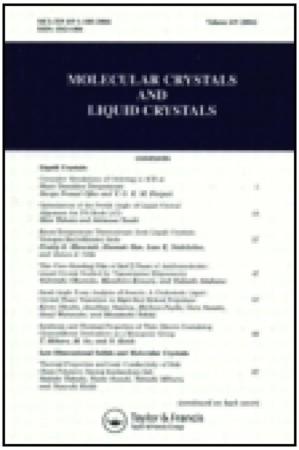

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ELECTRON-PHONON vs. ELECTRON-ELECTRON INTERACTIONS IN LOW DIMENSIONAL SOLIDS

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Abstract We present a general method to investigate the effect of electron-phonon coupling on the vibrational spectra of low-dimensional solids. The method, originally developed to deal with charge transfer crystals, is extended to conjugated polymers and to metal-halogen chains. We show that quadratic electron-phonon coupling is essential to properly define the reference state and to determine sets of transferable e-ph coupling constants.

INTRODUCTION: LINEAR AND QUADRATIC ELECTRON-PHONON COUPLING

The distinctive and most interesting physical properties of quasi one-dimensional (1D) solids are generally related to the presence of low lying electronic excitations. These electronic states are strongly coupled to the phonon system and, among other effects, originate in the vibrational spectra several peculiar features which are hardly accounted for by traditional spectroscopic methods. However, once the role of electron-phonon (e-ph) coupling is properly recognized, vibrational spectra become a valuable source of information on both vibrational and electronic properties. In this paper we present a general method to evaluate the strength of e-ph coupling from the analysis of the vibrational spectra of various classes of 1D half-filled systems.

The signatures of e-ph coupling (vibronic features) in the vibrational spectra of 1D solids can be qualitatively accounted for in terms of linear e-ph coupling. In his pioneering work on the vibrational spectra of charge transfer (CT) crystals with a dimerized segregated stack structure,[1] M.J.Rice proposed that the totally symmetric molecular vibrations are coupled to the CT electron via the modulation of on-site energies (electron-molecular vibration or site-diagonal e-ph coupling). A linear response theory (LRT) approach allowed him to demonstrate that the involved modes are softened and borrow intensity from the nearby CT band, giving rise to strong infrared (IR) absorptions, polarized along the stack axis. Several extensions of the Rice's approach to CT crystals with different (mixed, trimerized, tetramerized...) stack structure have been subsequently proposed,[2] showing that linear e-ph coupling can strongly affect both Raman and IR spectra.

The amplitude mode (AM) formalism developed by B.Horovitz[3] to describe the Raman and IR spectra of polyacetylene (or more generally of conjugated polymers) is also strictly related to the Rice's model. In polyacetylene (PA) the totally symmetric (a_g) phonons couple to the electrons via the CT integral modulation (bond-diagonal e-ph coupling). A LRT approach shows that this coupling originates a softening of the involved modes. The softening is strongly dependent on the electronic structure, hence on the conjugation length, on the presence of defects, and so on. Moreover, in doped and photoexcited samples, where defects lower the local symmetry, a_g modes acquire large IR intensities.

Linear e-ph coupling has also been recently proposed[4] to account for several features of the optical spectra of halogen-bridged metal complexes (MX chains; M =Pt,Pd,Ni.., X =halogen). In these systems the symmetric M-X stretching vibration modulates the on-site metal energy. Among other spectral features, this site-diagonal e-ph coupling is responsible for the appearance of long progressions of overtones in resonance Raman spectra.

In spite of their success, linear e-ph coupling theories cannot provide a quantitative description of vibronic effects in 1D solids. The main problem of linear e-ph coupling models is the lack of unambiguous definition of the reference state. As a consequence, the physical meaning of the fundamental microscopic parameters of the theory, i.e. the reference frequencies and the linear e-ph coupling constants, is obscured. Both parameters are then treated as adjustable quantities and are extracted from experiment by means of non-linear fitting procedures, often yielding non-reliable estimates. A precise physical meaning can instead be given to the microscopic parameters in models accounting for quadratic e-ph coupling. This is easily understood in the Herzberg-Teller (HT) approach sketched below.

In the crude adiabatic approximation the electronic hamiltonian ($\mathcal{H}_e$) does not depend on nuclear coordinates (**R**). HT introduce the **R**-dependence by expanding $\mathcal{H}_e$ on the **R** basis. Consistently with the harmonic approximation the expansion is carried out up to the second order, yielding the following e-ph hamiltonian:

$$\mathcal{H}_{e\text{-}ph} = \sum_{i} \frac{\partial \mathcal{H}_e}{\partial R_i} R_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 \mathcal{H}_e}{\partial R_i \partial R_j} R_i \, R_j \tag{1}$$

where i counts nuclear coordinates. $\mathcal{H}_{e\text{-}ph}$ acts as a perturbation on the **R**-independent eigenstates of $\mathcal{H}_e$, yielding **R**-dependent states. The second derivatives of the ground state energy on the R's give the force constant matrix (**F**) for the nuclear motion:

$$F_{ij} = F^{s}_{ij} + \langle G|\frac{\partial^2 \mathcal{H}_e}{\partial R_i \partial R_j}|G\rangle - 2 \sum_{F} \frac{\langle G|\frac{\partial \mathcal{H}_e}{\partial R_i}|F\rangle \, \langle F|\frac{\partial \mathcal{H}_e}{\partial \mathcal{R}_j}|G\rangle}{E_F - E_G} \tag{2}$$

where $|G\rangle$ and $|F\rangle$ are the ground and excited states of $\mathcal{H}_e$, and E_G and E_F are the corresponding energies. $F^{s}_{i,j}$ represents the skeleton force constant due to the contribution of the core electrons, i.e. of electrons which are not described by $\mathcal{H}_e$ (the deep level electrons in CT crystals or in MX chains, the σ-electrons in conjugated polymers).

As discussed above, the distinctive vibrational properties of 1D systems originate from the third term in Eq. 2, i.e. from the linear e-ph coupling, which involves CT-electron fluctuations and is strongly dependent on the excitation spectrum. On the other hand, the contribution from quadratic coupling only involves the ground state and is therefore expected to be similar for systems with similar ground state. The quadratic contribution is conveniently included in a reference force field F^o, which describes the potential due to the core electrons and to the ground state CT-electron distribution, but does not include CT-electron fluctuations.

In this view, the definition of the reference state for CT crystals appears rather obvious. CT crystals are molecular solids and the reference state for molecular vibrations is given by the isolated molecular units bearing the same charge they have in the crystal. Several years ago we recognized the role of quadratic e-ph coupling in CT crystals and the importance of a proper definition of the reference state.[5] This yielded reliable and transferable values of the fundamental microscopic parameters of the theory, i.e. the linear e-ph coupling constants.

On the contrary, for PA and MX chains the definition of a proper reference state is a more subtle problem. In these extended structures in fact the effect of CT electron fluctuations can hardly be disentangled from that of the ground state electronic distribution. In the following we shall shortly review the recently discussed definition of reference state for PA[6] (or more generally for conjugated polymers). Then a first reference state for MX chains will be proposed on the basis of the experimental data.[7]

POLYACETYLENE: REFERENCE STATE AND TRANSFERABLE e-ph COUPLING CONSTANTS

The HT approach is particularly useful in dealing with e-ph coupling in extended systems like PA. HT in fact describe the e-ph perturbation in terms of usual force constant matrices, thus allowing one to borrow valuable information from the well-settled field of molecular spectroscopy. From the point of view of molecular spectroscopy the reference force field for PA, which only involves the ground state electronic distribution, can be derived from the force field of a system with similar geometry but higher excitation energies. In a recent paper a reference force field (F^o) for PA has been proposed,[6] based on the well-known force field of butadiene. The force field is independent on isotopic substitution, whereas the kinetic energy matrix[8] (**G**) is completely determined by the nuclear masses and geometry. By diagonalizing the $\mathbf{GF^o}$ matrices the reference frequencies (ω_i^o) and normal modes (Q_i^o) are easily calculated for $(CH)_x$, $(CD)_x$ and $(^{13}CH)_x$. Once the quadratic coupling is included into the definition of the reference force field, one is left with the usual linear e-ph coupling, which is conveniently described on the $\mathbf{Q^o}$ basis:

$$\mathcal{H}_{e-ph} = \frac{2}{\sqrt{N}} \sum_i Q_i^o \, g_i \, B \tag{4}$$

where the sum runs over the 4 a_g modes of PA. B is the electronic operator which measures the amplitude of the bond-charge density wave.[6]

In the HT treatment the total force field on the $\mathbf{Q^o}$ basis becomes:

$$\Phi = \Phi^o - \Delta\Phi \tag{5}$$

with

$$\Delta\Phi_{ij} = \chi_b \, g_i \, g_j \tag{6}$$

where Φ^o is the diagonal matrix of the squared reference frequencies, and χ_b the electronic response to the phonon perturbation. The eigenvalues of Φ are the squared vibrational frequencies. If one inserts in the eigenvalue equation for Φ the experimental Raman frequencies (ω_i) of $(CH)_x$, as well as the ω_i^o, the χg_i^2 values can be obtained by solving a set of linear equations.[6]

In doped and photoexcited PA samples, defects locally break the inversion symmetry and make a_g modes IR active. The corresponding electronic structure is modified in respect of the perfect chain, and one expects that IR frequencies are still determined by Eq.5, but with different χ_b values. In Fig.1, left panel, we show the χ_b-dependence of the a_g frequencies of $(CH)_x$ as obtained with the coupling constants extracted from the Raman data of the pristine sample, taken with relative χ_b=1. The g_i values extracted from the Raman spectrum clearly allow us to satisfactorily reproduce the IR spectra of doped and photoexcited samples.

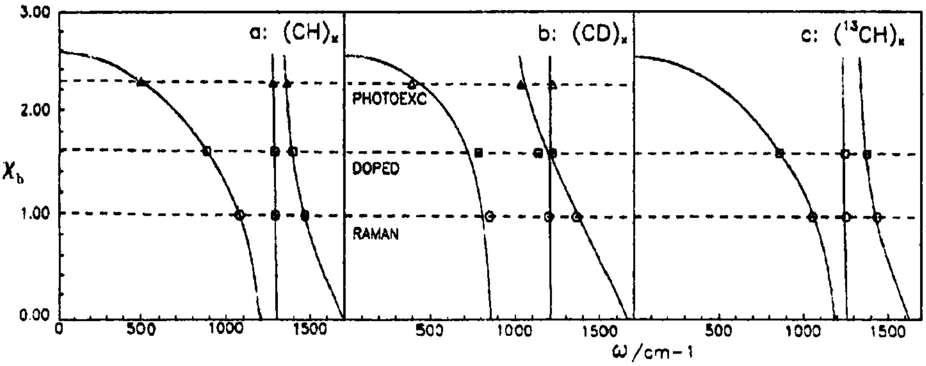

FIGURE 1 Relative χ_b vs. ω curves for PA and isotopic analogs (Ref. 6). Circles, squares and triangles indicate experimental frequencies.

The $\Delta\Phi$ matrix, and hence the χg_i^2, are defined on the Q^0 basis and depend on nuclear masses. However the $\Delta\Phi$ matrix can be easily transformed back to the (symmetrized) internal coordinate basis, the resulting ΔF matrix being independent on nuclear masses. This procedure[6] defines a new set of linear e-ph coupling constants γ_i which are transferable between isotopically substituted polymers. In Fig 1b and c we show the χ_b-dependence of the a_g frequencies of $(CD)_x$ and $(^{13}CH)_x$ as calculated with the γ_i values extracted from the Raman spectrum of pristine $(CH)_x$ sample. Once the quadratic coupling is properly accounted for, the same set of microscopic parameters (γ_i) satisfactorily reproduces the a_g frequencies of pristine, doped and photoexcited samples of $(CH)_x$ and of its deuterated and ^{13}C analogs.

The transferability of linear e-ph coupling constants defined on the (symmetrized) internal coordinate basis is thus proved for isotopically substituted polymers. However, since similar internal coordinates can be defined for different polymers containing similar chemical bonds, the transferability of the γ_i between different polymers is also expected and is currently under study.

MX CHAINS: A TENTATIVE REFERENCE STATE

MX chains, for instance ...Cl-Pt$^{3+\sigma}$-Cl Pt$^{3-\sigma}$ Cl-Pt$^{3+\sigma}$-Cl... (PtCl for short; the equatorial ligands, such as ethylendiamine, en, are not considered in the present treatment) offer a nice case to study site diagonal e-ph coupling. In fact only one mode, the Raman active symmetric M-X stretching, is coupled to the electron via the modulation of on-site Pt energy. The frequency perturbation due to linear e-ph coupling is given by the simple equation:[7]

$$\omega_s^2 = (\omega_s^o)^2 \{1 - \chi_v\, g_s^2\} \qquad (7)$$

where χ_v is the response of the electron system to the phonon perturbation and g_s the site-diagonal linear e-ph coupling constant. The determination of the reference frequency ω_s^o should follow the lines above sketched for PA. However, vibrational spectra of metal-halogen systems are far less studied than those of polyenes, and a reliable set of force constants is not available to construct the reference force field. On the other hand, an experiment recently carried out on PtCl gives some support to a first phenomenological definition of ω_s^o.[7]

It is known that ω_s has an anomalous pressure dependence, showing a decrease of about 15 cm^{-1} when the pressure increases to about 3 GPa.[9] However, the frequency (ω_a) of the antisymmetric Pt-Cl stretching, IR active and decoupled from the electronic system, is barely affected (slightly upshifted) by an analogous pressure increase.[7] The opposite behavior of ω_s and ω_a modes under pressure cannot be reproduced by traditional force fields. On the other hand, the lowering of ω_s with pressure is easily explained if e-ph coupling (Eq. 7) is taken into account.[7] If the electronic structure of the system is described in terms of a simple model (the trimer model),[4] then χ_v is only determined by the site-charge density wave amplitude (σ). Thus, as shown in Fig. 2, the ω_s lowering can be attributed to a decrease of σ under pressure (from ~ 0.89 to ~ 0.83 from ambient to 3 GPa). On the other hand, ω_a does not change appreciably with such a σ variation, and is nearly equal to the value of the isolated complex [Pt(en)$_2$Cl$_2$]$^{2+}$. It is therefore plausible to assume (as done in drawing

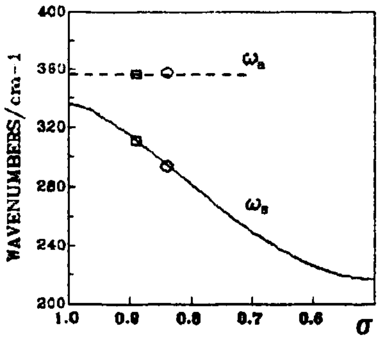

FIGURE 2 Calculated antisymmetric and symmetric Pt-Cl stretching frequencies (ω_a and ω_s) vs. site-CDW amplitude (σ). Squares and circles indicate experimental PtCl frequencies at ambient and 3 GPa pressure, respectively (Ref.7).

Fig. 2) that also ω_s^0 is constant and equal to the frequency of the isolated complex. The above assumption is certainly valid for σ close to 1; however, more work is required and is currently in progress to define more precisely the reference frequency and its possible variation with σ.

CONCLUSIONS

In early treatments of e-ph coupling in 1D systems only the linear term has usually been introduced. Whereas we recognize that this term is in fact essential to understand the distinctive features characterizing the vibrational spectra of low-dimensional solids, we stress the need to include quadratic e-ph coupling in *quantitative* treatments. Quadratic coupling renormalizes the reference frequencies and is required to properly define the reference state. When quadratic coupling is accounted for, the dimensionless linear e-ph coupling constants, $\lambda = \chi g^2$ (Eq. 6 and 7) can be accurately evaluated from the analysis of the vibrational spectra. To assess the strength of e-ph coupling, the χ value is also needed: It can be either calculated on the basis of proper models of the electronic structure,[6] or extracted from the analysis of the CT excitation spectra.[1,2,4,5] For the three classes of 1D solids considered here (half-filled CT crystals, conjugated polymers and MX chains) the e-ph coupling strength turns out to be about one order of magnitude smaller than electron-electron interactions.[2,6,7] This ratio is possibly subject to change for different classes of 1D solids.

In conclusion, we have presented a general method to obtain reliable estimate of e-ph coupling strength from optical data. The method provides a unified approach to the problem of e-ph coupling in low-dimensional solids and, defining sets of transferable coupling constants, allows one to properly deal with the variety of solids provided by modern chemical synthesis.

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