PHYSICAL REVIEW B, VOLUME 64, 020301(R)

Multiquanta breather model for PtCl

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(Received 10 October 2000; published 11 June 2001)

We study the many-quanta problem of an intramolecular vibrational excitation interacting with optical phonons, that may represent the nonlinearity from intrinsic electron-lattice interactions. In the adiabatic limit we calculate numerically the ground-state energy and the corresponding wave functions for N vibrational quanta. In the one-dimensional case we find strong redshifts in the overtone spectra and an increasing spatial localization as the number of quanta increases. Through model parameter fitting we achieve very good quantitative agreement with experimental resonant Raman scattering measurements in the quasi-one-dimensional charge transfer solid PtCl. Accurate analytical expressions for the redshifts are also obtained.

DOI: 10.1103/PhysRevB.64.020301 PACS number(s): 63.20.Ry, 63.20.Pw

Investigation of vibrational energy localization in crystals due to anharmonic effects has considerably increased over the last decade since Sievers and Takeno suggested[1] that energy localization can be induced through spatially localized nonlinear excitations that are solutions of discrete anharmonic lattices. The term ‘‘intrinsic localized modes’’ (ILM’s) or discrete breathers (DB’s) is presently used to distinguish nonlinear localization from disorder-induced localized modes. Following the original work a large number of theoretical studies have been devoted to the existence,[2] mobility[3] and thermodynamic[4] properties of DB’s in classical systems. Recently there has also been an increasing interest in the quantum character of breathers. Numerical diagonalization in anharmonic lattices[5] or strong electron-phonon coupled systems[6] has shown that analogous spatially localized modes can exist as eigenstates in quantum nonlinear lattices.

In spite of this theoretical activity the only microscopic experimental candidate for DB’s has been the anomalous Amide-I (C=O stretching) band with an unusual temperature dependence in ACN, attributed to a vibrational polaron formation.[7–9] Recently, however, resonant Raman scattering (RRS) measurements in PtCl, a quasi-one-dimensional charge density wave compound, have shown a strong redshift of the overtones,[10] stimulating interest in this area. The concept of multiquanta bound states in nonadiabatic and adiabatic Peierls-Hubbard models was used in order to explain this unusual redshifted multiquanta evolution of the fundamental frequency. In the former case a four-site model seems to fit the experimental results well.[10,11] In the latter adiabatic case the success of the adiabatic approach is restricted to a small number of bound quanta, since at higher energies the theoretical predictions deviate significantly from the experimental observations.[12] In the former case, the potential disadvantages are the large number of system parameters, the small lattice size used in the numerical calculations, and the assumption that the vibrational quanta are almost localized at a single unit cell scale.

In this work we use a simpler many-quanta effective model to describe the localization of the vibrational energy in molecular crystals. Our motivation is the simple picture offered in Ref. 12 for an intramolecular vibrational excitation on a trimer ($\mathrm{PtCl_2}$) caused by charge transfer between Pt^{4+} and Pt^{2+}, that is localized on a single lattice site. Since such excitations are delocalized in an extended lattice due to quantum mechanical tunneling, a coupling with an external field is necessary for breather formation. It is known that in materials like PtCl there is a very strong interaction of the electronic motion with the ionic arrangement.[13,14] The resulting nonlinearity through the electron-phonon coupling can be phenomenologically represented by an effective interaction of the intramolecular mode with a bath of another degree of freedom. Here, we represent the latter effectively by a soft optical phonon with frequency ω_0 lying in the range of the observed redshifts. The effective coupling of the intramolecular mode with optical phonons is easily connected with the calculated parameters of the underlying electron-phonon Hamiltonian,[14] using a first-order expansion of the electron-induced nonlinear potential close to the anticontinuous limit. In such a model an adiabatic treatment of the optical phonons leads to a generalized discrete nonlinear Schrondiger equation (DNLS), allowing the localization of the vibrational excitation.

Specifically, we consider a one-dimensional molecular chain described by classical Einstein oscillators with mass M and vibrational frequency ω_0. Assuming that an intramolecular vibrational excitation with on-site energy E_0 can hop from one site i to its nearest neighbors via the transfer matrix element J (described in a tight-binding model) and also that it is locally coupled with the oscillators, then the resulting Hamiltonian is given by

$$H=\sum_i \left[E_0\alpha_i^\dagger\alpha_i-J(\alpha_i^\dagger\alpha_{i+1}+\alpha_{i+1}^\dagger\alpha_i)\right] +\sum_i\left[\frac{1}{2M}p_i^2+\frac{M\omega_0^2}{2}x_i^2\right]+g\sum_i x_i\alpha_i^\dagger\alpha_i, \tag{1}$$

where $\alpha_i^\dagger$ and α_i are the creation and annihilation operators of the vibrational excitation obeying the standard bosonic commutation relations, x_i and p_i are the displacement from the equilibrium position and the momentum, respectively, of the ith oscillator, and g is the constant of the interaction which is assumed to be only on-site.

The Hamiltonian of Eq. (1) for a single intramolecular quantum reduces to the Holstein model.[15] In the adiabatic approximation its ground state always consists of a stable ILM solution (vibrational polaron).[16] Extending the calculations of Ref. 16, we introduce a many-body scheme in order to find the adiabatic ground state in the case of N vibrational quanta. For this purpose we consider a general N-quanta eigenstate of the Hamiltonian of Eq. (1):

$$|\Psi\rangle=\frac{1}{\sqrt{N!}}\sum_{j_1,j_2,\ldots,j_N} C_{j_1,j_2,\ldots,j_N}\alpha^\dagger_{j_1}\alpha^\dagger_{j_2}\ldots\alpha^\dagger_{j_N}|0\rangle, \tag{2}$$

where $|0\rangle$ is the vacuum state and $C_{j_1,j_2,\ldots,j_N}$ are the probability amplitudes for finding one quantum on site j_1, one on $j_2,\ldots,$ etc., and are normalized to unity. Due to the bosonic character of the vibrational quanta, the indices $j_1,j_2,\ldots,j_N$ are not necessarily different and

$$C_{j_1,j_2,\ldots,j_N}=C_{P\{j_1,j_2,\ldots,j_N\}}, \tag{3}$$

where P indicates all the possible permutations of the set $\{j_1,j_2,\ldots,j_N\}$.

In what follows we use the dimensionless quantities[16] $\tau=\omega_0 t$ (dimensionless time), $\epsilon_0=E_0/J$ (dimensionless on-site energy), $u_i=\sqrt{M\omega_0^2/J}\,x_i$ (dimensionless displacements), $k=g/\sqrt{JM\omega_0^2}$ (dimensionless coupling), and $\gamma=\hbar\omega_0/J$ (adiabaticity parameter). The adiabatic limit corresponds to the case $\gamma\rightarrow 0$.

We minimize the total energy with respect to $\{u_i\}$ in the adiabatic approximation (i.e., assuming $du_i/d\tau=0$) and using the stationarity condition

$$C_{j_1,j_2,\ldots,j_N}=\Phi_{j_1,j_2,\ldots,j_N}e^{-i(E/\gamma)\tau}, \tag{4}$$

where the coefficients $\Phi_{j_1,j_2,\ldots,j_N}$ are time independent and E is the sum of the tight-binding and the interaction energy. Then the distortion of the ith oscillator is given by $\partial(\langle\Psi|H|\Psi\rangle)/\partial u_i=0$, which implies (using $\dot{u}_i=0$)

$$u_i=-k\langle\Psi|\alpha_i^\dagger a_i|\Psi\rangle=-k\rho_i, \tag{5}$$

where the state $|\Psi\rangle$ is that of Eq. (2) and

$$\rho_i=N\sum_{i_1,\ldots,i_{N-1}}|\Phi_{i,i_1,\ldots,i_{N-1}}|^2. \tag{6}$$

In the derivation of the last equation we have taken into account Eq. (3). The quantity ρ_i/N gives the probability to find any quantum on site i.

The eigenvalue equation for the N-quanta stationary states is described by the following generalized DNLS equation:

$$E\Phi_{j_1,j_2,\ldots,j_N}=(N\epsilon_0-\Delta_N-k^2P_N)\Phi_{j_1,j_2,\ldots,j_N}, \tag{7}$$

where

$$\Delta_N\Phi_{j_1,\ldots,j_N}=\sum_{n_{j_1},\ldots,n_{j_N}}[\Phi_{n_{j_1},\ldots,j_N}+\cdots+\Phi_{j_1,\ldots,n_{j_N}}] \tag{8}$$

and

$$P_N\Phi_{j_1,\ldots,j_N}=[\rho_{j_1}+\cdots+\rho_{j_N}]\Phi_{j_1,\ldots,j_N}. \tag{9}$$

Here, the index n_{j_i} denotes the nearest-neighboring sites to site j_i. Equation (7), including a Hubbard term, has been obtained for $N=2$ in the study of the Holstein-Hubbard bipolaron problem.[17] As can be seen from Eq. (7) the ground-state solutions do not depend on the parameter γ. The latter affects the dynamical properties of the system (e.g., the normal modes), since it enters the equations of motion [see, for example, Eq. (6) of Ref. 16].

The total energy of the system, including the lattice energy, is given by

$$E_N=N\epsilon_0-\sum_{j_1,\ldots,j_N}\Phi^*_{j_1,\ldots,j_N}\Delta_N\Phi_{j_1,\ldots,j_N}-\frac{k^2}{2}\sum_i\rho_i^2. \tag{10}$$

The ground state of Eq. (7) with periodic boundary conditions is calculated numerically using the same method as in Ref. 16. The results show that, as in the one-quantum case, the ground state for the N quanta is always localized for any nonvanishing coupling strength forming a vibrational many-quanta polaron. These ILM's are gradually more extended as coupling k decreases. In the limit $k\rightarrow 0$ and for an infinite lattice we obtain $E_N\rightarrow N(\epsilon_0-2)$, which is the ground-state energy of N noninteracting fully extended (Bloch) vibrational quanta. For relatively large values of k the ILM's are completely localized at one site for any number of quanta, with total energy given by the anticontinuous limit expression [i.e., ignoring the term $\Delta_N\Phi_{j_1,\ldots,j_N}$ in Eq. (7)]:

$$E_N=N\epsilon_0-\frac{k^2}{2}N^2. \tag{11}$$

This expression has also been used by Scott *et al.* in the problem of ACN.[8]

In Fig. 1 we present with solid lines numerical results obtained from Eq. (7) for the binding energy $\Delta E_N=E_N-N(\epsilon_0-2)$ per quantum as a function of coupling constant for different number of bound quanta, N. It is clearly seen that the absolute value of the binding energy is an increasing function of N, resulting in strong redshifts of the overtone spectra. Also the wave function of the ground state becomes more localized as N increases. For this reason, the larger N, the more rapidly the total energy approaches the anticontinuous limit value of Eq. (11) (dashed lines in Fig. 1), as k increases. The ILM's stability in this adiabatic approach has been confirmed explicitly for the one-quantum[16] and two-quanta[17] cases. The higher quanta ILMs are not expected to lose their stability since they become even more localized.

The strong nonlinearity due to the coupling with the lattice leads to greater localization and increased redshifts at higher energies. Similar features are observed[10] in the ex-

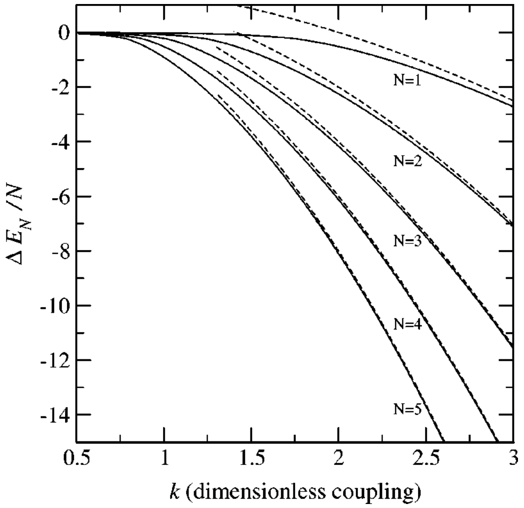

FIG. 1. The binding energy per quantum ($\Delta E_N / N$) as a function of the coupling constant *k* for different numbers of bound quanta ($N = 1,2,\ldots,5$). Solid lines represent numerical calculations. Dashed lines result from expression (11), valid for relatively large values of *k*.

perimental RRS overtone spectra of PtCl. Using our exact numerical procedure we can fit the experimental data of the overtone shifts of PtCl. According to our model the *relative* redshift of the overtones,

$$r_N(k,\epsilon_0) = \frac{NE_1 - E_N}{E_1}, \tag{12}$$

depends on two model parameters: the coupling constant *k* and the on-site energy ϵ_0 of the quanta.

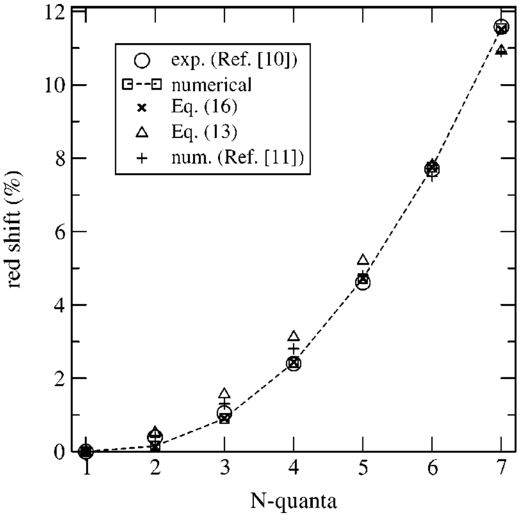

FIG. 2. Relative redshifts (%) of the Pt^{37}Cl overtone spectra as a function of the number *N* of quanta. Circles and crosses are experimental (Ref. 10) and nonadiabatic numerical (Ref. 11) results, respectively. Squares connected with the dashed line are obtained from numerical exact two-parameter fitting. Triangles result from the analytical one-parameter fitted expression in the anticontinuous limit. Data represented by × result from a more accurate analytical two-parameter fitted expression. (See text for details.)

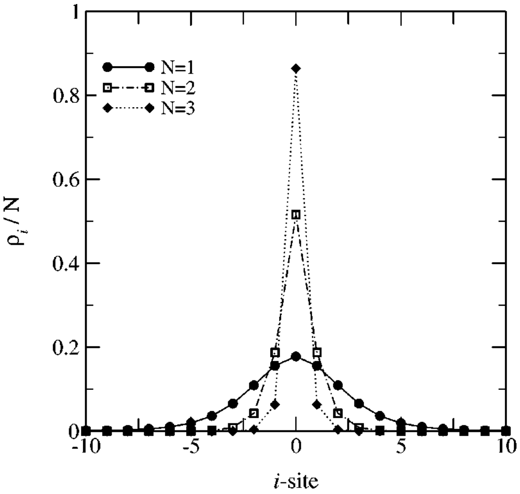

FIG. 3. The probability of finding any quantum on lattice site *i* (ρ_i / N) versus *i* for $N = 1$, 2, and 3 quanta. The coupling constant is $k = 1.19$.

In Fig. 2 we present the relative redshifts calculated from our numerical results through parameter fitting, and compare them with the experimental[10] and numerical[11] results for Pt^{37}Cl. The best fit is achieved for $k = 1.19$ and $\epsilon_0 = 191$. From these dimensionless values we obtain $J = 1.61\ \mathrm{cm}^{-1}$ in order to have the first peak at $304\ \mathrm{cm}^{-1}$, as observed in Ref. 10. For the fitted value of coupling constant *k* the probability to find any quantum on site *i* (ρ_i / N) is displayed in Fig. 3 for the one, two, and three vibrational quanta ILM's, respectively. We observe that the ILM corresponding to the second overtone ($N = 3$) is localized on almost one lattice site in agreement with the experimental observations.[10] However, the adiabatic single-quantum ($N = 1$) nonlinear renormalized vibrational polaron is extended to about 15 unit cells. As a result, in the framework of the semiclassical equations of motion, the ILM can uniformly propagate through the lattice.[18] Generally, the semiclassical mobility of such one-quantum ILM's is numerically tested[18] for $k < 1.5$. For Pt^{35}Cl the fitting parameters are $k = 1.15$ and $\epsilon_0 = 170$. The first peak at $312\ \mathrm{cm}^{-1}$ for this isotope[10] is obtained for $J = 1.86\ \mathrm{cm}^{-1}$.

In the anticontinuous regime ($k \gg 1$), where ILM's are localized at one site, an analytical expression is available for the relative red shifts, obtained through substitution of Eq. (11) in Eq. (12). Then

$$r_N(\beta) = \frac{1}{2\beta - 1}(N^2 - N), \tag{13}$$

where $\beta = \epsilon_0 / k^2$. This formula is not well suited to the case of PtCl since for small quanta numbers the ILM is not localized at a single unit cell (see Fig. 3 for $N = 1$ and 2). Fitting of expression (13) with the Pt^{37}Cl data is presented in Fig. 2 (triangles) for comparison of the one-site localized adiabatic redshifts, Eq. (13), with the corresponding nonadiabatic results.[11] We see that the analytical, one-parameter adiabatic fitting is slightly worse than the numerical, multiple-parameter nonadiabatic one. However, a more convenient analytical description of the PtCl redshifts can be found; as is clearly seen from Fig. 3, the one-quantum ILM is far from being single-site localized, and therefore its energy E_1 departs considerably from the anticontinuous limit value. However, accurate analytical relations for the energy E_1 at any value of coupling k are available.[16] In the PtCl case the one-quantum ILM is closer to the large vibrational polaron and thus a continuous approximation can be used, resulting in[15]

$$E_1 = \epsilon_0 - \left(2 + \frac{k^4}{48}\right). \tag{14}$$

The last formula provides a better description of the vibrational polaron energy for $k \lesssim 1.7$.[16] Moreover corrections of the anticontinuous expressions (11) for the energies E_N can be found using a variational method—as in the single quantum case[16]—in the framework of the Hartree approximation,[19] which results in

$$E_N = N\epsilon_0 - \left(\frac{k^2}{2}N^2 + \frac{2}{k^2} + \frac{1}{k^6N^2}\right). \tag{15}$$

The detailed calculations and the comparison of the variational results with the exact numerical will be presented elsewhere.[20] Using Eq. (12), where E_1 is given by Eq. (14) and E_N for $N \geqslant 2$ is given from Eq. (15), we obtain for the relative red shifts

$$r_N(k,\epsilon_0) = \frac{\left(\frac{k^2}{2}N^2 + \frac{2}{k^2} + \frac{1}{k^6N^2}\right) - \left(2 + \frac{k^4}{48}\right)N}{\epsilon_0 - \left(2 + \frac{k^4}{48}\right)}. \tag{16}$$

Fitting this expression with the Pt^{37}Cl data we find $k = 1.2$ and $\epsilon_0 = 195$. In Fig. 2 ($\times$'s) we plot Eq. (16) for the fitted values of parameters. This analytical relation approaches the experimental and the exact numerical data very well. A more accurate variational bridging of the continuous with the anticontinuous limit results is also possible.[20]

In summary, inspired by experimentally observed intrinsic localization of vibrational energy in PtCl, we have studied a Holstein-type model describing intramolecular *many*-quanta excitations coupled with optical phonons. The adiabatic treatment of the lattice allows the numerical calculation of the N-quanta ground state, which always forms an ILM. The inherent nonlinearity of the system results in stronger localization and correspondingly increased overtone redshifts at higher energies. Fitting the two parameters of our phenomenological model, we achieve very good agreement with experimental data in PtCl by a nonlinear renormalized one-quantum ILM extending over about 15 unit cells. In the adiabatic approximation we are able to deal with ILM's that extend to many lattice sites and are not restricted to a single site, as usually assumed in nonadiabatic studies.[21] Using the continuous approximation for the single-quantum energy and the anticontinuous limit for the many-quanta energy, an accurate analytical expression is obtained for the PtCl redshifts. The physical mechanism underlying our model to explain the PtCl ILM's is the formation of vibrational polarons (which should not be confused with electronic polarons). Possible application of the results presented in this work to other halogen-bridged mixed valence transition metal compounds or quasi-one-dimensional molecular materials remains to be tested. A limitation of the proposed model is that it does not take explicitly into account the electronic degrees of freedom—that are actually responsible for the resulting strong nonlinearity—and consequently cannot predict electronic properties of the ILM's. These can be approximately provided through the electronic rearrangement involved in molecular vibrations and will be discussed elsewhere.

We would like to thank A. P. Shreve for useful discussions and for providing the experimental data of Ref. 10. This research was supported by the Department of Energy, under Contract No. W-7405-ENG-36.

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