Vibronic contributions to resonant NLO responses: two-photon absorption in push-pull chromophores

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Two-photon absorption (TPA) spectra of push-pull chromophores are described in terms of a two-state model accounting for electron-vibration coupling. Vibrations have two main effects in TPA spectra. The most obvious one is the appearance of a vibrational structure in the spectrum; in this respect we find large Herzberg-Teller contributions. The second effect was not recognized so far: vibrational states contribute a new channel to TPA process, that shows up with a blue-shift and a distortion of the spectrum. Vibrational-channel contributions to other NLO responses are shortly discussed.

I. INTRODUCTION

The large non-linear optical (NLO) responses that characterize π-conjugated materials make them good candidates for innovative applications. Among other properties, large two-photon absorption (TPA) cross-sections are promising for different applications, ranging from optical storage to biological optical imaging. As a consequence, both experimental and theoretical works have received strong impetus and several interesting strategies have been proposed to improve NLO responses in general and TPA cross-section in particular. A presently highly debated topic concerns the importance of vibrational contributions to NLO responses of organic materials. The coupling of electronic and vibrational degrees of freedom (e-ph coupling) is very important in conjugated molecules and polymers, and is expected to originate large effects in systems with intrinsically non-linear behavior. General agreement is presently emerging about the importance of vibronic contributions to static NLO responses in conjugated materials. This can be easily understood: the static applied electric fields affect the electronic properties of the chromophore by affecting its π-electron distribution. Due to e-ph coupling, the applied fields then also act on the vibrational states by displacing nuclei, and this in turn reflects on the electronic distribution, in a feedback mechanism that amplifies non-linearity.

The situation is much more complex at optical frequencies. A fairly common statement is that nuclei are too massive to respond at optical frequencies, so that their contribution to NLO responses is irrelevant. In a recent paper, negligible vibrational contributions to non-resonant NLO responses have been demonstrated. Whereas for actual molecules with electronic excitation energies of the order of 1-2 eV and vibrational energies of about 0.1-0.2 eV it is difficult to find out a frequency range far enough from both electronic and vibrational resonances as to safely apply the approximations in Ref., one indeed does not expect really large effects of e-ph coupling in truly non-resonant NLO responses. As far as resonant processes are concerned, however, the above statement does not apply. Quite obviously it leads to erroneous conclusions if applied to incoherent measurements, i.e. to experiments where a ‘prepared’ state is allowed to relax for some time before further processing. Just as an example, we have already proved large and non-trivial effects of the coupling between electronic and slow degrees of freedom in time-resolved fluorescence and femtosecond hole-burning spectra of push-pull chromophores. But also in coherent resonant experiments (one- and two-photon absorption being simple examples) e-ph coupling is important. Just as in one-photon absorption (OPA) spectra, also in non-linear spectra e-ph coupling is responsible for structured, vibronically resolved band-shapes. Large effects of e-ph coupling have been recognized within the Condon approximation in TPA spectra of push-pull chromophores, and, within the same approximation, TPA, third harmonic generation (THG) and non-degenerate four-wave mixing spectra of the conjugated polymer polydiacetylene have been shown to be non-trivially affected by e-ph coupling. Recent ab initio calculations of TPA spectra of a few conjugated molecules showed sizable and, in

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some cases even large, Herzberg-Teller (HT) corrections, demonstrating once more the non-trivial role of e-ph coupling in conjugated systems.

The effects of e-ph coupling in NLO spectra calculated within the Condon and HT approximations are important and have to be included in any reliable spectral simulation. However they are not dissimilar in principle from standard effects in linear absorption spectra. In fact, within Condon and HT schemes, e-ph coupling only leads to a partitioning of the oscillator strength of a given electronic transition into several vibronic states, or occasionally (within HT) to a borrowing of intensity from an allowed transition to a forbidden one. Of course the spectral consequences of these well-known phenomena will be more and more complex and important the higher is the order of non-linearity, and the larger is the number of coupled electronic states involved in the process.4, 14. But in non-linear spectra e-ph coupling can have much more peculiar effects with no counterpart in linear absorption. In conjugated materials e-ph coupling is responsible for the appearance in infrared and/or Raman spectra of vibrational bands with large (sometimes really huge) intensities. 1, 21, 22. Then there are vibrational states, to mean states within the ground state vibrational manifold, that have large transition dipole moments and/or transition (Raman) polarizabilities. These states, if properly included in sum over states (SOS) expressions of NLO susceptibilities, provide an important purely vibrational channel to NLO responses, that adds to the standard electronic channel. Vibrational channel contributions to resonant NLO processes have not been recognized so far: here we demonstrate they can strongly affect the spectral properties of π-conjugated systems.

In the next Section we will concentrate on TPA spectra of push-pull chromophores described in terms of the simplest relevant model, the DA dimer with Holstein coupling 16. Within this model we are able to calculate numerically exact TPA spectra. We can then discuss the reliability of Condon and HT approximation schemes. We find sizable HT corrections to TPA spectra even for systems whose OPA spectra are well reproduced within the Condon approximation. Even more importantly, we demonstrate large contributions of the vibrational channel to TPA spectra. These contributions become dominant in the cyanine limit. In the discussion Section we extend the treatment to other non-linear techniques and shortly address the behavior of different π-conjugated systems.

II. TPA SPECTRA OF THE DA DIMER WITH HOLSTEIN COUPLING

The simplest relevant model to describe (low-energy) spectral properties of push-pull chromophores accounts for just two electronic states, |DA⟩ and |D+A−⟩, linearly coupled to a vibration, according to the following Hamiltonian (ℏ = 1)|13, 14.

\[
H = z_0(1 - \sigma_z) - \sqrt{2}t\sigma_x - \sqrt{2}\epsilon\omega_0Q\hat{\rho} + \frac{1}{2}(\omega_0^2Q^2 + P^2)
\]  

(1)

where \(Q\) and \(P\) are the coordinate and momentum for a harmonic vibration with frequency \(\omega_0\); \(\sigma_z\) and \(\sigma_x\) are the Pauli spin operators; \(2z_0\) is the energy gap at \(Q = 0\); \(\hat{\rho} = (1 - \sigma_z)/2\) is the ionicity operator measuring the amount of charge separation. The relaxation energy of \(|D^+A^-\rangle\), \(\epsilon\), measures the strength of the e-ph coupling. The above Hamiltonian assigns the two non-interacting (\(\sqrt{2}t = 0\)) states two harmonic potential energy surfaces (PES), as shown in Fig. 1a. Following Mulliken, we assume orthogonal basis states and neglect all dipole moment matrix elements but \(\mu_0 = \langle D^+A^- | \mu | D^+A^- \rangle\), so that the dipole moment operator can be written as: \(\hat{\mu} = \mu_0\hat{\rho}\).

When the interaction is switched on (without loss of generality we set \(\sqrt{2}t = 1\)) the two states mix and, in the adiabatic approximation, the ground and excited state PES, shown in Fig. 1b, are easily obtained by diagonalizing the relevant two-dimensional matrix as a function of \(Q\). As a consequence of e-ph coupling, i.e. of the relative displacement of the PES in Fig. 1a, the energy gap between the two basis states varies with \(Q\), so that the amount of mixing between the two states, measured by \(\rho = \langle \hat{\rho} \rangle\), also depends on \(Q\). Then, both the ground (\(|G\rangle\)) and excited state (\(|E\rangle\)) wavefunctions depend on \(Q\), and analytical expressions for the \(Q\)-dependent properties (energies, dipole moments, etc.) are easily obtained. In particular the energies of both states show a non-parabolic dependence on \(Q\), i.e. the two corresponding PES are anharmonic (Fig. 1b). This anharmonicity induced by e-ph coupling has large effects on static NLO responses 2, where high order \(Q\)-derivatives of the ground state PES are involved. It also strongly affects incoherent spectral measurements where the system tests large regions of the ground and/or excited state PES. On the opposite, anharmonicity is not expected to show up in vertical processes like OPA or TPA.

In any case, the analytical expressions for the ground and excited state PES allow for an exact solution of the corresponding vibrational problems. A detailed description of the adiabatic solution of the Hamiltonian in Eq. (1) is deferred to a subsequent publication 14. Basically, chosen a harmonic phonon basis to describe the vibrational problem on either surfaces, the corresponding Hamiltonian matrices are easily written down by expanding the relevant electronic energies in powers of \(Q\). Numerically exact vibrational eigenstates are then obtained provided that both the phonon basis and the \(Q\)-expansion are truncated at a sufficiently high order as to get convergence on the evaluated properties.
Similarly, the matrix elements of $\hat{\mu}$ on the complete adiabatic basis, are readily obtained from the $Q$-expansion of the relevant electronic dipole moments (either $\mu_G(Q) = \langle G | \hat{\mu} | G \rangle$, or $\mu_E(Q) = \langle E | \hat{\mu} | E \rangle$ or $\mu_{CT}(Q) = \langle G | \hat{\mu} | E \rangle$) closed on the relevant exact anharmonic vibrational eigenstates. For the calculations presented in this paper, we chose to describe the vibrational problem in either the ground or excited state PES on the basis of the eigenstates of a harmonic oscillator with frequency $\omega_i$, centered at the minimum of the ground state PES. With this choice we found that $\sim 20$ basis states and a similar number of terms in the $Q$-expansion of the electronic energies and/or dipole moments are more than enough to get convergence. We underline that the adiabatic approximation we adopt in the present treatment is very useful since it allows for a clear separation between states in the $G$- and $E$-manifolds, and then to distinguish between vibrational and vibronic excitations. The two kinds of states are completely mixed up in a truly non-adiabatic system. In any case, as far as the results presented in this paper are concerned, the reliability of the adiabatic approximation has been confirmed by the comparison with exact non-adiabatic results, obtained along the lines presented in Ref. [2].

OPA spectra are calculated as $\omega \text{Im}[\chi^{(1)}(\omega)]$, with the complex linear susceptibility, $\chi^{(1)}(\omega)$, defined as:

$$\chi^{(1)}(\omega) = \sum_g \sum_f \langle g | \hat{\mu} | f \rangle \langle f | \hat{\mu} | g \rangle \left( \frac{1}{\Omega_{fg} - \omega} + \frac{1}{\Omega_{fg} + \omega} \right)$$

(2)

where $|g\rangle = |G\rangle|0\rangle$ is the global ground state, $|f\rangle$ is an excited state, $\Omega_{fg} = \omega_{fg} - i\Gamma_f$ is the complex frequency of the $f \leftarrow g$ transition, defined in terms of the real transition frequency ($\omega_{fg}$) and of the damping factor of the $f$ state ($\Gamma_f$).

The summation in the above equation runs on all excitations, including vibrational excitations (in the $G$-manifold) as well as vibronic excitations (in the $E$-manifold). The sum on vibrational excitations describes of course the infrared (IR) absorption spectrum, and basically does not contribute to the electronic spectrum, dominated by terms that can be written as $\langle 0 | \mu_{CT}(Q) | v \rangle | v | / (\omega_{CT,v} - \omega - i\Gamma)$, where $|0\rangle$ is the lowest exact anharmonic vibrational state, $|v\rangle$ is the $v$-th exact anharmonic vibrational state in the $E$-manifold, and $\omega_{CT,v}$ is the $|G\rangle|0\rangle \rightarrow |E\rangle|v\rangle$ transition frequency.

In the following, we fix $\epsilon = 1$, and $\omega_i = 0.1$ as dimensionless parameters (in $\sqrt{2} t$ units). In the specific case of push-pull chromophores, a typical value for $\sqrt{2} t$ is $\sim 1$ eV [2-22], so that all the energy values can be approximately read in eV. We present results obtained for three different $\omega_i$ values, to model chromophores with a very low polarity ($\omega_i = 0.95$, $\rho = 0.35$), with intermediate polarity ($\omega_i = 0.66$, $\rho = 0.35$) and just in the cyanine limit ($\omega_i = 0.50$, $\rho = 0.5$). We notice that the properties of the system are symmetric with respect to the substitution $\omega \rightarrow 1 - \rho$. The upper panels in Fig. 2 report one-photon absorption (OPA) spectra: exact spectra (continuous lines) are compared to those obtained in the Condon (dotted lines) and HT (dashed lines) approximation schemes. Both Condon and HT schemes work within the harmonic approximation, and we calculate Condon and HT spectra in the best harmonic approximation for the ground and excited state PES, i.e. by truncating the expansion of the corresponding potential energies, around the ground state equilibrium position, up to the second order in $Q$. In the Condon approximation, the expansion of $\mu_{CT}(Q)$ is truncated at the zeroth order (constant) term, whereas in the HT approximation the linear term in the expansion of the numerator of $\chi^{(1)}$ is also accounted for. As it turns out from Fig. 2, both Condon and HT approximations are fairly good for OPA spectra. The minor deviations of HT from Condon spectra are irrelevant in the fairly broad spectra usually observed for polar chromophores in solution. Quite predictably, the harmonic approximation works well to describe electronic processes, and HT (and higher order) corrections to Condon spectra turn out small for allowed transitions.

Single beam TPA spectra can be calculated as $\omega \text{Im}[\chi_{TPA}(-\omega; \omega, \omega, -\omega)]$, where $\chi_{TPA}(-\omega; \omega, \omega, -\omega)$ is the TPA component of the third order complex susceptibility [2].

$$\chi_{TPA}(-\omega; \omega, \omega, -\omega) \propto \sum_{m, f, n} \langle g | \hat{\mu} | m \rangle \langle m | \hat{\mu} | f \rangle \langle f | \hat{\mu} | n \rangle \chi_{TPA}(n | g) \times$$

$$\left[ \frac{1}{\Omega_{mg} - \omega} + \frac{1}{\Omega_{mg} + \omega} \right] + \frac{1}{\Omega_{mg} - \omega} + \frac{1}{\Omega_{mg} + \omega}$$

(3)

where the triple sum runs on all excited states. Of course, if we are interested in TPA processes leading to the $E$-manifold, (i.e. processes measured for $\omega \sim \omega_{CT}/2$), then $f$ only counts vibronic excitations. But $m$ and $n$ run on both vibronic and vibrational excitations.

In all available studies of vibrational contributions to TPA spectra, all summations in Eq. (3) have been limited to vibronic excitations only, i.e. only the electronic channel to TPA has been accounted for. In this approximation, $\chi_{TPA}$ reduces to:

3
\[
\chi_{TPA}^{el}(-\omega, \omega, \omega, -\omega) \propto \sum_{u,v,w} \langle 0|\mu_{CT}(Q)|u\rangle \langle u|\mu_E(Q) - \mu|v\rangle \langle v|\mu_E(Q) - \mu|w\rangle \langle w|\mu_{CT}(Q)|0\rangle \times 
\]
\[
\left[ \frac{1}{(\Omega_{CT,u} - \omega)(\Omega_{CT,v} - 2\omega)(\Omega_{CT,w} - \omega)} + \frac{1}{(\Omega_{CT,u} + \omega)(\Omega_{CT,v} - 2\omega)(\Omega_{CT,w} - \omega)} \right] + 
\left[ \frac{1}{(\Omega_{CT,u} + \omega)(\Omega_{CT,v} + 2\omega)(\Omega_{CT,w} - \omega)} + \frac{1}{(\Omega_{CT,u} + \omega)(\Omega_{CT,v} + 2\omega)(\Omega_{CT,w} + \omega)} \right]
\]

where \( u, v \) and \( w \) run on vibrational states in the \( E \)-manifold, and \( \mu = \langle 0|\mu_G(Q)|0\rangle \) is the \((Q\text{-independent})\) ground state dipole moment. In the middle panels of Fig. 2 we report the electronic channel contribution to TPA spectra, calculated for the exact adiabatic eigenstates of the Hamiltonian in Eq. (1) (continuous lines). In the same figure, dotted and dashed lines refer to spectra obtained within the Condon and HT approximation schemes.

Even accounting for just the electronic channel to TPA absorption, we can already stress the importance of a proper modeling of e-ph coupling in TPA spectra. If e-ph coupling is not accounted for, both OPA and TPA spectra have a single Lorentzian shape, and are exactly superimposed if the TPA frequency scale is expanded by a factor of 2 with respect to the OPA scale. At the Condon level, the situation is not very different: e-ph coupling originates structured bands in both OPA and TPA spectra, but with similar shape, so that the two spectra are essentially superimposable in the absence of coupling. An obvious deviation is observed at \( \rho = 0.5 \), where, in the harmonic approximation, the TPA spectrum exactly vanishes due to the factor \( \mu_E - \mu \), proportional to \( 1 - 2\rho \) in the dimer model. At variance with OPA spectra, however, HT corrections are very important in TPA, at least for not too neutral molecules. For \( \rho = 0.35 \), the HT spectrum in the central panel of Fig. 2 has a qualitatively different shape from the Condon spectrum, with the 0-1 line acquiring intensity at the expense of the 0-0 line. Apart from the pathological \( \rho = 0.5 \) case, the HT approach offers a good approximation to the electronic channel contribution to TPA, confirming the reliability of the harmonic approximation to describe vertical electronic processes.

Up to now we have only considered the electronic channel contribution to TPA process, where e-ph coupling mainly contributes in defining vibronically structured band-profiles. We already got a fairly impressive result: the Condon approximation to TPA spectra is in general inadequate, even in cases where it works well for OPA spectra. However in TPA spectra, and more generally in non-linear spectra, vibrations have a much more important role than simply structuring the observed band-shapes. They in fact open a vibrational channel to non-linear processes. The lower panels in Fig. 2 show the total TPA spectrum, obtained from the imaginary part of \( \chi_{TPA} \) in Eq. (3), by allowing \( n \) and \( m \) indices to run on both vibrational and vibronic excitations. The comparison between continuous lines in the middle and lowest panels in Fig. 2 clearly demonstrates the importance of the vibrational channel to TPA process, with sizable effects on the absorption frequency, on the band-shape as well as on the total intensity. Overall, the vibrational channel increases the intensity of higher vibronic replicas at the expense of the lowest replicas, with effects that are most important at \( \rho \sim 0.4 \). This implies a blue-shift of the TPA spectrum if compared with the rescaled OPA spectrum. In the extreme case of \( \rho = 0.5 \), the blue-shift amounts to a vibrational spacing. Intensity effects are negligible for \( \rho \sim 0.2 \), but at \( \rho = 0.35 \) the vibrational channel amplifies TPA response by a 1.2 factor, that becomes a factor of 4 in the \( \rho = 0.5 \) case.

\[ \text{III. DISCUSSION} \]

Vibrational channel contributions to TPA process arise from terms in Eq. (3) where \( m \) or \( n \), or both \( m \) and \( n \) run on vibrational excitations, so that in each term contributing to the vibrational channel at least a factor like \( \langle 0|\mu_G(Q)|v\rangle \) appears, where \( v \) is one of the vibrational states in the \( G \)-manifold. The square of this term measures the absorption intensity of the \( v \)-th vibrational state. Since the fundamental vibration has by far the largest IR intensity, the vibrational channel to TPA is dominated by it. A first approximation to \( \chi_{TPA}^{vib} \) is then:

\[
\chi_{TPA}^{vib} \sim \left[ \sum_{v,w} \frac{\mu_IR(1)\mu_{CT}(Q)|v\rangle \langle v|\mu_E(Q) - \mu|w\rangle \langle w|\mu_{CT}(Q)|0\rangle}{(\omega_v - \omega)(\Omega_{CT,v} - 2\omega)(\Omega_{CT,w} - \omega)} \right] + \left[ \sum_{v} \frac{\mu_IR(1)\mu_{CT}(Q)|v\rangle \langle v|\mu_{CT}(Q)|1\rangle \mu_IR}{(\omega_v - \omega)(\Omega_{CT,v} - 2\omega)(\omega_v - \omega)} \right]
\]

where \( \mu_IR = \langle 0|\mu_G(Q)|1\rangle \) is the dipole moment of the fundamental vibrational transition. The relative importance of \( \chi_{TPA}^{vib} \) vs \( \chi_{TPA}^{el} \) goes as \( (\mu_IR/(\mu_E - \mu))(\omega_{CT} - \omega)/(|\omega_v - \omega|) \) or as its square, depending if the first or the second term
in the above equation is concerned. Since \(\mu_{IR} \propto \rho(1 - \rho)^{3/2}\), maximizes at \(\rho = 0.5\), whereas \(\mu_{E} - \mu \propto (1 - 2\rho)\) vanishes there, the relative importance of \(\chi_{TPA}^{ vib}\) increases fast towards the cyanine limit. On the other hand, the frequency of vibrational modes, \(\omega_v \sim 0.1 - 0.2\) eV, is not far from the laser frequency \(\omega \sim \omega_{CT}/2 \sim 0.5 - 1.5\) eV, so that the ratio \((\omega_{CT} - \omega)/(\omega_v - \omega))\) enhances the vibrational contribution over the electronic one by a factor ranging up to 3.

The solution of the two-state model in the adiabatic approximation allows for reliable estimates of the relative magnitude of electronic and vibrational contributions to TPA spectra and even more importantly offers a natural understanding of the physical origin of the different contributions. An obvious drawback of the two-state model is however the impossibility to account for the role of highly excited states. Of course, extending the sums in Eq. (3) to excited states (\(E'\)) higher than the lowest one (\(E\)) opens additional channels to the TPA process. These \(E'\)-channel contributions to TPA have \(n\) or \(m\) or both \(m\) and \(n\) in Eq. (3) running over vibronic states pertaining to the \(E'\)-manifolds. By closing over the vibrational states of these high-energy levels, one can roughly estimate the magnitude of \(E'\)-channel contributions in terms of the \(G \rightarrow E'\) and \(E \rightarrow E'\) transition dipole moments (beside of \(G \rightarrow E\)) and of the corresponding transition energies. At the best of our knowledge, experimental estimates of the \(E \rightarrow E'\) transition dipole moments are only available for coumarin 153 dispersed in CH\(_3\)CN. For this molecule, excited state transient absorption measurements yield a \(E \rightarrow E'\) transition dipole moment of around 10 D. Transition dipole moments of similar magnitude are also evaluated, from OPA spectra, for the two transitions \(G \rightarrow E\) and \(G \rightarrow E'\), occurring at energies of \(\sim 3.0\) eV and \(\sim 5.6\) eV, respectively. The joined analysis of electronic and vibrational spectra of the same molecule yields a \(\sim 0.23, \epsilon \sim 1\) eV and \(\omega_v \sim 0.2\) eV, in fairly good agreement with previous estimates on a similar dye (coumarin 102). Based on these data, the vibrational and \(E'\)-channel contributions to TPA spectra turn out of the same order of magnitude. In view of the fairly low polarity of coumarin 153 and of its fairly high \(\omega_{CT}\) frequency, we believe that for most push-pull chromophores the vibrational channel contribution to TPA spectra is larger than \(E'\)-channel contributions. In fact, preliminary ZINDO calculations on a few chromophores confirm that, at least for chromophores with intermediate polarity (\(\rho \sim 0.3 - 0.7\)), the vibrational contributions to TPA spectra are important and cannot be disregarded with respect to \(E'\)-channel contributions. Refined models for NLO responses accounting for plenty of excited states are bound to fail if no proper account is given for the contributions of vibrational states.

Besides TPA spectra, other NLO responses can be affected by the vibrational channel. Fig. 3 shows the amplitude of the third harmonic generation (THG) signal in the region \(\omega \sim \omega_{CT}/3\), for three different \(\rho\) values. Continuous lines refer to the total response, obtained by allowing the triple sums in \(\chi_{THG} = \chi^{(3)}(-3\omega; \omega, \omega, \omega)\) to run on both vibronic and vibrational excitations. Dashed lines instead account for the electronic channel to THG, obtained by summing only on vibronic states. The vibrational channel strongly affects THG response, with largest effects at \(\rho \sim 0.3\), where the response is amplified by a factor \(\sim 2\) in the shown spectral region. Calculations are performed using the complete expression for \(\chi_{THG}\), but, in the portion of the spectrum shown in the figure, the terms with a resonating denominator are clearly dominant, so that we can approximate \(\chi_{THG}\) as follows:

\[
\chi_{THG}(-3\omega; \omega, \omega, \omega) \sim \\
\sum_{f,m,n} \frac{(g|\mu|f)(f|m|n)(m|\mu|g)}{(\Omega_{fg} - 3\omega)(\Omega_{mg} - 2\omega)(\Omega_{mg} - \omega)} - \sum_{f,m} \frac{(g|\mu|f)(\mu|g)(g|\mu|m)(m|\mu|g)}{(\Omega_{fg} - 3\omega)(\Omega_{fg} - \omega)(\Omega_{mg} - \omega)}
\]

(6)

where \(f\) runs on vibronic excitations, just to guarantee an almost resonant denominator, \(\omega_{CT} - 3\omega\), and \(m, n\) run on both vibrational and vibronic excitations. The vibrational channel contribution to THG is more complex than for TPA. A few terms of \(\chi_{THG}^{ vib}\), obtained by allowing \(n\) or \(m\) or both \(m\) and \(n\) in the above equation to run on vibrational excitations, contain at the numerator \(\mu_{IR}\) or its square. A term however has a different numerator: \(\sum_{n,w}(0|\mu_{CT}(Q)|v)(v|\mu_{CT}(Q)|1)(1|\mu_{CT}(Q)|w)(w|\mu_{CT}(Q)|0)\), that is related to the non-resonant Raman intensity of the fundamental vibration. It is difficult to disentangle the contributions of the various terms to the observed signal, but the importance of Raman modes is suggested by the observation of the maximum vibrational contribution to THG just at \(\rho \sim 0.3\), where the non-resonant Raman intensity maximizes for the DA dimer model.

Having rationalized the vibrational channel contributions to TPA and THG spectra of the DA dimer model in terms of IR and non-resonant Raman intensity of coupled vibrations, we can shortly extend our discussion to different systems. In conjugated polymers the coupled vibrations are not IR active, whereas they have huge (non-resonant) Raman intensities. Then we expect no contribution from the vibrational channel in TPA spectra of pristine polymers, whereas the vibrational contributions to THG spectra can be important. A detailed description of NLO properties of polymers is difficult, in view of their fairly crowded excitation spectra. Preliminary results on a simple relevant model, the self-dimer with Peierls coupling, confirm large vibrational channel contributions to THG spectra, and negligible contributions to TPA spectra. Of course large vibrational contributions to TPA spectra can be expected for doped or photoexcited polymer samples, based on the very large IR intensities associated with charged solitonic or polaronic defects.
IV. CONCLUSIONS

In conjugated molecules and polymers e-ph coupling is very effective. It shows up with largely anharmonic PES, that, in conjugated polymers, often show more than a single minimum to signal the Peierls instability. A second fairly ubiquitous consequence of e-ph coupling is the large nuclear displacement upon electronic excitation, with well apparent effects in absorption and resonant Raman spectra. In systems with large e-ph coupling, static electric fields can draw nuclei out of equilibrium, and this is the basic reason why e-ph coupling is so effective in amplifying static NLO responses via anharmonic contributions. Fields at optical frequencies are too fast to displace nuclei, but in incoherent measurements nuclei are allowed to relax for a while following the application of the preparation pulses: once more e-ph coupling is important in defining the shape of the involved PES. Electron-phonon coupling largely affects vibrational spectra, with a softening of the relevant modes and a large increase of infrared and/or Raman intensities. Therefore in SOS expressions for the susceptibilities, vibrational states can give large contributions. For static susceptibilities this contribution indeed accounts for the anharmonicity of the ground state PES.

As far as resonant processes are concerned, the importance of the vibrational contributions has not been fully appreciated so far. Here we have analyzed TPA spectra of the DA dimer model — the simplest model relevant to push-pull chromophores — and proved that the vibrational contribution is very important in defining the shape, frequency and intensity of the signal. Including vibrational degrees of freedom has two major effects in TPA spectra, and more generally in resonant NLO processes. The first, fairly obvious, effect is the appearance of a vibronic structure in TPA spectra. This effect was already recognized; here we prove the validity of the harmonic approximation in this context, but the inadequacy of the Condon approximation. Specifically, HT corrections to TPA spectra are important even in cases when OPA spectra are well reproduced within the Condon approximation. The second effect of vibrations is more interesting and has not been recognized so far. Vibrational states in the ground state manifold in fact contribute a new and important channel to TPA process. The vibrational channel contribution shows up with a blue-shift of the TPA spectrum with respect to the rescaled OPA spectrum and with a large distortion of the TPA band-shape. These contributions are related to simple spectroscopic observables as inferred from vibrational and linear absorption spectra. This immediately leads to safe predictions about other systems. As a matter of fact, vibrational channel contributions to TPA spectra are related to the IR intensity of coupled modes, so that they are expected to be negligible in any polymer (but possibly dominant in doped and/or photoexcited polymers). THG spectra instead have contributions from Raman modes, so that large effects of e-ph coupling are expected in THG spectra of conjugated polymers.

The behavior of conjugated materials can only be understood by properly accounting for e-ph coupling, that affects in different ways and for different reasons the spectral properties of these systems. Common beliefs based on the behavior of other systems where e-ph coupling is not so effective, and/or extrapolated from our knowledge of their linear spectroscopic behavior need to be carefully reconsidered. A joint experimental and theoretical effort is needed to extract the correct physics out of these fascinating materials.

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FIG. 1. Potential energy surfaces sketched along the vibrational coordinate $Q$ for (a) the basis states ($\sqrt{2}t = 0$), and (b) the exact eigenstates ($\sqrt{2}t = 1$). Both panels refer to $z_0 = 0.95$ and $\epsilon = 1$. 
FIG. 2. OPA and TPA spectra calculated for $\epsilon = 1$ and $\omega_v = 0.1$ in units of $\sqrt{2}t$. Left, middle and right panels refer to $\rho = 0.2$, 0.35, 0.5, respectively. The vibronic and vibrational damping factors are fixed to 0.05 and 0.005, respectively. Upper panels report exact OPA spectra as continuous lines. Dashed and dotted lines correspond to spectra obtained in the HT and Condon approximation, respectively. Middle panels report the electronic channel contribution to TPA spectra; continuous, dashed and dotted lines refer to exact spectra and to spectra obtained in the HT and Condon approximation, respectively. Bottom panels show the total TPA spectrum including the vibrational channel contribution. The $x$-axis scale at the top and bottom of the figure report the energy of the OPA and TPA spectra, respectively. $y$-axes (arbitrary units) preserve the relative intensities.
FIG. 3. THG spectra calculated for the same parameters as in Fig. 1. Upper, middle and bottom panels refer to $\rho = 0.2$, 0.3, 0.5, respectively. THG spectra including the vibrational channel contribution (continuous lines) are compared with the purely electronic THG spectra (dashed lines).