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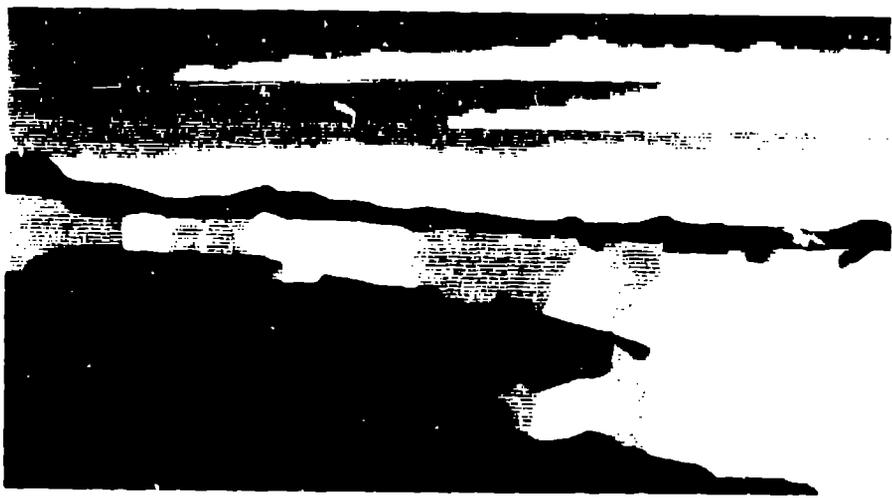
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## DYNAMICS AND PHOTOEXCITATION IN MX AND MXX' CHAIN SOLIDS

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### ABSTRACT

Nonlinear adiabatic dynamics associated with nonlinear excitations in MX and MXX' chain materials are numerically studied within a discrete, 3/4-filled, two-band, tight-binding extended Peierls-Hubbard model. Both Hartree-Fock (HF) adiabatic molecular relaxation and molecular dynamics techniques are employed to investigate the time evolution of solitons, polarons, bipolarons in charge-density-wave (CDW), bond-order-wave (BOW) and spin-density-wave (SDW) ground state materials. Photoexcitations are performed between (i) continuum levels, (ii) localized levels, (iii) continuum and localized levels. The subsequent formation and time evolution of excitons, defect pairs, breathers, and, for the MXX' solids, charge separation are studied in terms of energy levels and distortion patterns. These results are compared with the dynamics of previously studied 1/2-filled, one-band, SSH-type electron-phonon models, used for studying polyenes and polyynes, and experimental data.

### INTRODUCTION

Halogen-bridged mixed-valence transition metal linear chain complexes (MX chains),  $[ML_2][ML_2X_2] \cdot (Y_4)$  ( $M = Pt, Pd, Ni$ ;  $X = Cl, Br, I$ ;  $L$  and  $Y$  are various ligands and counterions), are interesting not only due to specific properties in the individual members of this class of materials, but, due to the wide range of ground states and attendant intrinsic defects experimentally available within relatively easily synthesized and well characterized crystals, the MX framework may be viewed as a template into which the appropriate  $M$ ,  $X$ ,  $L$ , and  $Y$  are lain to produce a material with virtually arbitrary desired properties. Thus we have put considerable effort in recent years into the theoretical modeling of the MX chain materials based on a two-band, 3/4-filled, tight-binding, Peierls-Hubbard Hamiltonian with on-site and intersite electron-phonon couplings. This effort has been recently reviewed [1], focusing on the calculation of relaxed geometries and optical absorption spectra. More recently, infrared and resonance Raman spectra were computed and compared with experimental data [2]. Our current theoretical studies of the electron spin resonance (ESR) spectra in pure MX materials [3], frustration effects at large electron-electron interaction strengths [4] and photoinduced and intrinsic electron-hole charge separation in mixed-halide MX materials [5], potentially very useful for device applications, are also included in these proceedings. References to the literature on the synthesis, characterization, and rele-

vant experiments may be found in the above, and in the experimental papers in these proceedings and those of ICSM '90 [6].

We focus here on the theoretical predictions for the dynamics of photoexcitation. It is worth noting that certain defect states, e.g. excitons, are inaccessible via impurity doping, but may be obtained during photoexcitation. This is illustrated below in the case of a weak CDW (delocalized) material PtI.

## DYNAMICS AND PHOTOEXCITATION

We have investigated the photodecay channel subsequent to photoexcitation in the ground state as well as in the presence of nonlinear excitations and impurities using adiabatic molecular dynamics [1,7]. In the present context adiabatic dynamics refers to the case when the energy corresponding to the bare phonon frequency is much smaller than the Peierls gap. For MX materials with heavy M and X atoms this condition indeed holds. The numerical procedure is an iterative two-step process. At a given time and fixed distortion pattern the electronic eigenvalue problem is solved [1]. In the next step the time evolution of distortion pattern is calculated by the classical ion dynamics. With this new distortion pattern the electronic eigenvalue problem is solved again. This process is carried out self-consistently and iteratively. We employed periodic boundary conditions. In a few test cases instantaneous as well as spatially homogeneous damping was also applied.

Photoexcitation was simulated numerically by manually removing an electron from an occupied state and instantaneously placing it in an unoccupied state. The system was allowed to evolve adiabatically with no further changes in electronic occupations. Fig. 1 shows the evolution on a PtI chain with 96 sites (48 Pt atoms and 48 I atoms) after a single electron is photoexcited across the Peierls gap, with the addition of the gap energy ( $E_g \approx 1.2$  eV) to the system. Periodic boundary conditions were employed. As is clear from Fig. 1(a), initially an exciton is formed within a phonon period. However, this exciton is unstable and, in principle, can decay into either (i) an electron polaron-hole polaron pair or (ii) a charged kink (i.e. electron and hole soliton) pair or (iii) a neutral kink-antikink pair. Based on the electronic occupancies of the excited state, the analysis of fully relaxed electronic states at later time and the energetics we find that the initially formed exciton evolves into a slowly separating neutral kink-antikink pair. Since the creation energy of the kink-antikink pair is smaller than the gap energy, the remaining energy goes partly into the kinetic energy of the kinks, partly into the acoustic phonons and partly in the form of a small amplitude localized "breather" (phonon bound state) between the kinks. Such a breather, a temporally and spatially coherent state of optical phonons [7], is clearly visible in Fig. 1(a). Alternatively, a breather is a charge-neutral, spatially localized, time-periodic, in general persistent, nonlinear lattice excitation which has important implications for subpicosecond time-resolved absorption experiments. It has distinct signatures in the intragap absorption. Since PtI is a delocalized system the initially formed exciton is extended over about 40 sites. Similarly, the breather is also quite extended.

Fig. 1(b) shows the time evolution of associated energy levels, in particular the characteristic gap states of a kink pair. Within  $\sim 200$  femtoseconds two continuum states are pulled into one (almost) degenerate midgap state indicating that the initial bound electron hole pair (exciton) quickly evolves into a kink-antikink pair. At the same time a breather level oscillates about the conduction band edge into the gap and persists with a time period larger than the phonon period.

We have also studied dynamics of photoexcitation in PtCl and PtBr. Unlike PtI, at later times lattice discreteness effects hinder complete separation of the kink-antikink pair in PtCl which is a very localized CDW system [1]. Results for a photoexcitation across the Peierls gap in a PtBr chain are shown in Fig. 2. The photodecay channel is found to be the same as in PtI except that the kink-antikink

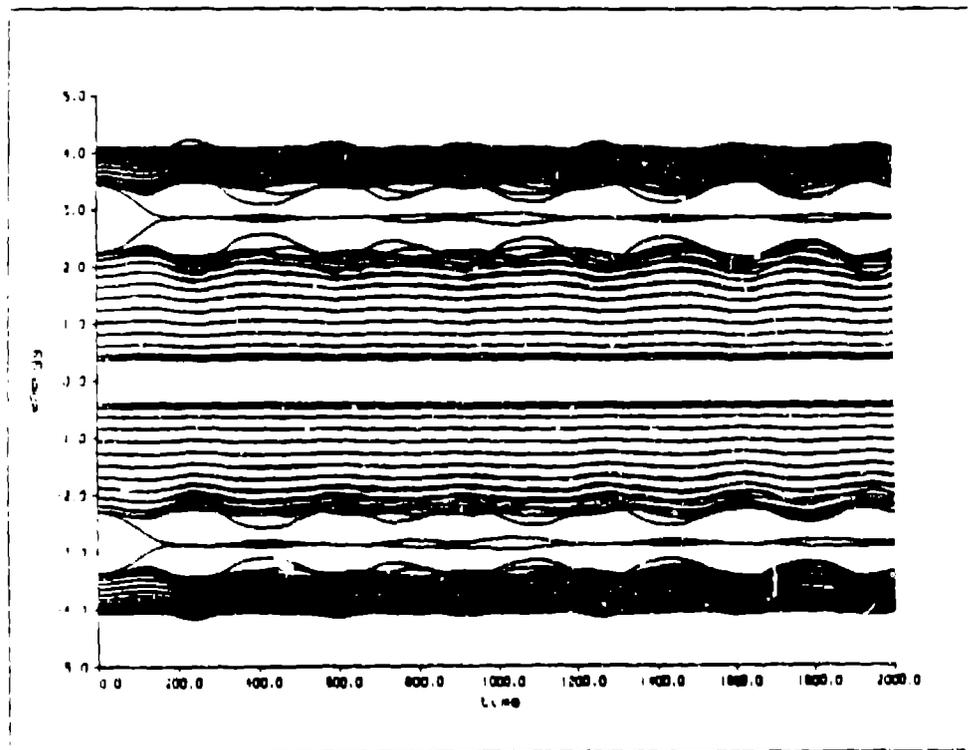
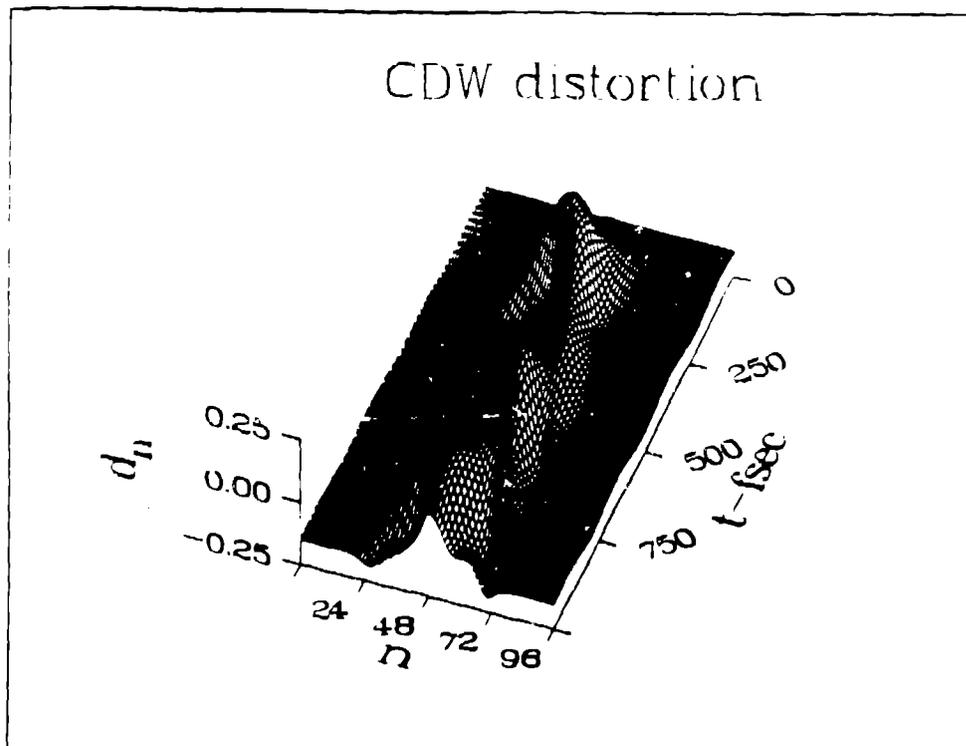


Fig. 1. Dynamics of photoexcitation in PtI: (a) CDW distortion as a function of time in units of  $10^{-16}$  seconds. For clarity the negative of CDW distortion is plotted. (b) Energy levels as a function of time for photoexcitation of the ground state.

### CDW distortion

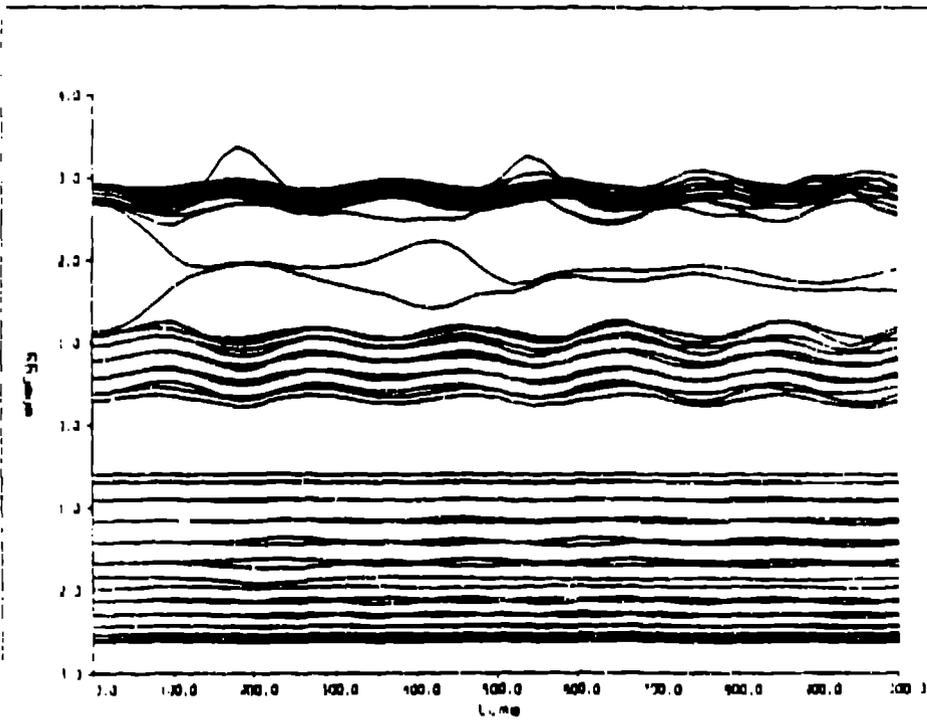
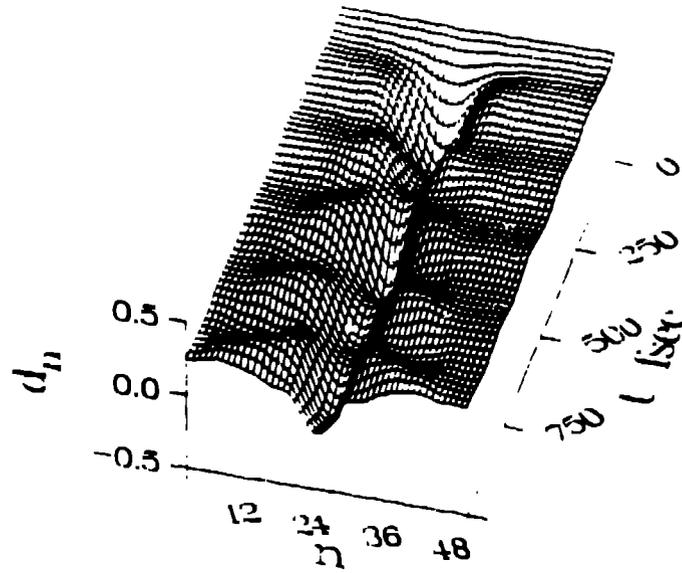


Fig. 2. Dynamics of photoexcitation in PtBr: (1) CDW distortion as a function of time in units of  $10^{-16}$  seconds. (b) Energy levels as a function of time for photoexcitation of the ground state.

pair is formed faster than in PtI and is less extended. A breather between the kink-antikink pair can also be seen.

Apart from a photoexcitation across the Peierls gap in the CDW ground state, we have also studied photoexcitations in the presence of polarons, kinks, etc., between intragap levels as well as between a localized level and a continuum (band) state. We find interesting photodecay channels other than the kink-antikink pair discussed above.

## CONCLUSIONS

We have presented an illustrative example of a theoretically calculated photodecay channel. A more detailed report of the dynamics of pure MX chain materials with weak electron-electron interactions will appear shortly [8]. Investigations of the influence of Coulomb interactions (both on-site Hubbard and longer-range terms) and site and bond impurities on the photodecay channel, in addition to dynamics studies for mixed-halide MX (MX<sub>2</sub>) materials, are in progress. These studies, combined with those mentioned in the introduction, will help both to further elucidate the experimental behavior of specific MX materials, as well as increase our general understanding of the role of competing electron-electron/electron-phonon interactions in all low-dimensional materials.

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