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Publisher: Taylor & Francis

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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

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Version of record first published: 17 Oct 2011.

To cite this article: E. J. Mele & G. Hayden (1985): Cluster Studies of Correlation Effects on the Excited States of Polyenes, *Molecular Crystals and Liquid Crystals*, 118:1, 19-29

To link to this article: <http://dx.doi.org/10.1080/00268948508076184>

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Cluster Studies of Correlation Effects on the Excited States of Polyenes

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Abstract The Hubbard-Peierls Hamiltonian is used to investigate the competing effects of electron phonon and electron electron interactions in the excited state spectrum for six electrons propagating on a six membered ring. With increasing U we find that the character of the lowest lying singlet excitation changes discontinuously from a polar state ($U < U_c$) which drives a structural relaxation analogous to soliton creation on the ring to an "excitonic" state ($U > U_c$) which favors polaron creation in the ring. Implications of the results for the excited state spectrum of $(CH)_x$ are discussed.

Introduction

Current theoretical models used to study photoexcitations in $(CH)_x$ and the related finite polyenes may be divided into two general classes. In one class are the models exemplified by the electron phonon model proposed by Su, Schrieffer, and Heeger (SSH) (1). These models describe the coupling of π electron bond orders to C-C bond lengths on the polymer backbone, and are commonly used to demonstrate, for example, that the equilibrium molecular structure in the ground electronic state is a dimerized (bond alternating) configuration. Parameterizations of this model have been found to yield a consistent semi-quantitative description of the magnitude of the bond alternation, the condensation energy and the phonon frequencies on the ground state surface (1,2). For long chains, models in this category predict an interesting symmetry breaking relaxation in the lowest electronic state, first analyzed in detail by Su and Schrieffer (3). This relaxation can be described as the formation and dissociation of two oppositely charged solitons in the bond alternation amplitude, which thus separate the excited carriers. Following this suggestion there have been a number of

experimental studies undertaken to examine the applicability of this description to photoexcitations in $(\text{CH})_x$ (4,5).

The second class of models have been studied extensively in the chemical community and emphasize the essential role of Coulomb correlations for a description of the excited states of these systems. Examples in this category are the configuration interaction studies on the Pariser-Parr-Pople (PPP) Hamiltonian by Schulten et al (6), Hudson (7) and more recently Soos and coworkers (8). These studies have emphasized that for finite polyenes, correlation modifies the rigid lattice excitation spectrum so that the lowest lying electronic state is not the ${}^1\text{B}_u$ state anticipated in the uncorrelated limit, but instead a state which has the same spatial symmetry as the ground state (${}^1\text{A}_g$) and which is dominated by two particle and higher independent particle excitations. This state is therefore not directly optically excited from the ground state, though there has been considerable evidence cited to implicate this state as a metastable state to which the photoexcited polyene may relax nonradiatively (9,10). In this theoretical work the effect of structural relaxation on the excited states is normally estimated by comparing bond orders in the ground and excited states; a self-consistent geometry optimization is conventionally not undertaken.

These two classes of models yield contrasting descriptions of the excited states of long polyenes. From experiments on finite polyenes, it is found that the width of the vibronic structure in optical excitation (~ 0.5 eV) is typically of the same order as the $2{}^1\text{A}_g - {}^1\text{B}_u$ splitting (~ 1.0 eV) obtained in the PPP models, which suggests that structural relaxation effects and correlation effects are of comparable importance. To obtain a better description of photoexcitations in $(\text{CH})_x$ it is therefore desirable to examine models containing features of both classes.

In the last several years there have been a number of studies analyzing the simultaneous effects of electron phonon coupling and electron electron repulsion on the ground state properties of long polyenes (11-14). These studies have demonstrated the persistence of dimerization in the presence of moderately strong repulsion and an interesting enhancement of dimerization for the weakly correlated ground state (12-13). As

noted above, the effects of correlation on the excited state spectrum are considerably more pronounced, and the situation is further complicated by the observation that the ordering of the excited states is sensitive to the variational freedom allowed for the many particle excited state wavefunction (6).

Here we examine the effects of lattice relaxation on the excited states of bond alternating structures in the presence of correlation for various strengths of the repulsion integrals. We confine our attention to finite systems which are sufficiently small to allow a rapid exact diagonalization of a Hubbard-Peierls Hamiltonian for the N electrons; in fact we limit our discussion to the case of six spin 1/2 particles propagating on a six membered ring. The motivation is to extract an intuitive picture of correlation effects from exact calculations on small systems which will both provide a qualitative description of phenomena occurring in longer systems and suggest an accurate approximate theory for longer systems. We are finding these calculations for $N=6$ helpful in both respects. In the following we outline our computational procedure and principal results, and close with some speculations about the behavior of larger correlated systems.

Computational Methods

For the calculations described below we adopt the Hubbard-Peierls Hamiltonian

$$\mathcal{H} = \sum_{i\sigma} (t_0 + \alpha x_i) a_{i\sigma}^\dagger a_{i+1\sigma} + \text{h.c.} \\ + \frac{1}{2} U \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + \frac{1}{2} K \sum_i x_i^2$$

(1)

where a_i^\dagger creates an electron with spin 1/2 on the i th site of an N -membered ring, t_0 is the nearest neighbor

hopping amplitude in an equal bond length reference structure, α is the derivative of this amplitude with respect to the bond length fluctuations (x_i), U is an on site two body repulsive interaction and K is a harmonic spring constant favoring the equal bond length structure. We apply this Hamiltonian to the case $N=6$; here 924 spin-space functions span the 6 particle Hilbert space, 175 of which are singlets. We generate 175 orthonormal basis functions to span the singlet space following the Serber coupling scheme (15). A computer code to extract matrix elements of H between these basis states was constructed and tested by reproducing known spectra in the $U = 0$ and large U limits (16). In the latter case the low lying spectrum of (1) is described by an effective Heisenberg spin Hamiltonian, and we have verified that our low lying neutral eigenfunctions reproduce the Bonner-Fisher results for $\langle S_z(i)S_z(i+j) \rangle$ in this limit (17).

For each electronic state we structurally equilibrate our model by computing the Hellmann-Feynman forces and combining these with the elastic forces from the last term in (1) to identify the net force on each site on the ring. A gradient descent procedure is then used to identify the potential energy minima in the ground and excited electronic states. To allow broken symmetry solutions we find it useful to manually displace the system from its highly symmetric configuration at various stages of the calculation. Although we searched the full six dimensional structural space the two most interesting distortions involve a relaxation from the sixfold symmetric structure to a threefold dimerized pattern (labelled by a distortion Q_d) and a relaxation from the sixfold structure towards a twofold bond alternating structure in which the bond alternation pattern slips at two sites on opposite vertices of the ring (labelled by a distortion Q_s). Only distortions preserving the circumference of the ring were considered (i.e. the ring is not permitted to breathe).

For $N=6$ even in the fully symmetric reference structure, quantization due to the finite system size opens a gap in the $U=0$ one electron spectrum. Consequently the ring is dimerized in the ground electronic state only when the dimensionless electron phonon coupling constant $\lambda = \alpha^2/Kt_0$ exceeds a critical value.

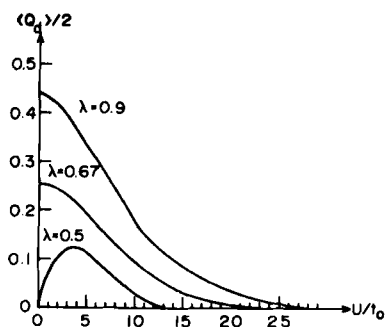


Fig. 1 Ground state dimerization amplitude as a function of U/t_0 for various coupling strengths

In Figure 1 the dimerization amplitude in the ground state is plotted as a function of U/t_0 for different values of λ . The smallest value of λ corresponds to the coupling adopted by Mazumdar and Dixit (12) for which the dimerization amplitude just vanishes at $U=0$ but is enhanced to a nonzero value only once U is turned on. Notice that for larger λ the dimerization amplitude is large and weakly U dependent for small U/t_0 and is finally suppressed in the large U limit. Dimerization is always lost above a critical repulsion strength; this is also a finite size effect. For $\lambda = 0.67$ for which more detailed results are given in Section III, the ratio of the strong to weak hopping amplitudes is three in the ground state equilibrium geometry at $U=0$. The virtue of working in this strong coupling regime is that here the $N=6$ ring most closely approximates the behavior of the long chain. For example in the strong coupling limit at $U=0$ the first excited electronic state drives a symmetry breaking relaxation which yields a twofold symmetric bond alternation pattern with two "kinks" at opposite vertices of the ring. For weaker λ the widths of these defects grow so that the kinks spread, interacting more strongly and weakening the dimerization amplitude more uniformly around the ring. Thus we believe that in the strong coupling regime we can extract behavior representative of the larger systems from these finite clus-

ter calculations. The principal and unavoidable disadvantage of the strong coupling limit is that quantitative comparison with the accepted parameterizations for $(\text{CH})_x$ cannot be made.

Results

We examine the effects of Coulomb correlation and lattice relaxation on the excited state spectrum by turning these interactions on in turn.

Vertical Excitation Spectrum

Level diagrams for the six particle singlet states are given in Figure 2 for three representative values of the repulsion integral ($U/t_0 = 0.1, 1.0$ and 5.0). In all cases the ring has been relaxed to the ground state equilibrium geometry which is the threefold (C_{3v}) dimerized structure (here $\lambda = 0.67$). The ground electronic state is the fully symmetric A_1 state in all cases. For $U=0$ the first excited state is fourfold degenerate separated by a small gap from a second

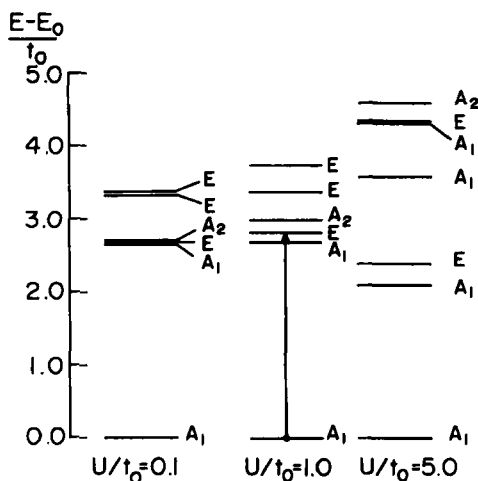


Fig. 2 "Rigid lattice" singlet states on the ring for $\lambda = 0.67$ at three representative values of U/t_0 .

fourfold degenerate excited state manifold. It is apparent that even a very weak U has a profound effect on these excited states. As demonstrated in the two right hand panels, U lifts the excited state degeneracy, and a second fully symmetric A_1 state appears at the bottom of the excited state band. In C_{3v} the E states are the polar states dipole accessible from the A_1 ground state; the lowest lying optical excitation is thus identified as the transition to the second singlet excited state. We believe that the low lying A_1 state is the ring analog of the 2^1A_g state discussed for the finite polyenes. Even for the simple case of $N=6$ we have not yet been able to extract a simple physical definition of the character of this state, but will refer to it as "excitonic" (18). Some important results from the $N=6$ study which we believe to be representative of larger systems are:

1. As $U \rightarrow 0$ the ground state is well separated from the low lying excited states by a gap. (For $N=6$ this gap has roughly equal contributions from the finite size of the ring and the ground state dimerization, clearly only the latter contribution persists into the large N limit.) Thus for sufficiently weak U the effect of electron repulsion on the ground state properties should be accessible through low order perturbation theory.

2. As $U \rightarrow 0$ the low lying excited state spectrum is very dense; this spectral region will be more congested for large N which will provide a large number of low lying single particle excitations. For even very weak U we expect these states to be strongly mixed and the independent particle degeneracy will be removed.

3. The lowest excited singlet to emerge from the independent particle "continuum" is the fully symmetric A_1 state. In the limit of very large U this state will ultimately describe a low lying spin wave in the system; however, in the parameter range of interest this state retains a large admixture of the charge transfer (ionic) configurations.

Lattice Relaxation Effects

The effect of lattice relaxation on the ordering of the low lying excited states is demonstrated in

Figure 3 and can be summarized in the following general observations. The relaxation which produces charged soliton pairs occurs on the polar, dipole accessible potential surface (labelled E in the ground state geometry); the energy gained in this relaxation is governed by the electron phonon coupling strength λ .

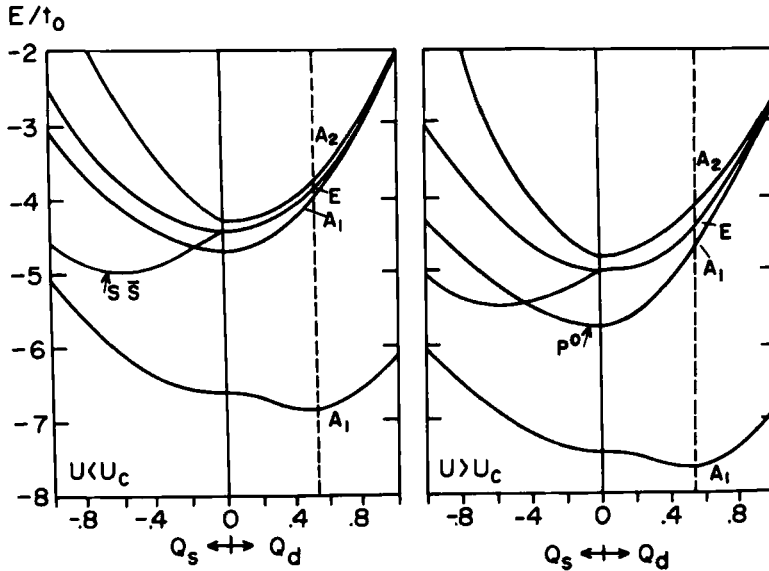


Fig. 3 Potential surfaces for the low lying singlets on the ring $\lambda = 0.67$. Q_d labels a distortion to a 3-fold symmetric bond alternating structure. Q_s labels a distortion to a 2-fold symmetric structure containing bond alternation defects at opposite vertices of the ring.

The lower lying excited A_1 state weakens the dimerization but does not favor kink formation; the splitting between this "excitonic" state and the E states increases with U. The lowest lying singlet excited state is thus determined by the competition between the lattice relaxation energy on the dipole accessible surface and the correlation stabilization energy on the lower

lying excitonic state. Two limiting behaviors are identified in Figure 3 for $U < U_c$ and $U > U_c$. In either case the ground state is clearly dimerized (the level diagrams of Figure 2 correspond to the vertical dashed cuts on this diagram; $\lambda = 0.67$). For $U < U_c$ the electron lattice interaction dominates and the structural relaxation in the excited state inverts the "vertical" state ordering. In the lowest excited state we obtain "kinks" in the dimerization amplitude at opposite corners of the ring, as expected in the SSH Hamiltonian. For $U > U_c$ the situation changes dramatically. The minimum energy configuration is now on the A_1 surface in the undimerized geometry; the analogous behavior for a long system would presumably correspond to a local reduction of the bond alternation amplitude, or polaron formation. It is interesting to note that these two kinds of relaxations involve separate potential surfaces, and therefore as U increases there should be a sudden transition from the conventional SSH picture to a new regime in which the lowest lying singlet is the self-trapped "excitonic" state. If a long range repulsion is retained, the charged solitons are presumably bound even for $U < U_c$, nevertheless there should be a discontinuous change in the character of the lowest lying singlet as the potential minima cross. For our model the transition occurs for $U_c/t_0 \sim 2$, however, this threshold is both N and λ dependent.

Extrapolation to Longer Systems

We are ultimately interested in understanding whether $(CH)_x$ is better characterized by the $U < U_c$ or the $U > U_c$ behaviors described above. It is interesting to note that in the conventional Pariser-Parr-Pople (PPP) parameterizations $U_{eff}/t_0 \sim 1.5$ which suggests that $(CH)_x$ is near the transition regime; this corroborates our observation in Section I that the extrapolated vibronic widths and the 1A_g binding energies are comparable. To investigate this question further we have applied the formalism of Section II directly to the PPP Hamiltonian for C_6H_6 ; here our results unfortunately were dominated by the limited size of the model.

We suspect that the general picture of Section III in which there is a competition between two kinds of

discrete many electron states will persist into the large N regime. It is interesting to speculate that if $(CH)_x$ is close to such a transition that the unfavorable state would remain as a metastable excited configuration. Thus for example if soliton formation is favored, as in the SSH picture, rapid nonradiative crossing to the "excitonic" state could trap a portion of the excited population. The excitations from and the kinetics of the decay of such a state would be of some interest. Alternatively if the self-localized exciton is lowest, relaxation to this level would still be limited by an intersurface crossing during the very rapid relaxation expected on the dipole accessible surface. The anomalously broad absorption edge in trans $(CH)_x$ suggests the dominance of a rapid large amplitude multiphonon process in the optically excited state which is uncharacteristic of the relaxations found in finite polyenes, or in cis $(CH)_x$. Several models associating this edge with the vibrational broadening due to soliton formation have been developed (19-21). A more thorough understanding of correlation effects in the excited states will await an extension of the Hubbard-Peierls theory to longer systems.

Acknowledgements: This work was supported by NSF under grant No. DMR 82-03484. EJM gratefully acknowledges support from the Alfred P. Sloan Foundation, and the additional assistance provided by the organizers of ICSM '84.

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