

Third harmonic generation and electron correlation in MX complex

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Abstract

Since the third harmonic generation (THG) is closely related to the energy gap, which is governed by the competition between the electron-phonon and electron-electron interactions, and the MX complex possess great flexibility of tuning the competition. Our theory shows that that the THG of the MX complex can be considerably enhanced by properly adjusting the e-p and e-e interactions.

The halogen-bridged mixed-valence transition metal (MX) complex has the chain structure, and each chain consists of alternating transition metal M (Pt, Pd, Ni) and halogen X (Cl, Br, I) with the ligand groups L attached to the metals and counterions between the chains [1].

A wide variety of MX chain complex have been synthesized in good crystallinity, their prototype is Pt-Cl complex, which has been systematically studied both theoretically and experimentally. It is shown that the Pt-Cl complex has fairly high THG with $\chi^{(3)} \sim 4 \times 10^{-11}$ esu [2]. Although this value is rather small comparing to that of polyacetylene, the MX complex remains a promising nonlinear optical material due to the following aspects. First, MX complex possesses much higher chemical stability than that of the polymers; Next, the structure of crystalline MX complex is better ordered. One more feature, which is explored in this paper, is that the THG of the MX complex can be considerably enhanced by properly adjusting the competition between the e-p and e-e interactions. The point is that the THG sensitively depends on the energy gap E_g ($\chi^{(3)} \sim \frac{1}{E_g^3}$) [3], which is governed by the competition between the e-p and e-e interactions. In MX chain complex, both the e-p and e-e interactions can be changed by chemically varying M, X, L, by pressure or by doping. It can be shown that, in MX complex, the CDW gap induced by the e-p interaction can be reduced by increasing the e-e interaction. This effect can be used to enhance the THG.

The two-band tight binding model of the MX complex reads [4]

$$H = \sum_{l\sigma} \left\{ (-t_0 + \alpha \Delta_l) (c_{l+1\sigma}^\dagger c_{l\sigma} + h.c.) + [\varepsilon_l - \beta_l (\Delta_l + \Delta_{l-1})] c_{l\sigma}^\dagger c_{l\sigma} \right\} + \frac{K}{2} \sum_l \Delta_l^2 + \sum_l U n_{l\uparrow} n_{l\downarrow}, \quad (1)$$

where $c_{l\sigma}^\dagger$ ($c_{l\sigma}$) creates (annihilates) an electron at site l with spin s , $n_{l\sigma} = c_{l\sigma}^\dagger c_{l\sigma}$. X atoms sit in the odd number of sites and M in even. Thus $\varepsilon_l = [\varepsilon_X, \varepsilon_M] = [-e_0, e_0]$, $\beta_l = [\beta_X, \beta_M] = [\beta, \beta]$, $U_l = [U_X, U_M]$, for $l = [odd, even]$, and Δ_l is the bond length deviation from uniform lattice spacing of the nearest neighboring X and M atoms. When the e-p interaction dominates, the ground state is CDW

$$\Delta_l = \Delta \left(\cos \frac{\pi l}{2} - \sin \frac{\pi l}{2} \right), \quad (2)$$

and the spectrum of Hamiltonian (1) can be obtained by using HF approximation. We can write the Bloch wave functions as

$$|k, s, j\rangle = \frac{1}{\sqrt{N}} \sum_{l=-N/2}^{N/2} \exp(i4kla) [C_{1\sigma}^{(j)}(k)|4l+1, s\rangle + C_{2\sigma}^{(j)}(k)|4l+2, s\rangle + C_{3\sigma}^{(j)}(k)|4l+3, s\rangle + C_{4\sigma}^{(j)}(k)|4l+4, s\rangle], \quad (3)$$

where, j is band indices, k is the wave vector and s is the spin of the state. The CDW parameter Δ is determined by minimizing the total energy

$$E_{total} = \sum_{j,k,\sigma}^{occ} \varepsilon_{k,\sigma}^{(j)} + \frac{1}{2} K \sum_l \Delta_l^2 - \sum_l U_l \rho_{l\uparrow} \rho_{l\downarrow} \quad (4)$$

where $\rho_{l\sigma} = \langle c_{l\sigma}^\dagger c_{l\sigma} \rangle$ and $\rho_l = \rho_{l\uparrow} + \rho_{l\downarrow}$. Then the energy gap E_g can be obtained, Fig. 1 shows that the e-e interaction reduces the energy gap E_g . It is contrary to the effect in polymers, where the e-e interaction initially enhance the energy gap [5].

With the wave functions and spectrum obtained from H , the THG can be calculated from the following formula [3]

$$\chi^{(3)}(\Omega; \omega_1, \omega_2, \omega_3) = \frac{e^4}{6\hbar^3 V} \sum_{k,s} \sum_P \left\{ \frac{\Omega_{vc}(\Omega_{vv} - \Omega_{cc})^2 \Omega_{cv}}{(\omega_{cv} + \omega_1)(\omega_{cv} + \omega_1 + \omega_2)(\omega_{cv} - \Omega)} - \frac{1}{2} \left[\frac{\Omega_{vc} \Omega_{cv} \Omega_{vc} \Omega_{cv}}{(\omega_{cv} + \omega_1)(\omega_{cv} - \omega_2)(\omega_{cv} - \Omega)} + \frac{\Omega_{vc} \Omega_{cv} \Omega_{vc} \Omega_{cv}}{(\omega_{cv} + \omega_1)(\omega_{cv} - \omega_2)(\omega_{cv} + \Omega)} \right] + \frac{(\Omega_{vv} - \Omega_{cc}) \Omega_{cv}}{(\omega_{cv} + \omega_1 + \omega_2)(\omega_{cv} - \Omega)} \frac{\partial}{\partial k} \left(\frac{\Omega_{vc}}{\omega_{cv} + \omega_1} \right) - \frac{(\Omega_{vv} - \Omega_{cc}) \Omega_{vc}}{(\omega_{cv} - \omega_1 - \omega_2)(\omega_{cv} + \Omega)} \frac{\partial}{\partial k} \left(\frac{\Omega_{cv}}{\omega_{cv} - \omega_1} \right) - \frac{1}{\omega_{cv} + \omega_1 + \omega_2} \frac{\partial}{\partial k} \left(\frac{\Omega_{vc}}{\omega_{cv} + \omega_1} \right) \frac{\partial}{\partial k} \left(\frac{\Omega_{cv}}{\omega_{cv} - \Omega} \right) \right\}, \quad (5)$$

where

$$\hbar\omega_{cv}(k) = E_c(k) - E_v(k) \quad (6)$$

is the energy difference between the conduction and valence bands, $\Omega = -(\omega_1 + \omega_2 + \omega_3)$, and

$$\Omega_{nn'}(k) = \int dr u_{nk}^* \frac{\partial}{\partial k} u_{n'k} \quad (7)$$

is the dipole transition strength, where $u_{nk}(r)$ is the amplitude modulation part of Bloch wavefunctions and n, n' are band indices, $n, n' = c, v$.

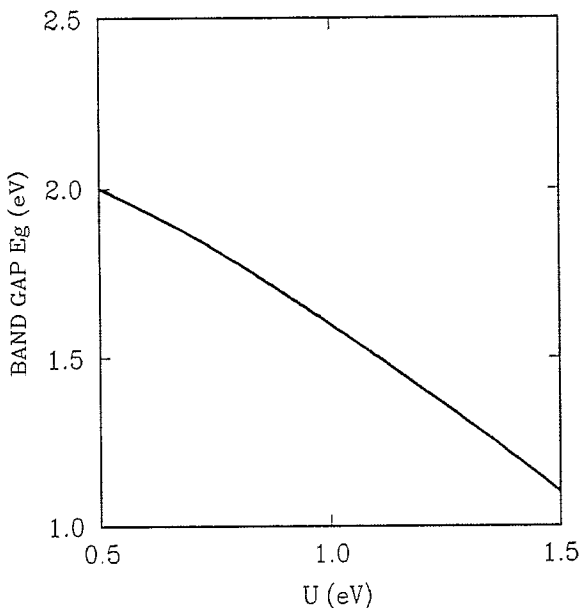


Figure 1 The band gap as a function of U.

In non-resonant region $\chi^{(3)}$ does not sensitively depend

on the frequency, the susceptibility $\chi^{(3)}(0)$ with zero frequency can be used as the limit of low frequency. The dependence of $\chi^{(3)}(0)$ on the e-e interaction is shown in Fig. 2, which indicates that the THG is enhanced by the e-e interaction. The parameters in Hamiltonian (1) are chosen as:

$$t_0 = 1.54\text{eV}, \alpha = 2.38\text{eV}/\text{\AA}, e_0 = 0.924\text{eV}, \beta = 0.143\text{eV}/\text{\AA}, K = 3.91\text{eV}/\text{\AA}^2.$$

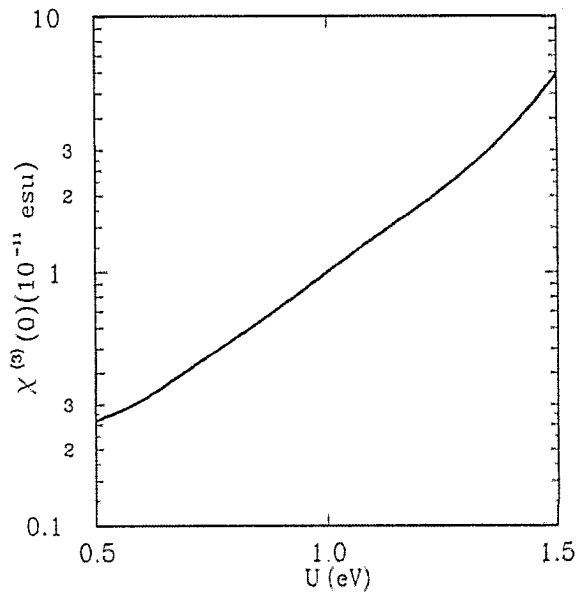


Figure 2 The dependence of THG on Hubbard U.

The physical reason of this enhancement is what we have analyzed above, mainly the e-e interaction reduces the CDW gap, and $\chi^{(3)}$ sensitively depends on the gap.

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