneously broadened. We assume a Gaussian distribution for exciton energies in the sample,

$$g(\omega) = \frac{1}{\sqrt{2\pi}\ \Delta\omega} \exp\left[-\frac{1}{2}\left(\frac{\omega-\omega_c}{\Delta\omega}\right)^2\right] \tag{1}$$

with the parameters ω_c and $\Delta\omega$ to be determined by fitting the data. The imaginary part of the linear susceptibility is calculated[7] by adjusting these parmeters. As it turns out, we can reproduce the experimental spectrum by choosing the most probable frequenccy $\omega_c = 2.35$ eV and the width $\Delta\omega = 0.12$ eV. The result is shown in Fig. 1(b).

With the distribution (1) in mind, we proceed to calculate the nonlinear optical susceptibility due to excitions of frequency ω_x and average our result over this distribuiton. Thus, we start with the Hamiltonian

$$H(\omega_x) = \omega_x a^\dagger a + \omega b^\dagger b + \lambda a^\dagger a(b^\dagger + b)$$
$$-[\mu^* a(E_p^* e^{i\omega_p t} + E_t^* e^{i\omega_t t}) + h.c.] \tag{2}$$

where $a^\dagger$ (a) and $b^\dagger$ (b) stand for the creation (annihilation) operators for the exciton and the phonon with corresponding frequencies ω_x and ω, respectively. The coupling constant for the exciton-phonon interaction is denoted by λ, and the dipole moment matrix element of the exciton is given by μ. The pump (probe) field has the amplitude E_p (E_t) and frequency ω_p (ω_t). Only one single phonon mode in the $C \equiv C$ stretch which couples most strongly to the exciton is consiered here because no qualitative change is expected by including more modes in similar problems.[8]

Since we are not interested in any quantity that is sensitive to the quantum number counting, we neglect quantum fluctuations and deal with mean values of the operators. Thus, we write

$$\alpha = \langle a \rangle, \qquad \beta = \langle b \rangle \tag{3}$$

and the equations of motion become classical. For convenience, we define the Rabi frequencies

$$\Omega_{p,t} = \mu E_{p,t} \tag{4}$$

and detunings

$$\Delta_p = \omega_x - \omega_p \qquad \Delta_t = \omega_p - \omega_t \tag{5a,b}$$

In what follows, we discuss the steady-state solution.[9] As is always true in pump-probe experiments, the pump field E_p is much stronger than the probe field E_t which can then be treated as a small perturbation. The unperturbed soluton can be obtained by setting $E_t = 0$ and the results are[10]

$$\alpha_0 = \Omega_p/(\Delta_p - \lambda_p n - i\gamma_x) \tag{6a}$$

$$\beta_0 = -i\lambda n/(i\omega + \gamma) \tag{6b}$$

where $\lambda_p = 2\lambda^2\omega/(\omega^2 + \gamma^2)$, and the exciton number $n = |\alpha|^2$ is determined by

$$\lambda_p^2 n^3 - 2\Delta_p \lambda_p n^2 + (\Delta_p^2 + \gamma_x^2)^2 n - |\Omega_p|^2 = 0 \quad (7)$$

It is noted that we have introduced phenomenologically the damping rates γ_x and γ for the exciton and the phonon in the solutions, respectively.

Equation (7) may have one or three real roots depending on the parameters λ_p, Δ_p, Ω_p and γ_x. There exists a threshold value Ω_p^o of the pump intensity below which Eq. (7) can have only one real root. Our numerical study shows that this threshold for three real roots changes when the other parameters change. In fact, we find that Eq. (7) can have only one real root when $\Delta_p \lesssim 2\ \gamma_x$ no matter what λ_p and Ω_p may be because of the complicated nonlinear interactions between the driving field and the excitons. Corrections $\delta\alpha$ and $\delta\beta$ due to the presence of the weak test field are known from numerical analysis[11] to be oscillating with frequency Δ_t around α_o and β_o, respectively. Thus we have

$$\alpha = \alpha_o + \delta\alpha_1 e^{i\Delta_t t} + \delta\alpha_2\, e^{-i\Delta_t t} \quad (8a)$$

$$\beta = \beta_o + \delta\beta_1\, e^{i\Delta_t t} + \delta\beta_2 e^{-i\Delta_t t} \quad (8b)$$

The susceptibility experienced by the test field is given by [10]

$$\chi_t^{(i)}\ (\omega_x) = n_o\ |\mu|^2\ \delta\alpha_1^{(i)}/\Omega_t, \quad i = 1, 2, 3. \tag{9a}$$

$$\frac{\delta\alpha_1^{(i)}}{\Omega_t} = \frac{\Delta_p - \lambda_p\ n^{(i)} + \Sigma_i\ - (\Delta_t - i\gamma_x)}{(\Delta_p - \lambda_p n^{(i)} + \Sigma_i)^2 - \Sigma_i^2 - (\Delta_t - i\gamma_x)^2} \tag{9b}$$

$$\Sigma_i = \frac{2\lambda^2 \omega n^{(i)}}{\Delta_t^2 - i\gamma\Delta_t - \omega^2} \tag{9c}$$

where the superscript i labels the ith root $n^{(i)}$ of Eq. (7). The susceptibility induced by the pump field alone should be given by

$$\Delta\chi_t^{(i)}(\omega_x) = \chi_t^{(i)}(\omega_x)]_{\Omega_p \neq 0} - \chi_t^{(i)}(\omega_x)]_{\Omega_p = 0} \tag{10}$$

This equation, as we have noted earlier, expresses only contributions from those excitions of frequency ω_x. To compare with experimental results, an average over the exciton energy distribution must be taken, that is,

$$\Delta\chi_t = \frac{1}{\sqrt{2\pi}\ \Delta\omega} \int_{-\infty}^{\infty} d\omega_x\ \exp\left[-\tfrac{1}{2}\left(\frac{\omega_x - \omega_c}{\Delta\omega}\right)^2\right] \sum_{i=1}^{3} n^{(i)} \Delta\chi_t^{(i)}(\omega_x) / \sum_{i=1}^{3} n^{(i)} \tag{11}$$

RESULTS AND DISCUSSION

Equation (11) is employed to calculate the absorption spectrum in the neighborhood of $\omega_t = \omega_p$ where the behavior of a hole has been carefully investigated experimentally.[6] Parameters used in our numerical work are chosen according to experiments.[5] They are $\omega_c = 2.35$ eV, $\Delta\omega = 0.12$ eV, $\omega = 0.25$ eV, $\omega_p = 2.1$ eV, $\gamma_x = 0.0004$ eV, $\gamma = 0.0002$ eV, $\lambda = 0.01$ eV and $n_o|\mu|^2 = 2.5 \times 10^{-4}/\pi$ eV. In Figs. 2 and 3, the width and depth of the hole are plotted as functions of the pump field intensity, respectively. It is observed from Fig. 2 that the full width at half the maximum (FWHM) is oscillatory as Ω_p increases. The nonlienar behavior of the hole depth is also evidently seen in Fig. (3). For the range of the incident laser intensity $0.0001 \leq \Omega_p \leq 0.0003$ eV for which measurements are made, both the width and the depth are found in qualitative agreement with experiments. We have also found that the absorption reaches saturation at about $\omega_p \sim 0.0011$ eV not shown in the figure.

It is perhaps enlightening to point out that the detuning Δ_p is actually a variable in this model because ω_x is not fixed but is characterized by the distribution (1). As a consequence, it is always possible to find for any given Ω_p, a $\Delta_p > 2\gamma_x$ so that Eq. (7) has three distinct real roots. Since different exciton numbers n imply different lattice relaxation energies which then lead to different positions and widths of the hole. Thus, there are generally three distinguishable susceptibilities that have to be averaged before the integration over ω_x. In fact, our numerical calculations show little or no anomaly when $\Delta_p \lesssim 2\gamma_x$ or $\Omega_p < \Omega_p^o$. It should also be emphasized that extreme care should be taken in the evaluation of the integral in Eq. (11). We use 10000 mesh points for the integration range of 2 eV, about twice the distribution shown in Fig. 1(b).

Finally, we note that the calculated hole width increases monotonically with increasing pump intensity for a fixed exciton frequency ω_x. It is therefore the inhomogeneous distribution (1) that causes the oscillatory variation. This implies that the interation of the pump field with excitons (both real and virtual) of various frequencies interferes and results in the width change as well as the saturation of the depth. To understand fully the physical processes that are responsible for this anomaly, a more careful study including dispersion and dephasing effects are being carried out and results will be reported elsewhere in the near future.

ACKNOWLEDGEMENTS

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4. See, e.g., Nonlinear Optical Properties of Organic Molecules and Crystals, ed. D. S. Chemla and J. Zyss (Academic, New York, 1987).
5. L.X. Zheng and Z. V. Vandemy, Private Communication.
6. L.X. Zheng, R. B. Benner, Z.V. Vardeny and G. L. Baker, to be published.
7. For the linear case, it is straightforward to find the absorptive part of the susceptibility $\mathrm{Im}\,\chi(\omega_x) = n_x|\mu|^2\,\gamma_x/[\gamma_x^2 + (\omega_x - \omega_t)^2]$. For inhomogenously broadened medium, it follows that $\mathrm{Im}\,\chi = \int_\infty^\infty d\omega_x\, g(\omega_x)\,\mathrm{Im}\,\chi(\omega_x)$.
8. X. Li, D.L. Lin, T.F. George and X. Sun, Phys. Rev. B 41, 3280 (1990); 42, 2977 (1990).
9. The time duration of a pulse of the pump field is about 2 ps while the exciton mean lifetime is ~1 ps. Hence it is all right to treat the problem in the steady state
10. D. L. Lin, X. Li and T.F. George, to be published.
11. X. Li, Z.D. Liu, D. L. Lin and T.F. George, Phys. Lett. (in press)

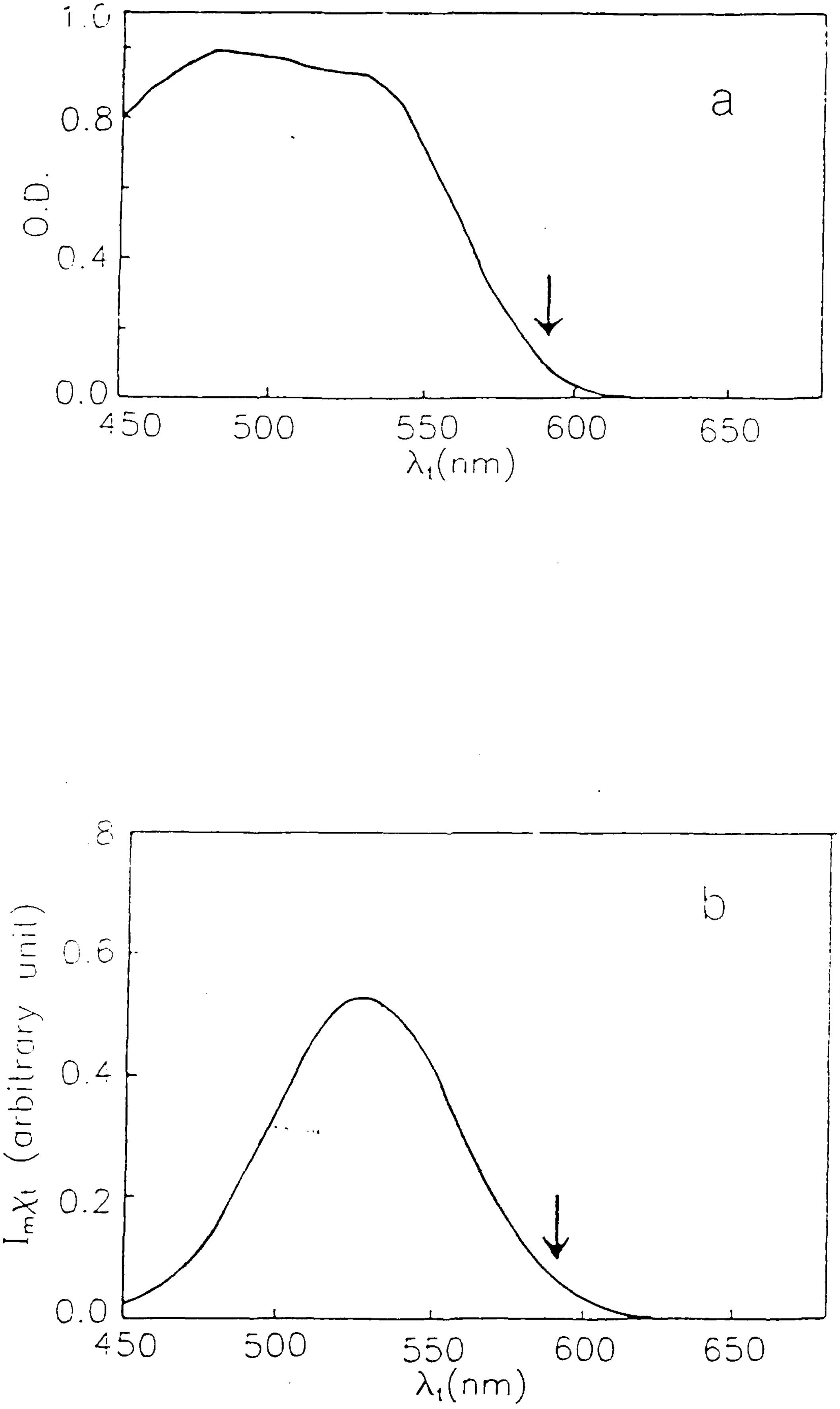
FIGURE CAPTIONS

1(a). Optical density versus the incident laser wavelength observed experimentally for a PDA-4BCMU film from Ref. 6.

(b). Absorptive part of the linear susceptibility as a function of the incident laser wavelength calculated with parameters $\omega_c = 2.35$ eV and $\Delta\omega = 0.12$ eV.

2. FWHM of the hole in the vicinity of $\omega_t \approx \omega_p$ in the differential absorption spectrum calcualted as a function of the Rabi frequency of the pump field.

3. Calculated hole depth near $\omega_t \approx \omega_p$ in the differential absorption spectrum as a function of the Rabi frequency of the pump field.



1.0
0.8
0.4
0.0
O.D.
450
500
550
600
650
λt(nm)
a
8
0.6
0.4
0.2
0.0
ImXt (arbitrary unit)
450
500
550
600
650
λt(nm)
b

Fig.1,

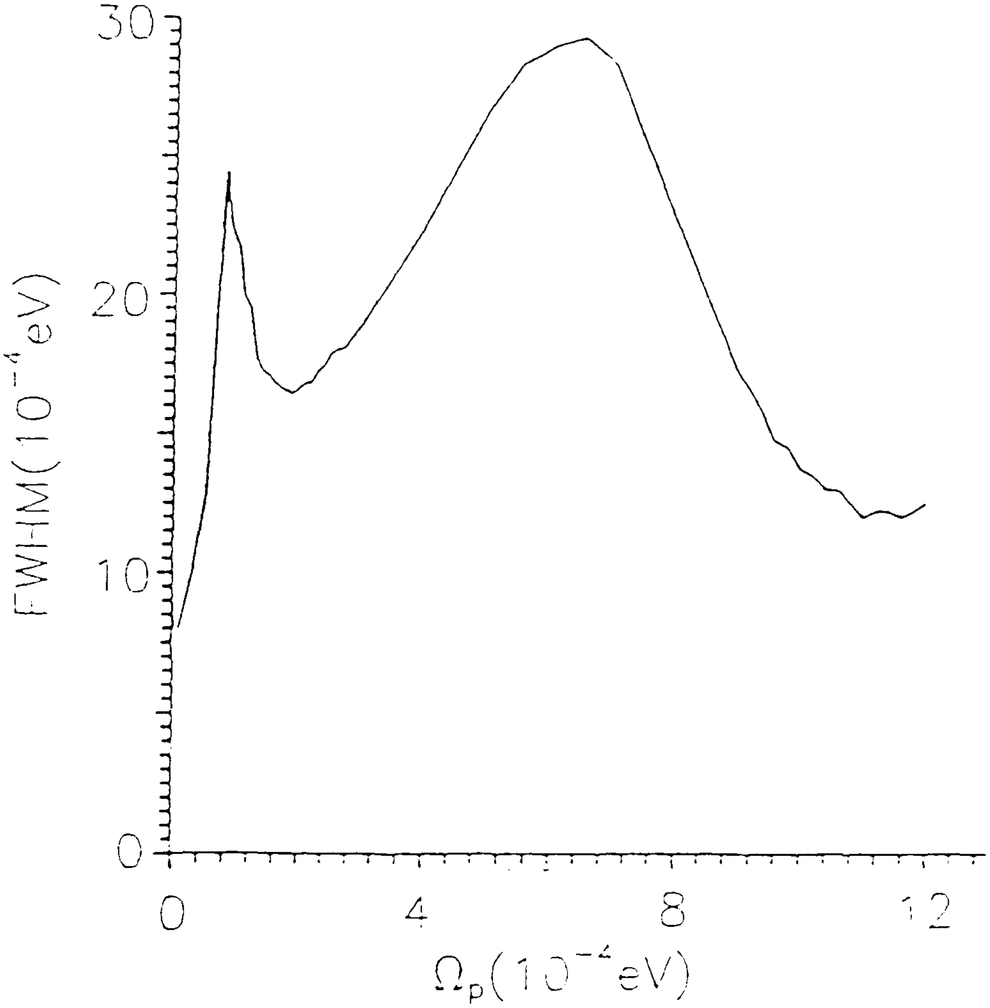


Fig. 2.

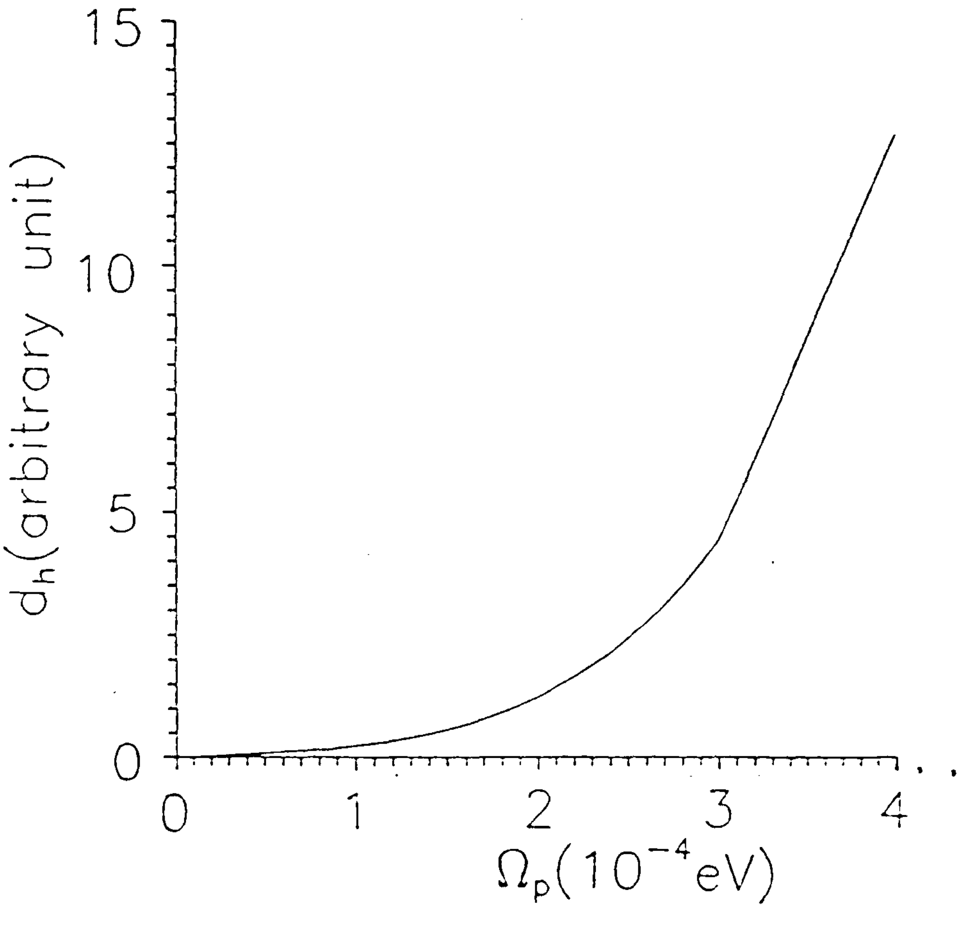


Fig. 3.