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Two-band model description of electroabsorption and third-harmonic generation in 1-D MX linear chains

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Abstract

Within a two-band model, we investigate the electroabsorption (EA) and third-harmonic generation (THG) processes in halogen-bridged mixed-valence Pt complexes: PtCl, PtBr and Ptl. For PtCl, the theoretical THG spectrum shows three peaks, corresponding to (i) a three-photon resonance at 0.83 eV originating in a M(etal)-M(etal) transition; (ii) a two-photon resonance at 1.5 eV from an M-M band-edge transition; and (iii) a three-photon resonance at 1.6 eV from an M-X transition. The latter two peaks account well for the twin-peak structure seen experimentally. We show that the twin-peak intensity strongly decreases from PtCl to PtBr and disappears for Ptl. We also discuss the theoretical EA spectra due to localized defects (polarons, bipolarons, kinks, and excitons).

There is considerable interest in the study of the nonlinear optical (NLO) properties of quasi-one-dimensional materials [1]. The halogen-bridged mixed-valence metal complexes (MX linear chain) exhibit a large NLO response [2]. By changing the metal (M=Pt, Pd, Ni), the halogen (X=Cl, Br, I) or the ligands (X, ethylamine, ethylenediamine, cyclohexanediamine) attached to the metals, the electronic properties can be tailored in an almost continuous fashion. Furthermore, the MX chains can be synthesized as well-ordered 1-D crystals [3]. The PtX systems display a charge density wave (CDW) behavior, with decreasing CDW strength from PtCl to PtBr and to Ptl. Isawa *et al.* have measured the third-harmonic generation (THG) spectrum of PtCl [2]; this presents a broad peak near 1.8 eV with a $\chi^{(3)}$ value around 3×10^{-11} esu, comparable to those in conjugated polymers [4]. The THG data for PtBr and Ptl are not available yet. Wada and Yamashita have carried out electroreflectance measurements on the PtX systems [5]; the EA data can be then obtained from a Kramers-Kronig transformation. In this work, we apply a two-band model to calculate the THG and EA spectra for the PtX systems. We also discuss the EA features associated with intrinsic defect states (i.e., polaron, bipolaron, polaron-exciton, and kink).

Gammel *et al.* have developed a two-band model to describe the PtX CDW systems and extensively studied their electronic structure, localized intrinsic defect excitations, lattice dynamics, and phonon spectra [6]. The two-band CDW Hamiltonian reads:

$$H = \sum_{l, \sigma} [(-t_0 + \alpha \Delta_l)(c_{l, \sigma}^\dagger c_{l+1, \sigma} + h.c.) + (-1)^l \epsilon_0 - \beta_l (\Delta_l + \Delta_{l+1})] c_{l, \sigma}^\dagger c_{l, \sigma} + K_{MX} \sum_l \Delta_l^2 + K_{MM} \sum_l (\Delta_{2l} + \Delta_{2l+1})^2 \quad (1)$$

Eq. (1) includes as parameters the on-site energy difference $2\epsilon_0$, hopping t_0 , on-site (β) and inter-site (α) electron-phonon coupling, and the effective spring constants for M-X and M-M bonds. We

use the parameter values suggested in Ref. [6] and set $K_{MM} = 3K_{MX}$. The adiabatic self-consistency condition is obtained as:

$$K_{MX} \Delta_l + K_{MM} (\Delta_l + \Delta_{l+1}) \delta_{l, \text{odd}} + K_{MM} (\Delta_l + \Delta_{l+1}) \delta_{l, \text{even}} = -\alpha_l \sum_{\sigma} \langle c_{l, \sigma}^\dagger c_{l+1, \sigma} + h.c. \rangle + \beta_l \langle n_l + n_{l+1} \rangle \quad (2)$$

Eq. (1) is then solved iteratively for the ground state and different kinds of local excitations with Eq. (2) and constraint $\sum_l \Delta_l = 0$ until a minimum energy lattice distortion is attained. The optical absorption is evaluated by the Golden rule as:

$$\alpha(\omega) = \sum_{as} |M_{as}|^2 \delta(\hbar\omega - (\epsilon_s - \epsilon_a)) \quad (3)$$

For a 1-D solid, both quantum-lattice fluctuations [7] and structural inhomogeneities induce an absorption linewidth broadening of gaussian type. We thus convolute the delta-function in Eq. (3) as $\delta(x) \propto \exp[-(x/2\eta)^2]/\eta$, with the full width at half maximum $\Gamma = 2\eta/\ln 2$. We apply Ott-Ward's Sum-Over-States perturbation theory [8] to calculate the THG of PtX. This method has been widely used in the description of NLO properties in linear conjugated polymers [9]. For the EA, which corresponds to the difference in absorption with and without application of a static electric field, we add a term $-F \sum_l e_l$ to Hamiltonian (1). Then, the EA is calculated as $\Delta\alpha(\omega) = \alpha(\omega, F) - \alpha(\omega, F=0)$.

The theoretical THG spectra for PtCl, PtBr, and Ptl are plotted in Fig. 1. For PtCl, which has the strongest CDW amplitude of the three, the THG spectrum consists of three peaks: (i) at 0.83 eV, which originates in a three-photon resonance to the M-M transition (at 2.5 eV within our parameters); (ii) at 1.5 eV, from a two-photon resonance to the band-edge transition (namely, from the bottom of valence band to the top of conduction band); and (iii) at

1.6 eV, from a three-photon resonance to an M-X transition. The 1.5 eV peak corresponds to what has been obtained by Sun *et al.* within a one-band CDW model to explain the observed THG peak [10]. We also depict in Fig. 1(a) the experimental results of Isawa *et al.* [2]. The experimental THG spectrum appears to have a twin-peak structure around 1.6-2.0 eV, in agreement with our two-band model result (peaks ii and iii above), indicating the necessity of using a two-band description. We find the twin-peak structure to decrease in intensities when going to weaker CDW systems (see Fig. 1(b), 1(c)); actually, it disappears for PtI. The theoretical static $\chi^{(3)}$ values for the three materials are 2.05×10^{-12} esu, 2.97×10^{-11} esu, and 6.12×10^{-10} esu, for PtCl, PtBr, and PtI, respectively.

Figure 1. Theoretical γ_{THG} spectra (in units of 10^{-14} esu) in : (a) PtCl, where the dots represent the experimental results of Isawa *et al.* [2]; (b) PtBr; (c) PtI.

We have analyzed the EA within the two-band model for the ground state of PtI earlier [11]. Here we calculate the EA from the intrinsic localized excitations, polaron, bipolaron, and kink, for which we present the spectra in Fig. 2 (taking PtBr as example, $F=300$ kV/cm, and setting a small $\eta=0.03$ eV for demonstrating clearly the structures due to localized states). There is obvious asymmetry between the positive and negative species due to the CDW. However, the band states present identical structures. It would be most interesting to investigate such features experimentally.

Figure 2. Theoretical EA spectra (arb. unit) for the localized states in PtBr: (a) positive polaron (solid line) and negative polaron (dashed line); (b) neutral (solid line), positive (dashed line), and negative (dotted line) kinks.

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REFERENCES

1. D.S. Chemla and J. Zyss (eds.), *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic, New York, 1987.
2. Y. Iwasa, E. Funatsu, T. Koda, M. Yamashita, H. Kobayashi, and K. Kubodera, *Mol. Cryst. Liq. Cryst* 217 (1992) 37; Y. Iwasa, E. Funatsu, T. Hasegawa, T. Koda, and M. Yamashita, *Appl. Phys. Lett.* 59 (1991) 2219.
3. N. Matsushita, N. Kojima, T. Ban, and I. Tsujikawa, *Bull. Chem. Soc. Jpn.* 62 (1989) 1785.
4. J.L. Brédas, C. Adant, P. Tackx, A. Persoons, and B.M. Pierce, *Chem. Rev.* 94 (1994) 243.
5. Y. Wada and M. Yamashita, *Phys. Rev. B* 42 (1990) 7398.
6. J. T. Gammel, A. Saxena, I. Batistic, A. R. Bishop, and S. R. Phillpot, *Phys. Rev. B* 45 (1992) 6408.
7. R. H. McKenzie and J. W. Wilkins, *Phys. Rev. Lett.* 69 (1992) 1085.
8. B. J. Orr and J. F. Ward, *Mol. Phys.* 20 (1971) 513.
9. See for instance, Z. Shuai and J. L. Brédas, *Phys. Rev. B* 44 (1991) 5962; *ibid.* B 46 (1992) 4395.
10. X. Sun, L. M. Li, R. T. Fu, and K. Nasu, *Synth. Met.* 57 (1993) 3986.
11. Z. Shuai D. Beljonne, J. L. Brédas, A. Saxena, and A. R. Bishop, submitted to *Phys. Rev. Lett.* (1994).